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ATOMIC STRUCTURE AND SPECTRAL LINES

BY THE SAME AUTHOR

WAVE MECHANICS

Being a supplementary volume to "Atomic Structure and Spectral Lines"

THREE LECTURES ON ATOMIC PHYSICS

ATOMIC STRUCTURE AND SPECTRAL LINES

BY

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TRANSLATED FROM THE FIFTH GERMAN EDITION BY

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VOLUME I

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EXTRACT FROM THE PREFACE TO THE FIRST GERMAN EDITION

AFTER the discovery of spectral analysis no one trained in physics could doubt that the problem of the atom would be solved when physicists had learned to understand the language of spectra. So manifold was the enormous amount of material that had been accumulated in sixty years of spectroscopic research that it seemed at first beyond the possibility of disentanglement. An almost greater enlightenment has resulted from the seven years of Röntgen spectroscopy, inasmuch as it has attacked the problem of the atom at its very root, and illuminates the interior. What we are nowadays hearing of the language of spectra is a true "music of the spheres" within the atom, chords of integral relationships, an order and harmony that become ever more perfect in spite of the manifold variety. The theory of spectral lines will bear the name of Bohr for all time. But yet another name will be permanently associated with it, that of Planck. All integral laws of spectral lines and of atomic theory spring originally from the quantum theory. It is the mysterious *organon* on which Nature plays her music of the spectra, and according to the rhythm of which she regulates the structure of the atoms and nuclei.

September, 1919

AUTHOR'S PREFACE TO THE FIFTH GERMAN EDITION

IN this new edition the subject-matter will be subdivided, and will appear in two volumes. The present volume, which constitutes the first portion, contains the older quantum theory, and is in part an abbreviation and in part an extension of the fourth German edition of the original work. The second volume will be an elaboration and completion of the supplementary volume, which originally appeared under the title " Wave Mechanics."

It has become clear that it is possible to understand the new theory only by building it up from the old theory. For this purpose the present volume necessarily treats not only of the basic experimental facts, but also of the orbital ideas so far as they are required for introducing the quantum numbers, and for serving as models for the wave-mechanical calculations. The final results are always given in the form in which they are presented by the new theory. Consequently, it has been necessary to refer frequently to the supplementary volume, and to leave occasional gaps in the proofs.

The first seven chapters have in the main been abbreviated. The methods involved in Hamiltonian mechanics, which I ventured to place only in the Appendix previously, have here been taken up in the text, as their technique has now become generally familiar. Conversely, I have transferred the instructive method of Rubinowicz for deriving the selection rules, which were previously given in the text, to the Appendix. Chapter VIII., which treats of multiplet structures, has been extended by the inclusion of the model of the spinning electron and of Pauli's Principle. Chapter IX., on Band Spectra, has been kept short, and does not claim to be in any way complete ; it contains only what is essential for wave-mechanics.

Special thanks are due to my colleague, Dr. K. Bechert. He has not only sacrificed much time in checking the formulæ and in correcting the proofs, but also in making several independent contributions, for example, to Chapters VII., VIII., and IX. Mr. H. Raether kindly prepared the index.

A. SOMMERFELD

MUNICH,
November, 1931

TRANSLATOR'S PREFACE

THE English rendering of the latest edition of Professor Sommerfeld's classic work will, it is hoped, be no less welcome than the previous English edition. It comes at a time when a certain definite stage has been arrived at in our knowledge of the structure of the atom. Much that was speculative only a few years ago has now become confirmed by subsequent experimental researches, whereas in some cases our views have had to be modified. As a useful model for interpreting the main features of spectroscopic phenomena the Rutherford-Bohr atom must still be regarded as indispensable. No harm can come from its provisional or conditional acceptance, so long as it is not treated too literally or too respectfully. Although wave-mechanics and quantum mechanics are available whenever difficulties arise in the last details of refinement of spectroscopic evidence, the less-mathematically minded physicist will probably prefer to deal with a concrete model to the deficiencies of which he is not blind.

It was the expressed wish of the author that the translation should not be too literal and that slight modifications should be left to the discretion of the translator. It is hoped that the exercise of this privilege has caused no change in sense while conferring freedom of idiom. I wish to take this opportunity of again thanking Professor Sommerfeld for his repeated assistance and courtesy. He has earned the gratitude of physicists throughout the world for carrying out so successfully the monumental task of giving a comprehensive and lucid exposition of modern atomic physics. He, himself, and his collaborators have contributed no mean share to these results, indeed, a great deal more than may be gathered from the author's own modest statements and references.

Acknowledgment must be made to Dr. E. Gwynne Jones (Beit Research Fellow of the Imperial College of Science and formerly Research Scholar of University College, Nottingham) for writing the section on hyper-fine structure, which has received the approval of the author. The addendum at the end of the text has been added by the translator.

The thanks of the translator are due to Mr. R. G. Horner, B.A., for kindly checking and correcting the proofs, a task to which he has devoted much time and care. The index was prepared with the help of Miss Barbara Hitchcock, B.Sc.

HENRY L. BROSE

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CHAPTER I

INTRODUCTORY FACTS

§ 1. Retrospect of the Development of Electrodynamics

IN the first half of the nineteenth century Electrodynamics consisted of a series of disconnected elementary laws. Formed analogously to Newton's Laws of Gravitation, they asserted the existence of direct action at a distance, which, starting from the seat of an electric charge or of magnetism and leaping over the intervening space was supposed to act at the seat of a second electric or magnetic charge.

Opposed to this there arose in the second half of the nineteenth century a view which followed the course of the continuously extended electromagnetic field from point to point and moment to moment; it was called the "Field Theory" in contradistinction to the "Theory of Action at a Distance." It was propounded by Faraday, worked out by Maxwell, and completed by Heinrich Hertz. According to this view the electromagnetic field is represented by the course, in space and time, of the electric and magnetic lines of force. Maxwell's equations teach us how electric and magnetic lines of force are linked with one another, how magnetic changes at any point of the field call up electrical forces, and how electric currents are surrounded by magnetic forces. The intervening medium, even if non-conducting, is supposed to have a certain transparency (permeability) and receptivity (dielectric capacity) towards magnetic and electric lines of force; hence at every point of space it influences the distribution of the electromagnetic field according to its constitution at that point.

The greatest triumph of this view occurred when Hertz succeeded in connecting *light*, the phenomenon of physical nature with which we are most familiar, with *electromagnetism*, which was at that time the most perplexing phenomenon. After Maxwell had already surmised that light was an alternating electromagnetic field (he succeeded in calculating the velocity of light from purely electrical measurements made by Kohlrausch), Hertz produced his "rays of electric force," which, just like light, are reflected, refracted, and brought to a focus by appropriate mirrors, and which are propagated in space with the velocity of light. The electric waves produced by Hertz had a wave-length of several metres. From them an almost unbroken chain of phenomena leads by way of heat rays and infra-red rays to the true light rays, whose

wave-lengths amount to only fractions of μ. The greatest link in this chain came later as a direct result of Hertz's experiments, namely, the waves of wireless telegraphy, whose wave-lengths have to be reckoned in kilometres. (Nauen sends out waves having a wave-length of 12 kilometres, or 7½ miles); the smallest and most delicate link is added at the other end of the chain, as we shall see, in the form of Röntgen rays, and the still shorter γ-rays which are of a similar nature; likewise the ultra-γ- or cosmic radiation (but see the closing paragraph of § 5).

Hertz died on 1st Jan., 1894, at the age of thirty-seven years. It would be natural to conclude that the later years of his short life and the work of his followers were occupied with the development of his wave experiments and of his theory of electromagnetic fields. But the last experimental paper by Hertz, " Concerning the Passage of Cathode Rays through Thin Metallic Layers " (1891), already pointed in a new direction.

The field theory had diverted attention from the origin of lines of force, and had chiefly served to illuminate their general course in a regular distribution of the field. The next question was to study the *singularities* of the field, the charges. The best conditions for doing so are offered by *cathode ray tubes*, which have a very high vacuum exceeding that of the so-called Geissler tubes (which were investigated by Plücker and Hittorf). Here we have electricity in a pure form, unadulterated by ordinary matter, and, in addition, moving in a straight line at an extremely high speed; cathode rays are corpuscular rays of negative electricity. It is true that Hertz as well as his eminent pupil Lenard first clung to the opposite view, namely, that the rays were undulatory in character; but Hertz had recognised the important value of the investigation of cathode rays for the future. Thus he had in this way helped personally in attracting workers from the field of physical knowledge just opened up by him towards pioneer work in a new field. In the sequel, the greatest interest became centred not in the propagation of the lines of force but in the charges, as the origin of these lines of force. The original theory of Maxwell which had been perfected by Hertz retained its significance for phenomena on a large scale, such as those of electrotechnics and wireless telegraphy, and gave an easy means of determining the mean values of the electrical *phase quantities* (i.e. quantities that define the state of the field). But to render possible deeper research leading to a knowledge of elementary phenomena a deepened view became necessary. Maxwell's Electrodynamics had to give way to Lorentz's Dynamics of the Electron; the theory of the continuous field became replaced by the discontinuous theory, that of the atomicity of electricity. So the theory of action at a distance and the theory of action through fields was succeeded by the atomistic view of electromagnetism, the theory of electrons.

§ 2. The Atomicity of Electricity. Ions and Electrons

The theory of the atomicity of matter has existed ever since there was a science of chemistry ; it is indispensable if the fundamental chemical law, that of multiple proportions, is to be intelligible. Nevertheless there has been no lack of opponents to atomicity. Goethe was one of them. It was repugnant to him to destroy the beautiful appearance of phenomena by dismembering matter and adding human elements. The eminent scientist and philosopher Ernst Mach regarded the " Atomic Hypothesis " as merely transitory. He favoured the description of events in terms of continuously distributed matter and continuously acting laws. The last opponent of atomic theory was the keen-witted author of works on Energetics, Wilhelm Ostwald (who has now been converted to a belief in atoms). Objections to the theory have died into silence in the face of its sweeping successes in all branches of physical knowledge. The perfect explanation of the Brownian molecular movements which confirms by ocular demonstration in the case of fluids the branch of atomic hypothesis concerned with the theory of heat has contributed much to this acceptance. No less impressive is the confirmation of the atomic structure of solid bodies which was given by Laue's discovery and which will be discussed in Chapter IV.

A necessary consequence of the atomicity of matter is the atomicity of electricity. This was stated simultaneously by Helmholtz and Stoney. Helmholtz remarked in his Faraday Lecture * of 1881, as a result of the laws of electrolysis which Faraday discovered and expressed numerically : " If we assume atoms of chemical elements, we cannot escape from drawing the further inference that electricity, too, positive as well as negative, is divided into definite elementary quanta that behave like atoms of electricity. Each ion,† as long as it is moving in the liquid, must remain associated with an electrical equivalent for each of its valency units."

Faraday's Law of Electrolysis actually states : *One and the same quantity of electricity, in discharging through various electrolytes, always sets free chemically equivalent quantities of the dissociated products.* In the case of univalent elements quantities are called chemically equivalent when they are in the ratio of their corresponding atomic weights, thus

1 grm. of H.	35·5 grms. of Cl.	107·9 grms. of Ag.

* Helmholtz, *Vorträge und Reden*, Vol. 2, p. 272. The parallel work of Stoney bears the title : " Physical Units of Nature," and appeared in February, 1881, in the Proceedings of the Dublin Phil. Soc., and in Vol. 11 of Phil. Mag.

† As is well known, ions are the " wandering " constituents of electrolytes during electrolysis, the cation being the positively charged constituent which moves in the direction of the positive current, " downwards," so to speak, the anion being the negatively charged constituent which moves " upwards."

To liberate these quantities, we always require, according to Faraday's Law, to make the same quantity of electricity pass through the electrolytes, namely, Faraday's constant:

$$F = 96{,}494 \text{ coulombs } * = 9649{\cdot}4 \text{ c.g.s. units.}$$

The constant ratios of weight (1 grm. H, 35·5 grms. Cl, and 107·9 grms. Ag) become intelligible to us on the supposition of the atomicity of matter: 1 grm. of H is composed of just as many atoms of H as 35·5 grms. of Cl contains Cl atoms, or 107·9 grms. of Ag contains Ag atoms. The equivalent charge F which is the same for each then becomes clear to us in the same way if we accept the atomicity of electricity: the equivalent charge F consists of just as many atoms of electricity or "elementary charges *e*," as 1 grm. of H contains H atoms, or 35·5 grms. of Cl contains Cl atoms, and so forth. There is associated with every univalent atom (or more generally with every univalent ion) an elementary charge *e*, whilst there are associated with every divalent atom or ion two elementary charges, and so forth for atoms of higher valency. Just as the atomicity of matter is a direct outcome of fundamental *chemical* facts, so the atomicity of electricity is a direct outcome of fundamental *electrochemical* facts.

For the sake of brevity of expression we shall define two further terms. Following Ostwald we shall take a *mol* to be that number of grammes which is given by the number expressing the molecular weight of the substance in question. Thus 1 mol of H_2O = 18 grms., and 1 mol of H_2 = 2 grms. (In the case of monatomic elements we use the term grammatom instead of mol, e.g. 1 grammatom of H = 1 grm.) Furthermore, **Loschmidt's number L** denotes the number of molecules (or atoms, respectively) contained in one mol (or grammatom) of the substance in question. For example, in the case of water, or dissociated hydrogen, this number will be defined by the equations

$$18 \text{ grms.} = Lm_{H_2O} \text{ and } 1 \text{ grm.} = Lm_H \text{ respectively,}$$

whereby m_H denotes the mass, measured in grammes, of a hydrogen atom, and m_{H_2O} denotes the mass, similarly measured, of a molecule of water. With regard to this term it must be mentioned that recently, in German physical literature, the expression "Avogadro's number" is often used in place of "Loschmidt's number," for the reason that it also plays a part in Avogadro's law of gases. But as Loschmidt was the first to determine this number successfully (by means of the kinetic theory of gases), it seems more in keeping with the facts to associate his name with it. The fact that he made his calculations for the cubic centimetre, and not for the mol, is a mere matter of form. If necessary the number L as defined above could be called "**Loschmidt's number per mol.**"

* A coulomb = $\frac{1}{10}$ of the so-called absolute unit of charge, that is the unit of charge defined in the c.g.s. system and measured electromagnetically.

The equivalent charge F contains, as we saw, just as many elementary charges e as 1 grm. of hydrogen contains atoms of mass m_H, or, as we may now say, the electrochemical equivalent contains L elementary charges e. We therefore write

$$9649{\cdot}4 \text{ c.g.s. units} = Le \qquad 1 \text{ grm.} = Lm_H$$

whence $$\frac{e}{m_H} = 9649{\cdot}4 \frac{\text{c.g.s. units}}{\text{grm.}} \qquad \frac{1 \text{ grm.}}{m_H} = L \quad . \quad . \quad (1)$$

The ratio of the charge to the mass is called the **specific charge** of the ion in question. In the case of the positive hydrogen ion, this specific charge is thus 9649·4, whereas for the divalent positive copper ion it is

$$\frac{2e}{m_{Cu}} = \frac{2 \cdot 9649{\cdot}4}{63{\cdot}6}$$

and for the univalent negative chlorine ion, it is

$$\frac{-e}{m_{Cl}} = -\frac{9649{\cdot}4}{35{\cdot}5} \text{ and so forth.}$$

Electrolysis shows, as Helmholtz pointed out, that positive as well as negative electricity is composed of elementary quanta $\pm e$. But there is a great difference between positive and negative electricity in a certain respect. We know positive electricity only as an ion, that is, associated indissolubly with ordinary matter: as we saw above, negative electricity also presents itself in electrolysis in the form of ions. But we also know the latter in its free state, dissociated from all ordinary matter, as detached electricity, so to speak. This is an all-important result of the researches on cathode rays, to which we have already referred in the preceding paragraph, and to which we shall again refer in the next.

The special position occupied by negative electricity, its occurrence as pure atoms of electricity, calls for a special name. Following the example of Stoney,* we shall call the negative atom of electricity the **electron.** On the other hand, we shall follow Rutherford in calling the smallest positive ion, namely the hydrogen ion, the **proton;** in spite of its being burdened with the mass of the hydrogen atom it plays the part of the **atom of positive electricity.**

In saying that the electron is not encumbered by ordinary matter, we do not imply that it is devoid of inertia. On the contrary, the mere presence of electric charges, or, generally, of energy of every kind, entails a certain mass effect. The mass which is associated with the electron in this way used to be called "electromagnetic" mass. This term is, however, as the newer developments of fundamental physical conceptions in the theory of relativity compel us to recognise, too narrow: not

* Cf. Trans. Dublin Phil. Soc., Vol. 4, 1891. In the mathematical development of the theory of electrons by H. A. Lorentz (*An Attempt at a Theory of Electrical and Optical Phenomena in Moving Bodies*, Leiden, 1895), the word electron does not occur: Lorentz retains the word ion in this essay.

only do electric charges produce a mass effect, but so does the cohesive energy that keeps the charge together and prevents it, in a way as yet unknown to us, from exploding. Therefore we nowadays prefer to speak outright of the *electronic mass* m, and to regard it as a fact presented by our experiments with cathode rays.

A great gap divides the electronic mass, as regards its magnitude, from the ordinary masses of atoms and ions. The electronic mass m is about 1800 times as small as the mass m_H of the lightest atom. Accordingly, the *specific charge of the electron*, the ratio of the elementary charge e to the electronic mass m, is in the same proportion greater than the specific charge of the hydrogen atom. From optical observations—measurements of spectral lines, to which we shall refer in Chapter II, and measurements of resolved spectral lines, to which we shall refer in Chapter VI—we have as the best value of this ratio according to our knowledge of the present time :

$$\frac{e}{m} = 1{\cdot}761 \,.\, 10^7 \quad . \quad . \quad . \quad . \quad (2)$$

Direct measurements, however, carried out with cathode rays, which are deflected by magnetic and electric fields (cf. § 3), give a somewhat greater value,* namely,

$$\frac{e}{m} = 1{\cdot}769 \,.\, 10^7 \quad . \quad . \quad . \quad . \quad (2a)$$

There are good reasons for assuming that (2) represents the correct value.†

The general course of the refraction of light in passing through transparent bodies (solids and gases), as calculated on Drude's Theory of Dispersion, gives us values of $\frac{e}{m}$ of the same order of magnitude. Now, we see electrons at work in the conduction of currents through metals, as also in radioactive processes, in the production of Röntgen rays (X-rays), in the photo-electric effect, and so forth. From this we conclude : *the electron is a universal element of structure of all matter.* Whether it is flowing along slowly in an electric current, or hastening through space at an extremely high rate as a cathode ray ; whether it is emitted in radioactive disruption or in a photo-electric process ; whether it is vibrating in our lamps (or, as we should nowadays prefer to express it, "jumping" in our lamps) ; or whether it effects the course of light in

* Cf. for this and the subsequent numerical data the meticulous discussion of all fundamental physical constants by R. T. Birge, Phys. Rev. Supplement, **1**, 1, 1929.

† Evidence in support of this view is given by the results of experiments which have been very carefully carried out by F. Kirchner in the physics department of Munich University. They are based on the direct measurement of the velocity of the cathode rays along the lines of a somewhat old method due to E. Wiechert ; these results have not yet been published, but they are known to give precisely the spectroscopic value of $\frac{e}{m}$.

telescopes, it is always the same physical unit, proving its identity by exhibiting the same charge and the same mass,* in particular by keeping the ratio of charge to mass constant.

If we now wish to form a picture of the electron in accordance with the foregoing statements, only scant material offers itself. An electron is, like every negative charge, essentially nothing more than a place at which the electric lines of force from all directions end. In the case of an electron at rest, these lines of forces are straight lines that come in uniformly from all directions. But the same picture holds, according to the ideas of the theory of relativity, for an electron moving in any way whatsoever, so long as the picture of the lines of force is regarded as being conceived by an observer moving with the electron, that is if the lines of force are drawn in a space that participates in the motion of the electron. In other cases, when the electron moves with regard

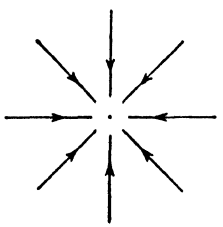


FIG. 1A.

Electron.

$$\frac{e}{m} = 1{\cdot}761 \,.\, 10^{7}$$
$$e = 1{\cdot}591 \,.\, 10^{-20}$$
$$m = 0{\cdot}903 \,.\, 10^{-27}$$

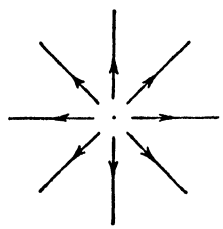


FIG. 1B.

Proton.

$$\frac{e}{m_H} = 9649$$
$$e = 1{\cdot}591 \,.\, 10^{-20}$$
$$m_H = 1{\cdot}649 \,.\, 10^{-24}$$
$$L = \frac{1}{m_H} = 0{\cdot}606 \,.\, 10^{24}.\dagger$$

to the observer who is mapping out its field, the electric lines of force would still, indeed, be straight lines, but would become compressed towards the central plane which is perpendicular to the direction of motion, and, moreover, would be accompanied by magnetic lines of force.

From the point of view of our present ideas, it is better to refrain from endeavouring to give the electron a definite volume or size. This could be calculated only on the assumption that the whole mass effect is electro-magnetic in origin, and this assumption is, on account of the

* The " same mass " is more correctly expressed by the " same rest mass," i.e. mass which is not moving with respect to the system of reference, cf. § 4, equation (2) of this chapter.

† Loschmidt's number often given in foreign books as number of mol. per c.c. at N.T.P. $= 2{\cdot}7 \,.\, 10^{19}$.

necessity for a cohesive energy (*vide* above), not justified. Moreover, we should be compelled in this case to make the arbitrary assumption that the electronic charge e occupies uniformly either the volume or the surface of a sphere, for which there is no support in our experience. Nevertheless it is worthy of remark that in whatever way the detailed calculation is carried out we arrive at a *sub-atomic* value for the extent of the electron ; its diameter comes out to about 10^5 times smaller than that of an ordinary atom.

The picture of the proton shows itself to be quite similar to that of the electron. As the lines of force start out from positive charges, they are to be furnished with arrows in the reverse direction to that for electrons ; they are likewise rectilinear and uniformly distributed, if we here also suppose the observer to be at rest relatively to the proton.

The extent of the proton is also of sub-atomic dimensions (of the size of the nucleus). It is often stated that the proton is considerably smaller than the electron ; but this assertion rests on the purely electromagnetic interpretation of mass, which we are disinclined to adopt here.

We have attached to our figures the characteristic values of the specific charge and also the values of the absolute charge and mass, and so have epitomised in them the properties of the electron and the proton. We shall report on the origin of these numerical values partly in the next chapter. Concerning the values of m_H and L the reader is referred to Note 1 on page 93 ; the value given above for m_H corresponds to a hydrogen atom whose atomic weight is imagined to be 1.

§ 3. Cathode Rays and Canal Rays

The cathode of a vacuum tube is, according to the terminology that we explained in connexion with the word cation (cf. note on p. 3), the electrode to which the positive current flows, that is from which the negative current emerges. The fact that the cathode rays start from the cathode is already an indication that we are dealing with a flow of negative electricity. In the case of a high vacuum and a sufficiently high potential difference, this flow does not follow the form of the tube as in the case of the ordinary Geissler tubes, but propagates itself rectilinearly from the cathode along the normals of the latter. Assuming the results of the decades of research on cathode rays ranging from Hittorf to J. J. Thomson and Lenard, we shall speak of **cathode ray particles,** or rather, of **cathode ray electrons.** These electrons owe their velocity to the potential gradient at the cathode, so that the kinetic energy of the electron is equal to the work that the drop in potential does on the electron. Inasmuch as the kinetic energy is proportional to the electronic mass m, and the amount of work is proportional to the electronic charge e, we see that the velocity v of the electron is determined by its specific charge $\frac{e}{m}$ and by the voltage drop of the vacuum

tube * V (volts multiplied by 10^8). The formula (which is nothing more than the law of the conservation of energy) is

$$\frac{mv^2}{2} = eV, \; v = \sqrt{\frac{2e}{m}V} \quad . \quad . \quad . \quad (1)$$

A good apparatus for studying cathode rays is a Wehnelt tube (potential difference 110 volts, pressure about 0·1 mm. of mercury, cathode carrying a spot of CaO, which, at a red heat, assists the emission

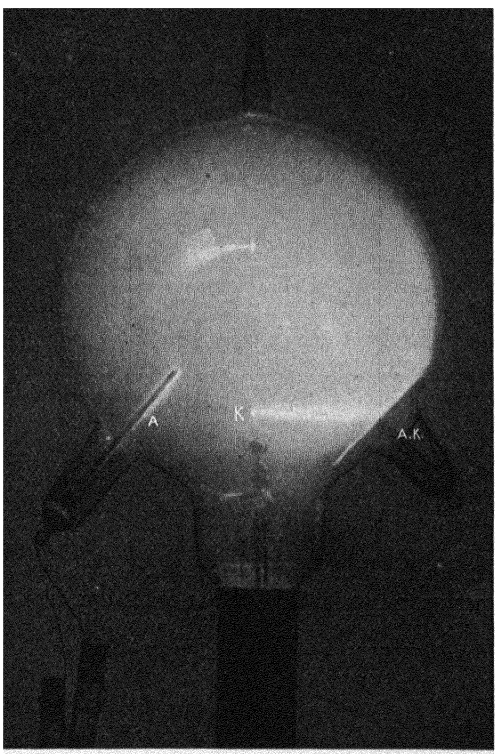


FIG. 2A.—Wehnelt tube. Rectilinear motion of electrons in the absence of external forces.

of electrons). The phenomena of illumination in the tube, which are very striking, are due only indirectly, as we must mention at the outset, to the cathode ray electrons, and arise from the impact of the latter with the remains of the gaseous content whose atoms are thus excited. By means of our tube we now confirm the following mechanical laws :—

1. *In the absence of external forces a body describes a straight line with*

* The potential difference expressed in volts is converted into absolute electromagnetic c.g.s. units by multiplying by 10^8.

constant velocity. Corresponding to this law we see in Fig. 2A how the beam of cathode rays are emitted perpendicularly to the cathode K, and disappear into the anti-cathode AK. (Above the beam of cathode rays we see in this and in the following picture a bright image that is formed by reflection from the glass sides.) The anti-cathode is not in general connected with the source of voltage, and is to be distinguished from the anode A. The fact that the beam of cathode rays diverges (becomes " scattered ") as its distance from its source increases, is due

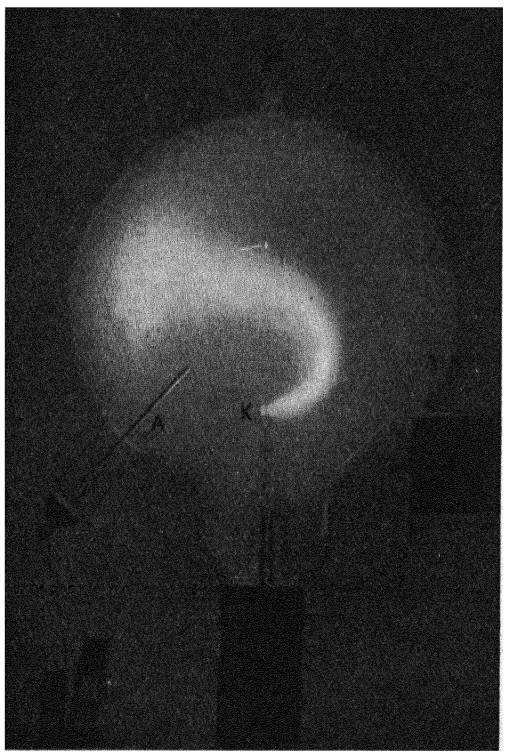


FIG. 2B.—Circular or spiral motion (as the case may be) of electrons in the magnetic field of a bar magnet MM.

to the influence of the remaining gas molecules on the paths of the electrons. The high value of the velocities of the electrons compared with the relatively small voltage of 110 volts is worthy of notice. From (1) it follows, that, in round figures,

$$v = 6 \cdot 10^8 \text{ cms. per sec.} = \tfrac{1}{30} c,$$

where $c = 3 \cdot 10^{10}$ cms. per sec. = velocity of light.

2. *Under the influence of a centripetal force, that is, one which is everywhere perpendicular to the orbit, a body describes a circle at a constant*

rate. The centripetal force is equal to the inertial resistance which is directed perpendicularly to the orbit and is called the "centrifugal force." We shall produce the centripetal force that is necessary for the experiment by a magnetic field, which arises from an ordinary bar-magnet MM. A magnetic field acts on moving charges ("current-elements") with a force that is perpendicular to the magnetic lines of force and to the direction of motion. In Fig. 2B the magnetic lines of force run from the back to the front, so that the centripetal force in question lies in the plane of the page. We see the beam of cathode rays become curved under its influence into a circle (or into a spiral, if the initial direction of the cathode rays and the direction of the magnetic field are not exactly perpendicular to one another: in our case we should then get a curve of variable curvature because the magnetic field is not homogeneous). It is pretty to see how the circle increases or decreases as the magnet moves away or approaches. Expressing this in a formula we find that if H denotes the intensity of the magnetic field, ρ the radius of the circle (more generally the radius of curvature of the curve), then

$$evH = m\frac{v^2}{\rho} \quad . \quad . \quad . \quad . \quad (2)$$

On the left is the centripetal force due to the magnetic field, on the right is the inertial resistance of the electron, or, expressed shortly, the centrifugal force. In this case, too, as we see, the ratio $\frac{e}{m}$ occurs as a determining factor. From (2) we get

$$v = \frac{e}{m}\rho H \quad . \quad . \quad . \quad . \quad . \quad (2a)$$

3. *In a homogeneous and parallel field of force, as, for example, is represented by gravity on the earth's surface, a body describes a parabola, the form of which depends on the value g of the acceleration in falling, or, more generally, on the acceleration in the field of force in question.* In our tube we generate the necessary field of force as an electric field by charging the anti-cathode negatively, as by connecting it with the cathode by hand. The field that results in this way is confined to the neighbourhood of the anti-cathode, and is tolerably homogeneous there. The cathode rays that previously disappeared at the anti-cathode are now bent backwards into a parabolic shape (cf. Fig. 2C, p. 12). (Above the anti-cathode there is a kind of dark space that somewhat disturbs the regularity of the parabola.) If F is the field intensity, then we get for the accelerative force that acts in this case,

$$g = \frac{e}{m}F \quad . \quad . \quad . \quad . \quad . \quad (3)$$

These and similar experiments clearly lead to determinations of $\frac{e}{m}$ by various methods. We may, for example, combine (1) and (2*a*),

eliminate v, and determinate $\frac{e}{m}$ from the three measurable quantities ρ, H, V. This value, when it was first discovered, led to *the discovery of the electron.* For as it was almost 2000 times greater than the value of $\frac{e}{m_H}$ that was derived from experiments in electrolysis, it pointed to the existence of a micro-mass which is almost 2000 times smaller than the mass of the hydrogen atom.

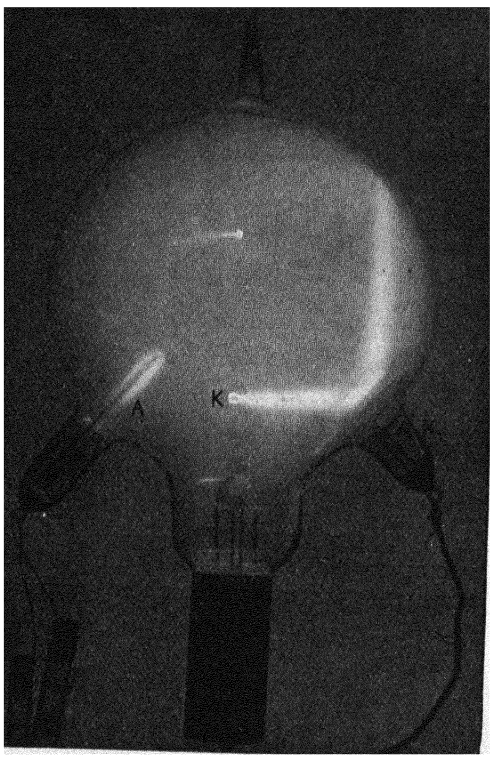


FIG. 2c. – Parabolic motion of electrons in a homogeneous electric field.

Certain results connected with the absorption of cathode rays are of particular interest for questions of atomic structure. Lenard was the first to lead the cathode rays out of their captivity in the tube by allowing them to enter into the air through extremely thin metal folia (so-called Lenard windows). Although they here also soon came to a dead stop owing to repeated obstruction by air molecules, they nevertheless clearly exhibited their corpuscular existence independently of the producing tube. Systematic experiments on absorption now showed that

the absorption, i.e. the stopping of an electron, depends solely on the *mass* of the atoms of the absorbing substance, not on its physical state or its chemical composition. On the other hand, according to the kinetic theory the mean sum (average) of the *cross-sections* of the atoms would be the decisive factor in the collisions and hence in the stoppage of a cathode ray. The comparison of the actual circumstances with those of the kinetic theory led Lenard to form the following picture of the structure of matter : Only a vanishingly small fraction of the space apparently occupied by matter is really impenetrable (at least for rapid cathode rays) ; the electrons can fly without obstruction through the whole intervening space. The impenetrable centres are called **dynamids** by Lenard.* They are regarded as electric fields of force, and exercise an attraction on the electrons, which are, however, no longer effective for great velocities at a moderate distance from the centres of force. In the case of small velocities the range of action of the attraction increases up to the extent of the range of action given by the kinetic theory of gases. Lenard has to set the number of dynamids per atom proportional to the mass of the atom, that is to the atomic weight, to get the law of absorption for rapid cathode rays.

The whole method of representation developed by Lenard as early as 1903 coincides strikingly with the nuclear theory that Rutherford built up in 1913 from a totally different set of facts (*vide* Chap. II, § 1). We need only replace **dynamid** by **nucleus,** and **number of dynamids per atom** by **nuclear charge,** to translate Lenard's results into the language now in use. In addition, the sub-atomic size of the dynamids, as calculated by Lenard, is in approximate agreement with the order of magnitude of the nuclei, as deduced by Rutherford. Proportionality of the number of dynamids with the mass of the atom then denotes proportionality of the nuclear charge with the atomic weight (cf. Chap. II, § 1). A difference which, however, is essential for the fruitfulness of the picture consists in the circumstance that, in the case of an element whose atomic number is Z (and which, in some cases, then has the atomic weight 2Z), Lenard assumes Z individual dynamids, generally separated in space, whereas Rutherford assumes a single nucleus carrying a charge Z.

The antithesis **electron** and **positive ion** is analogous to that of **cathode rays** and **canal rays.** The canal rays also obtain their velocity as a result of the potential drop at the cathode, but they run backwards, in the direction opposite to that of the cathode rays (Goldstein, 1886). They are thus oppositely charged to the particles of the cathode rays ; they are accordingly **positive rays.** To enable them to pursue their paths backwards from the cathode, the latter has to be pierced with holes (" canals "). The canal rays, like the cathode rays, follow rectilinear paths. They are likewise deflected by magnetic or electric fields, but in a direction opposite to that of cathode rays, corresponding

* Ann. d. Physik, **12,** 714 (1903).

to their reversed charge. Besides this, the deflection is considerably less than in the case of cathode rays. For if these deflection experiments are used to determine the specific charge of the particles in the canal rays, we find a value having the order of magnitude of the electrochemical equivalent, and indeed we get the exact value $\frac{e}{m_H}$, as given in § 2, Fig. 1B, in the case of canal rays of hydrogen, that is when the tube is filled with hydrogen ; we get a value 200 times as small in the case of canal rays of mercury (atomic weight of mercury = 200), that is when the tube contains mercury, and so forth. It may be mentioned that in the latter case, we also get multiples of this value, a fact that points to a multiple charge of the mercury atom (to the number of eight elementary quanta, according to J. J. Thomson). In the former case we observe in addition to the full equivalent charge, also half of this quantity, and this points to the formation of positively charged hydrogen molecules (mol-ions as contrasted with atom-ions).

Altogether, the conditions in the case of canal rays are not so typically simple and easy to grasp as in the case of cathode rays. This is due to the frequent transference of charges among the ions of the canal rays (W. Wien). They become neutralised after a short distance by taking up electrons, and become positively charged again through the loss of one or more electrons in subsequent collisions (sometimes they become negatively charged owing to the absorption of electrons). On the other hand, for this very reason the phenomena in the case of canal rays are much more manifold and instructive, inasmuch as the canal rays, as ions, possess the power of emitting light of their own (J. Stark). The luminescent phenomena of canal rays (cf. Chap. VI, the Stark effect) have furnished modern physics with invaluable material in just the province that concerns us here.

The contrary character possessed by ions and electrons manifests itself, too, in the velocities of canal rays and cathode rays. The relatively large mass of the ions of canal rays, for a constant voltage of the tube, assumes a much smaller velocity than the small mass of the electrons of cathode rays. The corresponding velocities are theoretically in the ratio of the square roots of the masses of the electrons and the ions, since equation (1) remains valid for velocities that are imparted to the ions of canal rays. In the case of cathode rays we get for a tension of 30,000 volts, for example, a velocity of 10^{10} cms. per sec. $= \frac{c}{3}$; in the case of canal rays we scarcely get beyond $2 \cdot 10^8$ cms. per sec. $= \frac{c}{150}$.

So far, in the case of both the ion and the electron, we have been concerned only with the measurement of the *specific* charge. On the other hand, we also mentioned the *absolute* value of the elementary charge e at the end of the preceding section as being an equal, invariable,

and universal quantity for ions and electrons. We must therefore complete our account by stating how the elementary charge itself may be determined. It is obvious that if we know the absolute charge then (by comparing it with the specific charge) we can also find the electronic mass m and the absolute mass of the hydrogen atom m_H, as well as the Loschmidt number $\frac{1}{m_H}$ and the mass of all other atoms. The values of m, m_H, and L found in this way are also noted at the end of the preceding section.

There are many ways of deriving the elementary charge e. The pioneer work in this question, as in others connected with electron theory, was done by Sir J. J. Thomson.* From our discussions about the theory of spectral lines we shall get a spectroscopic determination of e which promises to give us the most accurate value (cf. the final paragraph of Chap. VIII). At present, however, the surest road seems to be that which has been followed with particular success by Millikan.†

A macro-ion, that is a charged particle of matter composed of many atoms, preferably a drop of oil on account of its shape, is kept suspended by balancing an electric field against its weight, or it is allowed to drop slowly by altering the field or its own charge. By means of radiation from radioactive bodies or Röntgen rays (X-rays) the charge may be varied to the extent of one or several units of charge e. By noting the times taken to fall in the case of one and the same particle, we get the data necessary for calculating both the size of the particle and also its charge. The result of measurements repeated by Millikan over a span of several years is ‡

$$e = (4{\cdot}774 \pm {\cdot}004)10^{-10} \quad . \quad . \quad . \quad . \quad (4)$$

In contrast with this the spectroscopic determinations, which are, however, not yet complete (reflection of X-rays by an artificial grating), give a higher value, namely,

$$e = 4{\cdot}80 \,.\, 10^{-10} \quad . \quad . \quad . \quad . \quad (4a)$$

In (4) and (4a) the elementary charge is given in so-called **electrostatic units** (E.S.U.). We may express its value in **electromagnetic units** (E.M.U.), which are usual in the case of the specific charge, by dividing the above value by $c = 3.10^{10}$: §

$$e = (1{\cdot}591 \pm {\cdot}001)10^{-20} \quad \text{E.M.U.} \quad . \quad . \quad (5)$$

This was the value noted at the end of the preceding section.

* It must be mentioned, however, that the first value for e was obtained by J. S. Townsend in the Cavendish Laboratory. See in this connexion A. A. Millikan's account in his book, *The Electron.—Transl.*

† Phil. Mag. (6), **34**, 1 (1917).

‡ Birge (*loc. cit.*) obtains from Millikan's observations the value

$$e = (4{\cdot}768 \pm 0{\cdot}005)10^{-10}.$$

§ The exact value of c is 2·99796 ± 0·00004.

§ 4. α- and β-rays

Not only are canal rays and cathode rays produced artificially, but they also occur naturally, being emitted during the disintegration of radio-active elements. **The positively charged α-rays correspond to the canal rays, and the negatively charged β-rays correspond to the cathode rays.** These natural corpuscular rays are much more violent and tempestuous than those produced artificially. In this way they testify directly to the immense stores of energy available in the interior of the atom, which cannot even be approached by the energy of the particles produced in the best modern X-ray tubes.

The velocity of the α-rays of radium C amounts to $2 \cdot 10^9$ cms. per sec. It is about ten times as great as the velocity attained by canal rays. It follows from equation (1) of the preceding section that the energy that is necessary to produce this ten times greater velocity is 100 times greater than, or, if we take into account the carriers of the α-rays (*vide* below), even 400 times greater than the canal rays of hydrogen. Hence, whereas we work a canal ray tube by means of a potential difference of 30,000 volts, i.e. 30 kilo-volts (KV), we should require a voltage of about 12,000 KV to produce the energy of α-rays. A comparison of cathode rays with β-rays gives similar results. We may produce artificial cathode rays having a velocity ranging from $\frac{c}{3}$ to $\frac{c}{2}$, whereas natural β-rays are known whose velocities differ by only 1 per cent. and less from c. Since, as we shall see later, the velocity of light, c, represents an unsurpassable limit of velocity for all material particles, a limit which may be approximated to only when the energy applied is increased without limits, we see that to a velocity which approaches to within 1 per cent. of c, there corresponds a voltage of the same order of magnitude as was just given for α-rays.

For cases in which the velocities of the β-rays approximate so closely to the velocity of light, it is clearly convenient to express these velocities by giving their ratio to c instead of giving their absolute values v in cms. per second. This ratio, which is always a proper fraction, is usually denoted by the letter β, thus :

$$\beta = \frac{v}{c}, \quad 0 < \beta < 1 \quad . \quad . \quad . \quad . \quad (1)$$

From experiments on the deflection of α- and β-rays the specific charge has been found to be *half* the value of the *equivalent charge* $\frac{e}{m_H}$ in the case of α-rays, and considerably greater in the case of β-rays, namely, of the *order* of *magnitude* of the *specific charge of the electron*, $\frac{e}{m}$. The latter discovery confirms our above statement that β-rays are particularly rapid cathode rays. But the former discovery confronted

physicists with a difficult choice from which experiments on deflection offered an escape only after the effect of each single α-particle could be successfully demonstrated, that is, after a means of counting α-particles had been discovered. A decision had to be pronounced in favour of one of the three following possibilities, all of which were compatible with the value of the specific charge of the α-ray particle :—

1. $\frac{e}{m_{H_2}}$, i.e. the α-particles, are singly charged hydrogen molecules (that is molecules, each of which carry a unit charge).

2. $\frac{e}{m_x}$, i.e. the α-particles are singly charged atoms of an element x, hitherto unknown, and having the atomic weight 2.

3. $\frac{2e}{m_{He}}$, i.e. the α-particles are doubly charged helium atoms (atomic weight of He is 4·00).

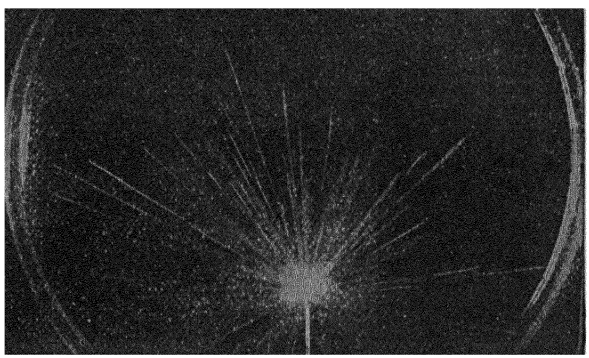


FIG. 3A.—Wilson-photograph of α-particles starting out from the end of a wire coated with radioactive material.

The experimental researches mentioned have demonstrated the truth of the third suggestion. This means that the *radioactive elements are able to produce from within themselves doubly charged positive helium atoms.* By proving the presence of lines of the He spectrum physicists succeeded in confirming this conclusion by direct observation.

In consequence of this we now understand the difference between the general properties of α- and β-rays. On account of their great mass ($4m_H$), the α-rays pursue their paths with great persistency. They shatter the obstacles which they encounter in the form of air molecules. The latter in this way become ionised, that is, they become split up into positively and negatively charged ions. And, indeed, the α-rays in their passage through atmospheric air form several thousand ions in every millimeter of their paths. The β-rays, on the other hand, being of extremely small mass, are much more easily deflected from their

paths. They exert a comparatively small influence on the air molecules with which they come into contact and form ions only now and then (5 or 10 per mm. according to their velocities).

These properties of α- and β-rays were exhibited in a striking way by some beautiful photographs of C. T. R. Wilson,* which have often been reproduced and which we must consider here also. His method consisted in bringing a radio-active substance into the vicinity of a sealed vessel which contained super-saturated water vapour ; by this means, α- and β-rays were introduced into the closed chamber. The gaseous ions which are formed by these rays serve, just as in the case of the gaseous ions or particles of dust that are instrumental in the production of rain in the atmosphere, as nuclei about which the super-saturated water vapour may condense when the moist air is suddenly allowed to expand. The drops of water which thus form and collect rapidly are what we see on the photographs.

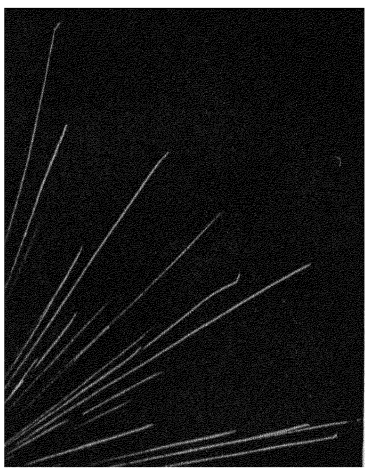


FIG. 3B.—Wilson-photograph of α-particles : large mass, small deviation, strong ionisation. At the ends of several tracks hooks are clearly visible.

The path of an α-particle is characterised on the plates as a dense, apparently continuous, mark (indicative of strong ionisation), but, in reality, it consists of individual drops of condensed vapour. In general, its course is a straight line (due to its great mass). Fig. 3A shows a sheaf of α-rays which start out from the end of a wire which has been made radioactive. Fig. 3B was produced by α-rays that originate at a point of convergence outside the picture. Several of them show, towards the ends of their paths, where their speeds have already been much reduced, pronounced hooks (sudden bends). We here call particular attention to this apparently subsidiary phenomenon for the reason that, as we shall see later (Chap. II, § 2), far-reaching consequences arise through it.

On the other hand, the path of a β-particle is deflected much more often and much more easily (on account of its small mass), and is punctuated only rarely with drops of water vapour, as is manifest on the photographic negative (this indicates feeble ionisation). In Fig. 4 we see in particular, besides diffusely scattered drops of water, the paths of

* The most recent and most complete pictures are given in Proc. Roy. Soc. **104, 1** and 192 (1923).

two such β-rays, of which one is strongly curved several times. In Fig. 5, we see, in addition to the thick (highly magnified) path of an α-particle (with a pronounced hook towards the end), several traces of the paths of β-rays.

To shed further light on the nature of β-rays we shall enlist the aid of another scientific document, one of the deflection-pictures obtained in the famous experiments on β-rays by Kaufmann : * it is here reproduced about six times magnified. The sheaf of β-rays emitted by a radium salt and singled out by means of a series of fine apertures is exposed to the simultaneous action of a magnetic and an electric field. The lines of force of both fields are parallel to one another and to the photographic plate. The electric lines of force divert the β-ray electrons from their ordinary paths, to the right in our figure, to the left when the field is reversed by a commutator. The magnetic lines of force cause a deflection at right angles to themselves ; in Fig. 6 this is upwards. Both deflections depend on the velocity. The greater the velocity, the smaller the deflection. For each velocity of the β-electron, therefore, a different " deflected point " or, if we also reverse the field each time, a different deflected point-pair will be recorded on the plate to the right and left. Now since this beam of β-rays may contain all possible velocities reaching almost to the velocity of light, a continuous section of line marked by the points of deflection will be produced, or, rather, two branches of a curve are produced that converge towards the point of departure of the undeflected beam. The latter path is also recorded on the plate, thanks to the photographic action of the γ-rays which cannot be deflected (cf. § 5). From formulæ (2) and (3) of the preceding section we can easily verify that the branches of the curve would have to be two parabolas that touch, having a common vertical tangent at



FIG. 4.—Wilson-photograph of β-particles : small mass, large deviation, weak ionisation.

* W. Kaufmann performed these experiments in the period 1901-1906 : a résumé of them is given in Ann. d. Phys., **19**, 487 (1906).

the undeflected point if the electronic mass m were constant, that is, the same for all velocities. As an experimental fact the two branches do not touch (cf. the tangents t and t' which have been sketched into Fig. 6), but run into one another at a certain angle. From this it is to

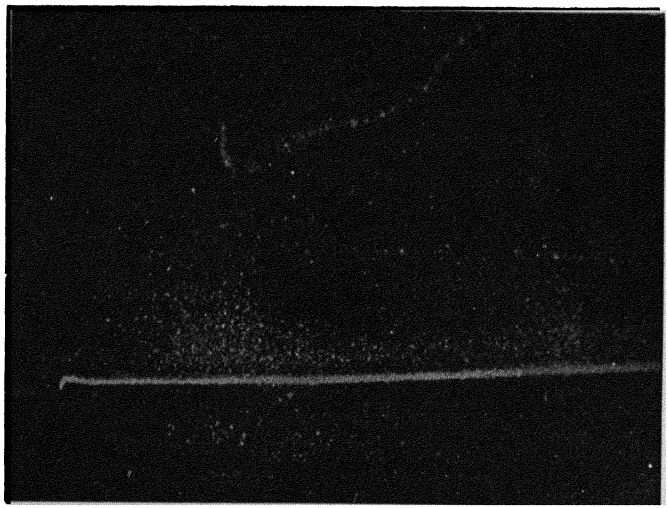


FIG. 5.—Wilson-photograph of an α-particle and a β-particle taken together. At the end of the track of the α-particle is a distinct hook.

be inferred that *the electronic mass depends on the velocity and that it increases beyond all limits as it (the velocity of the electron) approaches that of light.*

This result excited great astonishment, as is easy to understand, for it shattered the time-honoured dogma that mass is constant. But Kaufmann wished to read still more from his negatives. He wished to learn from them according to what law the mass of the electron alters with the velocity. In this connexion there were two opposing theories which led to different forms for this law, namely, the older theory of the absolute ether (the original theory of Lorentz, elaborated in particular by Abraham for the questions here under consideration), and its younger rival, the theory of the relativity of motions (founded by Einstein). The latter theory gives rise to a particularly simple form of the law governing the change of mass with motion, namely to the formula :

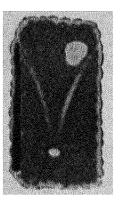


FIG. 6.—Kaufmann-photograph of deflected β-rays. The electric and magnetic fields are parallel to one another and to the photographic plate.

$$m = \frac{m_0}{\sqrt{1 - \beta^2}} \quad . \quad . \quad . \quad . \quad (2)$$

In it β is the velocity, as explained in equation (1), expressed in terms of the velocity of light c; m_0 is the "rest" mass corresponding to the velocity $\beta = 0$; m is the mass of the moving electron. The theory of relativity asserts that this formula is true not only for the electronic mass m, but also for any arbitrary mass of matter. This means that *every arbitrary mass must increase as β increases and must become infinitely great when $\beta = 1$*. From this the thesis, stated right at the beginning of this section, that the velocity of light represents for all velocities of material bodies a limit that cannot be exceeded, i.e. that the velocity of light can only be approached asymptotically but never exceeded, would already follow as a natural consequence.

It can easily be grasped from this that the deflection experiments of β-rays were regarded for a long time as the *experimentum crucis* which was to decide for or against the doctrine of the relativity of motions, and that they were thus to determine our fundamental views of space, time, motion, and the ether. So far as Kaufmann's experiments are concerned, it has been proved that they were not sufficiently accurate to give a decisive answer. Later experiments have established more and more definitely the correctness of the relativistic formula for mass (2). In our spectroscopic discussions later we shall likewise arrive at a confirmation of this formula by a method that far exceeds all others in accuracy (see the final section of Chap. VIII).

We might well close our brief survey of corpuscular rays here, were it not that we have still to discuss several general questions dealing with the nature of electricity. Are we to regard electricity as *unitary* or *dualistic?* Is it made of matter or of energy, of substance or of force?

The question as to whether it is of one kind or of two kinds was proposed long ago particularly with reference to Voltaic currents. Does only one type of electricity or do two contrary types, move (in opposite directions) along a conducting wire? The controversy remained unfruitful for a long time. It was only when R. C. Tolman * used the most highly refined methods of modern experimental technique that the question was settled. We may now assert that what flows in a conducting wire is negative electricity; every conduction current in metals is a current of electrons. In this domain our view is *unitary*.

In the realm of atomic physics, however, we are inclined to take the dualistic view. A positive charge signifies more than the absence of a negative charge. *Positive electricity is always associated with atomic masses.* We have thus to deal with two types of electricity that differ not only in sign but also in nature. They are represented by the electron and the proton.

There is no reason why we should not claim these two representatives as *negative* and *positive electrons*, respectively. Just as all negative electricity consists of the ordinary negative electrons, so all matter, according to the old hypothesis of Prout and the newest results of

* Cf., for example, Phys. Rev., **21**, 525 (1923).

Aston (cf. Chap. III, § 2) resolves into an aggregate of protons and electrons. Hence, as the fundamental elementary constituent of matter and of positive electricity, the positive hydrogen ion deserves the name of positive electron. In using the term " positive and negative electron," we have already adopted the dualistic view, even if not the dualism of two elements of a like type, but of two that differ radically in respect of mass.

In the following respect, too, there is a difference of type between negative and positive electricity. We can picture an atom (or a body) as highly charged negatively as we like, that is, we can add to it any number of negative electrons. But we can increase the positive charge only to a certain maximum amount so long as we do not considerably alter the mass. For we can abstract from the atom only just as many electrons as it possesses from the outset. In the case of the He-atom, as we shall see, this maximum limit is already reached when it has two positive charges, in the case of the H-ion when it has only one. A further increase in the positive charge could be effected only by simultaneously increasing the mass, that is, by adding positively charged matter.

This really furnishes us at the same time with the answer to the second question, as to whether we are to imagine electricity as a substance. To us nowadays negative electricity certainly denotes a substance. It is one of two universal and fundamental substances of which positively charged matter is the other ; both are equally entitled to being called such. If we regard an unalterable constitution as the characteristic of substance, then the charge (positive as well as negative) is more truly a substance than matter (electronic mass or ordinary mass). As a matter of fact we saw, as an inference from Kaufmann's experiments, that every mass varies according to its state of motion at the time under consideration (more correctly, according to the state of motion relative to the observer in question). In the case of the theory of relativity, too, no change in the electric charge enters into question. *In consequence of its absolute immutability the* **charge,** *in contradistinction to the mass, proves itself to be* **true substance.** *The charge and the mass are hereby indissolubly associated with one another, the negative charge with the electronic mass, the positive charge with the hydrogen mass.*

§ 5. Röntgen Rays and γ-rays

Röntgen's discovery was made in the year 1895. He was working with a highly evacuated cathode ray tube and observed the presence of penetrating rays that started out from the part of the tube at which the cathode rays struck the glass wall. These rays propagate themselves in all directions in straight lines from their source and are not deflected by a magnet.* For this reason Röntgen himself had looked on his "X-rays"

* The older developments of the work with which we are concerned in this section have been collected together by R. Pohl, *Die Physik der Röntgenstrahlen,* Braunschweig, 1912 (Sammlung Wissenschaft).

as wave-radiation. At first it remained undetermined whether they were longitudinal or transverse in character. As we know, improvements in the construction of X-ray tubes have brought it about that the X-rays are no longer produced at the glass wall but at an *anti-cathode* placed in the path of the beam of cathode rays : it is found preferable to make the anti-cathode of a metal with a high melting-point (e.g. platinum, tungsten, molybdenum, etc.). The cathode rays that strike it are thus brought to rest. By giving the cathode the shape of a soup-plate the focal point of the beam of cathode rays is made as small as possible.

The question whether the rays were longitudinal or transverse was decided by Barkla ten years after Röntgen's discovery. Even in the original researches of Röntgen it had been ascertained that all bodies, especially metals, on which X-rays impinge, serve as sources of new (" secondary ") X-rays. In the same way *secondary* X-rays generate *tertiary* X-rays. Now, Barkla discovered that *primary* X-rays are *partially polarised*, *secondary* X-rays are *wholly polarised* in certain directions. He succeeded in proving this with the help of tertiary X-rays, that is with the help of the secondary rays produced by secondary rays. For reasons to be given later, Barkla used as the generator of secondary rays not metals, but substances that are composed only of light atoms (charcoal, paraffin, paper). We must parenthetically mention another product of the action of impinging X-rays, namely, *secondary cathode rays*, which were discovered in 1900 by Dorn. They occur simultaneously with secondary X-rays, and are similar in velocity to the primary cathode rays that produced these X-rays.

Polarisation signifies that a ray favours a certain plane passing through it more than the one perpendicular to this plane. In the case of longitudinal vibrations, that is, vibrations that occur in the direction of the ray, there is symmetry about the ray and no such preference can be imagined. Longitudinal radiation must therefore be unpolarised. In the case of transversal vibrations, however, a favoured plane is determined by the direction of vibration and the direction of the ray. It is only when no direction of vibration is favoured that a ray composed of transverse vibrations can be unpolarised. We here interpret the direction of vibration not as being the direction of a motion of matter, but only of the electric force which participates in the wave-radiation. With this electric force is associated a perpendicular magnetic force.

Let us first discuss in a general sense the production of electromagnetic waves. In doing so, we shall adopt the standpoint of classical electrodynamics and of the theory of electrons. The fact that the newest developments have led to the partial rejection of this view is not to disturb us for the present.

A charge e which moves non-uniformly radiates energy, for it generates an electromagnetic field which propagates itself with the velocity of light. (A charge moving with uniform motion, such as a

cathode ray particle, carries its electromagnetic field along with it, and hence does not radiate.) Consequently the intensity of the radiated field is in general proportional to the acceleration * $\dot{\mathbf{v}}$ of the charge ; in particular, in the direction r = OP (cf. Fig. 7, in which O is the position of the charge, P that of the observer, briefly called the reference point (*Aufpunkt*), it is proportional to the component of acceleration $\dot{\mathbf{v}}_n$, which lies in the plane through $\dot{\mathbf{v}}$ and r, and which is perpendicular to r.

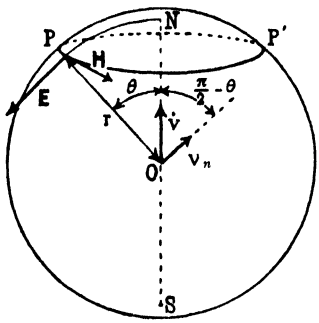


FIG. 7.—The field, according to classical electrodynamics, of a charge situated at O moving non-uniformly with acceleration $\dot{\mathbf{v}}$.

We describe a sphere through P, about O as centre, with the radius r, and mark as its north and south poles N and S, the two points at which the acceleration vector, when produced, meets the sphere. Let us fix the position of P on the sphere by means of the angle θ (complement of the geographical latitude). Then

$$\dot{\mathbf{v}}_n = \dot{v} \sin \theta.$$

The electric force lies in the meridian plane ONP, the magnetic force is the tangent to the small circle PP'. These forces are of equal magnitude if, as is natural, we measure $\mathbf{E}$ in the electric (" electrostatic ") system and $\mathbf{H}$ in the magnetic (" electromagnetic ") system, namely,

$$\mathbf{E} = \mathbf{H} = \frac{e\dot{\mathbf{v}}_n}{c^2 r} \quad . \quad . \quad . \quad . \quad (1)$$

(the charge e is measured in electrostatic units, just like $\mathbf{E}$). The dependence of these quantities on r, as expressed in the equation, may easily be seen *a priori*. During the process of emission of radiation, the same flux of energy passes through each spherical shell. Since the surface of each increases proportionately to r^2, the specific flux of energy $\mathbf{S}$, the so-called Poynting vector, must decrease as r^2 increases. But, if we disregard the factor $\frac{c}{4\pi}$ which depends on the system of measurement, $\mathbf{S}$ is equal to the product of $\mathbf{E}$ and $\mathbf{H}$ (at least, when $\mathbf{E}$ and $\mathbf{H}$ are perpendicular to one another) ; thus in our case :

$$\mathbf{S} = \frac{c}{4\pi}\mathbf{E}\mathbf{H} = \frac{e^2\dot{\mathbf{v}}^2}{4\pi c^3 r^2} = \frac{e^2\dot{v}^2}{4\pi c^3 r^2} \cdot \sin^2\theta \quad . \quad . \quad (2)$$

* Following Newton, we indicate the increase with respect to time by a dot thus :

$$\dot{\mathbf{v}} = \frac{d\mathbf{v}}{dt};$$

in the case here considered in which the velocity is supposed to have a constant direction, v denotes the value of $\dot{\mathbf{v}}$ when the direction is disregarded.

From this (by integrating over the surface of the sphere) we get for the total flux of energy:

$$\mathbf{S} = \frac{2}{3}\frac{e^2\dot{v}^2}{c^3} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Our representation (1) of the field is a necessary consequence of the established principles of electrodynamics. It shows the *transversal character of the field* (**E** and **H** are perpendicular to r, that is, to the direction of the ray **S**). In addition, it shows that *in the longitudinal direction, that is, in the direction of the acceleration* $\dot{\mathbf{v}}$, *the emission of radiation becomes zero* ($\sin\theta = 0$). This fact is used practically in wireless telegraphy: in the direction of the antenna (that is, of the alternating current, corresponding to our $\dot{\mathbf{v}}$) the emission is zero: it is a maximum in the direction at right angles to the antenna. The position of **H**, too, corresponds to the well-known circumstances that attend the passage of alternating currents through a wire: the lines of magnetic force are circles around the wire (corresponding to our small circle PP′ in Fig. 7).

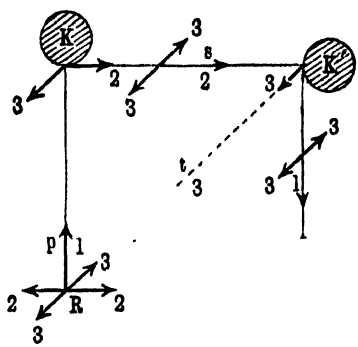


Fig. 8.—Transversal nature of Röntgen rays. Unpolarised rays vibrating in the directions 2 and 3 are emitted by the tube at R. The secondary rays from K in the direction 2, vibrate in the direction 3 only. The tertiary rays from K′ in the direction 1, also vibrate in the direction 3 only, while the intensity in the direction 3 from K′ vanishes altogether.

After these preliminary remarks, we have now to imagine secondary X-rays to be produced in the following circumstances: Every body, whether solid, liquid, or gaseous, is built up of electrons and positively charged matter. In Fig. 8, let 1 be the direction of the primary beam from R (Röntgen, or X-ray, bulb), to K (the scattering body). We assume that at the outset the primary ray is unpolarised. Let us then resolve the electric force, as shown at the bottom of the figure on the left, along the two perpendicular directions 2 and 3, which are perpendicular to 1; we get two equally intense component forces along 2 and 3. When the component 3 has arrived at the surface of K, it sets the electrons in motion along the direction 3. These electrons thus become the source of a new radiation. This radiation gives us, as we saw, no intensity along 3, but maximum radiation in the direction 2. In the same way the component force 2 sets the electrons of K into motion. The radiation thus produced gives no intensity in the direction (2), but maximum radiation in the direction 3. From this it follows that the secondary radiations s, which are propagated in the direction 2, are

derived from electronic vibrations in the direction 3 and likewise vibrate in this direction. *They are thus completely polarised.* (The same is true of the secondary rays that are propagated in the direction of 3 and which vibrate in the direction 2 ; and it is true of all secondary rays that are propagated at right angles to the primary direction 1. The secondary rays that are obliquely inclined to 1 are partially polarised.)

But how can we recognise the complete polarisation of the secondary ray *s*, seeing that we have no Nicol at our disposal for X-rays ? By repeating the process, we place a second scattering body K′ in the path of the secondary ray *s* and measure the tertiary X-rays. These are produced by electronic vibrations that take place exclusively in the direction 3. They emit maximum radiation in the direction K′1, and none at all in the direction K′3. *The perpendicular set of lines pst in the directions* 1, 2, 3 *proves by the vanishing of the intensity of the tertiary rays* K′3 *both the complete polarisation of the secondary rays and the transversal nature of the primary rays.*

In Barkla's experiments the scattering bodies K and K′ consisted of charcoal. The intensity of the tertiary rays was measured electroscopically by their ionising action on the air space of a condenser (ionisation chamber), which is very sensitive towards X-rays and which had already been perfected in the original experiments of Röntgen. Provided that the primary radiation was fully unpolarised, K2 and K3 would have to show the same degree of intensity under similar conditions of measurement. In reality, as Barkla, and later Bassler, found, the secondary rays already show differences of intensity with direction. *They thus indicate a partial polarisation of the primary radiation.*

The latter circumstance leads us still more deeply into the process of production of the primary X-rays. In Fig. 9 let K be the plate-shaped cathode and AA the anti-cathode. When the cathode rays strike the anti-cathode, they are arrested ; their average direction of retardation is represented in the figure by the arrow $\dot{\mathbf{v}}$. This change of velocity causes radiation to be produced, which is the shorter in wave-length and the more intense, the greater the change of velocity. *This radiation is to be regarded as the reason* (or better, *a reason*) *for the occurrence of X-rays.* The resultant field is described by the earlier Fig. 7. In it the direction SN is now represented by the direction KA of the cathode rays. The electric force lies in the meridian planes, that is, now, in the plane KAR through the cathode ray and the X-ray. The process of formation of X-rays thus points directly at a favoured plane for the electric force. *The observations* (of Barkla and others) *have confirmed this position of the plane of polarisation.*

According to our argument we should actually expect a complete polarisation of the primary X-rays if the retardation were to occur in one definite direction, namely, in that of the arrow $\dot{\mathbf{v}}$ in Fig. 9. But this

is certainly not the case. Rather there are changes in the direction of the impinging cathode rays while they are being brought to rest by the material of the anti-cathode. Through them the direction of the arrow **v** and hence also of the direction of polarisation becomes blurred. But there is a still deeper reason for the incompleteness of the polarisation.

Barkla has discovered that every material substance when bombarded with cathode rays emits a radiation characteristic of the substance (called "**characteristic radiation**" *Eigenstrahlung*). Whereas we may compare the radiation considered just above ("**impulse radiation**" *Bremsstrahlung*) with the forced vibrations that occur in mechanics—as a necessary consequence of the sudden stoppage—this characteristic vibration corresponds to the free or natural vibrations of mechanics. Through the agency of the cathode rays the electrons of the material of the anti-cathode are thrown out of their positions of rest (or out of their stable orbits) and tend to return to these. In doing so they emit the frequencies natural to, or characteristic of, the material of which the anti-cathode is composed. This circumstance gives the process a resemblance to optical fluorescence, in which, likewise, a frequency of vibration occurs, which is characteristic of the fluorescent material but differs from the frequency of the incident radiation. The phenomenon occurs freely, being excited by the cathode ray but, especially in regard to direction, is not subject to conditions. *Thus the characteristic radiation is unpolarised, and the total radiation (impulse radiation + characteristic radiation) is only partially polarised.*

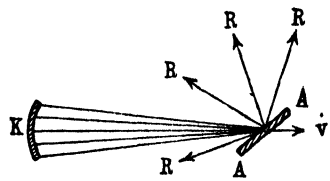


FIG. 9.—Diagrammatic representation of the retardation experienced in the anti-cathode A by the cathode rays coming from the cathode K. The Röntgen rays are emitted in all directions.

As a result of the polarisation experiments above discussed, there is no doubt that the radiation of X-rays is of the transverse wave type.

Nowadays we speak of Röntgen light or X-ray light and distinguish it from visible light only by its greater hardness (penetrative power). This general character of Röntgen light is shown very strikingly in a photograph, here reproduced in Fig. 10, by C. T. R. Wilson. In contrast with the former photographs (Figs. 3, 4, 5), we see here no rectilinear or curved corpuscular paths, but a thick beam of rays that traverse the space of the condensation chamber in a horizontal direction. This beam of rays is made visible to us photographically not *directly* but *indirectly* by the secondary cathode rays (see p. 23), that is, by the electrons that have been set free from air molecules and molecules of water vapour by the X-rays, and which fly out laterally and irregularly, and cause the water vapour to condense.

The *hardness* of Röntgen light represents what we usually call *colour* in the case of ordinary light. Great hardness denotes great frequency of vibration or small wave-length. Moderate hardness or greater " softness " denotes smaller frequency and greater wave-length. This terminology introduces no difficulty in the case of characteristic radiation. We called this free vibration and are tempted to ascribe to it a period (or a series of periods) of vibration characteristic of the material of the anti-cathode. This we may actually do, for experimental researches have fully confirmed this conclusion. The characteristic radiation is not only " characteristic " but also " homogeneous." It consists of a few sharply defined kinds of vibration, each of which corresponds to a homogeneous monochromatic type of light. When we have become acquainted with the spectral resolution of X-rays (Chap. IV), we shall see that the characteristic radiation assumes the form of a line-spectrum.

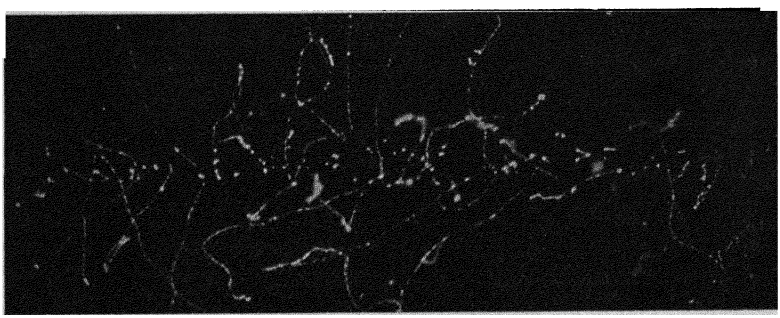


FIG. 10.—Wilson-photograph of secondary cathode rays produced in water vapour by a primary beam of Röntgen light passing from right to left.

To supplement our earlier statements we must add the following: As the atomic weight of the body emitting the characteristic radiation increases, so does the hardness and the intensity of the characteristic radiation. Anti-cathodes of heavy metals produce copious and hard characteristic radiation, whereas charcoal, paraffin, etc., produce only scant characteristic radiation, which is soft, being absorbed after traversing only a few centimetres of ordinary atmospheric air, and which, therefore, hardly deserves the name of Röntgen radiation. Hence we understand why Barkla, to prevent being disturbed by the characteristic radiation of the scattering body, had to use bodies of small atomic weight for his experiments on polarisation. On the other hand, makers of X-ray appliances had to resort to heavy metals for their anti-cathodes so as to make use of characteristic vibration as well as the impulse radiation.

Our explanation of hardness does not seem to be so readily applicable to the case of impulse radiation. The process of impulse radiation is

a single event ; that is to say, it is non-periodic. Consequently the conceptions of period of oscillation and wave-length here seem out of place. Now, it is a simple mathematical truth that a single unperiodic occurrence may be represented as composed of a number of purely periodic occurrences superposed on each other. For example, the crack of a gun may be represented by a continuous series of musical tones, if these are chosen of the proper intensity and phase (Fourier's integral representation of an arbitrary function). The physical realisation of this mathematical mode of representation is called the *spectrum* of the occurrence in question. From the moment that the spectrum of such an event can be specified, the spectral picture will be preferred on account of its fixed quantitative character. This moment had arrived, in the case of X-rays, when Laue made his discovery. Since then, we speak of the spectrum, wave-length, and frequency of vibration in the case of impulse radiation too. Accordingly the spectrum is not, as in the case of the characteristic radiation, a line-spectrum but a *continuous spectrum*. It resembles the spectrum of white light, and is therefore occasionally called the *white Röntgen spectrum*. The difference between the white Röntgen spectrum and that of the white light of the sun, for example, lies only in the order of magnitude of the dominant region of wave-lengths, of the region of maximum intensity. The mean wave-length of this region is in the case of X-ray spectra 10,000 times smaller than in that of the solar spectrum.

As we see, the hardness of the characteristic radiation depends on the atomic weight of the emissive material of the anti-cathode. On the other hand, the hardness of *impulse radiation depends essentially on the voltage of the X-ray bulb*, or on what is the same, according to equation (1) of § 3, the velocity of the impinging cathode rays ; as is well known, the hardness increases with the voltage of the bulb. In the language of spectra this means that the *region of wave-lengths of greatest intensity in the continuous spectrum shifts towards the smaller wave-lengths as the voltage increases*. We shall pursue this fundamental law further in the next paragraph. To do so, we must discard the view-point of classical electrodynamics here adopted, and must build up on the basis of the modern quantum theory.

For our special purpose—atomic structure and spectral lines—the characteristic radiation with its line-spectrum, which is characteristic of the emitting atom, will of course be more important than the impulse radiation with its continuous spectrum essentially conditioned by the voltage of the tube. But first we have yet to call attention to various observations about the latter that are intelligible on the basis of classical electrodynamics and mechanics.

We inquire into the total *scattered secondary radiation* that is emitted per unit of time by a body (radiator) struck by primary X-rays. The scattered secondary radiation, in contrast with the simultaneous secondary characteristic radiation of the radiator, has the same hardness, or

in more precise terms, the same continuous spectrum as the primary radiation. Compare, however, § 7 of the present chapter. Its intensity, calculated for a single emitting electron, is given by equation (3). We shall write it down here for unit volume of the radiator and take n as the number of atoms per unit volume, Z the number of electrons per atom. (The radiator is assumed to be a chemical *element*; in the case of a compound the various atoms would have to be differentiated.) We then obtain from (3)

$$S = \frac{2}{3}\frac{e^2\dot{\mathbf{v}}^2}{c^3}nZ \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This implies the assumption that the quantities of energy emitted by the individual electrons of the atom become simply superposed, an assumption which no longer holds for white light (cf. Note 1) and which even in the case of excitation by X-rays is not true for all directions of the scattered radiation (cf. again Note 1).

The acceleration $\dot{\mathbf{v}}$ of the individual electron is closely connected with the electric intensity of field $\mathbf{E}_p$ of the primary X-ray which impinges on it by the equation

$$m\dot{\mathbf{v}} = -e\mathbf{E}_p \quad . \quad . \quad . \quad . \quad (5)$$

In (5) we have assumed the electron to be free. If it is bound to a position of rest, the restoring force has to be added. In the case of sufficiently hard X-rays, we may discard this force; in the case of optical frequencies it must be taken into account (cf. Note 1). By inserting (5) into (4) we get

$$S = \frac{2}{3}\frac{e^4}{m^2c^3}\mathbf{E}_p^2 nZ \quad . \quad . \quad . \quad (6)$$

On the other hand, we determine the energy P of the primary radiation that falls per unit time on unit area of the radiator and excites secondary radiations in it. We get (cf. eqn. (2), in which $\mathbf{H} = \mathbf{E} = \mathbf{E}_p$),

$$P = \frac{c}{4\pi}\mathbf{E}_p^2 \quad . \quad . \quad . \quad . \quad (7)$$

From (6) and (7) we get

$$\frac{S}{P} = \frac{8\pi}{3} \cdot \frac{e^4}{m^2c^4} \cdot nZ \quad . \quad . \quad . \quad . \quad (8)$$

The energy S is produced at the expense of the energy P and hence causes a decrease in the latter, an "absorption through scattering." The ratio $\frac{S}{P}$ is called the "absorption coefficient due to scattering" and is designated by s. From it we pass on to the absorption coefficient of mass $\frac{s}{\rho}$ by dividing by the density ρ. Whereas s is a measure of the

scattering per unit of volume, $\frac{s}{\rho}$ is a measure of the scattering per unit of mass. Now

$$\rho = nm_{\mathrm{H}}\mathrm{M} = n\frac{\mathrm{M}}{\mathrm{L}} \quad . \quad . \quad . \quad . \quad (9)$$

in which M is the atomic weight if hydrogen = 1; and thus $m_{\mathrm{H}}\mathrm{M}$ is the mass of a single atom, and $nm_{\mathrm{H}}\mathrm{M}$ is the mass of the atoms contained in unit volume, i.e. it denotes the density ρ; $\mathrm{L} = \frac{1}{m_{\mathrm{H}}}$ is (see p. 4) "Loschmidt's number per mol."

From (8) and (9) we get

$$\frac{s}{\rho} = \frac{8\pi}{3}\frac{e^4\mathrm{L}}{m^2c^4}\frac{\mathrm{Z}}{\mathrm{M}} = \mathrm{K}\cdot\frac{\mathrm{Z}}{\mathrm{M}} \quad . \quad . \quad . \quad (10)$$

which is J. J. Thomson's formula.

The factor K is a universal quantity independent of the nature of the radiator. Its value may be calculated according to the data at the end of § 2 in Figs. 1A and 1B. In doing this, it must be observed that we have here reckoned e in electrostatic units, and hence according to the remark at the end of § 3 we must divide it by c to reduce it to electromagnetic units. We then obtain

$$\frac{e}{mc} = 1{\cdot}77\,.\,10^7,\ \frac{e\mathrm{L}}{c} = 9{\cdot}65\,.\,10^3,\ \frac{e}{c} = 1{\cdot}59\,.\,10^{-20}$$

and hence

$$\mathrm{K} = 0{\cdot}40 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

From this we can determine the ratio $\frac{\mathrm{Z}}{\mathrm{M}}$ from (10) if the absorption coefficient of mass is found by observation. Such observations have been made by Barkla (for air) and by Barkla and Sadler (for C, Al, Cu, Ag). In the case of air, C and Al, the value obtained (in cms. and grms.) is

$$\frac{s}{\rho} = 0{\cdot}2 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

For Cu and Ag, greater values * (0·4 and 0·5) were found, but in their cases we are no longer dealing with pure scattering, for secondary characteristic radiations occur, as well as scattered secondary rays, and these increase the demand for primary radiation and hence increase the absorption coefficient of mass. Taking this into consideration we may say: *for small atomic weights measurements lead to the uniform value* 0·2 *for* $\frac{s}{\rho}$, *whereas for greater atomic weights the values obtained do not contradict the assumption that the same value holds generally to a certain*

* Appreciably smaller values than 0·2 are obtained if very hard rays are used for the incident light. We revert to this question in Note 1.

degree of approximation so long as we are concerned only with the absorption due to scattering. Now, from (10), (11), and (12) the remarkable result follows:

$$\frac{Z}{M} = \frac{0{\cdot}2}{0{\cdot}40} = \frac{1}{2} \quad . \quad . \quad . \quad . \quad (13)$$

The number of electrons per atom is half as great as the atomic weight (proved for atomic weights smaller than 27).

From the secondary rays we return once more to the primary rays and inquire whether their mode of generation (sudden stoppage of cathode rays at the anti-cathode) can be proved in greater detail by observations. To answer this we must first generalise formulæ (1) a little. These formulæ related to the radiation emitted by a single electron that was subjected to an acceleration $\dot{\mathbf{v}}$, but that possessed no velocity comparable with c. They cannot, therefore, be applied to rather rapid cathode rays $\left(\beta = \frac{v}{c} = \frac{1}{3} \text{ (say)}\right)$ without some modification. They must be replaced, if β is not very small, by *

$$\mathbf{E} = \mathbf{H} = \frac{e\dot{\mathbf{v}}_u}{c^2 r(1 - \beta\cos\theta)^3} = \frac{e\dot{\mathbf{v}}}{c^2 r}\,\frac{\sin\theta}{(1 - \beta\cos\theta)^3} \quad . \quad (14)$$

in which θ denotes, as in Fig. 7, the angle between the direction of the X-ray under consideration and the direction of $\dot{\mathbf{v}}$ (being the same as the direction of the generating cathode ray). As regards the system of units the remarks on page 24 again apply here. In place of (2) we then get for the energy radiation $\mathbf{S}$ at the angle θ and measured per unit of time and surface:

$$\mathbf{S} = \frac{e^2\dot{\mathbf{v}}^2}{4\pi c^3 r^2}\,\frac{\sin^2\theta}{(1 - \beta\cos\theta)^6} \quad . \quad . \quad . \quad (15)$$

This is the radiation emitted during any arbitrary moment of the process of stopping according to classical electrodynamics: β denotes the velocity still left at this moment, divided by c. It can be shown that essentially the same formula represents the elementary process of emission according to the most recent wave-mechanical view of the quantum theory. We take the term "elementary process" to stand for the retardation caused by an individual atom of the anti-cathode, assuming that the velocity v_1 decreases down to a definite final value v_2. The quantity β that occurs in (15) then denotes the ratio of the arithmetic mean $(v_1 + v_2)/2$ to c.

Whereas formerly it was possible to use only massive anti-cathodes, physicists have recently succeeded in approximating to the ideal case of the elementary process by using very thin metal foil (only a few μ's thick). The dotted curves a and b in Fig. 11 represent some of the

* These formulæ are obtained from the equations (1) by means of a relativity transformation. Cf., for example, Riemann-Weber, 7th edn., 1929, Vol. II, p. 421, eqn. (20).

results obtained by H. Kulenkampff,* in particular those for which $v_2 = 0$ (short wave-limit of the continuous spectrum; cf. p. 41). Besides these, Fig. 11 shows the theoretical curves given by formula (15), namely, for the values $\beta = \frac{1}{20}$, $\frac{1}{4}$ and $\frac{1}{3}$. The experimental curves a and b correspond to the values $\beta = 0{\cdot}124$ and $\beta = 0{\cdot}182$.

The figure must, of course, be extended to three dimensions, by rotating it about the direction of the cathode ray. For $\beta \cong 1$ we should obtain a pear-shaped curve for the emission with a maximum near $\theta = 0$. For $\theta = 0$ itself, and also for $\theta = 180°$ the emission would, by (15), on account of the factor $\sin^2\theta$, be equal to zero in all circumstances, as has already been discussed above in the case of secondary radiation. Consequently, this inference is not in general confirmed, either by the more accurate wave-mechanical calculations or by observation. With regard to the dimensional relationships in the figure, we must remark that all the theoretical curves are drawn for the same $\dot{\mathbf{v}}$, whereas in the experimental curves the scale chosen, which is in itself arbitrary, is such that they approximate to the scale of the theoretical curves. The maxima of the theoretical and experimental curves have been designated by small circles. We see that the experimental maxima fit in well with the sequence of theoretical maxima.

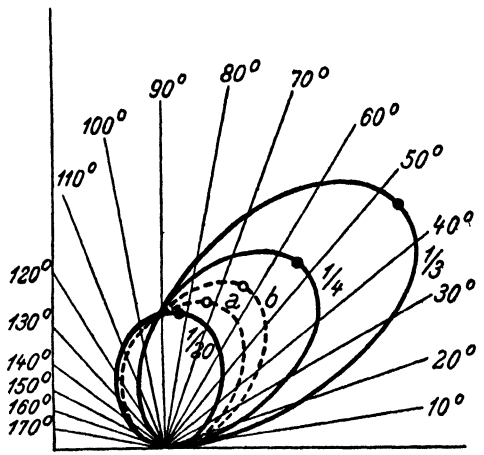


FIG. 11.—Polar diagram (radius-vector = intensity) of the intensity distribution of the continuous Röntgen rays. Compare the curves representing equation (15) (unbroken lines—β-values shown against the curves) with the experimental results of H. Kulenkampff (broken lines—a corresponds to $\beta = 0{\cdot}124$; b to $\beta = 0{\cdot}182$). For the sake of clearness the curves for b and $\beta = \frac{1}{4}$ are not shown between 90° and 180°.

This progressive *advance of the maximum* was derived by the author theoretically as long ago as 1909.† Besides the *differences of intensity* primary X-ray radiation exhibits *differences in hardness*.

The radioactive γ-rays bear the same relation to X-rays as α- and β-rays bear to the canal and cathode rays; likewise they cannot be deflected by electric or magnetic fields. We have already encountered them in Kaufmann's photograph (Fig. 6 of the previous paragraph) at

* Ann. d. Phys., **87**, 632 (1926).

† Physik. Zeitschr., **10**, 969 (1909)

the point of non-deflection on these. The γ-rays, too, may in principle be resolved spectrally. The result has been a line-spectrum of γ-radiation which links up continuously with the hardest characteristic X-rays and extends towards the region of decreasing wave-lengths to waves about twenty times smaller. In any case the difference in hardness between X-rays and γ-rays is far from being as great as that between visible light and X-rays (the ratio of the wave-lengths is in the latter case given by a factor of about 10^{-4}). Whether, in addition to the line-spectrum, there is also a *continuous background in the γ-spectrum* has not yet been proved. Experiments carried out by Edgar Meyer * and Kovarik † seem to favour a one-sidedness in the emission of γ-rays, similar to that which occurs in the case of Röntgen rays, but, in conformity with the greater hardness, this characteristic is correspondingly more strongly pronounced. The γ-rays, too, produce scattered secondary radiation and secondary β-radiation. In radium-therapy, γ-radiation alone is effective : it is surmised that its effectiveness is due solely to the secondary β-radiation generated in the diseased tissues, which thereby causes their disintegration (cf. Fig. 10, in which the corresponding process is exhibited for the case of air that is traversed by X-rays). In particular, it is the γ-rays of RaC and MsTh2 (cf. Table 1 of § 7 in this chapter) that are applied in medical practice.

All things considered, there is no doubt about the similarity in nature between γ-rays and X-rays.

A type of radiation which exceeds γ-radiation in hardness is *cosmic* or *ultra-γ-radiation* (also called *Hesssche Strahlung* in Germany, after its discoverer Hess). Its hardness exceeds that of γ-radiation by a factor of about 20. The origin and nature of this radiation is a subject of lively discussion at the present time. It is probable that it will give us information on extraordinary atomic processes which cannot be observed on the earth (building up or dismembering of atomic nuclei, transformation of atoms or protons into radiation, *Zerstrahlung*). The cosmic origin of this radiation would be established with certainty if the observation becomes confirmed that the radiation varies periodically with sidereal time. On account of its similarity to γ-radiation, it has hitherto been regarded as obvious that cosmic radiation is *undulatory* in character. This assumption has recently been called into doubt ‡ in favour of a corpuscular interpretation, in which cosmic radiation is regarded as consisting of extremely rapid corpuscles. Actually the properties of β-rays of a velocity very nearly equal to that of light approximate in every respect to the properties of wave-radiation ; they acquire an increasingly greater power of penetration and become more and more difficult to deflect. On account of the uncertainty of the subject, we are compelled to close the discussion with these brief

* Ann. d. Phys., **37**, 700 (1912) ; cf. also E. Buchwald, *idem*, **39**, 41 (1912).
† Phys. Rev., **14**, 179 (1919).
‡ W. Bothe and W. Kolhörster, Zeits. f. Physik, **56**, 751 (1929).

remarks, although cosmic radiation promises to reveal important information on the problem of the origin and destruction of matter.*

§ 6. The Photo-electric Effect and its Converse. Glimpses of the Quantum Hypothesis

Like the modern development of the doctrine of cathode rays (cf. § 2), so the knowledge of the photo-electric effect is to be traced back to a paper by H. Hertz (*Concerning an Effect of Ultra-violet Light on Electric Discharge*, 1887). Following in Hertz's footsteps, Hallwachs showed that when a metal plate is exposed to short wave radiation, it becomes positively charged ; and it was Lenard † who recognised that the true cause of this whole category of phenomena was to be sought in the corpuscular negative rays, **the photo-electric cathode rays.** Their specific charge $\frac{e}{m}$ was found to be equal to that of ordinary cathode rays, but their velocity was found to be many times smaller than the latter. Whereas in the Wehnelt tube we met with particularly slow cathode rays excited by a voltage of 110 volts, the photo-electric cathode rays, when reduced in the same way to an imagined excitation voltage, correspond to only one or two volts (according to equation (1), p. 9). They thus have a velocity that is ten times smaller than the velocity in the Wehnelt tube (cf. p. 8).

The following discoveries of Lenard are of very great importance.‡ The *intensity* of the exciting light has *no* influence on the *velocity* of the excited photo-electric cathode rays ; the intensity determines only the *number* of electrons emitted, which is exactly proportional to the intensity. But the velocity of the escaping electrons depends primarily on the *colour* of the exciting light. Ultra-violet light produces the quickest photo-electrons, and that is why its photo-electric activity was discovered first (by Hertz). Red light endows the photo-electrons with so small a velocity that in the case of most *metals* (it is difficult to demonstrate the photo-electric effect in the case of non-conductors) they remain embedded in the surface. The alkali metals alone form an exception in this respect for reasons that are connected with their chemical behaviour in other directions (with their electropositive character).

A far higher degree of photo-electric activity than that of ultra-violet light is possessed by X-rays.

To bring into prominence the essential peculiarity of these discoveries we shall refer to the well-known conceptions of thermo-

* See Translator's Note, p. 596.

† P. Lenard, *Erzeugung von Kathodenstrahlen durch ultraviolettes Licht*, Wiener Akademie, **108**, 1649 (1899).

‡ P. Lenard, *Über die lichtelektrische Wirkung*, Ann. d. Phys., **8**, 149 (1902).

dynamics in this connexion. Thermodynamics investigates the conditions that govern the transformation of heat into work and, in particular, then, the production of kinetic energy. It teaches us to recognise temperature as the measure of the work-value of heat. Heat of higher temperature is richer, is more readily able to be transformed into work than heat of lower temperature. Work may be regarded as heat of an infinitely high temperature, as unconditionally available heat.

In the case of the photo-electric effect, too, we are dealing with the production of kinetic energy, which is drawn from the energy supply of the incident radiation (the fraction that is absorbed). We should expect more intense light to produce a greater photo-electric effect, than less intense light. But this, as we saw, is not true. The work-value (*Wertigkeit*) of the light is not determined by its *intensity* but by its *frequency*. Blue light has great efficiency, red light but little. The intensity determines only the quantity, but not the quality of the photo-electric action. These facts are very strange, and depart greatly from the usual theoretical conceptions: they could not be explained on the basis of classical mechanics and optics. The key to them was furnished by the modern *theory of quanta*.

The quantum theory is a child of the twentieth century. It came to life on 14th December, 1900, when Max Planck gave the *Deutsche Physikalische Gesellschaft* a method of deriving the law of black body radiation, discovered by him shortly before, on the basis of a novel physical idea. As is well known, we apply the term **black body radiation** to that condition of equilibrium of heat radiation which comes about in a space enclosed by bodies of any kind, but at the same steady temperature. The term itself is due to the fact that radiation of precisely this intensity and spectral composition is also emitted by a black body, that is, a non-reflecting body at the same temperature.

The problem of radiation is rooted, on the one hand, then, in thermodynamics, in the laws of the equilibrium of heat and, on the other hand, in electrodynamics, in the laws according to which light- and heat-vibrations are excited, propagated, and absorbed. Planck spent years of consistently planned work in seeking to penetrate into the realm of electrodynamics with thermodynamic principles. To retain agreement with observation and experiment he finally saw himself compelled to take a bold step leading away from the high road of our usual wave theory and to propound his *hypothesis of energy-quanta*. He postulated that *energy of radiation of any frequency ν, whatsoever can be emitted and absorbed only in whole multiples of an elementary quantum of energy*,

$$\epsilon = h\nu \quad . \quad . \quad . \quad . \quad . \quad (1)$$

h is Planck's **quantum of action.** From measurements of radiation Planck soon succeeded in determining the value of his constant:

$$h = 6{\cdot}55 \,.\, 10^{-27} \text{ erg sec.} \quad . \quad . \quad . \quad . \quad (2)$$

(Its dimensions are : energy × time, the same as those of the mechanical " action " that occurs in the *Principle of Least Action.*)*

This postulate does indeed upset our usual ideas of the wave theory. If wave energy is propagated continuously in space and becomes dispersed, how can it then condense at individual places so as to be absorbed in quanta of finite size ? Moreover, how can it be emitted in finite quanta if, according to the laws of classical electrodynamics (cf., for example, equation (2) of p. 24), every change of motion of the centre of vibration, which emits radiation, is accompanied by an instantaneous emission of radiation ?

The hypothesis of energy-quanta, however, also affects classical statistics, that is, the method by which, for example, in the kinetic theory of gases we calculate the average result of many individual events which are not known to us separately. Like every problem of heat, so the problem of the equilibrium of radiation is ultimately a statistical question. The radiation that we observe is composed of an immense number of separate rays and separate events that occur in the emitting body. Now, Planck's investigations showed that classical mechanics could never lead to Planck's law of radiation, which has been verified by observation so brilliantly, and that, on the contrary, it would lead to a spectrum of heat radiation that would be in flagrant contradiction to the facts of experience.

It was precisely this statistical aspect of radiation that engaged the special attention of the discoverer of the quantum theory. He purposely brought the elementary atomic phenomena which lie at the basis of radiation under one scheme, by operating with a " harmonic oscillator," a configuration that emits and absorbs radiation in a manner different from that of the real atoms. Einstein (and also Stark) maintained the opinion that the quantum conception must be valid not only in the statistical equilibrium of radiation, but also in the elementary atomic phenomena. Einstein † called his extension of the principles of the quantum idea " a heuristic view-point concerning the production and transformation of light."

Disregarding for the present all obstacles we shall follow Einstein and describe the photo-electric effect thus. The radiation that is active photo-electrically is absorbed in energy-quanta $h\nu$ according to equation (1), and, in a manner depending on its vibration number ν, it may generate an amount of kinetic energy $h\nu$ in the electrons dislodged from the metal. In this process the kinetic energy that we measure in our observations is less than that originally absorbed since the electron, in passing through the surface of the metal, has to perform work to get away. This work of escape P keeps the free electrons back in the metal

* The value which is regarded as most correct at the present time is
$$h = (6{\cdot}547 \pm 0{\cdot}008) \,.\, 10^{-27} \text{ erg sec.}$$

† Ann. d. Phys., **17**, 132 (1905); cf. *idem*, **20**, 199 (1906), *Zur Theorie der Lichterzeugung und Absorption.*

if there is no photo-electric excitation, and it is different for different conductors. The difference in the values of P for two different metals finds expression in Volta's series of contact potentials, and is equal to the difference between the two contact potentials. Accordingly, we get for the velocity of escape v of the electrons, if m denotes the electronic mass :

$$\frac{mv^2}{2} = h\nu - \mathrm{P} \quad . \quad . \quad . \quad . \quad (3)$$

If we are dealing, not with the ordinary photo-electric effect at a metallic surface, but with the corresponding effect at the individual atom (in a non-conductor or a gas), then P does not denote the work of escape from the surface of the metal but the work of escape from the atom (the so-called work of ionisation).

At the time that Einstein set up the relation (3), only qualitative evidence was available on which it could be based : the velocity of electrons emitted photo-electrically increased with increasing frequency of the exciting light (greater $h\nu$) and with the increasing electropositive character of the metals (smaller P) : ultra-violet light had been found to be more effective than red light ; potassium, which is situated at the extreme end of the electropositive metals, was more sensitive than copper and silver. Quantitatively, Einstein could confirm the law only so far as order of magnitude was concerned. The wave-length of blue light is

$$\lambda = 0{\cdot}4\mu = 4 \,.\, 10^{-5} \text{ cms.}$$

The vibration number (frequency, or number of vibrations per second) corresponding to it is

$$\nu = \frac{c}{\lambda} = \frac{3}{4} \,.\, 10^{15} \text{ sec}^{-1}$$

and the corresponding energy-quantum according to equation (1) is

$$h\nu = 6{\cdot}55 \,.\, 10^{-27} \,.\, \tfrac{3}{4} \,.\, 10^{15} = 5 \,.\, 10^{-12} \text{ ergs.}$$

According to (3) the kinetic energy of the escaping electrons is just as great, provided that we disregard the work of escape P for the present. Now, if we calculate the potential V which a cathode ray tube would have to possess to produce the same kinetic energy $\frac{1}{2}mv^2$ in a cathode ray tube, we also get

$$e\mathrm{V} = 5 \,.\, 10^{-12}.$$

If we take for e its value in the electromagnetic system, that is,

$$e = 1{\cdot}6 \,.\, 10^{-20} \text{ (see p. 15)}$$

we get

$$\mathrm{V} = 3 \,.\, 10^{8} \text{ electromagnetic C.G.S. units} = 3 \text{ volts.}$$

The same order of magnitude, namely, 1 to 2 volts, characterises the contact difference of potential between two somewhat distant metals of

the Voltaic series, and hence also our work of escape P (which is, so to speak, the difference of contact potential of the metal relative to a vacuum). For the kinetic energy of the escaping electrons there then remains, according to (3), if we take P into account in our calculation, likewise an amount of 1 or 2 volts, corresponding to the above-mentioned order of magnitude of the results of observation.

The order of magnitude changes if we pass from visible light to Röntgen light (X-rays). The wave-length of the latter is, as we mentioned in the preceding paragraph, about 10^4 times smaller, and hence their vibration frequencies about 10^4 times greater than the corresponding quantities in the visible region. If we carry out the same calculations for X-rays as made just above for blue light, we get for the kinetic energy of X-ray photo-electric cathode rays, or for the potential corresponding to this energy, in place of 3 volts, 30 kilovolts, that is, a voltage such as is usual for working a moderately hard X-ray tube. Clearly, the work of escape P, being only of a few volts, is to be neglected in comparison with a voltage of this magnitude. We thus arrive at an amount of energy that corresponds to that of the secondary cathode rays mentioned on page 23, of which we said that it is equal to that of the corresponding primary rays. This shows that the secondary cathode rays are to be regarded as a photo-electric effect of the primary X-rays and that their energy, too, is expressed by Einstein's formula so far as the order of magnitude is concerned.

Ten years after Einstein had proposed his law, it became clear that it was not only true in order of magnitude but that it also gave the exact, quantitative expression for the photo-electric effect. This was shown in particular by Millikan * for the case of the sharply defined greatest energy which monochromatic light (light corresponding to a definite spectral line) is capable of generating. For if we plot the greatest energies that are obtained by using various spectral lines in a diagram (the energies as ordinates and the vibration frequencies of the spectral lines used to produce them as abscissæ), the line connecting the points plotted exhibits a linear increase, the magnitude of which is given by the constant h.

That there is a maximum value of the energy generated and that just this and not some mean value of the energy follows Einstein's law is, in fact, to be expected according to quantum ideas. For the energy-quantum $h\nu$ denotes the energy which the incident radiation initially puts as a maximum at the disposal of the electron for the purpose of photo-electric emission. This energy can, indeed, be reduced through secondary losses of energy in the metal, but it can never be exceeded. We have, therefore, to regard the photo-electric maximum of energy as being primarily given and determined by the theory of quanta. It appears that this maximum of energy obeys Einstein's law very accurately.

* R. A. Millikan, *A Direct Photo-electric Determination of Planck's "h,"* Phys. Rev., 7, 356 (1916).

We demonstrate this in the following diagram (Fig. 12) by Millikan, which has been obtained for the case of *lithium ;* the result for sodium looks quite similar. Millikan used as a source of light five mercury lines in succession. The corresponding five points of observation are indicated in the figure by small circles. The frequency number of the line corresponding to the shortest wave-length, the so-called resonance-line of mercury $\lambda = 2536$Å (Å = Ångström unit = 10^{-8} cms. = $\frac{1}{10}\,m\mu$) is $\nu = 118 \cdot 10^{13}$; this number and the frequencies of the other lines can be read off from the figure along the x-axis at the top. Opposite the Li-plate is a so-called Faraday cage (carefully sheltered from electrostatic influences) which is connected with the electrometer : the plate gives up the photo-electric cathode rays, released by incident radiation, to this Faraday cage. The plate and the cage are kept in a vacuum.

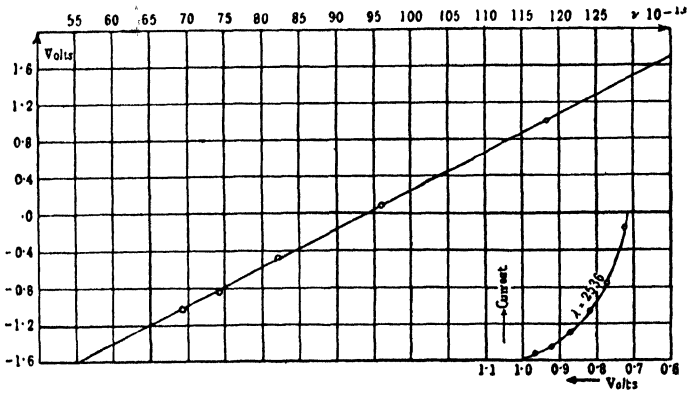


FIG. 12.—Proof of the Einstein photoelectric equation. The small auxiliary diagram shows how Millikan determined the reversing potential for which the photoelectric current produced by the incident light (Hg, $\lambda = 2536$) just equals zero. In the main figure the frequency number of the light necessary for the liberation of photo-electrons is plotted against the corresponding reversing potential.

If the plate is now charged positively, the ejected electrons experience a restoring force. A certain intensity of charge just suffices to turn back all electrons, including those that are emitted perpendicularly to the plate with the maximum velocity. The reversing potential, in volts, corresponding to this charge is at the same time, according to the law of energy, a measure of the maximum kinetic energy of the escaping electrons. Corresponding to every vibration frequency of the incident light there is a different photo-electric maximum of energy, that is, a different voltage of the reversing potential. Millikan next proceeds, by means of an auxiliary figure (see Fig. 12, the right-hand bottom corner), to determine graphically the voltage of the reversing potential for which the photo-electric current becomes just equal to zero.*

* Cf. also the criticism of this mode of procedure by O. Klemperer, Zeits. f. Physik, **16**, 280 (1923).

In the main part of Fig. 12 this voltage number is plotted as the ordinate, and the same is done in the case of the other four frequencies. The points obtained lie beautifully on a straight line (departing from it by less than 0·5 per cent.). The inclination of the line, expressed in C.G.S. units, is

$$h = 6{\cdot}58 \,.\, 10^{-27} \text{ erg sec. in the case of Li}$$
$$\text{and } h = 6{\cdot}57 \,.\, 10^{-27} \text{ erg sec. in the case of Na.}$$

These values agree sufficiently well with Planck's value of h in equation (2).

In the realm of X-rays, too, we may regard Einstein's law as an *exact* expression of the facts and not only as being correct in order of magnitude : here we may state it in the simplified form in which the work of escape P is omitted (cf. p. 39). Thus we write

$$eV = \frac{mv^2}{2} = h\nu \quad . \quad . \quad . \quad . \quad (4)$$

If we read this equation from right to left, it represents the process of generating secondary cathode rays by primary X-rays : it determines from the frequency ν of a monochromatic Röntgen radiation the maximum velocity v of the cathode rays which this radiation is able to release when it impinges on any arbitrary substance, and it likewise determines the corresponding voltage that is equivalent to the maximum velocity generated in the cathode rays. We here have, as in the photo-electric effect, *the transformation of wave-radiation into corpuscular radiation*. The same equation, however, represents *the transformation of corpuscular radiation into wave radiation*. For if we read it *from left to right*, V denotes the voltage of the X-ray tube. This produces the primary cathode rays of velocity v : when the latter strike the anti-cathode, they produce X-rays, namely, characteristic radiation, and impact radiation. The spectrum of the impulse radiation is, as we saw in the previous paragraph, continuous. This spectrum stretches from a small ν (soft X-rays) up to a *sharply defined limit in the region of short frequencies*, which corresponds with the hardest X-rays that can be produced by the voltage V ; the frequency corresponding to this limit is given by equation (4). So, here too, the *relation between the voltage* V *of the tube and the limiting frequency* ν *is expressed by Einstein's linear law*. As V increases, the short wave limit of the continuous spectrum moves to higher frequencies. The frequency of the greatest intensity, as also the average hardness of the radiation, becomes displaced in the same sense. The well-known law (cf. p. 29), that the hardness increases with the voltage of the tube, is thus likewise a consequence of Einstein's law ; it is, in a sense, a more sketchy form of it.

In particular, we get as a direct result of the double reading of Einstein's law the equality, emphasised above (p. 23), between the velocity of primary and secondary cathode rays. The production of

secondary cathode rays from primary X-rays appears as the converse of the phenomenon of the production of primary X-rays from primary cathode rays.

The existence of the short wave limit of the continuous spectrum is a leading feature in the complete picture of X-ray phenomena. There seems no possibility of success in attempting to explain it from the point of view of the classical theory of radiation. However we may care to picture the details of the phenomenon of impulse radiation, the resolution of the radiation emitted into Fourier terms would, according to classical electrodynamics, lead to a spectrum that would stretch to infinity on the side of higher frequencies. Thus the existence of the short wave limit is an unmistakable hint that we must go further than the classical theory of radiation and work out a quantum theory. Einstein's law formulates this fact as compactly and precisely as can be desired. As in the case of the photo-electric effect, the measurement of the short wave limit of the continuous X-ray spectrum may be elaborated so as to lead to a precise determination of the constant of radiation h.

We have now to take only one step further to arrive from Einstein's law at one of the main pillars of Bohr's theory of spectral lines.

We have seen how energy of monochromatic frequency $h\nu$ is taken up by a metal atom and how it reappears as kinetic energy of a photo-electron. If we now suppose that the absorbed energy of vibration does not suffice to release the electron from the atom, then it will only effect a re-adjustment in the atom, in which the atom passes from a lower to a higher step of energy. We can imagine this transition to be similar to that of a weight which is lifted from a lower initial position to a higher final position. If w_1 and w_2 ($> w_1$) are the initial and final energies of the atom, respectively, then we get, as a counterpart to Einstein's photo-electric equation, *Bohr's fundamental equation for a phenomenon of optical absorption :*

$$h\nu = w_2 - w_1 \quad . \quad . \quad . \quad . \quad (5)$$

Here the primary energy originates in the incident radiation ; the consequence is a change of configuration of the atom. If, however, we suppose that the primary energy originates in the change of configuration of the atom, of which the initial energy is w_1 and the final energy $w_2 < w_1$, then we may here, too, expect a radiation to appear thus :

$$h\nu = w_1 - w_2 \quad . \quad . \quad . \quad . \quad (6)$$

This radiation is now strictly *monochromatic*, if we assume that in this case w_2 as well as w_1 is fixed as a discontinuous quantity by the configuration of the atom. In equation (6) we have *Bohr's fundamental equation for the phenomenon of optical emission.*

Like Einstein's law, this extension of it by Bohr claims to be valid with absolute accuracy in the entire spectral region from the slowest heat rays to the most rapid X-rays and γ-rays. Thus this quantum

law regulates in the same way as Einstein's law the transition of wave radiation into corpuscular radiation as well as the reverse process; it governs the phenomena of absorption as well as those of emission, in optical regions as well as in the region of high frequencies. There is no doubt that we are here dealing with one of the most mysterious of physical laws.

§ 7. Wave Theory and Quantum Theory. Compton Effect

Heinrich Hertz,* in his discourse at the Heidelberg Session of the Science Research Society (*Naturforschergesellschaft*) in 1889, drew certain general conclusions from his experiments on electrical waves and made the following remarks about the nature of light:

"What is light? Since the time of Young and Fresnel we know that it is a wave-motion. We know the velocity of the waves, we know their lengths, and we know that they are transverse. In short, our knowledge of the geometrical conditions of the motion is complete. Any doubt about these things is no longer possible; a refutation of these views is unthinkable by the physicist. The wave-theory of light is, from the point of view of human beings, a certainty."

Has this certainty meanwhile been shattered? Yes and no! In all questions of *interference* and *diffraction* the wave-theory has not only maintained its position, but has actually gained new ground. It has extended its range of validity towards the side of small wave-lengths as far up as Röntgen and γ-rays, and towards the side of great wave-lengths as far down as the waves of wireless telegraphy, whose length is measured in kilometres. In all questions, however, which, in Einstein's language (cf. p. 37), concern the *production* and *transformation* of light we must operate with "light quanta" (photons), that is, with centres of energy which move away from the source with the velocity of light.

It does not appear that the *dualism*, light-wave and light-quantum, is capable of being overcome. This conviction is strengthened by the circumstance that in the case of corpuscular radiation and of matter generally a similar dualism has manifested itself. The new wave-mechanics, which will be discussed in the second volume of the present work, signifies that matter must be treated *partly as wave and partly as corpuscle*, as the former in problems involving deflection and diffraction, as the latter in questions involving transference of energy, as also even in the formulation of the fundamental wave-equation. A more penetrating critical analysis of physical experience (given by Heisenberg's Uncertainty Relation) makes it possible for the two methods of description, the wave and the corpuscular view, to avoid coming into conflict with one another. But this aspect, too, we shall reserve for the second volume.

* Gesammelte Werke, **1**, 340.

We shall now deal with the corpuscular view of light, which has enjoyed its greatest triumph in the *Compton effect*. We shall initiate our discussion by first fixing our attention on the *Doppler effect*.

It is well known from astro-physics that the spectrum of a star is slightly displaced to the violet or the red end of the spectrum according as the star moves towards or away from the observer. The relative displacement is equal to the ratio of its velocity in the line of vision to the velocity of light, that is

$$\frac{\Delta\nu}{\nu} = -\frac{\Delta\lambda}{\lambda} = \frac{v}{c}\cos\theta \quad . \quad . \quad . \quad . \quad (1)$$

where θ denotes the angle between the line connecting the star with the observer, and the direction of the velocity v. What holds for stars and their spectra also holds for every radiating atom. Equation (1) therefore gives us the change in the wave-length of any spectral line (for example, the D-line of the sodium atom), which the atom moving relatively to the observer emits as compared with that emitted by an atom at rest.

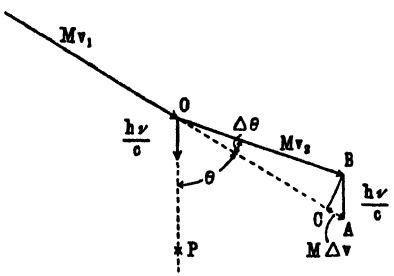


FIG. 13.—Momentum exchange in the Doppler effect. The particle has initial momentum Mv_1, the emitted light quantum momentum $h\nu/c$, and the particle after emission momentum Mv_2.

It seems almost impossible to understand the Doppler effect except from the point of view of the classical wave-theory: if the emitting source is approaching us the wave-surfaces become compressed together, and we have a shortening of the wave-length ($\Delta\lambda < 0$); if the source is moving away from us the wave-surfaces become drawn apart, and we have an increase of wave-length ($\Delta\lambda > 0$), and we arrive directly at formula (1). In the face of these remarks it is extremely instructive to see how we can understand the same formula equally well from the point of view of light-quanta.*

We assume that the radiating atom does not emit a spherical wave, but that it emits a quantum in one direction, for example, in the direction OP towards the observer (Fig. 13). This quantum has the energy $h\nu$. It imparts to the emitting atom a recoil in the reverse direction. The magnitude of this recoil is $\frac{h\nu}{c}$. If we do not wish to proceed on primitive corpuscular lines we can base this assumption on a very general consequence of the theory of relativity, namely, the **Law of Inertia of Energy.**

* Cf. E. Schrödinger, Physikal. Zeits., **23**, 301 (1922). Our treatment differs in form from that of Schrödinger.

Einstein regards this law as the most important result of the special theory of relativity. It states: *every amount of energy represents a mass. Every amount of energy in motion represents a momentum. The magnitude of the mass is equal to the magnitude of the energy divided by* c^2. According to this law the mass which moves with our light-quantum is *

$$\mu = \frac{h\nu}{c^2} = \frac{h}{c\lambda} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Since, like its equivalent energy, it moves with the velocity of light c, it has the momentum (impulse):

$$\mu c = \frac{h\nu}{c} = \frac{h}{\lambda}.$$

Thus, the law of *conservation of momentum*, which is the foundation pillar of mechanics, and of which the law of *conservation of energy* is only a consequence, demands that the atom should experience a recoil $-\frac{h\nu}{c}$, as was asserted above.

Using these two laws of conservation, we now construct the change of direction and the change of velocity of the atom due to the recoil. Let v_1 be the original velocity, Mv_1 the original momentum, v_2 and Mv_2 the velocity and momentum after the emission. Let the emission occur at an angle θ with respect to the original direction of the velocity. Let the angle with respect to the changed direction of the velocity be $\theta + \Delta\theta$. We construct the latter by drawing the recoil OB at the continuation OA of the original momentum. We mark off $Mv_2 = OB$ and $Mv_1 = OA$, and so obtain in the line CA the change in the value of the momentum. We calculate it from the triangle ABC, which we may assume as approximately rectilinear and right-angled. We get

$$M\Delta v = M(v_1 - v_2) = \frac{h\nu}{c}\cos\theta \quad . \quad . \quad . \quad (3)$$

We have thus applied the law of conservation of momentum. We still have to make use of the law of conservation of energy. Let w_1 and w_2 be the energy of the atomic configuration before and after the emission. According to the preceding section, equation (6), the following frequency is emitted by the atom at rest in the change of configuration $w_1 \rightarrow w_2$:

$$h\nu = w_1 - w_2 \quad . \quad . \quad . \quad . \quad (4)$$

The frequency emitted by the moving atom differs from this: let it be $\nu + \Delta\nu$. It follows from the energy-equation thus: $\frac{M}{2}v_1^2 + w_1$ is the total energy of the atom before emission, $\frac{M}{2}v_2^2 + w_2 + h(\nu + \Delta\nu)$ is

* It is obvious that the rest-mass of the light-quantum is equal to zero. Otherwise the mass moving with the velocity c would have to be infinitely great.

the energy of the atom after emission + energy of the emitted light-quantum. Hence

$$\frac{M}{2}v_1^2 + w_1 = \frac{M}{2}v_2^2 + w_2 + h(\nu + \Delta\nu) \quad . \quad . \quad (5)$$

Substituting from (4), we obtain

$$h\Delta\nu = \frac{M}{2}(v_1^2 - v_2^2) = M\Delta v\frac{v_1 + v_2}{2} \quad . \quad . \quad . \quad (6)$$

If we write $\bar{v}$ for the arithmetic mean of the velocities v_1 and v_2 and substitute for the change of momentum $M\Delta v$, its values from (3), then, dividing by $h\nu$, we have

$$\frac{\Delta\nu}{\nu} = \frac{\bar{v}}{c}\cos\theta \quad . \quad . \quad . \quad . \quad (7)$$

which is precisely equation (1), with the difference that $\bar{v}$ now takes the place of v, which is of no consequence. It is a characteristic feature that h cancels out in passing from (6) to (7). This circumstance, which is in a certain sense accidental, helps us to understand why we can explain the Doppler effect just as well from the point of view of the classical wave-theory as from that of the quantum-theory, which we have here adopted.

In the above discussion we have apparently been inconsistent in setting the recoil equal to $\frac{h\nu}{c}$ instead of to $\frac{(h\nu + \Delta\nu)}{c}$. If we use the latter value instead, our result becomes changed only in terms of the second order, that is, in terms involving $(\bar{v}/c)^2$. But if we wished to take into account such terms, we should have to calculate relativistically from the outset and should, in particular, have to write down a different expression for the kinetic energy of the atom. In this case, as has been emphasised by Schrödinger, we should obtain the rigorous Doppler formula in the sense of the theory of relativity.

We now come to the effect which was discovered by Arthur Compton * and explained by him on the quantum theory. This effect occurs when X-rays are scattered ; it is demonstrated by an apparatus similar to that on page 25. Hard X-rays (for example, from a molybdenum anti-cathode) fall on a radiator of low atomic weight (carbon, paraffin). The incident and also the scattered radiation is resolved spectrally (cf. Chap. IV, § 2). It is then found that a part of the secondary spectrum is displaced with respect to the primary spectrum towards the side of the long waves by an amount $\Delta\lambda$ which depends only on the

* The earliest communications by Compton are: Phys. Rev., **21**, 483 (1923); Phil. Mag., **46**, 897 (1923). Cf. in particular Fig. 1 of the last-mentioned reference which clearly shows the way in which the change of wave-length depends on the angle of scattering θ. The theory given by Debye in Physikal. Zeits., **24**, 161 (1923), corresponds almost exactly with Compton's own theory.

scattering angle θ. The results of experiment agree perfectly with the theoretical formula :

$$\Delta\lambda = 2\Lambda \sin^2 \frac{\theta}{2} \text{ where } \Lambda = \frac{h}{m_0 c} \quad . \quad . \quad . \quad (8)$$

Λ is a universal length having the numerical value

$$\Lambda = 0{\cdot}024 \,.\, 10^{-8} \text{ cm.} = 0{\cdot}024 \text{ Å.}$$

Its physical meaning may be characterised as follows by equation (2) : it is the wave-length of the light-quantum *whose mass μ is equal to the rest mass m_0 of the electron.*

To bring out clearly the fundamental significance of Compton's result, we must bear in mind that the scattering of X-rays is similar in nature to the reflection of ordinary light. Both phenomena are explained according to the classical theory (cf. Note 1 of the Appendix) by the sympathetic vibration of the electrons on which the light or the X-rays impinge. This sympathetic vibration occurs, from the classical point of view, exactly in rhythm with the incident wave-radiation. If observation shows that in a part of the scattered X-ray beam there is in fact a change of wave-length, this signifies that the classical wave-theory can account for only a part of the phenomena (the unchanged radiation).

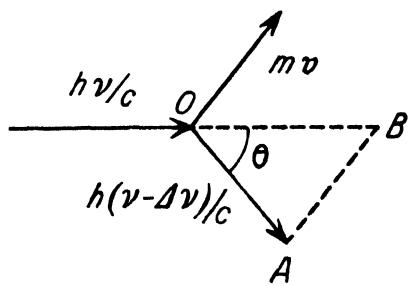


FIG. 14.—Momentum exchange in the Compton effect. The incident light-quantum has momentum $h\nu/c$, the emitted light-quantum momentum $h(\nu - \Delta\nu)/c$, and the recoil electron momentum mv.

Equation (8) is derived by Compton and Debye, exactly as above in the Doppler effect, by simply applying the laws of conservation of momentum and energy. The earlier figure applies to our present case if we suppose the corpuscular momenta Mv_1, Mv_2, formerly used, to be now replaced by the momenta of the incident and scattered wave-radiation, respectively, and the earlier ray $h\nu$ by a corpuscular stream of electrons. Instead of the closed momentum triangle OAB of Fig. 13, whose sides are Mv_1, Mv_2, $h\nu/c$, we then get the closed momentum triangle of Fig. 14, whose sides are $\frac{h\nu}{c}$, $h(\nu - \Delta\nu)/c$, mv. Here θ is the angle of scattering, namely, the angle between the deflected ray OA and the continuation of the primary ray OB. The fundamental physical assumption of Compton's theory is : if an X-ray quantum is deflected by an atom, then some electron of the atom takes up energy and momentum differences that become liberated in the process. The electron that is alone effective in this act is treated as a free electron, in spite of its belonging originally to the atomic configuration ; this is justified

in view of the great energy of the X-ray quantum, at least for the more loosely attached electrons of the atom. The deflection of the X-ray quantum by the amount θ of the angle of scattering hence becomes possible only because an electron experiences a reaction of such a direction and magnitude as satisfies the laws of conservation. This postulate fixes uniquely not only the change of frequency and wave-length of the X-ray quantum, but also the magnitude and direction of the motion of the ejected electron.

In the triangle OAB of Fig. 14 we have by the cosine law,

$$\left.\begin{aligned} m^2v^2 &= \left(\frac{h\nu}{c}\right)^2 + \left(\frac{h(\nu-\Delta\nu)}{c}\right)^2 - \frac{2h\nu}{c}\frac{h(\nu-\Delta\nu)}{c}\cos\theta \\ &= \left(\frac{h\nu}{c}\right)^2\left[1 + \left(1-\frac{\Delta\nu}{\nu}\right)^2 - 2\left(1-\frac{\Delta\nu}{\nu}\right)\cos\theta\right] \end{aligned}\right\} \quad . \quad (9)$$

Neglecting the term $\left(\frac{\Delta\nu}{\nu}\right)^2$ we write for this :

$$\frac{m}{2}v^2 = \frac{1}{m}\left(\frac{h\nu}{c}\right)^2\left(1-\frac{\Delta\nu}{\nu}\right)(1-\cos\theta) \quad . \quad . \quad (10)$$

The energy law gives

$$h\nu = h(\nu-\Delta\nu) + \frac{m}{2}v^2, \quad . \quad . \quad . \quad (11)$$

that is,

$$\frac{m}{2}v^2 = h\Delta\nu.$$

From (10) and (11) it follows that

$$\Delta\nu = \frac{h\nu^2}{mc^2}\left(1-\frac{\Delta\nu}{\nu}\right)(1-\cos\theta)$$

for which we may now write

$$\frac{c\Delta\nu}{\nu(\nu-\Delta\nu)} = 2\,\Lambda\sin^2\frac{\theta}{2}, \quad \Lambda = \frac{h}{mc} = 0{\cdot}024\,\text{Å} \quad . \quad (12)$$

We now show that the left-hand side denotes just the change of wave-length $\Delta\lambda$ observed by Compton. Actually we have

$$\Delta\lambda = (\lambda+\Delta\lambda) - \lambda = \frac{c}{\nu-\Delta\nu} - \frac{c}{\nu} = \frac{c\Delta\nu}{\nu(\nu-\Delta\nu)} \quad . \quad (12a)$$

Thus equation (12) is identical with our assertion (8), except that in the definition of Λ we have instead of the rest mass m_0 the mass m of the motion, which may be set equal to m_0 in the non-relativistic treatment.

If we wish to take into account the refinements of relativity, we must set $m = m_0/\sqrt{1-\beta_2}$ in (9), so that (9) now becomes

$$\frac{m_0^2\beta^2}{1-\beta^2} = \left(\frac{h\nu}{c^2}\right)^2 4\left(1-\frac{\Delta\nu}{\nu}\right)\sin^2\frac{\theta}{2} + \left(\frac{h\Delta\nu}{c^2}\right)^2 \quad . \quad . \quad (13)$$

Here the term which was previously neglected is taken account of in the last term on the right-hand side. Correspondingly, we must write for (11),

$$m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right)=h\Delta\nu \quad . \quad . \quad . \quad (14)$$

According to the theorem of the inertia of energy, the energy of the moving electron is equal to mc^2 and the energy of the stationary electron is m_0c^2, so that the excess of energy of the moving electron is given by the difference of these expressions, that is, the kinetic energy of the moving electron :

$$E_{kin}=(m-m_0)c^2=m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}}-1\right) \quad . \quad . \quad (15)$$

which we shall use in equation (14). From (14)

$$\frac{1}{\sqrt{1-\beta^2}}=\left(1+\frac{h\Delta\nu}{m_0c^2}\right)^2,$$

or, if we take the 1 across from the right to the left-hand side, and multiply throughout by m_0c^2,

$$\frac{m_0\beta^2}{1-\beta^2}=\frac{2m_0h\Delta\nu}{c^2}+\left(\frac{h\Delta\nu}{c^2}\right)^2 \quad . \quad . \quad . \quad (16)$$

It is very striking that when we equate the right-hand sides of equations (13) and (16) the quadratic term in $\Delta\nu$ cancels out. In this way Compton's result (12) comes out, *even when no terms are neglected*, with the definition given for Λ in (8).

Besides the wave-length of the scattered radiation the magnitude and the direction of the velocity of the expelled electron are given uniquely by the preceding formulæ. The ratio of the kinetic energy of the electron to the energy $h\nu$ of the incident light-quantum is, for example, by (15), (14), (12) and (12*a*) :

$$\frac{E_{kin}}{h\nu}=\frac{\Delta\nu}{\nu}=2\Lambda\sin^2\frac{\theta}{2}\cdot\frac{\nu-\Delta\nu}{c}=\frac{2\Lambda\sin^2\theta/2}{\lambda+2\Lambda\sin^2\theta/2} \quad . \quad (17)$$

In the last step of the transformation we must replace $\nu-\Delta\nu$ by $\lambda+\Delta\lambda$ and $\Delta\lambda$ in accordance with equation (8). The ratio (17) thus always comes out as a rather small value, even for very hard X-rays ; for example, when $\lambda=10$, $\Lambda=0{\cdot}24$ Å and $\theta=\pi/2$, it becomes equal to only 1/11, and amounts to 1/2 only when $\lambda=\Lambda$ and $\theta=\pi/2$. In comparison with the photo-electrons, whose energy is of the order of magnitude of the incident $h\nu$, the " Compton electrons " have a considerably smaller value. The direction of their momentum depends of course on the direction θ of the scattered ray, but always has a positive and, in general, predominant component in the prolongation of the incident ray, part of whose momentum it is, of course, that is transferred to the Compton electron.

The fact that in addition to the displaced scattered radiation an undisplaced radiation, which is coherent with the primary radiation, also presents itself can be reconciled with the above theory. We need only suppose that in this process the momentum of the primary radiation is taken up by the *whole* atom ; the change in the frequency of the light-quantum then becomes inappreciable, cf. (8) where the electronic mass m_0 would in this case have to be replaced by the atomic mass M.

We must call special attention to a characteristic feature of formula (8), as contrasted with formula (1) for the Doppler effect, that $\Delta\lambda$ is independent of the absolute value of the wave-length. From this it follows that the *relative* change of wave-length becomes the more marked the smaller the wave-length itself is. In the case of hard γ-rays, where λ is of the order of magnitude of our Λ, the change $\Delta\lambda$ becomes comparable with the primary wave-length λ of the γ-radiation. According to Compton there is evidence of this in experimental results.

This is not the place to enter into the question of the experimental confirmation of the preceding theory, for example, in photographs obtained with Wilson's cloud chamber (cf. Fig. 10, § 5, of the present chapter). This confirmation leaves practically nothing to be desired at the present time, which is seven years after Compton's discovery. But there are other questions, such as the intensity of the displaced Compton line as compared with the undisplaced line and its dependence on the nature of the scattering atom which cannot be answered at all on the above simple corpuscular theory ; rather, they require the methods of wave-mechanics and hence can be treated only in the second volume.

It suggests itself to us to inquire whether a similar effect to that obtained with X-rays is to be expected in the visible region. It is clear that compared with the weaker energy-quanta of the visible region even the most loosely bound valency electrons cannot be regarded as free. The energy of the incident light-quantum does not, therefore, suffice to produce a recoil electron ; the momentum of the scattered light-quantum becomes transferred, as in the case of the undisplaced Compton line, to the atom as a whole. Moreover, it is not long since we have become acquainted with an optical effect which in many respects forms a counterpart to the Compton effect, namely, the Raman * effect. Raman has shown that the energy of the light-quantum can be modified by the scattering molecule, in the scattering process, in that either a part of its energy is retained as internal energy of the molecule or internal energy of the molecule becomes added to that of the light-quantum. This brief outline of the Raman

* The first communications on the effect were : C. V. Raman and K. S. Krishnan, Indian Journal of Physics, **2**, March, 1928 ; cf. also Nature, **121**, 501, and **122**, 12 (1928).

effect contains in it the corpuscular theory which was given by Smekal * long before Raman made his discovery.

Recapitulating, we may say that the Compton effect demonstrates very impressively the dual nature of radiation : the main features of the phenomenon, the transference of energy and momentum, are represented most naturally by the light-quantum theory of radiation and the corpuscular theory of the electrons, whereas the finer features, the questions of intensity and distribution, are represented by the wave-theory of light and the wave-mechanics of electrons, which has been modelled on it.

§ 8. Radioactivity

Hitherto we have considered only the physical manifestations of radioactive processes. A few remarks about the chemical carriers involved must now be added.

A characteristic feature of radioactivity is that it occurs essentially only in the case of the elements of greatest atomic weight. Uranium (*Ur-ahn* = *original ancestor* of the radium family) is the heaviest element, having an atomic weight 238·14. Thorium, the parent substance of the thorium family, is the second heaviest of the elements that were known before radioactivity (as its atomic weight = 232·12). It is therefore allowable to regard atoms that are too heavily loaded with matter as hypertrophic configurations that are unstable and disintegrate into simpler forms.

We shall take for granted the sum-total of radio-chemical research in the form of the genealogical tree given in Table 1. How it became possible to set up these lines of descent will be made clear below (in the theory of disintegration), and also partly in the next chapter (§ 5, " Laws of Displacement "). It need only be remarked here that without this theory as a kind of Ariadne's thread it would have been impossible to find a means of locating the members of this manifold series of new elements. On the other hand, we must mention that it is only the extraordinary sensitiveness of electroscopic observations of radioactivity, a sensitiveness which far exceeds that of the balance, that has enabled us to prove the existence of the products of disintegration, for these are often present in only very minute quantities.

We distinguish three radioactive families, the *uranium-radium*, the *thorium*, and the *actinium* families. It is very probable that the actinium series branches off from the uranium series, on account of the circumstance that uranium and actinium minerals occur together. But it is not yet known how this branching occurs in detail. Accordingly, we trace the actinium descent only as far back as protoactinium, which was discovered by Hahn and Meitner.

* A. Smekal, Naturwissenschaften, **11**, 873 (1923).

Our lines of descent exhibit in the upper row the development from the parent substance to the three emanations (inert gases); in the lower row the development is shown from the emanation to a final product, having the character of lead. In the actinium series it is AcD (actinium lead); in the thorium series it is ThD (thorium lead). In the radium series the analogous product RaD is not the final product, since the members RaE, RaF (= polonium), and RaG (= radium lead) are linked with it as later products. The similarity of the three lines of descent between the emanations and the D-products is shown not only in the number of products of disintegration and their position in the natural series of elements (cf. the table of isotopes in § 2 of Chap. III) but also in their mode of disintegration (denoted in our table by the letters α and β printed above the arrow used to signify transformation; γ denotes that γ-rays are present). At corresponding positions in the genealogical trees the disintegration is effected either by an α-transformation (emission of helium) or a β-transformation (electron emission). The notation here adopted takes due account of this parallelism in the disintegration. It has been suggested by Stefan Meyer and Schweidler, and differs from that formerly in use (which arose historically and which is thus less systematic) in the names given to the C- and D-products.

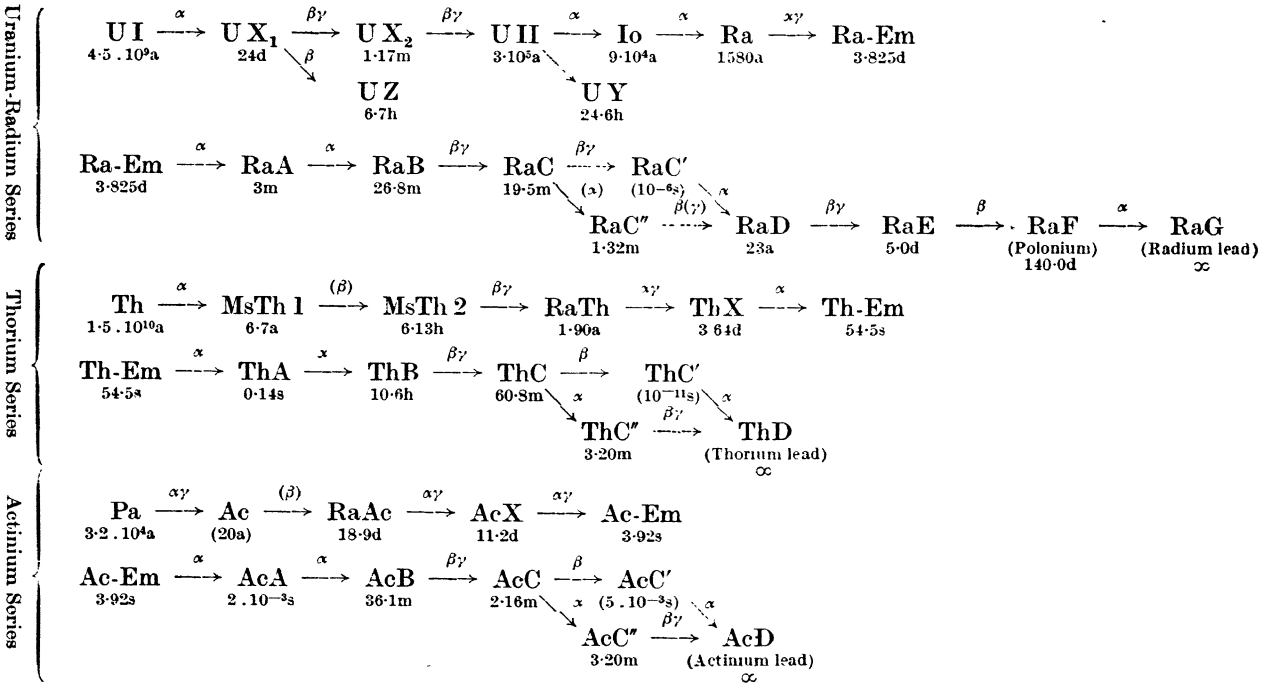
Below the symbol of each element we have recorded the "**half-value time**"; this is the time which has elapsed when half the body is disintegrated. It is proportional to the "mean duration of life" of the element. We shall explain later how it is determined. The abbreviations a, d, h, m, s, denote: year (*annus*), day, hour, minute, second. We thus have long-lived elements with spans of life stretching over millions of years (UI has a half-value time of $4{\cdot}5 \cdot 10^9$ years, and Th has one twice as long) and short-lived elements which live only for seconds or fractions of a second. The elements whose lives are shortest are to be found among those designated by C′:

$$\text{RaC}' \text{ has } 10^{-6} \text{ seconds, AcC}' \ 5 \cdot 10^{-3}, \text{ ThC}' \ 10^{-11}.$$

These numbers, like all the bracketed half-value times, have been found, not by observation, but by calculation. There is also a certain parallelism between the half-value times of the three families, in particular in the above-mentioned region between the emanation and the lead group.

The branching between RaC and RaD over RaC′ and RaC″, and the exactly corresponding branching of the Th- and Ac-trees is of special interest. The fact that RaC is transformed into different products (RaC′ and RaC″) according as it disintegrates by a β- or an α-transformation, is intelligible. But the fact that these products, when subjected to the same transformations but interchanged (i.e. by an α- and a β-transformation respectively), resolve into the same element RaD will be made plausible by the displacement laws of Chap. III, § 2, but it is not empirically certain. (The transitions which are uncertain

TABLE 1 *



* The abbreviations in the table denote: U = uranium, Ra = radium, Io = ionium, Em = emanation, Th = thorium, Ac = actinium, Ms = meso, RaTh = radio-thorium (etc.), Pa = protoactinium. The numerical values are taken in part from the before-mentioned book by K. Fajans.

in this sense are indicated by dotted lines in the table.) Another branch leads to UZ, which was discovered by Hahn;* its further evolution is not yet known.

We thus see that in virtue of these ramifications there are represented in our genealogical tree not only children and grand-children but also brothers.

Our next step is to give a short account of the laws of radioactive disintegration. These laws arise directly and are of an extraordinarily simple type. Being fully independent of temperature and pressure, they thus differ fundamentally from the laws that govern ordinary chemical transformations. Nor are they dependent on whether the active substance is present as an element or a salt, whether it is pure or mixed with other substances. Everything seems to support the view that we are not dealing with an action of one atom on another but rather with some inner atomic process.

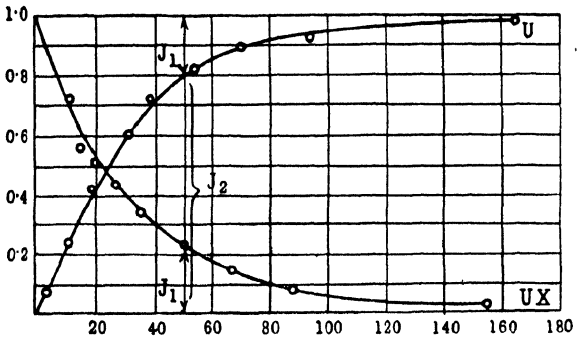


FIG. 15.—Rise and fall of the β-ray emission for U and UX. The UX contained in a U-preparation is separated out chemically at time $t = 0$. The (diminishing) β-ray emission of this UX and the (increasing) emission of the U, always add up to the same initial value of unity.

In Fig. 15 we consider a particularly simple case, namely, that of the decay of UI to UX_1 and UX_2 with the further branch leading to UZ, or, as we shall find it simpler and briefer to express it in the sequel, from U to UX; this is the process which stands at the beginning of our genealogical tree.

Let us take the β-ray activity as an indicator. That is we shall suppose the α-rays to be eliminated by absorption for the sake of our present argument.† Only the β- and γ-rays penetrate into the electroscope, ionise the air, and produce a charge which flows into the leaves of the electroscope, and which serves as a measure of the number of ions formed. But since γ-rays are ineffective in forming ions as com-

* Ber. d. D. Chem. Gesells., **54**, 1131 (1921); Naturwiss., 1921, p. 84; Zeits. f. physikal. Chem., **103**, 461 (1923).

† $\frac{1}{10}$ mm. of Al are sufficient to absorb the most rapid α-rays almost entirely.

pared with β-rays, we need here regard the activity as referring solely to β-ray activity; "inactive" means "producing" no β-rays.

The preparation with which we start is not pure uranium but already contains a certain very small percentage of UX. It is possible to precipitate the latter from the uranium by repeated application of barium sulphate. The UX thus isolated carries away the whole activity of the preparation with it, and the U itself is left behind entirely inactive at first. In the figure we have thus set the initial activity of U equal to zero, and that of UX equal to 1. From these initial states onwards the activity of the UX diminishes regularly to zero, whereas that of U simultaneously recovers and increases from 0 to 1. By comparing the two curves we see that their ordinates at each corresponding point add up to 1. If $J_1(t)$ is the activity of UX at the time t, and $J_2(t)$ that of U at the same moment, then we have

$$J_2(t) = 1 - J_1(t) \quad . \quad . \quad . \quad . \quad (1)$$

Hence although these products are distinct from one another (chemically, and, for example, separated by a considerable distance in space) they yet continue to act in full accord with one another: the activity lost by the one is gained by the other; the sum of their activities is constant just as would have been the case if we had not separated them chemically.

According to the disintegration theory of Rutherford and Soddy, the explanation is as follows. The constitution of the atom, and this alone, invests any arbitrarily chosen atom with a certain *probability* that it will disintegrate in an arbitrarily chosen unit of time. This probability is called the **radioactive constant** (or decay constant) of the atom. From this there follows the essential principle of the theory of disintegration: **The number of atoms that decay per unit of time is equal to the radioactive constant multiplied by the number of atoms still present** (namely, equal to the probability of decay of an atom multiplied by the number of atoms). On the other hand, the activity of the prepared substance is, except for a constant depending on the apparatus, equal to the number of atoms that decay per unit of time (in our case the atoms disintegrated by the β-transformation). In conjunction with the above principle, this leads to

$$J(t) = C\lambda n \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where J = activity at the time t, C = the apparatus constant, λ = the radioactive constant, and n = the number of radioactive atoms at the time t.

We next apply this principle to the two curves of Fig. 15.

I. In the case of UX isolated from its parent substance, the number of atoms n is changed only through the decay of the atoms present. Therefore the number of atoms that decay in time dt is $-dn$. From

this, and from the principle of the disintegration theory we get the following differential equation for the disintegration of UX :

$$-dn = \lambda n dt \quad . \quad . \quad . \quad . \quad (3)$$

Thence it follows that if n_0 denotes the initial number of atoms of UX, and if e is the base of natural logarithms,

$$n = n_0 e^{-\lambda t} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and, by (2),

$$J(t) = C\lambda n_0 e^{-\lambda t} \quad . \quad . \quad . \quad . \quad (5)$$

In our figure we chose our unit so that $J(0) = 1$. Hence we must set

$$C\lambda n_0 = 1 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and thus get

$$J_1(t) = e^{-\lambda t} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The curve in Fig. 15, *which was obtained from direct observation, agrees exactly with this exponential law.* Its rate of decline allows us to determine the decay or radioactive constant λ.

II. In the case of the U that has been purified of UX, let N be the number of uranium atoms at the time t, N_0 the initial number, Λ the radioactive constant of uranium. The decay again takes place according to the law (3), which now assumes the form

$$-dN = \Lambda N dt, \qquad N = N_0 e^{-\Lambda t} \quad . \quad . \quad . \quad (8)$$

Now, the radioactive constant Λ of the uranium is extremely small compared with the radioactive constant λ of the UX, i.e.

$$\Lambda \ll \lambda \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Hence, within a period of observation that is not reckoned in millions of years, we may reasonably set

$$\Lambda t = 0, \qquad e^{-\Lambda t} = 1 \quad . \quad . \quad . \quad . \quad (10)$$

and hence, by (8),

$$N = N_0, \qquad -\frac{dN}{dt} = \Lambda N_0 \quad . \quad . \quad . \quad (11)$$

Measurement of the activity in this case discloses nothing of this change, since it is an α-transformation. For this measurement depends only on the β-transformation of the UX. Now a UX-atom arises from each U- atom. If the latter were not to decay, we should have simply $dn = -dN$ and, by (11),

$$\frac{dn}{dt} = \Lambda N_0, \qquad n = \Lambda N_0 t \quad . \quad . \quad . \quad (12)$$

The number n of UX-atoms and therefore also the activity $J(t)$ of UX would thus increase uniformly with the time, and would thus be represented by a straight line in Fig. 15, namely, the initial tangent of the curve there shown as $J_2(t)$. But the increase does not continue indefi-

nitely, for the UX-atoms decay in their turn : a state of equilibrium is gradually reached, in which just as many UX-atoms decay as are formed. If n_0 is the number when equilibrium is reached, then the number of UX-atoms which decay per unit of time is, according to (3), λn_0, the number of those being formed is equal to the U-atoms that are decaying, and equals ΛN_0, by (11). Hence, in radioactive equilibrium,

$$\lambda n_0 = \Lambda N_0 \quad . \quad . \quad . \quad . \quad (13)$$

In the state of radioactive equilibrium, the number of atoms of parent substance and product are in the inverse ratio of the corresponding radioactive constants..

This state of equilibrium existed during the initial separation of the U and the UX. The equilibrium number n_0 just calculated is thus identical with the initial number of atoms n_0 of UX in equation (4). In the state of equilibrium the activity of UX will be, according to (2) and (6),

$$J_2 = C\lambda n_0 = 1.$$

Our curve $J_2(t)$ which was originally an oblique straight line thus gradually curves round into a horizontal straight line, which is at unit distance from the time axis.

If, further, we wish to find the law of curvature, we must complete (12) thus :

$$\frac{dn}{dt} = \Lambda N_0 - \lambda n$$

by taking account not only of the production of the UX-atoms but also of their decay. As a result of (13) this equation may be written

$$\frac{dn}{dt} + \lambda n = \lambda n_0$$

and may be integrated by simple mathematical rules, if we take into consideration the initial conditions $n = 0$, $t = 0$, thus :

$$n = n_0(1 - e^{-\lambda t}).$$

By multiplying this by $C\lambda$ we get the activity $J_2(t) = C\lambda n$. From (6) we get for the latter,

$$J_2(t) = 1 - e^{-\lambda t} \quad . \quad . \quad . \quad . \quad (14)$$

Thus $J_2(t)$ increases according to the same exponential law as that by which $J_1(t)$ decreases. $J_2(t)$ and $J_1(t)$ sum up to unity.

This is the full explanation of Fig. 15. The same diagram gives us the semi-decay time of UX. For this, the relation holds,

$$e^{-\lambda t} = 1 - e^{-\lambda t} \text{ or } e^{-\lambda t} = \tfrac{1}{2} \quad . \quad . \quad . \quad (15)$$

The abscissa of the point of intersection is thus the time which has elapsed when the exponential function has diminished to a half of its initial value, i.e. since the time $t = 0$. In our case the curve tells us that the half-value (or semi-decay) time t_H is equal to 23·8 days.

In addition to the half-value time we also arrive at the radioactive constant. For from (15) it follows that

$$\lambda t_H = \log_e 2 = \cdot 693 \quad . \quad . \quad . \quad . \quad (16)$$

The radioactive constants are in the inverse ratio of their half-value times. The values of these times are given in Table 1.

Closely related to the conception of half-value time we have the conception of *mean length of life* or *average life*. If we denote the latter by t_L, we get in place of (16),

$$\lambda t_L = 1 \quad . \quad . \quad . \quad . \quad . \quad (17)$$

For, as in social statistics, we define the mean length of life by first multiplying each age by the relative number of the individuals that just attain this age but do not exceed it and then summing all these products of age and relative number. In our case, as we see from (3) and (4), $-dn$ is the number of atoms which at the time t decay within the time-interval dt, and n_0 the total number of atoms initially present, thus

$$\frac{-dn}{n_0} = \lambda e^{-\lambda t} dt$$

signifies the relative number with which we are here concerned. By multiplying it with the corresponding t and summing for all t's, we get the required average length of life :

$$t_L = \int_0^\infty t\left(\frac{-dn}{n_0}\right) = \int_0^\infty te^{-\lambda t}\lambda dt \quad . \quad . \quad . \quad (18)$$

Equation (17) follows simply from this definition if we multiply both sides of (18) by λ and introduce $x = \lambda t$ as a new variable of integration :

$$\lambda t_L = \int_0^\infty xe^{-x}dx = 1.$$

By comparing (16) with (17) we see that we get the average lengths of life of the radioactive elements by dividing the numbers of Table 1 by ·693.

In general, conditions are not so simple as in the example we have so far discussed. This simplicity was due in the first place to the fact that the life of U is very long compared with that of UX_1. We made use of the resultant simplification ($\Lambda \ll \lambda$) in passing from equation (8) to equation (11). The fact that UX was to comprise both the products UX_1 and UX_2 has already been mentioned above. But then the further fact comes into consideration that the life of UX_2 ($t_H = 1{\cdot}17$ minutes) is very short compared with the life of UX_1 (cf. Table 1), and that the life of UII is relatively again extraordinarily long ($t_H = 3{\cdot}10^5$ years). The result is that immediately following on the disintegration of each UX_1-atom, i.e. at intervals of probably about a minute, the decay of

the new-born UX_2-atom and the transition to the UII-atom takes place. The decay is accompanied by β- and γ-radiation, and therefore increases the ionisation produced by the decay of UX_1. The addition of the decay of UX_2 does not, however, bring about to any appreciable extent a delay in the rate at which the activity dies down, or a change in the exponential law given by the curve. This allowed us to use the short term " UX," as referring to a uniform product, in our explanation of Fig. 15, thus treating the two elements UX_1 and UX_2 conjointly as was the practice formerly before these two elements had been separated. Nor does the activity of UII, which remains after the decay of UX_1 and UX_2, cause a change in the course of the activity curve, since, being an α-activity, it evades measurement.

We get a complete picture of the great possibilities of the theory of decay only when we consider the course of the activity in a case in which several products of approximately the same length of life participate. The classical example is given by the precipitate which is produced by radium emanation. This precipitate consists of a mixture of RaA, RaB, RaC, which becomes transformed into the long-lived RaD. The theory of decay enables us to separate the contributions of these different components to the total activity and to determine the half-value period for each of them. We cannot, however, go into further details here, and shall therefore merely touch on several points of general significance.

The Geiger-Nuttall rule establishes a relationship between the life-period of the α-particles and their velocity: *the shorter the life-period the greater the velocity*. In other words, the more unstable an element is, the more vigorous the explosion. If we plot the life-period as the logarithm of the half-value period against the velocity as the logarithm of the range,* the Geiger-Nuttall relation is represented by a *straight line* in the case of every family, and these straight lines are approximately parallel for the different families. Deviations from straightness occur only at the ends of these lines, that is, only in the case of elements of very short or very long life-periods.

We next inquire: is radioactivity a peculiarity of the heavy metals uranium and thorium, or is it a general property of matter? The only certain result that can be adduced as evidence is that *potassium* and *rubidium* exhibit a weak β-activity. Hence, although the high atomic weight undoubtedly favours radioactive disintegration, it is not the only decisive factor. The conditions for potassium are fairly accurately known. There are two kinds of potassium (isotopes, cf. Chap. III, § 2), one of atomic weight 39 and another, which occurs less often, of atomic weight 41. According to Hevesy it is only the latter that is radioactive.

Then there is the second question: Whence does the energy of

* For example, the range as measured in air is proportional to the cube of the velocity.

radioactive actions come ? At the beginning of § 4 we saw that the energy of the α- and β-rays is many times more than that which any of our present technical means will allow us to produce in the case of canal and cathode rays. When the rays are kept back in the prepared substance, they produce and maintain an increase in the temperature of the substance, which is several degrees higher than that of the surrounding air. The heat energy generated by 1 grm. of radium amounts to about 100 calories per hour. A familiar problem of long standing asks how the energy which the sun loses by radiation is continually replaced. In this case, too, reference has been made to the apparently inexhaustible supplies of energy derived from radioactive processes. Whence does all this energy come ? The answer is : from the interior of the atom, or, more precisely, from the innermost part of the atom, from the " nucleus " of the atom. We thus indicate the rôle which has to be assigned to radioactivity in our theory of the atom. The sources of energy which thus manifest themselves to the outer world are of an order of magnitude quite different from the energies of other physical or chemical processes. They bear witness to the powerful forces that are active in the interior of the atoms (in the nuclei). This inner world of the atom is generally quite shut off from the outer world. It is not influenced by the temperature or pressure conditions that exist outside. It is governed by the law of probability, the law of spontaneous decay that can in no wise be influenced. Only as an exception is a door left open which leads from the inner world of the atom into the outer world. The α- and β-rays that are hereby emitted are emissaries from a world otherwise closed.

CHAPTER II

THE HYDROGEN SPECTRUM

§ 1. Nuclear Charge and Atomic Number. The Atom as a Planetary System

THE absorption of cathode rays and the dependence of the absorption on the velocity led to the view (cf. Chap. I, § 3) that matter has a perforated structure.

Rutherford came to the same conclusion, expressed in a quantitative form, by experiments on the scattering of α-rays. In passing through thin metal leaves a beam of α-rays at first undergoes a general scattering. Just as the shots from a gun at a target, so the points of impact of α-particles cluster about a mean position of greatest probability, the prolongation of the incident beam of α-particles, and occur less and less frequently in all other directions as we move outwards from this mean position. A fluorescent screen, such as is used in spinthariscopes, allows us to observe and count the impacts of individual particles owing to the scintillation produced. But there are occasional departures from the incident direction, which amount to as much as 150°. They are few in number (e.g. in the case where platinum is the scattering leaf and α-rays from radium C are used for the scattered radiation, only 1 in 8000 of the incident particles are deflected through angles $> 90°$) : but this number is much greater than is to be expected according to the law of scattering for small angles. Rutherford * and his collaborators, Geiger and Marsden,† made an accurate investigation of the distribution of these abnormal deflections among the various angular segments for a series of metal laminæ, using α-rays of various velocities. We have already met with corresponding abnormal deflections in Wilson's photographs, in the form of hooks at the end of the α-ray tracks produced, not by atoms of metal, but by air molecules. We reproduce in Fig. 16 the picture of a particularly striking case (this is an enlargement of a portion of our former picture, Fig. 3*b*).

What has happened to the α-particle at this bend ? Rutherford traces the effect back to very intense electric fields that start out from a very small element of space, the " nucleus." Since the magnitude of

* Phil. Mag., **21**, 669 (1911). † *Ibid.*, **25**, 604 (1913).

the abnormal deflections increases with the atomic weight of the deflecting element, the intensity of the deflecting field must also increase with the atomic weight. If we consider the field produced by a point-charge concentrated in the nucleus, and if we suppose this charge to act according to Coulomb's law, we can calculate the magnitude of the charge that is necessary to account for the observed deflections. At the suggestion of Rutherford, Chadwick * made very careful measurements of the deflections caused by thin laminæ of Pt, Ag, and Cu, and succeeded in determining with an accuracy of about 1 per cent. the charges that must be assumed in the corresponding nuclei. He obtained the numbers 77·4, 46·3, and 29·3 for Pt, Ag, and Cu respectively, expressed as multiples of the elementary charge e. These numbers agree, within the limits of error, with the position of the corresponding element in the periodic system, namely, with the atomic numbers 78, 47, and 29. Thus, following Rutherford, we enunciate the fundamental thesis: *The nuclear charge is equal to the atomic number numerically.* If in the general case we designate the atomic number by Z, then the nuclear charge of each element is Ze.

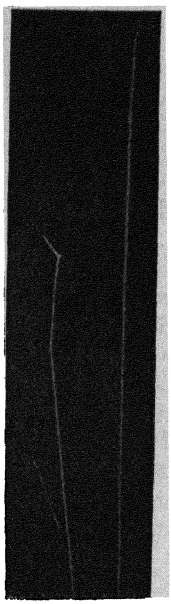


Fig. 16.—Wilson-photograph of α-particles in water vapour. The distinct hook on the left shows where scattering by a positive nucleus has taken place.

The nuclear charge, in itself, might just as well be negative as positive, that is, the deflections might be regarded just as well as due to attractions instead of to repulsions. But our general observations about ions and electrons lead us to decide in favour of the positive sign for the nuclear charges. For the nucleus must possess not only a considerable charge but also a high resistive power, that is, must have a great mass, in order to bring about the great deflections of the α-particles. Now it was the positive charge (cf. p. 21) that was, by nature, associated with gravitational matter, whereas the negative charge was a property of the light and mobile electron. Electrons, as centres of negative charges, may be adduced to explain the small deflection in the regular scattering, whereas we must fall back on the heavy positive nucleus to explain the abnormal deflections.

We thus arrive at the following summarised statement. *The positively charged α-particle is repelled by the positively charged nucleus, if it passes exceptionally close to the latter. In the neighbourhood of the*

* Phil. Mag., **40**, 734 (1920).

nucleus there is an atmosphere of negative charges, electrons, by which the α-particle is attracted. These attractions, which are superposed according to the laws of chance, explain the *regular scattering of slight angular deflection,* whilst repulsions explain the *comparatively rare bends of great angle.*

Observations of α-rays also allow us to make deductions about the size of the nuclei. The distribution of the deflections among various angles was calculated by Rutherford and Chadwick on the assumption that the nuclear charge is concentrated at a point. So far as the observed deflections agree with those calculated, they thus show that the size of the nucleus did not interfere with the paths of the particles. In the case of gold, Darwin * has obtained a value $3 \cdot 10^{-12}$ cms. as the possible upper limit for the "size" of the nucleus; in that of water he obtained $2 \cdot 10^{-13}$ cms. This estimate by no means precludes the nucleus from being actually smaller, but it cannot be larger if a disagreement with the observations of α-rays is to be avoided. We may thus at least affirm with certainty that *the nucleus* (as also the electron, see p. 8) *can be at most of sub-atomic size.*

On the whole, atoms must be electrically neutral. Consequently the number of electrons † per atom must equal the number of elementary positive charges concentrated in the nucleus. Hence we get our second thesis. *The atomic number is equal to the nuclear charge (numerically), and both are equal to the number of electrons around the nucleus.*

This thesis is supported by a result arising from the theory as well as from the measurement of Röntgen radiation—the value found for the amount of scattered radiation per atom. As we saw earlier (Chap. I, § 5, eqn. (13)), this amount led us to conclude that the number of excited electrons per atom that emit scattered radiation is equal to half the atomic weight. Whereas in the case of optical waves only the outside or loosely bound electrons (so called dispersion or valency electrons) perceptibly vibrate in sympathy—the inner electrons are too rigidly fixed to be affected by the optical excitation to which they are exposed—the X-rays, which are of high frequency, affect the inner electrons (those nearer the nucleus). The above result about the scattered radiation was interpreted by us earlier as follows. *The total number of electrons in the atom is approximately equal to half the atomic weight and is exactly equal to the atomic number of the element,* which, for its part, is approximately equal to half the atomic weight.

So far our theses are supported by a comparatively meagre number

* C. G. Darwin, Phil. Mag., **27**, 506 (1914); cf. Rutherford, *ibid.*, 494 (1914).

† In more accurate language, we mean the number of electrons present in the atom *outside the nucleus.* For, later, the facts of radioactivity will compel us to assume that there are also electrons in the interior of the nucleus. In determining the nuclear charge these are subtracted from the positive charge present. Hence "nuclear charge" denotes, not the positive charge of the nucleus, but *the algebraic sum of the positive charge of the nuclear matter and the negative charge of the electrons contained in the nucleus.* For further remarks see § 6 of Chapter III.

of observations. In the next two chapters we shall use the facts of the periodic system and of X-ray spectra to establish the above statements on a firmer basis. Assuming these results for the moment, we affirm : *for each step forward in the periodic system of the elements the nuclear charge grows exactly by one unit and the nuclear mass becomes increased by approximately two units.* For since the electrons contribute only a vanishingly small amount to the atomic weight, the latter must be represented essentially by the mass of the nucleus. And further : *each element in the periodic system contains one electron more than the preceding element* (we do not here take into consideration the nuclear electrons mentioned in the last footnote).

Historically it was *van den Broek* * who first formulated the idea of an order number (atomic number) which increases with the nuclear charge and number of electrons ; he adduced chemical facts to support it.

The question arises : How can the electrons of the atom maintain themselves in opposition to the attractive action of the nuclear charge ? Will this action not cause them to fall into the nucleus ? The answer—a possible one, which is particularly simple and satisfactory—is furnished by the conditions of the solar system. The earth fails to fall into the sun for the reason that it develops centrifugal forces owing to its motion in its own orbit, and these forces are in equilibrium with the sun's attraction. If we transfer these ideas to our atomic model we arrive at the following view. **The atom is a planetary system in which the planets are electrons. They move in orbits about the central body, the nucleus.** The atom of which the atomic number is Z is composed of Z *planets each charged with a single negative charge, and of a sun charged with* Z *positive units.* The *gravitational attraction,* as expressed in Newton's law, is represented by the *electrical attraction* as given by Coulomb's law ; these laws are alike in form. There is a difference in that the planets repel one another in our atomic microcosm—likewise according to Coulomb's law—whereas, in the case of the solar macrocosm they undergo *attraction* not only from the sun but also from themselves.

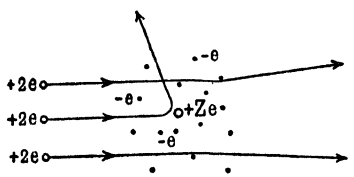


FIG. 17.—Scattering of a beam of α-rays by the nucleus and electrons of an atom of atomic number Z.

Bearing in mind the picture of the planetary system, let us once again consider the phenomenon of α-ray deflection. We shoot an α-particle, a *comet,* through our planetary system. In general it pursues a rectilinear path (as is shown in the top and bottom paths of Fig. 17) and is attracted (scattered) only slightly by the nearest small

* Physikal. Zeits., **14**, 32 (1913).

planets. But if it strikes the sun directly or passes near by (central path of Fig. 17), it undergoes a comparatively great and immediate repulsion. It then describes a hyperbolic orbit, in the focus of which is the nucleus ; the angle of deflection is equal to the angle between the two asymptotes of the hyperbola.

This astronomical description of the phenomenon hints, too, at the method of calculation, and Rutherford was the first to apply it in the discussion of the measurements of α-ray deflections and on it he founded his nuclear theory.

But we must emphasise even at this early stage that the vivid and picturesque planetary model has had to be given up as a result of the developments of the last decade, and has had to give way to a less concrete and more diffuse idea. Wave mechanics forces us to ascribe to the revolving electrons definite places at definite times, and we must be satisfied with calculating the statistical mean of such places. Nevertheless, essential features of these orbital types (both of elliptic and hyperbolic orbits), namely, their quantum numbers, and energies are also taken up in wave-mechanics. It is therefore indispensable to elaborate this picture of the planetary system in the present first volume in order that we may refine it still further by wave-mechanics in the second volume.

In the next chapter we shall describe the atomic models to which we shall be led by adopting the idea of the planetary system. In this chapter we restrict our remarks essentially to the model for hydrogen.

The reason for this is easy to understand : it is only in the case of the hydrogen atom that we are dealing with the simplest problem, that of *two bodies ;* all the other atoms bring us face to face with the notorious difficulties of the problem of three and more bodies.

1. **The hydrogen atom** (Niels Bohr,* 1913). The simplest atom is the hydrogen atom ; for this, $Z = 1$. It consists of *a nucleus with one positive charge, and of an electron that revolves about this nucleus.* The orbit of the electron is, as in Kepler's planetary problem, an ellipse at which the nucleus is situated. We have as a particular case a circular orbit, where the nucleus is situated at the centre.

2. **The hydrogen ion or proton.** After it has lost its only electron the hydrogen atom consists solely *of a solitary nucleus of vanishingly small spatial dimensions as compared with atomic dimensions.*

From this model we may immediately infer that *it is impossible to picture as a physical reality a hydrogen ion carrying two positive charges.* If a chemist should ever succeed in producing such a one, we should be compelled to declare all that follows in this book to be false. W. Hammer † proved its non-existence and corrected an older and

* The writings of Bohr that laid the foundation to this theory appeared under the title : " On the Constitution of Atoms and Molecules," 1913, in Phil. Mag., **26,** 1, 476, 857. See also " Three Lectures on Atomic Physics," N. Bohr ; cf. also the reference to § 7, page 118.

† Ann. d. Phys., **43,** 686 (1914).

contrary result of J. J. Thomson.* The impossibility of having a hydrogen atom with a double positive charge is connected with the general difference between positive and negative charges, which was emphasised at the end of Chapter I, § 4: a negative charge may be increased to any extent, a positive charge only to a certain limit, namely, to that at which all electrons have been removed from the atom.

3. **The ionised helium atom.** Whereas the neutral helium atom (one nucleus and two electrons) represents a problem of three bodies and so does not come up for discussion here, the positively charged helium atom, the He-ion, that is, a helium atom from which one electron has been removed by electrical or thermal means, is again very simple. Consisting of a *doubly charged nucleus and one electron*, it is represented by the same picture as the hydrogen atom. It is hydrogen-like (*wasserstoffähnlich*), and so also comes under the simple mathematical scheme of the two-body problem.

It differs from the H-atom only in size. It is easy to understand that the two-fold attraction of the He-nucleus on the electron diminishes the orbit of the rotating electron as compared with that of the electron that rotates around the singly charged H-nucleus, and, indeed, it is reduced to one-half the size.

4. **The α-ray particle.** The next picture, that of doubly ionised helium, the helium atom with two positive elementary charges, is very characteristic and satisfactory. It is, like the simply positive hydrogen ion, a mere nucleus without real extension. The unique part played by this system as an α-particle in radioactive phenomena now becomes clear. The enormous penetrative power of α-particles, their comet-like intrusion into the planetary systems of foreign atoms, their double positive charge, which corresponds to the loss of all electrons in the helium, the non-existence of three-fold positively charged helium, give it a special rôle. In addition, the circumstance that, hitherto, a characteristic light emission of α-rays has never been observed, speaks in favour of our model. In the first chapter we spoke of the luminescence of canal rays and of the similarity of nature between canal rays and α-rays. This similarity, as we now see, cannot extend to the luminescence. We are acquainted with helium canal rays that consist of neutral and also of simply ionised helium atoms. These are recognised, among other methods, by the characteristic lines that they radiate out. To render this emission of spectral lines possible, there must be present at least one electron, which alters its position during the process of

* Sir J. J. Thomson, *Rays of Positive Electricity*, 1913. Thomson emphasises the certainty of this statement by the following words on p. 53 of this book: "No hydrogen atom with more than one charge has ever been observed, though as the hydrogen lines occur practically on every plate more observations have been made on the hydrogen lines than on those of any other element." But Thomson established positive charges to the number of 8 units in the case of mercury; cf. Chapter I, § 3.

emission. But the doubly ionised helium atom is devoid of electrons, and hence of the means of radiating. It becomes immediately obvious that the helium nucleus, in travelling as an α-ray through the atmosphere or other matter with its enormous velocity (almost $\frac{1}{10}$. velocity of light), cannot carry an electron with it on the way or draw one to itself.*

It must also be mentioned that already in Fig. 17 we have made use of the exceedingly minute size of the α-particle. When, arguing from this figure, we derived an upper limit for the nuclear size of an atom, deducing it from the deflection of α-ray comets, we assumed tacitly that the α-particles could be justifiably treated as points. In more correct language, this determination of size gave us the sum of the nuclear radii of the atom in question and of the helium atom. Inasmuch as the sum was found to be sub-atomic, it was clear that, besides the atomic nucleus under consideration, the α-particle itself can have no appreciable size.

Whereas objections may be raised against the later spectral evidence of our atomic theory, on the ground that it requires diverse theoretical intermediate steps, the observable properties of the α-particle follow directly from our fundamental views of nuclear charge and nuclear size, of atomic number, and the number of associated electrons in the atom.

Our picture of the α-particle is so convincing that it seems justifiable to infer from it that there is no gap between hydrogen and helium in the periodic system. Rydberg imagined that there were grounds in the chemical system of arrangement of the elements which led him to conclude that two elements existed between hydrogen and helium. In that case, however, He would not have the nuclear charge 2 but 4. The α-particle would not be a pure He-nucleus, but an He-nucleus with 2 external electrons. But this would be incompatible with the general results obtained experimentally with α-particles. Moreover, the exact calculation of X-ray spectra furnishes evidence against a general increase of the atomic-number Z which would become necessary for the remaining elements if two unknown elements had to be interposed at the beginning of the periodic table. We shall therefore regard the atomic number $Z = 2$ to have been proved to be correct for helium.

5. **Doubly ionised lithium** (Li^{++}) **and trebly ionised beryllium** (Be^{+++}). It has recently been found possible to follow the analogy of the singly charged helium atom by producing the next successive two-body systems, namely, the doubly charged lithium atom (Li^{++}), with its three positive nuclear units of charge and one electron, and the trebly

* Experiments by Henderson (Proc. Roy. Soc., **102**, 496 (1923)) and Lord Rutherford (Nature, **112**, 305 (1923)) have shown that even a fast α-particle very often attaches an electron to itself in its flight, but that the distances over which it exists as He^+ are extremely small compared with the distances over which it is a pure He-nucleus. With decreasing velocity (at the end of its range) the probability increases for the He^+-ions and neutral He-atoms also occur.

charged beryllium atom (Be^{+++}), with its four units of positive charge in the nucleus and its one electron. Like He^{+} they come into the simple scheme of the hydrogen problem. We shall discuss this question more fully in § 5.

§ 2. Empirical Data about the Spectra of Hydrogen. The Principle of Combination

Before we deal with the spectra of the simplest element H, for which $Z = 1$, it may be convenient to make some preliminary remarks about spectra in general.

Whereas solid bodies emit a continuous spectrum when they glow, we observe in the case of gases and vapours (in addition to continuous regions) **line-spectra** and **band-spectra.** The former belong to the atom, the latter to the molecule, whereas continuous emission spectra can occur in the case of atoms as well as of molecules. Hence in a Geissler tube the hydrogen must first dissociate into atoms before its line-spectrum can appear. In the case of iodine vapour, on the other hand, the band-spectra disappear in proportion as the dissociation of I_2 into I progresses. The line-spectra consist of individual well-defined lines or complexes of lines; the band-spectra appear, if the dispersion is small, as shaded bands (often accompanied by "flutings" ("*Kannelierungen*")), but they resolve under higher dispersion into a great number of neighbouring lines.

Within the line-spectra regular sequences of lines may be grouped together into **series.** The distances between successive lines decrease according to definite laws in each series as we proceed towards the violet end, and the lines accumulate at a series limit which is usually accessible only by extrapolation. At the same time the intensity of the lines decreases regularly towards this limit of the series, either, as is the rule, from the beginning of the series, or from a definite point later. The series character is particularly marked in the first three columns of the periodic system (alkali metals, alkaline earths, and earths). The lines of a band-spectrum accumulate at the **heads** of the bands, but do not become infinitely dense there as in the case of the series lines at the series limit; the heads of the bands lie partly towards the violet and partly towards the red.

Line-spectra and band-spectra occur during absorption as well as during emission. Indeed, the absorption spectra, in the form of Fraunhofer lines, primarily played the determining part in the historical development of the measurement of wave-lengths. Absorption spectra have a characteristic advantage over emission spectra in that, in general, they have a more complete set of lines. Whereas, under ordinary conditions, only few lines of the emission series are sufficiently intense to be observed (for example, those of the hydrogen series are known from photographs of nebular clusters as far as the 33rd member of the

series, and in vacuum-tubes, at the most as far as the 20th member), the absorption series, also under laboratory conditions, may be counted almost up to the series limit, and they number as many as 60 lines.*

In Fig. 18 we show the absorption spectrum of the so-called principal series of lithium in the reproduction of a photograph taken by B. Trumpy. The wonderful regularity of the series law is brought out strikingly in this picture. On the right-hand side near the series limit the individual lines no longer appear separated. The photograph begins on the left with the third member of the series as the apparatus had been designed to reproduce the ultra-violet lines. The source of light used was a magnesium arc ; for this reason the emission lines of magnesium (the white lines) also appear on the plate.

The approximate distribution of the seven colours of the rainbow in the spectrum is as follows (λ given in Ångström units) :

$\lambda =$	8000	6450	5750	5500	4950	4550	4250	3500
	red	orange	yellow	green	blue	indigo	violet	

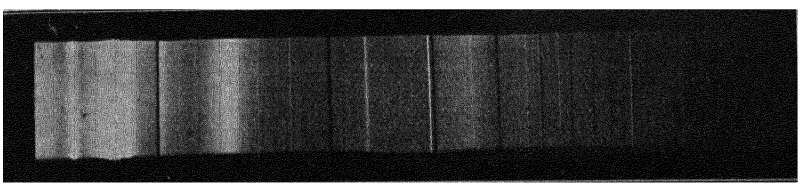


FIG. 18.—Absorption spectrum of Li (principal series) according to Trumpy. The dark absorption lines crowd together towards the series limit on the right. The bright lines are emission lines of Mg.

The first lines of the visible hydrogen spectrum were measured by Fraunhofer as absorption lines of the solar spectrum, and were called the C, F, *f*, *h* lines, respectively. Nowadays we call them H_α, H_β, H_γ, H_δ, Their distances apart are shown by wave-numbers (reciprocal wave-lengths) schematically in Fig. 19. In this case, too, we have the same regularity as in that of the Li-spectrum, indeed in a still purer form, since the law of the hydrogen series is essentially an integral law.

It was J. J. Balmer, a teacher at a secondary school in Basel (Bâle), who, at the instigation of Hagenbach, sought out this law and exposed its ideal form so clearly that we have nowadays to make only non-essential improvements on it (cf. the relativity correction in Chap. V). Balmer's formula became the model of all later rational spectral formulæ and constitutes the firm foundation of the theory of spectral lines.

* Wood and Fortrat (Astrophys. Journ., **43**, 73 (1916)) give measurements which extend as far as the 58th line of the absorption series of sodium.

Balmer wrote his formula * thus :

$$\lambda = h\frac{m^2}{m^2 - n^2} \quad . \quad . \quad . \quad . \quad (1)$$

The integral numbers m and n have the values $n = 2$, $m = 3, 4, 5, 6$, for H_α, H_β, H_γ, H_δ respectively. The factor h (which must not, of course, be confused with Planck's constant h) is, according to Balmer, if λ is measured in Ångström units ($1\text{Å} = 10^{-8}$ cms., cf. p. 40), equal to 3645·6.

Nowadays we write Balmer's formula thus (λ in cms., ν in cm.$^{-1}$) :

$$\frac{1}{\lambda} = \nu = \mathrm{R}\left(\frac{1}{2^2} - \frac{1}{k^2}\right) \qquad \left.\begin{matrix}\mathrm{R} = 109677{\cdot}8 \\ k = 3, 4, 5, \ldots\end{matrix}\right\} \quad . \quad . \quad (2)$$

Formula (2) arises from (1) (if we disregard the choice of units and the recent more exact determination of the numerical factor R) by setting in (1), $n = 2$, and

$$h = \frac{n^2}{\mathrm{R}} = \frac{4}{\mathrm{R}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

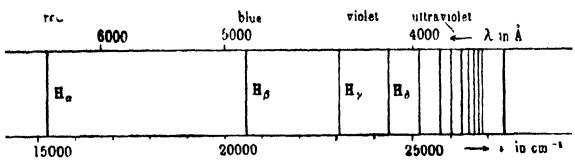


FIG. 19.—Balmer series of hydrogen.

R is the so-called *Rydberg constant* (Rydberg-Ritz wave-number) : ν denotes the *wave-number* (number of wave-lengths per cm.).

We must here add the following remarks. Following spectroscopic usage (with its possible disadvantages) we use the same letter ν for the *wave-length* as for the frequency (or vibration number, that is, the number of complete vibrations per second). So we have the following two meanings for ν, which differ in their dimensions :

$$\nu = \frac{1}{\lambda} = \text{wave-number (cm.}^{-1}\text{)} \quad . \quad . \quad . \quad (4)$$

$$\nu = \frac{1}{\tau} = \text{frequency (sec.}^{-1}\text{)} \quad . \quad . \quad . \quad . \quad (5)$$

* Ann. d. Phys., **25**, 80 (1885). Balmer remarked simply that the wave-lengths H_α, H_β, H_γ, H_δ, may be represented in terms of the " basic number " h, quoted in the text, thus :

$$\frac{9}{5}h,\ \frac{4}{3}h = \frac{16h}{12},\ \frac{25}{21}h,\ \frac{9}{8}h = \frac{36}{32}h.$$

Enlarging the fractions $\frac{4}{3}$ and $\frac{9}{8}$ for H_β and H_δ in the manner shown, he recognised the successive numerators as the squares, 3^2, 4^2, 5^2, 6^2, and the denominators as the differences of squares, $3^2 - 2^2$, $4^2 - 2^2$, $5^2 - 2^2$, $6^2 - 2^2$. With the discovery of the basic number h Balmer's formula so to speak blossomed into existence.

Hence it follows that

$$\text{frequency } \nu = \text{wave-number } \nu \times \text{velocity of light } c \quad . \quad (6)$$

We always imply the meaning (5) for ν, when, as in Chapter I, §§ 6 and 7, we speak of the energy-quantum $h\nu$: we imply the meaning (4) when, as in the present section, we are writing spectral formula. The Rydberg constant introduced in (2) also has the dimensions (4) of a wave-number.

The expression " Rydberg frequency " is therefore inappropriate as it suggests the dimensions sec.$^{-1}$. This term, in its true sense, should be applied to the quantity :

$$\begin{aligned} c\mathrm{R} &= (2{\cdot}99796 \pm 0{\cdot}00004) \,.\, 10^{10} \,.\, (109677{\cdot}759 \pm 0{\cdot}008) \\ &= (3{\cdot}28809 \pm 0{\cdot}00004) \,.\, 10^{15}\ \mathrm{sec}^{-1} \quad . \quad . \quad . \quad . \quad (7) \end{aligned}$$

(concerning the numerical values see p. 15, footnote, and p. 95). But on account of the uncertainty of the value of c, this true Rydberg frequency is not sufficiently exact for spectroscopic purposes.

We may form an idea of the great accuracy implied in writing down a number with seven figures (cf. R in (2)) if we recollect that the standard metre measure itself is defined only to within several μ's, that is at most to the millionth part of its length.

The fact that the accuracy of Balmer's formula is not overstrained may be recognised from the following table * which compares the observed and calculated values of the wave-lengths in international Ångström units (in air) for the first seven lines of the Balmer series :

TABLE 2

	$m = 3$	$m = 4$	$m = 5$	$m = 6$	$m = 7$	$m = 8$	$m = 9$
λ observed	6562·80	4861·33	4340·47	4101·74	3970·06	3889·00	3835·38
λ calculated	6562·80	4861·38	4340·51	4101·78	3970·11	3889·09	3835·43

This first example also serves to give the reader an idea of the extraordinary accuracy of spectroscopic measurement—accuracy of calculation and of measurement—which overshadows even the famous " astronomic accuracy."

Balmer concluded his short account in 1885 with the remark that the discovery of a corresponding " base number " h for elements other

* F. Paschen and R. Götze, *Seriengesetze der Linienspektren*, p. 24, Berlin, 1922. Compare A. Fowler, *Report on Series in Line Spectra*, London, 1922; this book appeared almost simultaneously with the preceding book. See also W. Grotrian, *Graphische Darstellung der Spektren von Atomen und Ionen mit ein, zwei und drei Valenz-Elektronen*, 2 vols., Springer, Berlin, 1928. The most comprehensive account of spectroscopy is, of course, given in the fundamental work by H. Kayser, *Handbuch der Spektroskopie*, Leipsic, 6 vols.; a seventh volume was written in conjunction with H. Konen.

than hydrogen would be very difficult, and would be possible only in the case of the most accurate measurement of wave-lengths. How astonished he would have been to learn that the same base number h, or rather (cf. 3) $R = \frac{4}{h}$, occurs in the spectra of all other elements. To have recognised this is, above all, the achievement of Rydberg, and to a lesser degree, of W. Ritz, who gave a more accurate expression.

The essential feature of Balmer's discovery is the denominator of the formula (1), in that he recognised it as the difference between two integers. From this we get formula (2) giving the difference of two "terms," the first being the **constant term,** which, at the same time, gives the series limit ($m = \infty$), the second being a **variable term.** This representation as the difference of two terms corresponds to the view of the wave-number as the difference of level between two energy-steps, which we treated in the preceding chapter (§ 6, eqn. (6)). Thus the terms inform us about the energy of the atom in its initial and its final state. *The object of spectroscopy is to find the series terms, namely, the atomic states and their energy-values.* The observing of spectral lines is only a means to enable us to arrive at the terms. *It is only when the spectral lines have been expanded into series and have been resolved into terms that the object of spectroscopy has been attained.*

Through his simple formula Balmer showed the way to the most general and most fruitful principle of spectroscopy, which was introduced in 1908 by W. Ritz, who recognised its fundamental importance, under the name, **"Principle of Combination."** Ritz formulated the principle in his original paper* thus: "By additive or subtractive combination, whether of the series formulæ themselves, or of the constants that occur in them, formulæ are formed that allow us to calculate certain newly discovered lines from those known earlier." But the fundamental importance of the principle of combination consists of the following: by expressing the wave-number of a spectral line as the difference of two terms, we define two different states or energy-levels of the atom in question. In this way several lines or series of lines determine several atomic states or energy-levels for the same element. The principle of combination now asserts that it is admissible to pass from any one of these levels to any lower level, and to derive from the difference of the two corresponding terms a new wave-number of the element. That this new wave-number happens to be obtained by additive or subtractive combination, as is stated in Ritz's original rule, is unessential. For example, if we represent two lines by means of the term-differences A − B and C − D, then we get new lines by combining the terms (B, D) and (A, C) with the wave-numbers D − B and C − A, which cannot thus be derived individually from A − B and C − D by the simple process of addition or sub-

* W. Ritz, Gesammelte Werke, published by the Schweizer Physikal. Gesellschaft, p. 162. Paris, Gauthiers Villars, 1911.

traction. In particular, when two terms of the original lines are equal to each other, we arrive at the new lines, as the special formulation of Ritz's law given above states, by addition or subtraction.

The principle of combination has maintained itself in the whole region of spectroscopy from infra-red to X-ray spectra as an *exact physical law* with the degree of accuracy that characterises spectroscopic measurement. It forms the foundation not only of the old theory of Bohr but also of the present wave-mechanical theory of spectra, and is, in essence, identical with Bohr's law in Chapter I, § 6, equation (6). But not all combinations that may be formed from the terms or energy-levels are equally probable. Rather, there are certain limitations ("rules of selection," cf. Chap. VII), that, in certain circumstances, reject certain combinations.

A first and particularly brilliant test of the principle of combination was offered by the hydrogen spectrum. Even Balmer himself raised the question whether the number n in his formula might not also take the value 3, but the state of spectroscopy at that time did not admit an answer. That is, he suspected lines with the wave-numbers

$$\nu = R\left(\frac{1}{3^2} - \frac{1}{4^2}\right) \qquad \nu = R\left(\frac{1}{3^2} - \frac{1}{5^2}\right), \text{ etc. .} \qquad (8)$$

Ritz demanded the existence of these lines on the ground of his principle of combination, since the first line of (4) may be obtained by forming the difference of the wave-numbers of H_α and H_β, while the second line may be obtained by forming the difference of H_γ and H_α, and so forth. Thereupon Paschen succeeded in finding in the infra-red region of the hydrogen spectrum intense lines of wave-lengths $\lambda = 18751{\cdot}3$ and $12817{\cdot}5$ Å, respectively, corresponding exactly to the previously calculated values.

Since that time there is no doubt that Balmer's formula must be written, in conformity with the conjecture of its discoverer, with two integers, thus :

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \qquad . \quad . \quad . \quad . \quad (9)$$

Paschen's lines form the first two members of the *infra-red series of hydrogen*, which are obtained by setting $n = 3, m = 4, 5, 6, \ldots$ Other terms of this "Paschen series" have been measured by F. S. Brackett,* who is also the first to have determined the first terms of the next successive series of wave-lengths $\lambda = 4{\cdot}05\mu$, which is given by $n = 4$, $m = 5$, and $\lambda = 2{\cdot}63\mu$, given by $n = 4$, $m = 6$ ($1\mu = 10^{-4}$ cms. $= 10^4$ Å). This Brackett series was completed by A. H. Poetker.† Lastly, A. H. Pfund ‡ found an infra-red line belonging to hydrogen at $\lambda = 7{\cdot}40\mu$, which is the first member of a "Pfund series" and corresponds to $n = 5$, $m = 6$.

* Astrophys. Journ., **56**, 154 (1922). † Phys. Rev., **30**, 418 (1927).
‡ Journ. Opt. Soc. Amer., **9**, 193 (1924).

What is the position with regard to the series that corresponds to the choice $n = 1$, $m = 2, 3, 4, \ldots$? It lies in the ultra-violet; its series limit $\nu = R$ is four octaves higher than the series limit of the ordinary Balmer series $\nu = R/4$, which also lies in the ultra-violet. The existence of this *ultra-violet* series of hydrogen was proved by Th. Lyman,* and is the final confirmation of Balmer's formula. The ground line of this " Lyman series " (which we might call the K-series of hydrogen, if we wished to follow the nomenclature of the X-ray spectra) is

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right), \qquad \lambda = 1215{\cdot}7 \text{ Å} \quad . \quad . \quad (10)$$

Balmer's formula (9) maintained itself in the sequel not only as a *sufficient*, but also as a *necessary* condition of the hydrogen lines. That is to say, not only are all the series of lines indicated by (9) actually observed in the case of hydrogen, but also no other lines belong to the hydrogen *atom* but those contained in (9). Up to the time (1913) when Bohr's theory was proposed, two further series were actually ascribed to hydrogen; they were given by the formulæ: †

$$\nu = R\left(\frac{1}{1{\cdot}5^2} - \frac{1}{\overline{m}^2}\right) \qquad \overline{m} = 2, 3, 4, \ldots \quad . \quad . \quad (11)$$

and

$$\nu = R\left(\frac{1}{2^2} - \frac{1}{(\overline{m} + \frac{1}{2})^2}\right) \qquad \overline{m} = 2, 3, 4, \ldots \quad . \quad (12)$$

They were called the " Principal Series " and the " Second Subordinate Series of Hydrogen," while Balmer's series itself was called the " First Subordinate Series," in accordance with a terminology that will be developed in Chapter VII, § 1.

The series (11) was originally measured by A. Fowler ‡ in the spectrum of a mixture of H and He; series (12) was discovered by Pickering in the spectra of nebular clusters (ζ-Puppis). According to Bohr's theory, however, both series are to be ascribed not to H but to He^+, that is, to ionised helium; at the same time formulæ (11) and (12) are to be remodelled and supplemented as follows (by multiplying numerator and denominator by 4):

$$\nu = 4R\left(\frac{1}{3^2} - \frac{1}{m^2}\right) \qquad m = 4, 5, 6, \ldots \quad . \quad (11a)$$

$$\nu = 4R\left(\frac{1}{4^2} - \frac{1}{m^2}\right) \qquad m = 5, 6, 7, \ldots \quad . \quad (12a)$$

Written in this way, they come under Balmer's form (9), with the difference that R is replaced by 4R, a fact that points to the double nuclear

* Astrophys. Journ., **23**, 181 (1906); **43**, 89 (1916).

† The current number has been called $\overline{m}$ here to distinguish it from the current number m of equations (11*a*) and (12*a*).

‡ Monthly Notices, **73** (1912).

charge of He (cf. eqn. (5) of § 4 of the present chapter), and with the further difference that the value of R in (11*a*) and (12*a*) does not agree exactly with the value of R in (9); this is explained by Bohr's theory of motion of the nucleus (cf. § 5 of the present chapter). The series (11*a*) and (12*a*) are the simplest examples of "spark lines," that is, of radiations which are emitted, not by the neutral, but by the ionised atom. The general theory of spark lines which we shall give in Chapters VII and VIII has been developed directly from the study of the spark lines of helium.

But our reasons for denying hydrogen the series (11) and (12) and ascribing them to helium are not only of a theoretical nature, but rest on experimental evidence given by precision measurements by A. Fowler * and F. Paschen,† to which we shall often have occasion to refer.

For the present we assert that the series (11) and (12) occur not only in mixtures of hydrogen and helium, but also in very pure helium.

We next remark that Pickering's series (12) includes only one-half of the lines represented by (12*a*), namely, those for which m is odd; the other half coincides nearly, but not quite (on account of the above-mentioned small difference in the value of R), with the ordinary Balmer series. In reality both together form a uniform series in that the lines of the one type arrange themselves according to intensity continuously with the lines of the other type.‡ It is therefore unjustifiable and arbitrary to detach one-half as the Pickering series and to ascribe it to hydrogen. The other half was overlooked earlier only because it could not be separated from the neighbouring true hydrogen lines. Further details on this point are given in § 5, Fig. 24.

The same is true of the relation between the series (11) and (11*a*). Of the lines represented by (11*a*), and actually observed, the series formula (11) represents only the members for which m is even. Hence, if we regard the series (11*a*), in the sense of (11), as the principal series of hydrogen, it becomes arbitrarily subdivided into two parts, of which only the one fits into the terminology of the hydrogen members. Actually, as Paschen shows, both parts as regards the intensity of their lines as well as the nature of their origin belong together, and form a uniform series.

We thus finally find our above assertion confirmed that the simple and integral character of spectral laws expressed in Balmer's formula represents a necessary criterion for emission by hydrogen. The spectral laws (11) and (12) that depart from the integral type, and thus do not come under Balmer's formula, do not belong to hydrogen but to ionised helium.

* "Series Lines in Spark Spectra," Proc. Roy. Soc., **90**, 426 (1914), and Phil. Trans., 1914.

† "Bohr's Heliumlinien," Ann. d. Phys., **50**, 901 (1916).

‡ This has been confirmed astrophysically in photographs of the O-stars taken by H. H. Plaskett, Publications of the Astrophys. Observ., Victoria (Canada), 1922.

Besides the Balmer spectrum, which, on account of its having four lines (H_α, H_β, H_γ, H_δ) in the visible region, is also called the four-line spectrum, hydrogen has a totally different kind of spectrum, the "many-lines spectrum" (*Viellinien-spektrum*) or "secondary spectrum." But this belongs to the molecule and not to the atom, and is to be regarded as a band-spectrum, although it does not exhibit the external characteristics of a band-spectrum. We shall revert to this question in Chapter IX.

Continuous spectra occur in the case of the hydrogen atom as well as in the case of the hydrogen molecule (cf. the beginning of the present section). It will not be possible to treat the continuous spectra completely, and to link it up appropriately with line- and band-spectra until we arrive at the second volume dealing with wave-mechanics.

§ 3. Introduction to the Theory of Quanta. Oscillators and Rotators

If we wish to penetrate further into the nature of the theory of quanta, we must not restrict ourselves to the special case of vibrational energy, which we treated alone in Chapter I, § 6. This case takes precedence historically; it led Planck to formulate from heat radiation a definition of his **quantum of action** h. The simple oscillator was used by Planck in a certain sense as a theoretical agent reacting to heat radiation; by means of it he developed his hypothesis of energy-quanta (see p. 36). This hypothesis is the foundation of the photo-electric law of Einstein, and also of its extension as Bohr's hypothesis concerning emitted and absorbed energy in atomic processes.

Adopting a more general standpoint, we shall consider instead of a special Planck oscillator *any arbitrary mechanical system whatsoever*, or, for the present, a little more specially, any *arbitrary moving point-mass*, whereby it matters little whether we assume it to be charged (an electron) or not.

We find it expedient to begin by enunciating the form that Newton gave the mechanical laws in his *Principia*, in particular his *Definitio II* and *Lex II* (*Definitio I* defines the conception of mass; *Lex I* is the law of inertia).

Definitio II: Quantitas motus est mensura ejusdem, orta ex velocitate et quantitate materiae conjunctim.

"The momentum (amount of motion) is the product of the mass and the velocity."

Lex II: Mutationem motus proportionalem esse vi motrici impressae et fieri secundum lineam rectam, qua vis illa imprimitur.

"The change in the momentum (amount of motion) is proportional to the impressed force and takes place in the direction in which that force acts."

In place of amount of motion we say **impulse** in order to emphasise

its directed character; we denote the impulse by p, and hence by *Definitio II* we have

$$p = mv \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As usual, we designate the position of the point by rectilinear co-ordinates x, y, z. For the sake of generalisation later, we shall, however, use, instead of different letters, different suffixes attached to the same letter thus: $q_1 = x$, $q_2 = y$, $q_3 = z$. The velocity is then given in magnitude and direction by

$$\dot{q}_k \Big(\text{where } \dot{q}_1 = \dot{x} = \frac{dx}{dt} \; \dot{q}_2 = \dot{y}, \text{ etc.} \Big),$$

and if p_1, p_2, p_3 are the corresponding components of the momentum or impulse then, by (1),

$$p_k = m\dot{q}_k \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The fact that the *dynamical* triplet of impulse co-ordinates occurs conjointly with the *geometrical* triplet of the co-ordinates of position is of great importance to us. Furthermore, the above formulation of the law of motion, Newton's *Lex II*, is of particular importance to us. It is wrong to speak of Newton's "Law of Acceleration." *It is not the kinematic quantity* **acceleration** * *but the dynamical quantity* **change of momentum** *that is regulated by this law.* In this sense we write down *Lex II* for each co-ordinate direction ($k = 1, 2, 3$) separately:

$$\dot{p}_k = \mathbf{K}_k = \frac{-\partial \mathrm{E}_{pot}}{\partial q_k} \quad . \quad . \quad . \quad . \quad (3)$$

In (3) we assume that the force $\mathbf{K}$ is derivable from a potential energy E_{pot} (function of the q_k's). The kinetic energy is

$$\mathrm{E}_{kin} = \frac{m}{2}(\dot{q}_1^2 + \dot{q}_2^2 + \dot{q}_3^2) = \frac{p_1^2 + p_2^2 + p_3^2}{2m}$$

by (2). We call the total energy, *considered as a function of* q_k *and* p_k, **Hamilton's function** H. We have

$$\mathrm{H}(q, p) = \mathrm{E}_{kin} + \mathrm{E}_{pot}, \qquad \frac{\partial \mathrm{H}}{\partial q_k} = \frac{\partial \mathrm{E}_{pot}}{\partial q_k}, \qquad \frac{\partial \mathrm{H}}{\partial p_k} = \frac{\partial \mathrm{E}_{kin}}{\partial p_k} = \frac{p_k}{m}.$$

Consequently we may write the fundamental equations (2) and (3) in the form

$$\frac{dq_k}{dt} = \frac{\partial \mathrm{H}}{\partial p_k}, \qquad \frac{dp_k}{dt} = -\frac{\partial \mathrm{H}}{\partial q_k} \quad . \quad . \quad . \quad (4)$$

* Of course, when the mass is constant $\dot{p} = m\dot{q}$ = mass × acceleration. But in general the mass is not constant; in the theory of relativity it is not even constant for a single particle of mass; and in ordinary mechanics it is not constant for a rigid body, for then the rôle played by mass is taken over by the moment of inertia, and this varies during motion. In these cases Newton's assertion about change of momentum remains valid, but not the statement about mass × acceleration which has wrongly become prevalent.

This *Hamiltonian* or *canonical* form of the equations of motion is remarkable not only on account of its symmetry but also because it remains preserved if any arbitrary new co-ordinates are introduced (cf. Note 2) and because it holds not only for an individual point-mass but also for any arbitrary mechanical system. For arbitrary co-ordinates and systems * the impulse p is defined by

$$p_k = \frac{\partial E_{kin}}{\partial \dot{q}_k} \quad . \quad . \quad . \quad . \quad (5)$$

in which the kinetic energy is *to be regarded as expressed as a function of the* q_k's *and the* $\dot{q}_k$'s. For the individual mass-point, (5) clearly becomes identical with (2) if rectangular co-ordinates are used.

The values of the co-ordinates q and p determine the corresponding state or **phase** (in Gibbs's terminology) of the system. To get a vivid picture of the state of motion in terms of the position (q) and the velocity or impulse (p), respectively, we imagine, in the case of an individual point-mass (which has three degrees of freedom), its three position co-ordinates q and its three impulse co-ordinates p drawn as perpendicular co-ordinate axes in a space of six dimensions, so that each point of this space represents a phase of our point-mass. In a system having f degrees of freedom this **phase-space** is of $2f$ dimensions.

Let us first restrict ourselves to systems of one degree of freedom, for which the general phase-space resolves into a single phase-plane.

We draw q and p as rectangular co-ordinates in the phase-plane of our system. In this plane we construct the *phase-paths* or *orbits*, that is, the sequence of those graph points that correspond to the successive states of motion of the system. Choosing any point as an initial state we may plot the phase-paths and with them densely cover the whole of the phase-plane. The characteristic feature of the quantum theory, however, is that it selects a discrete family of phase-orbits from the infinite manifold of phase-orbits. To define these selected orbits, we shall first consider the area of the phase-plane included between two arbitrary phase-orbits : we shall call such an area a **phase-area.** We then draw our family of orbits so that the phase-area between two neighbouring orbits is always equal to the quantum of action h. In this way h acquires the significance of the *elementary region* (or element) *of the phase-area.* We shall regard this significance as constituting the true definition of Planck's quantum of action h. We shall next illustrate these rather abstract ideas by

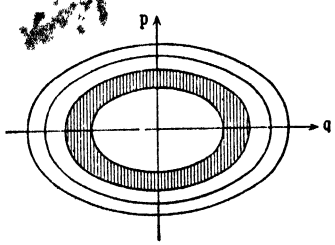


FIG. 20.—Phase orbits of a linear oscillator.

* We shall discuss how the definition is to be generalised for the case where the acting forces have no potential in Note 5 by a special example.

means of two very important special cases, that of the **oscillator** and that of the **rotator.**

We give the name **linear oscillator** to a point-mass m that is bound elastically to its position of rest, and that can be moved to either side of this central position only in a direction $x = q$ or its reverse, whereby it experiences a restoring force but no damping resistance. The oscillator is the simplest instance of a centre of vibration such as is assumed in optics in the form of a " quasi-elastically bound electron." We use the more accurate term " harmonic oscillator " if we wish to emphasise that the latter has a definite characteristic vibration independent of the amplitude. Let the vibration number or frequency of the oscillator (number of its free vibrations per unit of time) be ν. The vibration phenomenon is then expressed by

$$x = q = a \sin 2\pi\nu t \quad . \quad . \quad . \quad . \quad (6)$$

In this case the impulse p simply becomes equal to $m\dot{q}$ (according to (2), and in agreement with (5)). Hence

$$p = 2\pi\nu ma \cos 2\pi\nu t \quad . \quad . \quad . \quad . \quad (7$$

By eliminating t from (6) and (7) we get as our phase-orbit an ellipse in the p-q-plane having the equation

$$\frac{q^2}{a^2} + \frac{p^2}{b^2} = 1 . \quad . \quad . \quad . \quad . \quad (8)$$

in which the minor axis b is defined by

$$b = 2\pi\nu ma \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The area of the ellipse is then

$$ab\pi = 2\pi^2\nu ma^2 .$$

We next assert that this same quantity is also equal to $\frac{W}{\nu}$, where W denotes the energy, which remains constant during the vibration. If, for example, we calculate W at the time $t = 0$, the potential energy is zero, and the kinetic energy is

$$\frac{m}{2}a^2(2\pi\nu)^2 = W \quad . \quad . \quad . \quad . \quad (10)$$

and hence, actually,

$$ab\pi = \frac{W}{\nu} . \quad . \quad . \quad . \quad . \quad (11)$$

By altering W we get in the phase-plane the phase-orbits as a family of similar ellipses since, by (9), the ratio $\frac{b}{a}$ has the constant value $2\pi\nu m$. We have now to make the selected ellipses of this family succeed one another in such a way that the elliptic zones have each the same

area h. Hence, if we denote the difference between the energy-constants for two successive ellipses of the family by ΔW, we obtain from (11):

$$h = \frac{\Delta W}{\nu}, \quad \Delta W = h\nu \qquad . \quad . \quad . \quad (12)$$

If we number the ellipses thus: 0, 1, . . . n, and call the corresponding energies W_0, W_1, . . . W_n, it follows from (12) that

$$W_n = W_0 + h\nu n \qquad . \quad . \quad . \quad . \quad (13)$$

Whereas in the classical theory all points of the phase-plane are of equal value and represent possible states of the oscillator, the states for which the graph points lie on one of the ellipses of our family are distinguished. They represent the **stationary states** of the oscillator, that is, such states as the oscillator may pass through without cessation and without loss of energy, in other words, in the case of a charged point-mass, *without radiating energy*. But from time to time the oscillator changes its energy; it emits energy when its graph point jumps over to a smaller ellipse; it absorbs energy when its graph point is transferred to a larger ellipse. Emission and absorption occur in multiples of the energy quantum $h\nu$.

If we set $W_0 = 0$ in (13), we arrive at the first form of Planck's theory:

$$W_n = n\epsilon, \ \epsilon = h\nu \qquad . \quad . \quad . \quad . \quad (13a)$$

But if we assume that corresponding to the quantum state zero there is a certain "zero-point energy," and if we set this equal to $\frac{h\nu}{2}$, an assumption which is confirmed by wave-mechanics, we arrive at a second form of the theory which Planck proposed in 1911. The energy of the n^{th} quantum state then becomes

$$W_n = (n + \tfrac{1}{2})\epsilon = (n + \tfrac{1}{2})h\nu \qquad . \quad . \quad (13b)$$

We generalise this for any arbitrary mechanical system of one degree of freedom and assert that: *the graph-point of the system in the phase-plane is restricted, according to the quantum theory, to certain favoured "quantised" orbits. Each of these orbits encloses with its neighbouring orbit an elementary region of area h.* Let the n^{th} of these orbits (if closed) have the area

$$J = \iint dpdq \qquad . \quad . \quad . \quad . \quad (14)$$

wherein the integral is to be taken over *the interior of the n^{th} orbit.* If we perform the integration with respect to p (corresponding to the elementary formula $\int ydx$ for the area of a curve $y = f(x)$), we get

$$J = \int pdq \qquad . \quad . \quad . \quad . \quad (14a)$$

This integral is to be taken *along the n^{th} orbit itself*. We shall call (14*a*) the *phase-integral*.

We consider the precise formulation of the quantum hypothesis to consist in the postulate that the difference between the phase-integrals for two successive orbits must be equal to h :

$$\Delta J = h, \quad J = J_0 + nh \quad . \quad . \quad . \quad (15)$$

This postulate singles out of *the continuous manifold of all mechanically possible motions a discrete and infinite number of real motions, such as are possible according to the theory of quanta*. In contradistinction to this general form of the quantum hypothesis, the original hypothesis of energy-quanta that was formulated by Planck for the phenomena of heat radiation is only a special result of the general quantum postulate adapted to the oscillator. In the preceding, we were relieved from the task of evaluating the phase-integral (14) only because we were able to calculate the area of the ellipses directly from the formula $ab\pi$. In particular, if we assume $J_0 = 0$, we obtain from (15) the following formulation analogous to (13*a*) :

$$J = \int p dq = nh \quad . \quad . \quad . \quad . \quad (15a)$$

which formed the foundation of the older quantum theory, but which is not confirmed throughout by wave-mechanics.

From the oscillator we pass on to the **rotator.** This term is to denote a point-mass m, which rotates about a fixed centre uniformly in a circle of radius a. The natural co-ordinate of position is here the angle ϕ which the radius to the point-mass makes with an arbitrary initial radius $\phi = 0$. We thus set $q = \phi$. The kinetic energy is

$$E_{kin} = \frac{m}{2} a^2 \dot{q}^2 \quad . \quad . \quad . \quad . \quad (16)$$

In the case of uniform rotation the potential energy will certainly be independent of ϕ ; it is indifferent to us whether this energy depends on a since a is constant during the motion. Hence we may write

$$E_{pot} = \text{const.}$$

The impulse co-ordinate in this case corresponding to the co-ordinate q is by (5) and (16) :

$$p = ma^2\dot{q} \quad . \quad . \quad . \quad . \quad . \quad (17)$$

It signifies the moment of momentum with respect to the centre of the circular orbit. Since $\dot{q} = \text{const.}$, this moment of momentum (*Impuls-moment*) p is constant during the motion ; this, in fact, follows immediately from the equations of motion (4). Therefore the phase-orbit of the rotation (the orbit in the phase-plane q-p) is a straight line parallel to the q-axis (Fig. 21). Hence the phase-orbit is not a closed curve in

his case. Hence we have here first to define what is to be regarded as the area of the phase-orbit.

This is done as follows : the phase of the rotator (its position in the orbit and the direction of its momentum or impulse) becomes repeated after every complete rotation. Thus, the true phase-orbit is not an infinitely long straight line but a finite one that repeats itself. In the q-direction the phase-plane of the rotation has only the length 2π ; we may, for example, cut it along the lines $q = \pm \pi$ and join the edges so as to form a cylinder. The surface area of the cylinder between the n^{th} and the $(n-1)^{th}$ phase-orbit, being a rectangle on the base 2π, is equal to $2\pi(p_n - p_{n-1})$. We have to set this surface equal to h. We then get for the surface between the n^{th} and the zero phase-orbit, which is represented by the q-axis, the expression

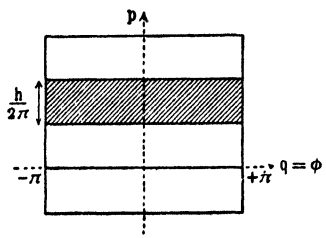


FIG. 21.—Phase orbits of a rotator.

$$2\pi p_n = nh \quad . \quad . \quad . \quad . \quad . \quad (18)$$

This is the surface that takes the place of the area of the closed curves in the case of the oscillator.

From this we see that **the rotator is to be quantised not in energy quanta but in quanta of moment of momentum. In the case of the rotator the moment of momentum must be a whole multiple of $\frac{h}{2\pi}$.** If, on the other hand, we calculate the energy (kinetic energy) of the rotator, then it follows from (16) and (17) that

$$E_{kin} = \frac{p\dot{q}}{2}$$

and from (18), when $\nu = \frac{\dot{q}}{2\pi}$,

$$E_{kin} = \frac{nh}{2}\frac{\dot{q}}{2\pi} = \frac{nh\nu}{2} \quad . \quad . \quad . \quad . \quad (19)$$

Here ν denotes the rotation frequency of the rotator (number of full revolutions per unit of time), which appropriately takes the place of the vibration number of the oscillator. Hence if we wish to speak of energy-quanta $h\nu$ in the case of the rotator, too (which is better avoided altogether), we should find *its energy to be not a whole multiple, but a half-multiple of the energy-element $h\nu$.*

We pass on from the case of the oscillator and the rotator to the case of *any* number of degrees of freedom. In this case we must demand not *one* quantum condition of the form (15) but f different quantum conditions, by which each of the f degrees of freedom in a certain sense becomes fixed. We infer this, as a general result, from

the perfect sharpness of the spectral lines, which allows us to conclude that the atomic phenomena underlying their origin are fully discrete. For this purpose the author has adopted a direct " heuristic " method,* which leads to the same results as those simultaneously obtained by Planck † as a consequence of a more systematic investigation into the treatment, along quantum lines, of systems of several degrees of freedom. The postulate of the author is : *we must impose the condition* (15*a*) *on each individual degree of freedom of the system, that is, we must postulate the value of the phase-integral for the k^{th} degree of freedom to be a whole multiple of h :*

$$J_k = \int p_k dq_k = n_k h \quad . \quad . \quad . \quad . \quad (20)$$

A little earlier than the author, W. Wilson ‡ developed the same postulate from the law of heat radiation.

By setting $n_k = 1, 2 \ldots$ in turn in (20) we fix the first, second . . . quantised phase-orbit of the k^{th} degree of freedom. Since the system is bound by each of its degrees of freedom to one of these orbits, the required definiteness of its motions is attained. " Degenerate systems," namely, systems for which the number of necessary conditions may be reduced, will be discussed in § 7.

We might generalise equation (20) in the sense of equation (15). In that case we should have to fix a value for ΔJ_k, and not for J_k itself, that is, we should have to leave the quantity J_0 that occurs in (15) undetermined for every co-ordinate. We shall, however, keep essentially to the original formulation (20) of the " quantum rules " in this volume, and shall make them more rigorous later in the second volume.

If it is to be possible for integrals of the form (20) to be integrated for every co-ordinate separately, that is, without a knowledge of the simultaneous behaviour of the remaining co-ordinates, then it must be possible to represent every p_k as a pure function of the corresponding q_k. In this case the mechanical system is called *separable*. This property is discussed in detail in § 6. The condition for it was first given in important papers by Schwarzschild ‖ and Epstein,¶ which linked up with papers published by the present author in 1915 and 1916. The quantum rule (20) has an exact meaning only when we restrict its application to separable systems, for it is only then that we can answer the question : what *co-ordinates* and what *limits of integration* are to be used in performing (20) ?

* " Zur Theorie der Balmerschen Serie," Sitzungsberichte der Münchener Akademie, Dec., 1915, and Jan., 1916, as also Ann. d. Phys., **51**, 1 (1916).

† M. Planck, " Die Struktur des Phasenraumes," Ann. d. Phys., **50**, 385 (1916).

‡ W. Wilson, " The Quantum Theory of Radiation and Line-spectra," Phil. Mag., **29**, 795, June, 1915. A historical account has been given by N. Bohr, cf. *loc. cit.*, p. 118, footnote 1, in which a work by Hn. Ishiwara, simultaneous with that of W. Wilson, is referred to.

‖ K. Schwarzschild, *Zur Quantentheorie*, Berlin, Sitzungsber., April, 1916, which appeared on 11th May, the date of Schwarzschild's death.

¶ P. S. Epstein, Ann. d. Phys., **50**, 489 (1916) ; and **51**, 168 (1916).

The co-ordinates q_k meant in (20) *are precisely those into which the system can be separated.* If there are several possible ways of effecting separation the types of orbit determined by the phase-integrals become different, but the energies in the orbits, which are the essential factors, agree.

The limits of integration must be fixed as follows : *the separation-co-ordinate q_k is to traverse in the course of integration the whole region that is necessary to characterise the phases of the system uniquely.* In the case of a cyclic co-ordinate ($q = \phi$, rotation) this region stretches from $-\pi$ to $+\pi$ (cf. Fig. 21, in which the plane is to be bent into a cylinder), the radius vector r extending from the region r_{min} to r_{max} and back again to r_{min}. Further examples will be given in this and in the next chapter.

Finally, it is to be noted that the phase-integral, in virtue of its geometrical significance as a surface in the (q, p)-plane, is necessarily a positive magnitude ; hence it follows that the " quantum-numbers " n_k are also necessarily positive numbers.

If we survey what we have learned from the quantum treatment of the oscillator and rotator and from the extension to general systems —all of which is based on the fact that spectral lines are sharply defined —we arrive at a totally new view of natural phenomena. The quantised states, those defined by integers, are favoured above all other possibilities in being stationary states of the system ; they do not link up continuously with each other but form a *net-work. Phase-space, regarded as the manifold of all conceivable states, including those which are not stationary, is traversed by the graph curves of the stationary orbits so as to form a network. The size of the meshes is determined by Planck's constant h.*

§ 4. Bohr's Theory of Balmer's Series

We here make the simplest assumptions possible : a nucleus of negligible size carrying a charge $+ Ze$, and an electron of charge $-e$ likewise concentrated at a point ; the mass of the nucleus is considered infinitely great compared with the mass m of the electron (that is, we are confronted with a " one body problem " instead of the actual " two body problem ") ; Coulomb's law is valid and likewise ordinary (pre-relativistic) mechanics ; the electron moves in a circle * about the nucleus and is a simple " rotator." Concerning these assumptions we remark that for hydrogen, in particular, $Z = 1$; the calculation with Z is worth doing because it also includes the case of He^+ and Li^{++} (cf. Chap. II, § 3, Nos. 4 and 6). The assumption that the nuclear mass is infinitely great is a good approximation even for hydrogen (according to earlier remarks, cf. equation (16) of the pre-

* We must remark that Bohr speaks more generally of elliptic orbits, even in his first paper, Phil. Mag., **26** (1913).

ceding section, $m : m_H = 1 : 1847$); but in the next section we shall let this assumption drop.

The orbit of the electron is fixed by two conditions, one prescribed by the classical theory, the other by the quantum theory. The classical theory requires that the external forces be in equilibrium with the inertial forces. The inertial force of circular motion is the centrifugal force :

$$\frac{mv^2}{a} = mv\omega = ma\omega^2$$

($v = a\omega$ is the linear velocity, ω the angular velocity of the rotating electron, a the radius of the orbit). The only external force is the Coulomb force of electric attraction $\frac{Ze^2}{a^2}$. Hence the condition of the classical theory is

$$ma\omega^2 = \frac{Ze^2}{a^2}$$

or

$$ma^3\omega^2 = Ze^2 \quad . \quad . \quad . \quad . \quad (1)$$

The quantum condition is given by the equation for the moment of momentum of the rotator,* namely, $2\pi p = nh$ (cf. eqn. (18), § 3, of this chapter).

With our present symbols the moment of momentum takes the form

$$p = mva = ma^2\omega.$$

Hence we get the quantum condition as

$$ma^2\omega = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad (2)$$

Dividing (1) by (2), we get

$$v = a\omega = \frac{2\pi Ze^2}{nh} \quad . \quad . \quad . \quad . \quad (3)$$

Inserting this value in (2),

$$a = \frac{n^2h^2}{4\pi^2mZe^2} \qquad \omega = \frac{8\pi^3mZ^2e^4}{n^3h^3} \quad . \quad . \quad . \quad (4)$$

We also write down the value of the period of revolution τ,

$$\tau = \frac{2\pi}{\omega} = \frac{n^3h^3}{4\pi^2mZ^2e^4} \quad . \quad . \quad . \quad . \quad (4a)$$

* It is worthy of remark that, before Bohr, J. W. Nicholson (Monthly Notices, **72** (1912), cf. in particular p. 679) set up the quantum condition for the rotator, and used it to interpret certain lines of the sun, as well as of nebulæ. Since, however, Nicholson did not determine the emitted radiation in terms of quanta, like Bohr, but only set it equal to the mechanical frequency, his theory is very different from that of Bohr.

Thanks to our two conditions, then, the two unknowns a and ω or τ are determined. *Both together demand that the electron move only in certain "quantised" circles on the* 1^{st}, 2^{nd}, . . . n^{th} *"Bohr circle"; n* is the "quantum number" of the orbit. The radii of the circles are proportional to the squares of the quantum numbers :

$$a_1 : a_2 : a_3 : \ldots a_n = 1^2 : 2^2 : 3^2 : \ldots n^2 \quad . \quad . \quad (5)$$

The times of revolution in the Bohr circles are proportional to the cubes of the quantum numbers :

$$\tau_1 : \tau_2 : \ldots \tau_n = 1^3 : 2^3 : \ldots n^3 \quad . \quad . \quad . \quad (6)$$

To bring out the analogy with the planetary system still more and to prepare for later generalisations leading to elliptic orbits, we recapitulate our results so far obtained in the form of Kepler's laws :

Kepler's First Law : *The planet moves in a circle at the centre of which the sun is situated.* There is a discrete infinite number of orbits ; the radius of the n^{th} orbit is given by the quantum number n.

Kepler's Second Law : *The radius vector from the sun to the planet describes equal areas in equal times.* The surface-constant of the n^{th} orbit (which is proportional to our moment of momentum p) is equal to n times Planck's quantum of action.

Kepler's Third Law : *The squares of the periodic times (of revolution) are proportional to the cubes of the radii of the orbits.* For, by (6) and (5), the time of revolution is proportional to n^3, and the orbital radius is proportional to n^2.

As above remarked, for hydrogen Z = 1. The radius of the first Bohr circle is therefore by (4), in the case of hydrogen,

$$a = a_1 = \frac{h^2}{4\pi^2 me^2} \quad . \quad . \quad . \quad . \quad (7)$$

We next determine the velocity v_1 in the first Bohr circle and divide it by the velocity of light c. We call the ratio $\frac{v_1}{c}$ simply α. By (3), we get

$$\alpha = \frac{v_1}{c} = \frac{2\pi e^2}{ch} \quad . \quad . \quad . \quad . \quad (8)$$

Using the values * : $e = 4{\cdot}77 \,.\, 10^{-10}$, E.S.U. $\frac{e}{m} = 1{\cdot}77 \,.\, 10^7 \,.\, c$ E.S.U., $h = 6{\cdot}55 \,.\, 10^{-27}$ (cf. p. 36), we get by calculation

$$a_1 = 0{\cdot}528 \,.\, 10^{-8} \text{ cm.} \qquad \alpha = 7{\cdot}28 \,.\, 10^{-3} \qquad \alpha^2 = 5{\cdot}31 \,.\, 10^{-5} \quad (9)$$

* Here and in the sequel e is to be taken as measured in ("electrostatic") units, as is evident from the above statement for Coulomb's law. According to the concluding remark of Chapter I, § 2, we should therefore multiply the given values of e and $\frac{e}{m}$ by $c = 3{\cdot}00 \,.\, 10^{10}$.

The value of α will be the determining factor in Chapter V—as the constant of the *fine structure* of spectral lines. From the value of a_1 we get for the diameter $2a_1$ of the hydrogen atom in its " normal state " the order of magnitude 10^{-8} cms., corresponding to the ideas that were gained about atomic size in other ways (kinetic theory of gases, etc.).

We next calculate the energy of the electron in its various orbits and take this opportunity to explain why we just now called the first orbit the normal state of the atom. We again designate the nuclear charge by Ze. The energy is composed of potential and kinetic energy. The potential (Coulomb) energy is, in view of (4),

$$E_{pot} = \frac{-Ze^2}{a} = -\frac{4\pi^2 mZ^2e^4}{n^2h^2} \quad . \quad . \quad . \quad (10)$$

The negative sign indicates attraction. In the case of repulsion we should have to exert work in bringing the electron from infinity up to the nucleus, as in the case of a spring that we set ; this would correspond to the positive sign. When the force is attractive, we correspondingly gain energy, and have thus to exert negative work.

In general we have the rule in a Coulomb field (see Note 3) that

$$E_{kin} = -\tfrac{1}{2} E_{pot} \quad . \quad . \quad . \quad . \quad (11)$$

We can immediately confirm this rule here. For, by (3),

$$E_{kin} = \frac{m}{2}v^2 = \frac{2\pi^2 mZ^2e^4}{n^2h^2} \quad . \quad . \quad . \quad (12)$$

and this is, by (10), actually identical with half of the negative potential energy with the sign reversed. If W denotes the constant value of the total energy then by (10) and (12)

$$W = E_{kin} + E_{pot} = \frac{-2\pi^2 me^2E^2}{h^2} \cdot \frac{1}{n^2} \quad . \quad . \quad (13)$$

Thus we may supplement our third Kepler law by stating that *the energy constants of the various orbits are inversely proportional to the squares of the corresponding quantum numbers.*

Our way of counting the energy entails that we give to an infinitely great orbit the energy zero. As a result of this the energy constant for all finite paths comes out negative. As we are concerned later only with differences of energy the negative sign causes no difficulty whatsoever, although it appears to contradict the nature of energy. But we should immediately arrive at a positive value for the energy if we were really to calculate the total energy of the moving electron, and thus count besides the kinetic and potential energies also, for example, the " proper " energy contained in the field of the electron. According to the view of the theory of relativity, the latter energy is simply equal to mc^2, that is, equal to an amount of energy, which is many times greater than the other parts of the energy and which would therefore make the

sign of the total amount positive. In the same way, we could include the still considerably greater positive proper energy of the nucleus. But since these proper energies are constant, they naturally cancel when we form energy-differences and they are, therefore, more conveniently left out of account from the very outset.

Our energy-constant W has the algebraically smallest value in the first (innermost) orbit. If we call it W_1, then in the 2nd and 3rd orbits, respectively, we have $W_2 = \frac{1}{4}W_1$, $W_3 = \frac{1}{9}W_1$. These amounts are $> W_1$, since $W_1 < 0$. Hence the electron can be lifted from an inner to an outer orbit only by an **addition of energy.** It can fall from an outer to an inner orbit when it **loses energy.** The innermost orbit is therefore most stable and represents, as we said earlier, the **normal state** of the revolving electron. As a rule the hydrogen atom is in this *unexcited* state. All the other states, in which the electron describes a more external orbit, are called " excited " states. The additional energy required to bring about this change of state may be transmitted to the atom electrically or thermally, by collisions with electrons or with other atoms.

According to the principles of the quantum theory the totality of excited and unexcited states represents a *discrete series* of possibilities. In this respect our atomic planetary system differs from the solar planetary system.* But our system also deviates definitely from classical electrodynamics. According to the latter theory, as we saw in Chapter I, § 5, an electron radiates energy when it is accelerated. Uniform rotation is an accelerated motion (on account of change of direction of velocity, although the magnitude of the velocity remains constant). But the quantum theory must postulate that its stationary orbits are *radiationless* (occur without the emission of radiation). This is immediately clear in the case of the ground orbit, in particular ; otherwise the atom would lose its energy in a very short time and we should have no permanent, invariable, atom at all.

The process of emission, like the other processes in the atom, is, according to the quantum theory, discontinuous. The continuous decrease of energy assumed in classical theory becomes replaced in the quantum theory by a broken line. This line is horizontal in parts, namely, when it represents the atom as being in a stationary quantised state ; it sinks by a finite amount when the atom passes from an excited to a quantised state of less energy, in particular, in passing to the ground state. According to what law does this discontinuous decrease of energy occur ?

These were brought together under Einstein's law (cf. Chap. I,

* We find it incumbent on us to mention the Titius-Bode rule, which states a simple arithmetical relationship holds approximately between the orbital radii of the planets. We cannot, however, persuade ourselves that this is also an expression of a quantum theory, and do not therefore find it possible to compare this rule with our laws for discrete atomic orbits.

§ 6), and were extended as far as Bohr's *frequency condition* for spectral emission (*loc. cit.* eqn. (6)) :

$$h\nu = W_n - W_m \quad . \quad . \quad . \quad . \quad (14)$$

This equation states that if the atom passes over from an initial state of energy W_n to a final state of lesser energy W_m, then the excess of energy is radiated out in the form of a monochromatic wave of light, the frequency ν of which is determined by just this equation (14). Each such transition thus causes an emission of well-defined light and is observed as a sharp spectral line. How the change of the liberated atomic energy into light-energy is effected is still a matter of mystery. Earlier, when dealing with Einstein's law, we emphasised that equation (14) does not rest on the ideas of the continuous electromagnetic field, but on the idea of light quanta (photons).

We now substitute the energy-value (13) in equation (14). Passing immediately from the frequency ν (sec^{-1}) to wave-number ν ($cm.^{-1}$), we divide the right-hand side of equation (14) by c (cf. p. 71, eqn. (6)). Let the quantum number for the final orbit be n, and for the initial orbit $m > n$. We get

$$\nu = RZ^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad . \quad . \quad . \quad (15)$$

when we have used the abbreviation

$$R = \frac{2\pi^2 me^4}{ch^3} \quad . \quad . \quad . \quad . \quad (16)$$

Since $Z = 1$ for the hydrogen atom we get from (15) precisely *the Balmer series in its general form* (9) on page 73, *and for R we have the significance of the Rydberg constant.* For other hydrogen-like atoms, He^+, Li^{++}, and so forth (15) holds if we write $Z = 2$, 3, etc.

But the sweeping success of Bohr's theory is not founded only on the derivation of Balmer's formula, but especially on the numerical calculation of the Rydberg-Ritz constant R that occurs in it. Before Bohr, A. E. Haas,* in particular, had already proved the universal nature of this constant, and had shown how it was very probable that it could be expressed in terms of h and electronic data. But Bohr's theory first brought complete clearness by giving the relation (16). If we use the values given on page 86 :

$$e = 4{\cdot}77 \,.\, 10^{-10} \qquad e/m = 1{\cdot}77 \,.\, 10^7 \,.\, c \qquad h = 6{\cdot}55 \,.\, 10^{-27}$$

then it follows that

$$R = 1{\cdot}09 \,.\, 10^5 \text{ cm.}^{-1} \quad . \quad . \quad . \quad . \quad (17)$$

This value of R agrees, except for the last, not quite certain, figure with the observed value in equation (2) of page 70, in which $R = 1{\cdot}09678$. Bohr's theory is thus confirmed very strikingly.

* Sitzungsber. Wiener Akad., March, 1900.

We shall now continue to reverse the sequence of results and use the theoretical formula for Rydberg's constant to correct one of the data occurring in it, namely, e, m or h. We actually know Rydberg's number to a degree of accuracy that we can never hope to attain in measurements of e, $\frac{e}{m}$ or h. This leads us to the *problem of spectroscopic units*, which we shall, however, be able to solve only in the next section when we have deepened the theory of Rydberg's constant. The problem is **to calculate the universal constants e, $\frac{e}{m}$, h from purely spectroscopic data with "spectroscopic accuracy."**

In Fig. 22 we once more summarise Bohr's theory graphically. The ultra-violet (Lyman) series ($n = 1$), the visible Balmer series ($n = 2$), and the infra-red Paschen series ($n = 3$), and the Brackett series, which is still more red, are indicated by the arrows denoting the corresponding electronic transitions.

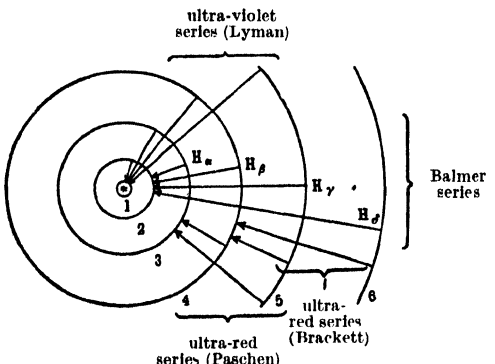


FIG. 22.—Diagrammatic representation of the origin of the hydrogen series from the electron transitions between the discrete circular orbits of the Bohr theory.

In Fig. 22 the different circular orbits have been drawn in one plane. This is, of course, arbitrary. The position of the orbit remains undefined in space and is, moreover, of no account for the problem of spectral lines, since this is concerned only with the energy-differences of the orbits. In the last section of the present chapter we shall discuss the question of orientating the hydrogen orbits in space, that is, of performing "spatial quantising." Further, we shall see in the next volume that the elementary ideas of orbits are banished by wave-mechanics and are replaced by statistical mean values.

§ 5. Relative Motion of the Nucleus

In the preceding section the nuclear mass was assumed to be infinite and the nucleus itself was assumed to be at rest. We now take into account the fact that the mass of the nucleus is finite and then see that it, too, will move. Our first Kepler Law on page 86 will now accordingly be enunciated thus:

The planet and the sun each move in a circle about their common centre of gravity.

In Fig. 23 let m be the mass of the planet, M that of the sun. According to the law of conservation of the centre of gravity, the centre of gravity S of m and M remains at rest. m and M move on their circles at the ends of a common diameter with the common angular velocity ω. Let a be the distance Sm, A the distance SM. Then

$$am = \mathrm{AM} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

from which it follows

$$a = (a + \mathrm{A})\frac{\mathrm{M}}{\mathrm{M} + m}, \qquad \mathrm{A} = (a + \mathrm{A})\frac{m}{\mathrm{M} + m} . \quad . \quad (2)$$

The *classical* condition (p. 85) now requires that the Coulomb attraction is equal not only to the centrifugal force of the planet, but also to that of the sun. Thus

$$ma\omega^2 = \mathrm{MA}\omega^2 = \frac{Ze^2}{(a + \mathrm{A})^2}.$$

This double equation reduces, on account of (1), to a simple equation. By substituting a from (2) and by using μ as the "resultant" mass of m and M, namely,

$$\mu = \frac{\mathrm{M}m}{\mathrm{M} + m}, \qquad \frac{1}{\mu} = \frac{1}{m} + \frac{1}{\mathrm{M}} \quad . \quad (3)$$

we get $$\mu(a + \mathrm{A})^3\omega^2 = Ze^2 \quad . \quad . \quad (4)$$

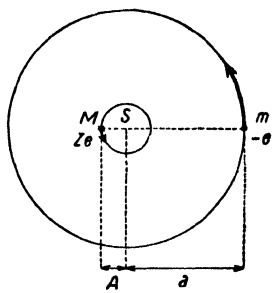


FIG. 23.—Motion of the nucleus in hydrogen. Both the nucleus and the electron move in circular orbits round the common centre of gravity.

The *quantum* condition next becomes added to the classical condition. This deals with the moment of momentum p of the rotator. The latter quantity is composed of the moment of momentum of the planet $ma^2\omega$ and that of the sun $\mathrm{MA}^2\omega$, thus :

$$p = ma^2\omega + \mathrm{MA}^2\omega,$$

by equations (1), (2), and (3) we write for p successively,

$$p = ma(a + \mathrm{A})\omega = \frac{m\mathrm{M}}{\mathrm{M} + m}(a + \mathrm{A})^2\omega = \mu(a + \mathrm{A})^2\omega \quad . \quad (5)$$

The quantum condition requires that $2\pi p = nh$, thus we get

$$\mu(a + \mathrm{A})^2\omega = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad (6)$$

Equations (4) and (6) agree with equations (1) and (2) of the preceding section, with the exception that μ and $a + \mathrm{A}$ takes the place of m and a. Consequently we may use the solutions for these equations obtained from (4) of the previous section. The result is

$$a + \mathrm{A} = \frac{n^2h^2}{4\pi^2\mu Ze^2}, \qquad \omega = \frac{8\pi^3\mu Z^2e^4}{n^3h^3} \quad . \quad . \quad (7)$$

The potential energy between the sun and the planet is now (cf. (10) of the preceding section)

$$E_{pot} = -\frac{Ze^2}{a+A} = -\frac{4\pi^2\mu Z^2e^4}{n^2h^2}.$$

The kinetic energy is again equal to half the potential energy with reversed sign (this theorem is proved in Note 3 at the end of the book for moving nuclei, too), hence the total energy is

$$W = E_{kin} + E_{pot} = -\frac{2\pi^2\mu Z^2e^4}{n^2h^2} \quad . \quad . \quad . \quad (8)$$

The circumstance that μ, the "resultant" mass of the sun and planet enters into this equation, points to the fact that we are now concerned with the energy-constant of the common motion of both masses (their relative motion). For this common motion there is a discrete series of quantised states of motion that are singled out of the manifold of all states of motion by the quantum number n, in exactly the same way as previously for the cases in which the planetary orbits were alone considered.

We now consider a transition from an initial state of motion (with the energy-constant W_m, quantum number m) to a final state of motion (with the energy-constant W_n, quantum number $n < m$), and assume that the energy set free again becomes transformed into monochromatic radiation, according to equation (14) of the previous section. The energy set free is derived now, not only from the planet but also from the sun during the transition; the sun's orbit alters simultaneously with that of the planet in a ratio definitely fixed by the change in the quantum numbers. The spectral formula obtained in this way is clearly again equation (16) of the previous section, but with μ in place of m. Consequently we get for Rydberg's constant

$$R = \frac{2\pi^2\mu e^4}{ch^3} = \frac{2\pi^2 me^4}{ch^3\left(1+\frac{m}{M}\right)} = \frac{R_\infty}{1+\frac{m}{M}} \quad . \quad . \quad (9)$$

Here we have inserted the value of μ out of equation (3), and have divided the denominator by M. The symbol R_∞ recalls the earlier value of R in equation (16) of the previous paragraph, which was actually obtained under the assumption that $M = \infty$. Equation (9) contains the following remarkable result:

Owing to the relative motion of the nucleus Rydberg's constant becomes reduced in the ratio $\left(1+\frac{m}{M}\right) : 1$. Rydberg's constant is least for hydrogen, for which its value is

$$R_H = \frac{R_\infty}{1+\frac{m}{m_H}} \quad . \quad . \quad . \quad . \quad (10)$$

Its value for the hydrogen-like He^+-ion being

$$R_{He} = \frac{R_\infty}{1 + \frac{m}{m_{He}}} = \frac{R_\infty}{1 + \frac{1}{4}\frac{m}{m_H}} \quad . \quad . \quad . \quad (11)$$

and, for increasing atomic weight, approaches the universal limit R_∞, which was designated as Rydberg's constant simply by R in the previous section.

This result, too, we owe to Bohr. He remarked at once that from the spectroscopic determination of R_H and R_∞, or, what is easier to carry out in practice, from the determination of R_H and R_{He}, the quantity m/m_H could be obtained. For it follows from (10) and (11) that

$$\frac{m}{m_H} = \frac{R_{He} - R_H}{R_H - \frac{1}{4}R_{He}} \quad . \quad . \quad . \quad . \quad (12)$$

The determination of m/m_H in equation (12) is equivalent to the determination of the specific electronic charge e/m. We actually have

$$\frac{m}{m_H} = \frac{e/m_H}{e/m} \quad . \quad . \quad . \quad . \quad (13)$$

Now, e/m_H is the specific ionic charge, the electrochemical equivalent * of § 2, Chapter I, that is, a quantity that is very accurately known (its value is 96,494 Coulombs). An exact spectroscopic determination of m/m_H denotes at the same time an exact knowledge of e/m, one that is presumably more accurate than can ever be obtained from experiments on the deflection of cathode rays. We have thereby come a step nearer to the goal that we set up as the problem of spectroscopic units in the preceding section : Instead of using the one value of $R = R_\infty$ in equation (10) of the previous section, we use the two values R_H and R_{He} out of the above equations (10) and (11), and we get, instead of one, two

* We must call attention to the following circumstance. The atomic weights are referred to oxygen = 16; the atomic weight of hydrogen does not then come out as 1 but as 1·0078. When we set the electrochemical equivalent 9649 of the mol. in Chapter I, § 2, equal $\frac{e}{m_H}$, we did not then imply that m_H was to stand for the mass of the true hydrogen atom, but for the mass of an imaginary atom which signifies the unit for the table of atomic weights. We shall distinguish the true hydrogen atom from this imaginary hydrogen atom m_H by using for the former the symbol m_H^*. They are then related by $m_H^* = 1{\cdot}0078\ m_H$. Loschmidt's number L, which refers accurately to the mol. of amount 1 grm., is not equal to $1/m_H^*$, but to $1/m_H$. When the relative motion of the nucleus, however, is taken into account we deal with the true mass m_H^* of the hydrogen atom, not with m_H. Consequently, to be exact, we should replace m_H in equation (13) by m_H^* and we should take $e/m_H^* = 9649{\cdot}4/1{\cdot}0078$. In the same way, we should write m_H^* for m_H in equation (10), but not in equation (11), because the true atomic weight of He is equal to four times the ideal, and not the real atomic weight of H. A correction should then also have to be applied to equation (12), when exact numerical calculations are desired, but we have left these out of account in the text.

equations for determining the three universal units e, e/m, and h. The necessary third such relation we shall get to know in Chapter V.

We must next broach the question as to how the difference between R_H and R_{He} may be made evident in practice. This is made possible by the series of ionised He, of which we spoke in § 2.

Ionised helium is of the type of hydrogen (*wasserstoffähnlich* = hydrogen-like). Accordingly its spectral lines are contained in the general formula (15) of Balmer's type, mentioned in the previous section, if we set $Z = 2$ in it. But the earlier $R = R_H$ is now to be replaced by R_{He}. From equation (15) of the previous paragraph, there thus arises in this way, if we set $n = 4$:

$$\nu = 4R_{He}\left(\frac{1}{4^2} - \frac{1}{m^2}\right) = \begin{cases} R_{He}\left(\frac{1}{2^2} - \frac{1}{\bar{m}^2}\right) \cdots & m = 2\bar{m} \\ R_{He}\left(\frac{1}{2^2} - \frac{1}{(\bar{m} + \frac{1}{2})^2}\right) \cdots & m = 2\bar{m} + 1 \end{cases} \tag{14}$$

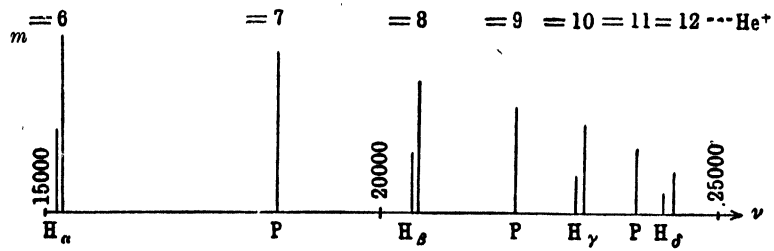


FIG. 24.—Diagrammatic representation of the spectrum of a mixture of ionised helium and hydrogen. The lines of the Pickering series (P) show their correspondence with the lines adjacent to the Balmer lines by the regular diminution of intensity in the series.

The subdivision into two parts (which is not really contained in the nature of the matter in question) brings into evidence the circumstance that the component for which m is even ($m = 2\bar{m}$) coincides very nearly with Balmer's series, whereas the other part ($m = 2\bar{m} + 1$) has the form of Pickering's series that was given earlier in equation (12) of page 74. The combination of the two partial series (which conforms with the nature of the matter in hand) into one uniform series corresponds to the earlier formula (12*a*) on page 74.

In Fig. 24 we exhibit the positions of the He^+-lines relatively to the Balmer lines. The lengths of the lines denote diagrammatically their intensity, on the assumption that we are dealing with a mixture of He^+ and of H. For this reason the Balmer lines are drawn shorter than the neighbouring He^+-lines. The difference in the position of the two series corresponds to the difference between R_{He} and R_H. Since $R_{He} > R_H$, the helium lines, as compared with the Balmer lines, are displaced a little towards the violet end. The lines P of Pickering's series, that is, the helium lines $m = 2\bar{m} + 1$, arrange themselves

between the helium lines $m = 2\bar{m}$, as emphasised on page 75, in order of steadily increasing intensity.

The researches of Paschen mentioned on page 75 give for the wave-lengths of the helium lines and the neighbouring Balmer lines the following values (here cut short at the first decimal place) in Ångström units, which confirm the displacement towards the violet, as predicted by theory.

TABLE 3

	He^+	H
$m = 6$ . . .	6560·1	6562·8 (H_α)
$m = 7$ . . .	5411·6	—
$m = 8$ . . .	4859·3	4861·3 (H_β)
$m = 9$ . . .	4561·6	—
$m = 10$ . . .	4338·7	4340·5 (H_γ)
$m = 11$ . . .	4199·9	—
$m = 12$ . . .	4100·0	4101·7 (H_δ)

According to our whole development of the question, this violet shift of the helium lines with respect to the Balmer lines may be regarded as a certain indication of the relative motion of the nuclei during the stationary forms of motion of the atom, or, more accurately, of the slightly different relative motion of the heavier helium nucleus compared with that of the lighter hydrogen nucleus. From the difference in the wave-lengths of the He^+-lines as compared with the H-lines, Paschen determined the value of R_{He} and R_H (for the lines of He^+ actually measured by him). More recent precision measurements by W. V. Houston * give the values

$$\left.\begin{aligned} R_{He} &= 109{,}722{\cdot}403 \pm 0{\cdot}004 \\ R_H &= 109{,}677{\cdot}759 \pm 0{\cdot}008 \end{aligned}\right\} \quad . \quad . \quad (15)$$

By equation (12) we obtain from Houston's values (cf. also the correction referred to in the footnote to p. 93)

$$\frac{m^*_H}{m} = 1839, \qquad \frac{e}{m} = 1{\cdot}761 \,.\, 10^7 \,.\, c \,. \quad . \quad . \quad (16)$$

By equations (10) or (11) we get from R_H or R_{He} that

$$R = R_\infty = 109{,}737{\cdot}42 \pm 0{\cdot}06 \quad . \quad . \quad . \quad (17)$$

Houston's value for $\frac{e}{m}$ in (16) is given on page 6, equation (2), as the spectroscopic value.

Of the series of ionised helium, we have here considered particularly that whose final quantum number is 4 (Pickering), and in § 2 we

* Phys. Rev., **30**, 608 (1927). For the calculation see also Birge, *loc. cit.*, p. 6, of Chap. I.

have briefly mentioned that whose final number is 3 (Fowler). Son representatives of the series whose final quantum numbers are 1 and have also been measured. Their succession of lines is identical wit that of the ordinary Lyman series and Balmer series except for th factor $Z^2 = 4$. Hence the corresponding lines lie in the extren ultra-violet; their wave-lengths result from those of the correspondir hydrogen lines by dividing by 4 (if we disregard the small difference i the constant R):

$$\nu = 4R\left(\frac{1}{1^2} - \frac{1}{2^2}\right), \quad \lambda = \tfrac{1\,2\,1\,6}{4} = 304,;$$

$$\nu = 4R\left(\frac{1}{2^2} - \frac{1}{3^2}\right), \quad \lambda = \tfrac{6\,5\,6\,0}{4} = 1640;$$

. . . . . .

The first measurements of the wave-lengths of the lines of these serie were made by Lyman.* Further lines were then discovered by Compton and Boyce,* so that now three lines of the series whose fina quantum is 2 (as far as $\lambda = 1085$ Å) are known, and five lines of th series whose final quantum number is 1 (as far as $\lambda = 234$ Å).

In the succession of hydrogen-like spectra the H- and the He^+ spectrum would now be followed by the spectrum of Li^{++}, that is, o doubly ionised lithium. This ionised atom again consists of a nucleus and an electron; its spectrum, hence, is of the general form of equation (15) of the preceding section with Z now equal to 3. On account of the relative motion of the nucleus we now write this equation as

$$\nu = 9R_{Li}\left(\frac{1}{n^2} - \frac{1}{m^2}\right), \quad R_{Li} = \frac{R_\infty}{1 + \dfrac{m}{m_{Li}}} \quad . \quad . \quad (18)$$

Edlén and Ericson † have measured the first two lines of the Lyman series, $n = 1$, $m = 2$, 3 in the spectrum of Li^{++}. They lie in the extreme ultra-violet at 135·0 and 113·9 Å, exactly at the place given by calculation from formula (18). R_{Li} has the value 109728·6. The "ground line" $n = 1$, $m = 2$, $\lambda = 75{\cdot}94$ Å of trebly ionised beryllium (Be^{+++}) has also been measured by the same investigators. Hence, we may close our discussion of the hydrogen-like spectra for the present with the statement: the frequency-equation (15), page 89, as well as its more rigorous form (9), page 92, which is obtained by taking into account the relative motion of the nucleus, are brilliantly confirmed by experiment.

§ 6. Introduction to Hamiltonian Mechanics

In § 3 we found it convenient to introduce the concepts of Hamiltonian mechanics. We shall now proceed to describe this theory

* Th. Lyman, Astrophys. Journ., **60**, 1 (1924); K. T. Compton and J. C. Boyce, Journ. of the Franklin Institute, **205**, 497 (1928).

† B. Edlén and A. Ericson, Nature, **125**, 233 (1930).

systematically, since it is so extraordinarily convenient for dealing with the most important problems of the quantum theory. This will at the same time prepare us for the foundations of wave-mechanics which links up closely with the formalism of Hamiltonian mechanics.

Our first objective is the derivation of *the partial differential equation of Hamilton and Jacobi*. We start out from d'Alembert's principle of mechanics (non-relativistic). This has the advantage that we need not restrict ourselves to considering mechanical systems of isolated point-masses, but may pass straight on to a mechanical system with any arbitrary internal relationships.

D'Alembert's principle states that the external forces are in equilibrium with the inertial resistances by virtue of the relationships between the parts of the system. In testing whether this equilibrium exists with respect to infinitesimal virtual displacements, namely, such as are compatible with the internal relationships of the system, we postulate that the work performed by the external forces and the inertial resistances (" virtual work ") must vanish.

Let the rectilinear components of the external forces be denoted in turn by K_k ; the inertial resistances, also resolved into rectangular components, are then given by $-\dot{p}_k = -m\ddot{q}_k$(cf. p. 77, eqn. (2)). For a system of point-masses which are described by n co-ordinates q_k, taken all in all, the principle then asserts that

$$\sum_{k=1}^{n}(K_k - \dot{p}_k)\delta q_k = 0 \quad . \quad . \quad . \quad . \quad (1)$$

Any connexions that may exist between the point-masses need not be taken into account, since they do no work in the virtual displacement δq_k.

We assume that the external forces have a potential. We then have

$$\sum_{k=1}^{n}K_k\delta q_k = -\delta E_{pot} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Further,

$$E_{kin} = \sum_{k=1}^{n}\frac{m_k}{2}\dot{q}_k^2, \quad \delta E_{kin} = \sum_{k=1}^{n}m_k\dot{q}_k\delta\dot{q}_k = \sum_{k=1}^{n}p_k\delta\dot{q}_k.$$

The sum on the right-hand side may easily be transformed. We have

$$\sum\dot{p}_k\delta q_k = \frac{d}{dt}\sum p_k\delta q_k - \sum p_k\delta\dot{q}_k = \frac{d}{dt}\sum p_k\delta q_k - \delta E_{kin} \quad . \quad (3)$$

in which we have used the last equation of those two lines above.

From (1), (2), (3) it therefore follows that :

$$\frac{d}{dt}\sum p_k\delta q_k = \delta(E_{kin} - E_{pot}) = \delta L.$$

$L = E_{kin} - E_{pot}$ is called the " Lagrange function " ; from its definition we see that it is quite independent of the choice of co-ordinates. By integrating from 0 to t (the variable under the integral is called τ to distinguish it from t), we get

$$\left[\sum_{k=1}^{n} p_k \delta q_k\right]_0^t = \int_0^t \delta L d\tau \quad . \quad . \quad . \quad . \quad (4)$$

From (4), as is well known, we immediately get Hamilton's principle of mechanics :

$$\delta \int_0^t L d\tau = 0 \quad . \quad . \quad . \quad . \quad (4a)$$

if we decide that δq_k is to vanish at the limits $\tau = 0$ and $\tau = t$, and that δt is to be zero along the path.

We next show that equation (4) holds not only for rectangular Cartesian co-ordinates, as we assumed earlier, but quite generally for arbitrary co-ordinates Q_k and momenta P_k. It is immediately clear from the meaning of L (see above) that the right-hand side of the equation is independent of the choice of co-ordinates. The same holds of the left-hand side, since it signifies the work of the impulses p_k during the virtual displacement of δq_k. Hence we must have

$$\sum_k p_k \delta q_k = \sum_l P_l \delta Q_l, \qquad k = 1, 2, \ldots n \; ; \; l = 1, 2, \ldots f$$

where $f < n$ denotes the number of degrees of freedom of the mechanical system and $n - f$ the number of equations of condition between the points of the system, which we imagine to be already fulfilled in introducing the new co-ordinates Q, P. The invariance of $\Sigma p_k \delta q_k$ may be worked out analytically as follows. We suppose the new co-ordinates Q_k to be given as functions of the rectangular co-ordinates q_k :

$$q_k = f_k(Q_1, \ldots Q_f) \quad \text{and} \quad Q_l = \phi_l(q_1, \ldots q_n) \begin{cases} k = 1, 2, \ldots n \\ l = 1, 2, \ldots f \end{cases} \quad . \quad (5$$

Then

$$\dot{Q}_l = \sum_{m=1}^{n} \frac{\partial \phi_l}{\partial q_m} \dot{q}_m \quad . \quad . \quad . \quad . \quad (6$$

We now calculate

$$p_k = \frac{\partial E_{kin}}{\partial \dot{q}_k}$$

and imagine E_{kin} to be expressed in terms of the new co-ordinates an velocities ; we then have

$$p_k = \frac{\partial E_{kin}}{\partial \dot{q}_k} = \sum_{l=1}^{f} \frac{\partial E_{kin}}{\partial \dot{Q}_l} \frac{\partial \dot{Q}_l}{\partial \dot{q}_k} = \sum_{l=1}^{f} \frac{\partial E_{kin}}{\partial \dot{Q}_l} \frac{\partial \phi_l}{\partial q_k}, \quad . \quad . \quad (7$$

the last step being on account of (6). On the other hand, we get for δq_k

$$\delta q_k = \sum_{m=1}^{f} \frac{\partial f_k}{\partial Q_m} \delta Q_m \quad . \quad . \quad . \quad . \quad (8)$$

so that we obtain from (7) and (8)

$$\sum_{k=1}^{n} p_k \delta q_k = \sum_{k=1}^{n} \sum_{l=1}^{f} \sum_{m=1}^{f} \frac{\partial E_{kin}}{\partial \dot{Q}_l} \frac{\partial Q_l}{\partial q_k} \frac{\partial q_k}{\partial Q_m} \delta Q_m$$

$$= \sum_{l,m} \frac{\partial E_{kin}}{\partial \dot{Q}_l} \delta Q_m \sum_{k} \frac{\partial Q_l}{\partial q_k} \frac{\partial q_k}{\partial Q_m}.$$

The last summation over k gives 0 when $l \neq m$, and 1 when $l = m$. Hence

$$\sum_{k=1}^{n} p_k \delta q_k = \sum_{l=1}^{f} \frac{\partial E_{kin}}{\partial \dot{Q}_l} \delta Q_l.$$

If we now take over the general definition for the impulse or momentum from (5), page 78,

$$P_k = \frac{\partial E_{kin}}{\partial \dot{Q}_k} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

we obtain the required result:

$$\sum_{k=1}^{n} p_k \delta q_k - \sum_{l=1}^{f} P_l \delta Q_l = \sum_{k=1}^{f} P_k \delta Q_k \quad . \quad . \quad . \quad (10)$$

The variations are at present still quite arbitrary. If we also imagine the moment t of the end of the orbit to be varied by δt, we have

$$\int_0^t \delta L d\tau = \delta \int_0^t L d\tau - L \delta t,$$

and we then obtain (4) if instead of the capitals Q_k, P_k we now again use the small letters q_k, p_k for the generalised co-ordinates:

$$\left[\sum_{k=1}^{f} p_k \delta q_k \right]_0^t = \delta \int_0^t L d\tau - L \delta t \quad . \quad . \quad . \quad (11)$$

If as we have hitherto assumed (cf. equation (2)) the potential energy does not contain the time, the energy law holds in the form

$$H = E_{kin} + E_{pot} = \text{const.} = W \quad . \quad . \quad (12)$$

Here (as on p. 77) H denotes the total energy of the system. From (12) it follows that

$$-E_{pot} = E_{kin} - W, \quad L = 2E_{kin} - W$$

$$\int_0^t L d\tau = 2 \int_0^t E_{kin} d\tau - Wt = S - Wt \quad . \quad . \quad (13)$$

The quantity

$$S = 2\int_0^t E_{kin} d\tau \quad . \quad . \quad . \quad . \quad (14)$$

here introduced has the dimensions of an action (erg sec), and is called the *action function* (*Wirkungsfunktion*).

If we substitute (13) in (11) we obtain

$$\left[\sum p_k \delta q_k\right]_0^t = \delta S - t\delta W - (W + L)\delta t = \delta S - t\delta W - 2E_{kin}\delta t. \quad (15)$$

As in the case of rectangular co-ordinates, E_{kin} is again a homogeneous quadratic function of the generalised velocities, so that we may use Euler's theorem and write

$$2E_{kin} = \sum \frac{\partial E_{kin}}{\partial \dot{q}_k}\dot{q}_k = \sum p_k \dot{q}_k.$$

From (15) we obtain

$$\left[\sum p_k \delta q_k\right]_0^t = \delta S - t\delta W - \sum p_k \dot{q}_k \delta t \quad . \quad . \quad (15a)$$

The integral (14) is to be taken over any mechanically possible path, as is shown by its derivation from d'Alembert's principle. Through fixing such a path by means of its initial conditions (initial position and initial momentum) S becomes a definite function of the time. By making the initial conditions variable, S appears as a function of $2f + 1$ variables (of the time, of f co-ordinates q_k^0 of the initial position and of f co-ordinates p_k^0 of the initial momentum). But instead of these $2f + 1$ variables we shall introduce other variables, namely (proceeding as for a ballistic problem), besides the co-ordinates q_k^0 of the initial point, the co-ordinates q_k of the end-point (" target point " ; " *Treffpunkt* ") and, simultaneously, instead of the time t between the initial point and the target point, the energy W (in ballistic terms, the " charge "). As a matter of fact, starting from a given initial point, we can reach a given target point by different paths and in various orbital times, according to the amount of energy available. The equation that accordingly exists between t, W, q_k and q_k^0 allows us to calculate t as a function of W, q_k and q_k^0 and to eliminate it by inserting this value in the upper limit of S. *In the sequel we accordingly regard* S, *the function of action, as a function of the co-ordinates* q_k *of the final position and of the co-ordinates* q_k^0 *of the initial position, and as a function of the energy* W. We take δS as standing for the expression

$$\delta S = \sum \frac{\partial S}{\partial q_k}\delta q_k + \sum \frac{\partial S}{\partial q_k^0}\delta q_k^0 + \frac{\partial S}{\partial W}\delta W \quad . \quad . \quad (16)$$

We suppose this value of δS inserted in the right-hand side of equation (15*a*). Designating the displacements δq_k for $t = 0$ and $t = t$ on the left-

hand side of (15*a*) by δq_k^0 and δq_k^t, we write, in place of (15*a*),

$$\sum_{k=1}^{k=f} p_k(\delta q_k^t + \dot{q}_k \delta t) - \sum_{k=1}^{k=f} p_k^0 \delta q_k^0 + t\delta W = \delta S \quad . \quad . \quad (15b)$$

Let the quantity δq_k^t be called the " variation *at* the end-point of the orbit." It signifies the virtual displacement to which we have subjected the orbital element at the time $\tau = t$. We must distinguish between this and the " variation *of* the end-point of the orbit," which, as in equation (16), will be called δq_k. The latter is now composed of two parts ; (1) of the virtual displacement δq_k^t that we have effected at the end of the orbit, and (2) of the lengthening of the orbit which corresponds to the alteration of the orbital time by the amount δt. We have to imagine the co-ordinate q_k to continue its course during the time δt with the velocity $\dot{q}_k$. The second part therefore becomes $\dot{q}_k \delta t$ and we have

$$\delta q_k = \delta q_k^t + \dot{q}_k \delta t.$$

If we insert this in the left-hand side of (15*b*) the following relation results, on which all that follows is founded :

$$\sum_{k=1}^{k=f} p_k \delta q_k - \sum_{k=1}^{k=f} p_k^0 \delta q_k^0 + t\delta W = \delta S \quad . \quad . \quad (17)$$

(where δq_k is the variation *of* the end-point of the orbit).

By comparing (16) and (17) and assuming δq_k, δq_k^0, δW as all independent of each other (no equations of condition), we obtain

$$p_k = \frac{\partial S}{\partial q_k} \quad (18) \qquad p_k^0 = -\frac{\partial S}{\partial q_k^0} \quad (18a) \qquad t = \frac{\partial S}{\partial W} \quad . \quad (18b)$$

If, now, S were known in any way as a function of the q_k's, then by (18) we should be able to derive the p_k's from S. But this does not really help us on. For, to determine S as a function of the q_k's, we should require previously to have integrated the equations of motion. Then, besides the successive positions of the system, also the corresponding momentum co-ordinates would be known and equation (18) would become superfluous.

We can, however, use equation (18) indirectly to find S. For if we insert (18) in the energy law (12)

$$E_{kin} + E_{pot} = H(p_k ; q_k) = W \quad . \quad . \quad . \quad (19)$$

where H denotes Hamilton's function, that is, the total energy, expressed as a function of the p_k's and q_k's, then we get *Hamilton's partial differential equation*.

$$H\left(\frac{\partial S}{\partial q_k} ; q_k\right) = W \quad . \quad . \quad . \quad . \quad (20)$$

It is of the first order and of the second degree (at least in the case of classical mechanics, since here E_{kin} is a quadratic function of the p_k's). We shall assume that we can integrate equation (20), that is, that we can specify a solution

$$S = S(q_1 \ldots q_f ; \alpha_1 \ldots \alpha_f)$$

containing f arbitrary constants of integration. One of these constants, say α_1, is merely added to S and is therefore of no account ; it does not enter into the expressions for the p_k's. But S also contains W as an essential constant arising from the differential equation. We shall call special attention to this by writing

$$S = S(q_1 \ldots q_f ; W\alpha_2\alpha_3 \ldots \alpha_f) + \alpha_1 \quad . \quad . \quad (21)$$

We shall see presently how, under certain circumstances (by separation of the variables), we can actually arrive at a solution of the differential equation (20) of the form (21). We first exhibit the inner relationship between the quantum theory and Hamilton's method involving the function of action, of which we spoke at the beginning of this note. It rests on the fact that our phase-integrals

$$\int p_k dq_k$$

allow themselves to be expressed directly by the function of action S.

On account of (18) we have

$$\int p_k dq_k = \int \frac{\partial S}{\partial q_k} dq_k = J_k \quad . \quad . \quad . \quad (22)$$

By the rule on page 84, about the integration limits of the phase-integral, J_k denotes the increase that S undergoes when the variable q_k traverses the region that comprises the complete description of all the phases of motion of the system. Fixing our attention on periodic motions (or " conditionally periodic " motions, see below), we suppose that in the integration q_k returns to its value at the outset, and we call J_k the *k^{th} modulus of periodicity of the function of action*. Our quantum conditions

$$\int p_k dq_k = n_k h$$

then require that the *moduli of periodicity of the action function be whole multiples of Planck's quantum of action.*

To see how the moduli of periodicity of S are determined we must consider a little more closely the integration of the differential equation (20). The only method that is successful is that of the *separation of the variables*. We shall illustrate it by a simple example.

Suppose we are dealing with an oscillator bound anisotropically in space. The restoring forces $-k_1x_1$, $-k_2x_2$, $-k_3x_3$ act on the point-

mass m in the directions of three mutually perpendicular axes $x_1x_2x_3$. If p_1, p_2, p_3, are the components of momentum ($p_k = m\dot{x}_k$), then

$$E_{kin} = \frac{p_1^2 + p_2^2 + p_3^2}{2m}, \quad E_{pot} = \frac{1}{2}(k_1x_1^2 + k_2x_2^2 + k_3x_3^2)$$

and the partial differential equation (20) then becomes

$$\left(\frac{\partial S}{\partial x_1}\right)^2 + \left(\frac{\partial S}{\partial x_2}\right)^2 + \left(\frac{\partial S}{\partial x_3}\right)^2 + m(k_1x_1^2 + k_2x_2^2 + k_3x_3^2) = 2mW \qquad (23)$$

This equation allows itself to be "separated" with respect to the variables x_1, x_2, x_3, that is, it allows itself to be resolved into the following three equations, that each depend on only one of the three variables :

$$\left.\begin{aligned} \left(\frac{\partial S}{\partial x_1}\right)^2 + mk_1x_1^2 = \alpha_1, \quad \left(\frac{\partial S}{\partial x_2}\right)^2 + mk_2x_2^2 = \alpha_2, \\ \left(\frac{\partial S}{\partial x_3}\right)^2 + mk_3x_3^2 = \alpha_3 \end{aligned}\right\} \qquad (24)$$

where α_1, α_2, α_3 are integration constants between which the following relation holds :

$$\alpha_1 + \alpha_2 + \alpha_3 = 2mW \qquad (25)$$

We thus have only two arbitrary constants ; the third constant is determined by these two and W.

Equations (24) give us

$$\frac{\partial S}{\partial x_i} = \sqrt{\alpha_i - mk_ix_i^2} = \sqrt{mk_i}\sqrt{a_i^2 - x_i^2} \qquad (26)$$

Here we have set

$$\alpha_i = mk_ia_i^2 . \qquad (27)$$

Equation (26) shows in conjunction with the mechanical meaning of

$$\frac{\partial S}{\partial x_i} = p_i = m\dot{x}_i \qquad (28)$$

that the variable x_i is limited to the region between $\pm a_i$ and that it can reverse its sense of motion only at the end-points $\pm a_i$ of this region. For if x_i were to overstep the region $\pm a_i$, then p_i would become imaginary, which is impossible. If x_i were to stop before getting to the boundaries of the region and reverse its direction at a point inside, then $\dot{x}_i$ would $= 0$ here ; but by (28) this would entail the vanishing of $\partial S/\partial x_i$, which is excluded by (26), since $\partial S/\partial x_i$ can vanish only at the limiting points $\pm a_i$. Thus *the variable x_i traverses the entire region $\pm a_i$ alternately in the increasing and the decreasing sense, reversing its sense of motion and the sign of p_i at the end-points of the region.* That is, the full region of variability of x_i stretches from $-a_i$ to $+a_i$ and back again to $-a_i$. We indicate this integration by adding a circle $\bigcirc$ to the integral sign. Our quantum conditions are then to be written in the form

$$J_i = \oint \frac{\partial S}{\partial x_i} dx_i = \sqrt{mk_i} \oint \sqrt{a_i^2 - x_i^2}\, dx_i = n_ih . \qquad (29)$$

Here the integral obviously denotes the circular surface whose radius is a_i. Thus we conclude from (29) that

$$a_i^2 = \frac{n_i h}{\pi\sqrt{mk_i}} \quad . \quad . \quad . \quad . \quad (30)$$

From (27) and (25) it then follows that

$$\alpha_i = \sqrt{mk_i}\frac{n_i h}{\pi}, \qquad \sum\sqrt{mk_i}\frac{n_i h}{\pi} = 2m\mathrm{W} \quad . \quad . \quad (31)$$

We finally introduce the vibration numbers ν_i, which correspond to the free oscillations of our point-mass in the three co-ordinate directions. These are given by

$$2\pi\nu_i = \sqrt{\frac{k_i}{m}}, \qquad \sqrt{mk_i} = 2\pi m\nu_i.$$

If we insert this in the second equation (31), we get

$$2m\mathrm{W} = \sum 2m\nu_i n_i h, \qquad \mathrm{W} = \sum n_i \nu_i h \quad . \quad . \quad (32)$$

The energy of our oscillator thus appears, as was to be foreseen, as an integral sum of energy-quanta $h\nu_i$ that correspond to the three partial vibrations ; our spatial oscillator, just like the linear oscillator in § 3, equation (13*a*), is quantised according to energy-elements.

A series of general remarks follow from this simple example.

(*a*) If Hamilton's differential equation of a system of f degrees of freedom allows itself to be fully separated as regards the co-ordinates $q_1 \ldots q_f$, that is, divided into parts that depend in turn on only one of the co-ordinates q_i, then, as in (24), f constants a_i appear, of which, however, only $f - 1$ are arbitrary. In this way we obtain by the method of separation of variables the complete solution of Hamilton's differential equation with the number of integration constants required in our former remarks. Together with the energy-constant W we have f parameters (we shall call them briefly the " constants α "), which, *according to classical mechanics, may be chosen freely within a continuous manifold, but, according to the quantum theory, are capable only of discrete values.*

(*b*) Just like the Hamiltonian equations so the partial equations derived from them by the process of separation in the co-ordinates q are of the first order and of the second degree. We shall assume that in Hamilton's equation only the squares (and not the products) of the $\frac{\partial \mathrm{S}}{\partial q_i}$'s occur ; this is equivalent to the kinetic energy being composed linearly of the squares of the p_i's. In this case we speak of the orthogonal co-ordinates q. If we calculate $\partial \mathrm{S}/\partial q_i$, then, as in (26), we obtain a pure square root of a function of q_i alone :

$$\frac{\partial \mathrm{S}}{\partial q_i} = \sqrt{f_i(q_i)} \quad . \quad . \quad . \quad . \quad (33)$$

Let a_i and b_i be two consecutive simple real roots of the function f_i in a region of values which is accessible to the co-ordinate q_i according to its mechanical significance; we then see from the same considerations as those applied in our special example, that if once q_i lies between the values a_i and b_i, then it swings permanently between these limits ("libration limits"). For each libration and for each co-ordinate q_i, S increases by a fixed modulus of periodicity. Just as in our example the periods corresponding to the various co-ordinates do not in general superpose exactly, and hence the orbit will not return into itself. We call this behaviour *conditionally periodic.** For further details, in particular concerning the conditions under which an asymptotic "limitation motion" occurs, in place of the "libration motion" we refer the reader to Charlier,† *Celestial Mechanics* ("Mechanik des Himmels").

(*c*) In all conditionally periodic systems the form of the orbital curve has the character of *Lissajous figures*. In Fig. 25 we draw the two-dimensional Lissajous curve which is described by the co-ordinates x_1x_2 of our example. The curve touches its envelopes $x_1 = \pm a_1$ and $x_2 = \pm a_2$ alternately. Exactly the same occurs in the general case, for which we denoted the corresponding limits for the co-ordinates q_i by a_i, b_i. The somewhat different appearance of, for example, figures which will be shown in Chapter VI to illustrate the Stark effect, is merely due to the fact that the co-ordinates q_i are not Cartesian but have been drawn as curvilinear co-ordinates in agreement with their physical significance. The Lissajous curve in this case does not nestle in a rectangle but in a curvilinear quadrangle.

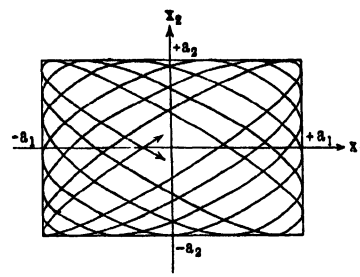


FIG. 25.—Form of the orbital curve of a conditionally periodic system having two degrees of freedom x_1, x_2.

(*d*) An essential difference, however, manifests itself if there happens to be a cyclic azimuth among the co-ordinates q_i of the system, that is an angular co-ordinate ϕ, which does not occur in the expression for the energy. In this case in place of equation (33), the following holds:

$$\frac{\partial S}{\partial \phi} = \text{const.} = p \quad . \quad . \quad . \quad . \quad (34)$$

* Non-separable problems can also have a conditionally periodic form for the orbits as E. Fues has shown (Zeits. f. Physik, **34**, 788 (1925), following the ideas contained in a paper by Kneser, Math. Ann., **84**, 277 (1921).

† Leipzig, 1902, Vol. I, pp. 85 *et seq.* The name "conditionally periodic" arose from the circumstance that when one or more conditions of commensurability (Note 5) became added to the motion, it "degenerated" into a truly periodic motion. The more appropriate term "multiply periodic" has been suggested by Bohr.

In ϕ we have no libration limits but the mass-point continually traverses the orbit around the origin of the co-ordinate system, according to the law of areas. The representation of the relativistic Kepler ellipse in Chapter V, § 1, gives us a picture of this behaviour. It is included between two enveloping circles instead of being hedged in by a curved quadrangle. The full region of variability for a cyclic co-ordinate stretches from $\phi = 0$ to $\phi = 2\pi$. Consequently the corresponding modulus of periodicity of S is

$$J_\phi = \int_0^{2\pi} p d\phi = 2\pi p$$

and the quantum condition becomes, as in the case of the simple rotator

$$2\pi p = nh \quad . \quad . \quad . \quad . \quad . \quad (35)$$

It is not necessary for the sequel to emphasise this frequently occurring exceptional case. Rather, use is to be made of it in defining the conditions of the conditionally periodic system.

(*e*) The general quantum conditions for a conditionally periodic system are, following on (33), for orthogonal co-ordinates q_i:

$$J_i = \oint \sqrt{f_i(q_i, W, \alpha_2 \ldots \alpha_f)} dq_i = n_i h \quad . \quad . \quad (36)$$

They furnish us with f equations for determining the f constants W, $\alpha_2 \ldots \alpha_f$. These constants, in particular also the energy W, are thus fixed by the quantum numbers n_i. *A discrete manifold is separated out from the continuous manifold of their values. In particular, the quantising of the energy pays due regard to the sharpness of spectral lines.*

(*f*) *Complex integration* offers the natural method appropriate for evaluating the integrals of the form (36). As we have already indicated by the sign $\bigcirc$, the path of integration is a closed one. It runs round the two branch points a_i, b_i of the square root, which we suppose connected by a branch incision; and, moreover, since the square root changes its sign in passing around the one or the other branch-point, and since the integrand of the phase-integral is necessarily positive (cf. p. 84) the path forwards must be traced on the positive, that backwards on the negative, edge of the incision. We re-model it (cf. Note 4) into any arbitrary course about the incision and may, in given cases, simplify it further by contraction into the singular points of the integrand. *Thus the most powerful instrument of the theory of functions, the method of complex integration, places itself beside the methods of higher mechanics in the service of the quantum theory.*

(*g*) Hitherto we have disregarded the real problem of integration of the differential equations of mechanics, that is, the representation of the motion in its dependence on time. We must now supplement our

remarks by a few statements about the method of calculating the orbits that constitutes the true achievement of Jacobi in this field. This is done most briefly by means of the theory of canonical transformations (see Note 2). We start out from the integral (21) of the Hamilton-Jacobi equation with the integration constants W, $\alpha_2, \alpha_3 \ldots \alpha_f$ (we shall in future continue to omit the unessential constant α_1) and perform the process of variation on it, obtaining

$$\delta S = \sum_1^f \frac{\partial S}{\partial q_k}\delta q_k + \frac{\partial S}{\partial W}\delta W + \sum_2^f \frac{\partial S}{\partial \alpha_k}\delta \alpha_k.$$

Using equation (18), we write this

$$\delta S = \sum_1^f p_k \delta q_k + \beta_1 \delta W + \sum_2^f \beta_k \delta \alpha_k \quad . \quad . \quad (37)$$

The quantities β here introduced are to be defined thus, as a comparison with the preceding equation shows :

$$\beta_1 = \frac{\partial S}{\partial W}, \quad \beta_k = \frac{\partial S}{\partial \alpha_k}, \quad k - 2 \ldots f \quad . \quad . \quad (38)$$

Equation (37) states that between the q_k, p_k as original variables, and the β_k, α_k (with $\alpha_1 = W$) as "new variables," the characteristic relation of the contact transformation, equation (19*b*) of Note 2, again holds. The function F* that occurred there is here again represented by S. As it does not contain t explicitly, equation (19*a*) of Note 2 assumes the form $H(p, q) = \overline{H}(P, Q)$; that is, in our case

$$H(p, q) = \overline{H}(W, \alpha_2 \ldots \alpha_f, \beta_1 \ldots \beta_f) = W \quad . \quad (39)$$

From this it follows that

$$\frac{\partial \overline{H}}{\partial W} = 1, \quad \frac{\partial \overline{H}}{\partial \alpha_k} = 0, \quad k = 2 \ldots f, \quad \frac{\partial \overline{H}}{\partial \beta_k} = 0, \quad k = 1. \ldots f. \quad (40)$$

Now the Hamiltonian equations hold in the new co-ordinates W, α, β, just as much as in the old co-ordinates p, q. Thus, in view of (40), we have

$$\frac{dW}{dt} = -\frac{\partial \overline{H}}{\partial \beta_1} = 0, \quad \frac{d\beta_1}{dt} = \frac{\partial \overline{H}}{\partial W} = 1, \quad . \quad . \quad (41a)$$

$$\frac{d\alpha_k}{dt} = -\frac{\partial \overline{H}}{\partial \beta_k} = 0, \quad \frac{d\beta_k}{dt} = \frac{\partial \overline{H}}{\partial \alpha_k} = 0, \quad k = 2 \ldots f \quad . \quad (41b)$$

These equations assert nothing new so far as W and α_k are concerned. They only confirm their constancy during the course of the motion. But concerning β_k they state that *the quantities $\beta_2 \ldots \beta_f$ are also constant during the motion, and that β_1 becomes equal to t* (except for an additive constant, which we can include in the reckoning of the

time). If we now compare this result with the equation of definition (38) of the β's, we have

$$t = \frac{\partial S}{\partial W} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$\beta_k = \frac{\partial S}{\partial \alpha_k} = \text{const.}, \quad k = 2, 3. \ . \ . \ . f \quad . \quad . \quad (43)$$

Equations (43) give $f - 1$ relations between the co-ordinates $q_1 \ . \ . \ . \ q_f$ of the orbit, which do not contain the time. They suffice to describe the *form of the orbit.* We call them the *orbital equations.* The constants $\beta_2 \ . \ . \ . \ \beta_f$, together with the α_k's and W, give the still wanting constants of integration of the problem. The course of the motion in time is represented by equation (42).

We have thus deduced—by the shortest way—the remarkable theorem of Jacobi: *the integrals of the equations of motion may, if a complete solution* S *of the partial differential equations is known, be obtained by mere differentiation.*

(*h*) We shall conclude this section with a few remarks on the origin of Hamilton's theory. Our account is based on two notes by F. Klein.* Hamilton was an astronomer who studied the course of rays of light in optical instruments. He found *ray optics* prevalent (Newton's emissive (corpuscular) theory of optics), in which the path of corpuscles of light in a medium which is homogeneous in sections or, more generally, in a non-homogeneous medium, is described by *total differential equations.* Hamilton endeavoured to link up this theory with that of *wave-optics,* which had just begun to come into being at that time,† by means of *partial differential equations.*

He recognised as the connecting link the *concept of the wave-surface.* In wave-optics this is defined as the surface for which the vibrations of light are in the same phase; in ray optics it may be defined as the orthogonal surface to the orbits of the light corpuscles. In every optical problem there is a family of wave-surfaces. Let this family be represented analytically by S = const., where the constant is the parameter of the family and S is a function of the co-ordinates $q_1, \ . \ . \ . \ q_f$. For the mechanics of light-corpuscles $f = 3$ and space is Euclidean; for the problems of general mechanics we must pass over into an f-dimensional space which, moreover, is in general non-Euclidean.

As we know from the theory of surfaces, the direction-cosines of the normal to the surface S = const. is determined by the ratios of the derivatives $\partial S/\partial q_k$. The momentum of the light corpuscles is in the direction of this normal, so that p_k is proportional to $\partial S/\partial q_k$. This at

* Gesammelte Abhandl., **2,** 601 and 603; they appeared originally in Jahresberichte d. Deutsch. Math. Ver., **1,** 1891, and Zeits. f. Math. u. Physik., **46,** 1901.

† Hamilton's papers on ray optics date from 1828 to 1837 (Trans. Irish Academy); his papers on dynamics date from 1834 to 1835 (Trans. Roy. Soc., London).

once tells us the geometrical meaning of our equation (18) and at the same time convinces us that the equation S = const. of the wave-surface is analogous to the postulate that Hamilton's function of action must be constant. The circumstance that the wave-surfaces are to be described by a partial differential equation is plausible geometrically, just as is the fact that its orthogonal trajectories may be derived by simple differentiation (see above, under (*g*)).

Jacobi took up and extended only that aspect of Hamilton's theory which could be dealt with by analytical mechanics. The optical aspect became lost to view, and was newly discovered by Bruns * in his theory of the *eikonal*. The eikonal is essentially the time taken by a ray of light to pass in an optical system from a given initial point to a variable final point. Hence the eikonal becomes identical with the phase in the undulatory theory, that is with the action function S. At the same time, Hamilton's principle, equation (4*a*), which we may also write in the form $\delta S = 0$, becomes merged into Fermat's principle of least time.

The relationship between ray optics and ordinary mechanics, which has here been sketched, was all-important for the discovery of wave-mechanics: just as ray optics is only a limiting case (wave-length small compared with the diffracting objects) and is in general to be replaced by wave-optics, so, according to Schrödinger, ordinary mechanics must be replaced, when we deal with atomic dimensions, by wave-mechanics.

§ 7. Elliptic Orbits in the Case of Hydrogen

In §§ 4 and 5 we have spoken only of the circular orbits of the electron of the hydrogen atom. This is obviously an unnecessary limitation. As in planetary systems so here we must fix our attention on the ellipse as the general form. In this sense we express Kepler's law in the form:

The electron moves in an ellipse, in one focus of which the nucleus is situated.

In the formulation of Kepler's law the relative motion of the nucleus is left out of account for the present: this defect can be remedied subsequently.

The motion in the ellipse represents a problem in *two degrees of freedom*, in that the position of the electron is determined by two co-ordinates, here by the polar co-ordinates measured from the focus, namely, the azimuth ϕ and the radius vector r. We treat the problem most simply † by the methods of the preceding section; that is, we start out from the Hamilton-Jacobi differential equation in the

* Abhandl. d. Leipziger Akad., **21**, 1895.

† In the previous English edition of this book (p. 234) the elliptic motion was treated in as elementary a manner as possible. It seems appropriate nowadays to follow the direct if somewhat thorny path of Hamilton's method, particularly in view of the trend towards wave-mechanics.

co-ordinates $q_k = r, \phi$. To be able to set up this differential equation we must first write down the total energy H as a function of the impulses or momenta p and the co-ordinates q.

We form the orbital element ds of the electron in polar co-ordinates:

$$ds^2 = dr^2 + r^2 d\phi^2.$$

From this we obtain the kinetic energy

$$\mathrm{E}_{kin} = \frac{m}{2}\left(\frac{ds}{dt}\right)^2 = \frac{m}{2}(\dot{r}^2 + r^2\dot{\phi}^2) \quad . \quad . \quad . \quad (1)$$

The potential energy is

$$\mathrm{E}_{pot} = -\frac{\mathrm{Ze}^2}{r} \quad . \quad . \quad . \quad . \quad (2)$$

where we again first denote the nuclear charge generally by Ze.

Corresponding to the position co-ordinates

$$q = \phi \text{ and } q = r, \text{ respectively,}$$

we have, by equation 9 of § 6 of the present chapter, the *impulse* or *momentum co-ordinates*

$$p = \frac{\partial \mathrm{E}_{kin}}{\partial \dot{q}} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We call them p_ϕ and p_r, and on account of (1) and (3),

$$p_\phi = mr^2\dot{\phi}, \quad p_r = m\dot{r} \quad . \quad . \quad . \quad . \quad (4)$$

By (1), (2) and (4) the energy law now runs:

$$\mathrm{W} = \mathrm{E}_{kin} + \mathrm{E}_{pot} = \frac{m}{2}(\dot{r}^2 + r^2\dot{\phi}^2) - \frac{\mathrm{Ze}^2}{r}$$

$$= \frac{1}{2m}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right) - \frac{\mathrm{Ze}^2}{r} = \mathrm{H}(p, q).$$

By the general rule on page 101, equation (20), we get from this the Hamilton-Jacobi equation if we replace p_r by $\partial \mathrm{S}/\partial r$ and p_ϕ by $\partial \mathrm{S}/\partial \phi$. Hence

$$\left(\frac{\partial \mathrm{S}}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial \mathrm{S}}{\partial \phi}\right)^2 = 2m\mathrm{W} + \frac{2m\mathrm{Ze}^2}{r} \quad . \quad . \quad (5)$$

Since ϕ does not occur explicitly (cyclic co-ordinate, see p. 105), we may next set

$$\frac{\partial \mathrm{S}}{\partial \phi} = \text{const.} = p \quad . \quad . \quad . \quad . \quad (6)$$

This integral of the differential equation is equivalent to the law of areas. For p_ϕ is by equation (4) the moment of the momentum mv, that is, the product of the arm r and the azimuthal component of the momentum $mr\dot{\phi}$. By the law of areas ("the radius vector sweeps out equal areas in equal times"; Kepler's second law) p_ϕ is, however,

constant during the motion, and this is also asserted by equation (6). The quantum postulate

$$J_\phi = \int_0^{2\pi} \frac{\partial S}{\partial \phi} d\phi = n_\phi h \quad . \quad . \quad . \quad . \quad (7)$$

hence gives us as the value of p :

$$2\pi p = n_\phi h, \quad \frac{\partial S}{\partial \phi} = \frac{n_\phi h}{2\pi} \quad . \quad . \quad . \quad . \quad (8)$$

The equation (7) is called the *azimuthal quantum condition;* it agrees with the earlier quantum condition of the rotator (see eqn. (18), p. 82) ; n_ϕ is the *azimuthal quantum number*. The limits of the integral in (7) correspond to the rule on page 84. They comprise the whole domain of values of the position co-ordinate ϕ. By substituting equation (8) in equation (5) we obtain

$$\left(\frac{\partial S}{\partial r}\right)^2 = 2mW + \frac{2mZe^2}{r} - \frac{n_\phi^2 h^2}{4\pi^2 r^2} \quad . \quad . \quad . \quad (9)$$

or

$$\frac{\partial S}{\partial r} = \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}} \quad . \quad . \quad . \quad (10)$$

with the abbreviations

$$A = 2mW, \quad B = mZe^2, \quad C = -\frac{n_\phi^2 h^2}{4\pi^2}.$$

We need not concern ourselves with the general integration of (5), but may immediately * form

$$J_r = \oint \frac{\partial S}{\partial r} dr = n_r h \quad . \quad . \quad . \quad . \quad (11)$$

(11) is the *radial quantum condition*, and n_r is correspondingly the *radial quantum number*. The limits of the integral must comprise the full range of values of r ; that is, r runs from r_{min} to r_{max}, and back to r_{min} again ; we denote this by attaching a circle to the middle of the integral sign. We may evaluate the integral by the method of complex integration and then obtain, as is shown in Note 4,

$$J_r = \oint \sqrt{A + \frac{2B}{r} + \frac{C}{r^2}}\, dr = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}}\right) \quad . \quad (12)$$

If we substitute this in (11) we get, in view of the meanings of A, B and C,

$$-2\pi i\left(-i\frac{n_\phi h}{2\pi} - \frac{mZe^2}{\sqrt{2mW}}\right) = n_r h \quad . \quad . \quad (13)$$

* W. Wilson deduced the above equations (11) and (7) from his general formulation of the quantum conditions, quoted on p. 83, slightly earlier than the author (Wilson's paper, Phil. Mag., 31 (161), 1916, was concluded in November, 1915, the author's in December, 1915). But Wilson made no application of these equations to Balmer's series.

(In determining the sign of $\sqrt{C}$ we must bear in mind the final remark in Note 4.) Equation (13) now reduces to

$$\frac{2\pi imZe^2}{\sqrt{2mW}} = (n_\phi + n_r)h,$$

or

$$W = -\frac{2\pi^2 mZ^2e^4}{h^2} \cdot \frac{1}{(n_\phi + n_r)^2} = -\frac{RhcZ^2}{n^2} \quad . \quad . \quad (14)$$

where we have taken the value of R from equation (16), page 89, and have set

$$n_\phi + n_r = n \quad . \quad . \quad . \quad . \quad (15)$$

We call n the quantum sum or, according to Bohr, the *principal quantum number*. Like n_ϕ and n_r, it is a positive integer. Bohr suggested using k for n_ϕ. Instead of this we shall later introduce the quantity (l), which is given to us by wave-mechanics.

The result (14) is of very great importance, and of impressive simplicity: *we have found for the energy of the elliptic orbits the same value as we found in equation* (13) *on page* 87 *for circular orbits; the quantum number n that occurred before is now replaced by the principal quantum number* $n_\phi + n_r$. We shall presently show that *the quantum conditions* (7) *and* (11) *select from the inherently continuous manifold of all possible ellipses a family of quantised ellipses which are given by the two positive whole numbers* n_ϕ *and* n_r, or, as we may say in view of (15) *whose size and form is determined by* n_ϕ *and* n_r. Equation (14) then states that *each of the quantised ellipses of our family is equivalent in energy to a definite Bohr circle.*

We realise the form of the ellipses best by determining their semi-major and semi-minor axes. For this purpose we require the aphelion and the perihelion distances, that is, r_{max} and r_{min}. We obtain these quantities by forming $p_r = m\dot{r} = \partial S/\partial r = 0$. By equation (9) this gives

$$2mWr^2 + 2mZe^2r = \frac{n_\phi^2 h^2}{4\pi^2}.$$

But for the major axis we clearly have

$$2a = r_{max} + r_{min},$$

that is,

$$a = \frac{-2mZe^2}{2 \cdot 2mW} = \frac{h^2n^2}{4\pi^2 mZe^2}, \quad . \quad . \quad . \quad (16a)$$

the last step following from (14). For the semi-minor axis b we have the familiar relationship $b^2 = a^2 - c^2$, where c denotes the distance of the focus from the centre of the ellipse. Hence it follows, as is immediately obvious geometrically,

$$b^2 = (a - c)(a + c) = r_{min} \cdot r_{max}.$$

Hence

$$b^2 = -\frac{n_\phi^2 h^2}{4\pi^2 \cdot 2mW} = \left(\frac{h^2 n n_\phi}{4\pi^2 m Z e^2}\right)^2,$$

$$b = \frac{h^2 n n_\phi}{4\pi^2 m Z e^2} = a\frac{n_\phi}{n} \quad . \quad . \quad . \quad (16b)$$

If, as in equation (7) on page 86, we write $\frac{h^2}{4\pi^2 m e^2} = a_1 =$ radius of the first Bohr circle as an abbreviation in equations (16*a*) and (16*b*), we get

$$a = a_1\frac{n^2}{Z}, \quad b = a_1\frac{n n_\phi}{Z} \quad . \quad . \quad . \quad (16c)$$

The equations (16*a*, *b*, *c*) show that the size and form of the ellipses is, in fact, fully determined by n_ϕ and n_r. We also observe that our value for a coincides with the radius of the circular orbit, having the same n (cf. eqn. (4), p. 85).

We may now also calculate the period of revolution τ from the law of sectorial areas. We know that

$$\frac{p_\phi}{m} = r^2\dot{\phi} = \frac{1}{m}\frac{n_\phi h}{2\pi}$$

denotes double the surface swept out by the radius vector in unit time, and hence is also equal to $\frac{2F}{\tau}$, where $F = ab\pi$ is the total surface of the ellipse. Hence it follows that

$$\tau = \frac{2mF}{p} = \frac{4\pi^2 m}{n_\phi h}ab = \frac{n^3 h^3}{4\pi^2 m Z^2 e^4} \quad . \quad . \quad . \quad (17)$$

that is, exactly the same value as for the circular orbit having the same n (eqn. (4*a*), p. 85).

Finally, we may conclude from (16*a*) and (17), as on page 86, that Kepler's third law also holds for our elliptic motion :

$$\frac{\tau^2}{a^3} = \text{const.} = \frac{4\pi^2 m}{Ze^2} \quad . \quad . \quad . \quad . \quad (18)$$

(In the astronomical case, we must replace Ze^2 by $m\mathrm{M}$, in agreement with Newton's law ; here M = sun's mass.)

If we had also taken into account the motion of the nucleus (cf. the beginning of this section), we should have had to replace the electronic mass m in all our formulæ by the " resultant " mass μ (cf. § 5). In place of R_∞ we should then have to substitute the general value R of equation (9), page 92.

We next take one ellipse of the family as the initial orbit of the electron (let the principal quantum number of the ellipse be m), another ellipse as the final orbit (its principal quantum number being n). In

order that the transition may be spontaneous and accompanied by the emission of energy we must have $m > n$. We calculate the emission of energy by the $h\nu$-law. We obtain, analogous to equation (15), page 89,

$$\nu = RZ^2\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad . \quad . \quad . \quad . \quad (19)$$

and in particular for hydrogen (for which Z = 1),

$$\nu = R\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad . \quad . \quad . \quad . \quad (20)$$

From the point of view of practical results, this spectral formula again gives only Balmer's series, but *it has a deepened theoretical significance and its origin has now multiple roots. By the admission of our elliptic orbits the series has gained no extra lines and has lost none of its sharpness.*

When the author, early in 1916, developed the above theory, he referred at the outset to a series of ways * by which the various possibilities of generation contained in a Balmer line may be made manifest.

1. In the natural state of the H-atom without a super-imposed field the various possibilities of generation coincide only accidentally, as it were, in one line. But if we allow an electric field to act on the luminescent atom, in the manner practised by Stark, the original quantum orbits will be disturbed. It is evident that the disturbance will affect the various ellipses differently ; it will therefore alter the energy of the various orbits differently in each case. The result is the so-called **Stark effect,** to which we shall return in Chapter VI. 2. Similar consequences follow from the application of a magnetic field and the result is the **Zeeman effect.** Here, too—both in our theory and in the older view based on the classical theory—the resolution of the lines is not due to new possibilities of vibration being generated but to the circumstance that lines which were originally coincident are differently displaced and hence separated by the magnetic field. We shall also study the Zeeman effect in Chapter VI.† 3. The most beautiful and most instructive manifestation of the quantum states that belong to the same Balmer line is, however, given by Nature herself without our agency in the fine structure of space-time conditions as reflected in **the fine structure of spectral lines.** This will be dealt with in Chapter V, to which we refer the reader. 4. The (in hydrogen) coincident lines may be separated by **an inner atomic field** in place of an external electric or magnetic field. Such an inner atomic field does not, indeed, occur in the case of hydrogen itself or atoms of the hydrogen type, but does in the case of all other atoms (neutral He, Li, etc.). In Chapter

* Sitzungsberichte der Münchener Akademie, 1915, p. 425, cf., in particular, § 6.

† It is more accurate to say that we shall first deal with the Zeeman effect for fields that are not too weak. The complications that occur in the Zeeman effect and also in the Stark effect when the fields are extremely weak are discussed in Chapter VIII.

VII we shall see that such atomic fields are the cause of the single Balmer series of hydrogen splitting up in the elements not of the hydrogen type into the series systems: Principal Series, First and Second Subsidiary Series, etc.

All these things are connected with a conception which was introduced into the quantum theory by Schwarzschild (cf. the quotation on p. 83). It is a question of the difference between *degenerate* and *non-degenerate* systems. A system of f degrees of freedom is degenerate if less than f quantum numbers are sufficient to fix its energy according to the quantum theory. The classical Kepler motion and, indeed, every purely periodic motion is fully degenerate, since the one principal quantum number n suffices alone. The relativistic Kepler motion is non-degenerate; on account of the smallness of the relativity correction it may, however, be called approximately degenerate. In the same way the degeneracy is partially counteracted by the electric field of the Stark effect, the magnetic field of the Zeeman effect, the inner atomic field and so forth. It is only in the case of non-degenerate systems that all the f phase-integrals come into action, as we mentioned earlier in introducing them (p. 82). The analytical criterion of degeneracy set up by Schwarzschild or taken over from celestial mechanics is developed later in Note 5 of the Appendix.

We next enumerate the various possible circular and elliptic orbits, which belong to a given value of $n = n_\phi + n_r$. We begin by remarking that:

(*a*) $n_r = 0$ denotes a circular orbit. This follows from the radial quantum condition (11), which shows that when n_r vanishes, so also does p_r, that is, $\dot{r}$, and so r must be constant.

(*b*) $n_\phi = 0$ denotes a degenerate ellipse, namely, the focal distance taken twice (to and fro). For when $n_\phi = 0$ we also have by (16*b*) that $b = 0$.

But this degenerate ellipse must be *excluded*. From the point of view of orbits the reason given was that if the electron were to traverse the focal distance it would necessarily collide with the nucleus. The view of wave-mechanics is much more satisfactory. In wave-mechanics the azimuthal quantum number, our n_ϕ or Bohr's k (see above), becomes replaced by the quantity:

$$l = n_\phi - 1, \quad l = 0, 1, 2 \ldots \quad . \quad . \quad . \quad (21)$$

From this it follows immediately that 1 is the smallest value of our quantum number n_ϕ that can occur according to wave-mechanics, or, in other words, that $n_\phi = 0$ is *forbidden*.

At the same time it follows from $n = n_r + n_\phi$ that the upper limit of n_ϕ is the value n, and hence that the upper limit of the wave-mechanical quantity l is $n - 1$. Accordingly for a given n we have precisely n possibilities of resolution into radial and azimuthal quantum numbers, corresponding to the n permissible values of l, namely, $l = 0, 1, 2 \ldots n-1$.

This is illustrated in the following tabulation, where we enumerate the various types of orbit according to the quantum numbers n and l (the significance of the expressions K —, L —, M —, N — shell will be made clear in the next chapter) :

$n = 1$, one possibility, K-shell

$l = 0$	$n_r = 0$		$a = a_1 = b$
	a circle		

$n = 2$, two possibilities, L-shell

$l = 1$	$n_r = 0$	$a = 2^2 a_1$	$b = a$
$l = 0$	$n_r = 1$	$a = 2^2 a_1$	$b = \frac{1}{2}a$

circle or ellipse of eccentricity $\epsilon = \frac{\sqrt{3}}{2}$

$n = 3$, three possibilities, M-shell

$l = 2$	$n_r = 0$	$a = 3^2 a_1$	$b = a$
$l = 1$	$n_r = 1$	$a = 3^2 a_1$	$b = \frac{2}{3}a$
$l = 0$	$n_r = 2$	$a = 3^2 a_1$	$b = \frac{1}{3}a$

circle or ellipses of eccentricities $\epsilon = \frac{\sqrt{5}}{3}$ or $\epsilon = \frac{\sqrt{8}}{3}$

$n = 4$, four possibilities, N-shell

$l = 3$	$n_r = 0$	$a = 4^2 a_1$	$b = a$
$l = 2$	$n_r = 1$	$a = 4^2 a_1$	$b = \frac{3}{4}a$
$l = 1$	$n_r = 2$	$a = 4^2 a_1$	$b = \frac{2}{4}a$
$l = 0$	$n_r = 3$	$a = 4^2 a_1$	$b = \frac{1}{4}a$

circle or ellipses of eccentricities $\epsilon = \frac{\sqrt{7}}{4}$

or $\epsilon = \frac{\sqrt{12}}{4}$ or $\epsilon = \frac{\sqrt{15}}{4}$.

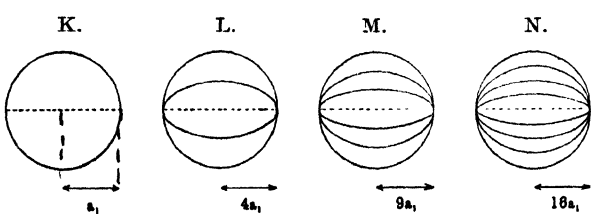


FIG. 26.—Shape of the orbit of the hydrogen electron for $n = 1, 2, 3, 4$ (from left to right). The orbits are drawn concentrically in order to show the relative sizes of the orbits which have the same value of n.

The diagrams drawn in Fig. 26 have not been drawn to the same scale (in order to save space) ; cf. the arrows a_1, $4a_1$, . . . drawn at the bottom. Moreover, for the sake of clearness the curves have been

depicted concentrically instead of confocally. If we draw them confocally we obtain the following picture instead :

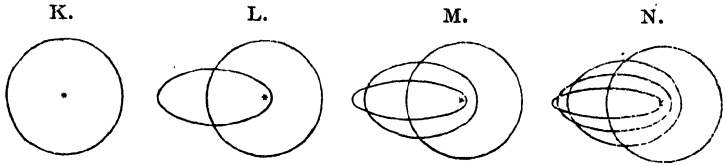


FIG. 27.—Orbits of the hydrogen electron for $n = 1, 2, 3, 4$ drawn confocally.

We introduce an abbreviated name for these different types of orbits ; we call them generally

$$n_l \text{ — orbits,}$$

a modification of Bohr's nomenclature n_k — orbits, which we find it necessary to supersede in conformity with our present-day knowledge ; hence we must associate with the letters K, L, M, N the following symbols :

K	L	M	N
1_0	2_1	3_2	4_3
	2_0	3_1	4_2
		3_0	4_1
			4_0

The orbits represented by the symbols in the top row are circles, and those below them are ellipses of increasingly great eccentricity.

Among all the electronic orbits that will engage our attention in the sequel the Kepler ellipse will occupy a special position : it is purely periodic. We know that in the two-body problem for any arbitrary law of attraction $f(r)$ purely periodic orbits occur in only two cases, namely, when $f(r)$ is proportional to r^{-2} (Kepler ellipse) or proportional to r^{+1} (two-dimensional harmonic oscillator). We shall see that the chief result of this section is intimately connected with this kinematic character of motion in Kepler orbits, this result being the fact that the energy depends only on the sum of the azimuthal and the radial quantum number.

For if we integrate the third equation on page 100, namely, the relationship,

$$\mathrm{E}_{kin} = \tfrac{1}{2}\sum p_k \dot{q}_k \quad . \quad . \quad . \quad . \quad (22)$$

with respect to t over the period τ of the motion, we obtain

$$2\int_0^\tau \mathrm{E}_{kin} dt = \sum \int p_k dq_k \quad . \quad . \quad . \quad (23)$$

The right-hand side is the sum of our phase-integrals for the different co-ordinates of the system. In a purely periodic motion (and only in

such) every co-ordinate q_k actually traverses its full range of variability (cf. p. 103), while the time t varies from 0 to τ. Thus in the notation of page 83 the right-hand side is

$$\sum J_k = \sum n_k h.$$

We denote the left-hand side of equation (23) by J ; in virtue of its definition from the kinetic energy it is independent of the choice of co-ordinates and, by equations (14) and (22) of § 6, is equal to the increase of the function of action after each complete revolution. If we follow Bohr * by demanding that

$$J = 2\int_0^\tau E_{kin}dt = nh \quad . \quad . \quad . \quad . \quad (24)$$

we are clearly in agreement with our rule for the phase-integrals, and we get simply that $n = \sum n_k$ (principal quantum number, sum of quanta).

The individual quantum number n_k refers to the co-ordinate q_k, and so has no physical meaning unless this co-ordinate is distinguished by the nature of the problem ; but the principal quantum number n is independent of the choice of co-ordinates.† In the case of the Kepler problem the ambiguity in the choice of co-ordinates may be easily followed. In the present section we have used polar co-ordinates. When we discuss the hydrogen atom in the electric field (Stark effect) in Chapter VI we shall use parabolic co-ordinates. In particular, we may apply parabolic co-ordinates to the case of a vanishingly small electric field, that is, to a pure Kepler motion. Lastly, we may use elliptic ‡ co-ordinates, namely, such that the Kepler orbit forms an ellipse of the co-ordinate system. In all these three co-ordinate systems the phase-integrals may be formed independently of one another, that is, the problem may be separated. We find that we obtain, according to the co-ordinate system used, various quantum conditions $J_k = n_k h$, that is, *different shapes* (eccentricities) for the quantised ellipse. But we always have the *same value for the energy* (because the value of W is determined simultaneously with the time-mean of the kinetic energy, see Note 3), and, as we may add, the same value for the *major axis a* and *the period* τ.

* N. Bohr, *On the Quantum Theory of Line Spectra*, Kopenhagen Academy, Vol. IV, 1918.

† The property of the quantum sum was first emphasised by the author in his first paper on Balmer's series (Münchener Akad., 1915, § 7), where the equation (23) of the text appears for the first time. The correct choice of co-ordinates presented particular difficulties at that time, which were shortly afterwards removed, however, by Schwarzschild and Epstein's rule of the separation of variables (cf. the references on p. 83).

‡ As always in the " problem of two fixed centres " ; the first centre is the nucleus, the second lies in the other focus and has the mass (charge) zero.

Hence we see equation (24) leads directly and without calculation to the essential elements that define the orbit; those elements which it does not yield, for example, the minor axis b, are dependent on the co-ordinate system and must therefore be of no importance physically. If, in spite of this, we did not give up using the special co-ordinates r, ϕ, the reasons are as follows:

(1) Our point of view is that the results of classical mechanics are limiting cases of relativistic mechanics. But in the relativistic treatment the quantising of the Kepler ellipses is fully determined, and it is not sufficient to introduce only the one quantum number n. At the same time, the use of polar co-ordinates is prescribed by the nature of the problem. This also justifies the n_i-orbits designated above, namely, as limiting cases of the corresponding relativistic orbital curves, which arise when the relativity correction is neglected.

(2) When we develop the theory of the periodic system in the next chapter we require, besides the major, also the minor axis and the form of the n_i-orbits, exactly as given above. Their use for this purpose may likewise be justified as a limiting process. If we are not dealing with hydrogen, but with more general atomic models, there must be added to the Coulomb field of force an additional field which arises from the electronic envelope around the nucleus, and which may be described to a first degree of approximation as a central field. The treatment of this case according to the quantum theory is similar to that of the relativistic case. The polar co-ordinates are also prescribed here as separation variables and give rise to two quantum conditions which fix the minor axis as well as the major axis and the energy. Our n_i-orbits, which we have so far developed for hydrogen, then result as limiting cases of the corresponding orbits in a central field of vanishingly small intensity.

(3) The process favoured by Bohr cannot be generalised by wave-mechanics, whereas this *is* possible with our process of quantising in polar (or parabolic) co-ordinates. For in the wave-mechanical treatment we must take into account *all* the degrees of freedom of the system; in the Kepler problem not even the plane polar co-ordinates are sufficient; rather we must treat the problem as spatial, as will be shown in the next section.

§ 8. Quantising of the Spatial Position of Kepler Orbits. Theory of the Magneton

In the preceding section we quantised the Kepler orbits with respect to **size** and **form,** by means of the azimuthal quantum number n_ϕ and the radial quantum number n_r. We wish to show that the quanta can perform still more: they also determine the **position of the orbits in space,** that is, they select from the continuous manifold of all possible positions of the orbits in space a discrete number of orbits that conform to certain quantum conditions.

It is possible to quantise spatially only, of course, when a certain favoured direction is given with respect to which we may measure the orientation of the orbits. Such a favoured direction may be given by an external field of force. But in this case we have no longer, even for the hydrogen atom, pure Kepler orbits. Rather, these are deformed by the external field of force. If we wish to manage with the Kepler orbits, notwithstanding this, we must pass on to the "limit when the force tends to zero." In this passage to the limit the disturbance of the orbits by the field of force vanishes, but on the other hand the possibility of them orientating with respect to the field of force remains. The reason for this is that, whereas the disturbance of the orbits is a phenomenon which varies *continuously* with the field of force, the orientation of the orbits is restricted to certain *discrete* possibilities.

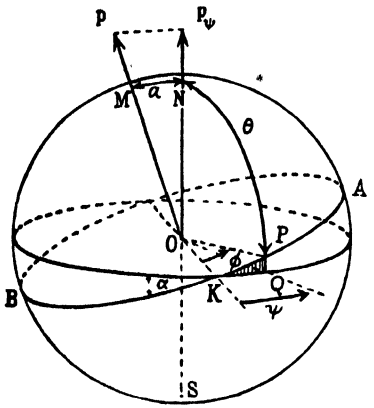


FIG. 28.—Position of the orbital plane BPA of the hydrogen electron relative to a magnetic field whose lines of force proceed from top to bottom of the diagram (parallel to NS).

We take the direction of the lines of force as the axis of a spatial polar co-ordinate system $r\theta\psi$; in Fig. 28 this is the axis SN. We assume the nucleus to be at rest at O; we draw the unit sphere (i.e. one of unit radius) about O as centre. Let the variable radius OP point to the present position of the electron. Let OK be called the line of nodes ("*Knotenlinie*"); it is the line of intersection of the equatorial plane OKQ and the orbital plane OKP. The great circle KPAB is the trace of the orbital plane on the unit sphere. The "latitude" θ is represented in the figure by PN, the longitude ψ, reckoned from the line of nodes, is represented by KQ; in addition, we consider the "orbital azimuth" ϕ, which is given by KP. Let α be the angle between the direction ON of the lines of force and the normal OM to the orbital plane; α appears in the figure as the arc MN, and at the same time as the angle at K in the spherical triangle KQP, which is shaded in the figure.

Corresponding to our three degrees of freedom $r\theta\psi$, we have now three quantum conditions:

$$\left.\begin{aligned} \int p_\theta d\theta &= n_\theta h \\ \int p_\psi d\psi &= n_\psi h \\ \int p_r dr &= n_r h \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (1)$$

The integration with respect to ψ is from 0 to 2π. The integration with respect to θ stretches from $\theta_{min} = \text{NA}$ to $\theta_{max} = \text{NB}$ and back again to θ_{min} (cf. p. 84); the integration with respect to r is, as before (cf. p. 111), from r_{min} to r_{max} and back again to r_{min}. Hence the radial quantum integral is not different from that obtained from the two-dimensional point of view, and determines the shape of the orbit in the same way. Similarly, we may take over from the case of the plane the azimuthal quantum number n_ϕ and the areal constant p = moment of momentum about the normal to the orbit, for which we have, by our above remarks,

$$\int_0^{2\pi} p d\phi = 2\pi p = n_\phi h \quad . \quad . \quad . \quad . \quad (2)$$

We assert that *the azimuthal quantum number n_ϕ is equal to the sum of the "equatorial" or "magnetic" quantum number n_ψ and the "latitudinal" quantum number n_θ*:

$$n_\phi = n_\psi + n_\theta. \quad . \quad . \quad . \quad . \quad (3)$$

The proof is contained in equation (23) of the preceding section.

By using first plane polar co-ordinates $r\phi$, and then space polar co-ordinates $r\theta\psi$, we obtain

$$\int p_r dr + \int p d\phi = \int p_r dr + \int p_\theta d\theta + \int p_\psi d\psi \quad . \quad . \quad (4)$$

If we cancel the radial phase-integral on both sides and substitute for the values of the others from (1) and (2), we obtain directly equation (3).

But we have the additional relationship

$$n_\psi = n_\phi \cos \alpha \quad . \quad . \quad . \quad . \quad . \quad (5)$$

between the quantum numbers n_ϕ and n_ψ. For p is the total moment of momentum of the revolving electron; p_ψ is its component in the equatorial plane. The former is drawn in Fig. 28 as a vector in the direction of the normal OM to the orbital plane, the latter as a vector in the direction of the normal ON to the equatorial plane. As Fig. 28 shows,

$$p_\psi = p \cos \alpha. \quad . \quad . \quad . \quad . \quad (6)$$

According to this p_ψ, just like p, is constant * during the motion. The equatorial quantum condition (1) comes out, if calculated, as

$$2\pi p_\psi = n_\psi h \; . \quad . \quad . \quad . \quad . \quad (7)$$

* If we had used Hamilton's method here, that is, if we had set up the partial differential equation in the space co-ordinates r, θ, ψ we should have seen from the analysis immediately that

$$p_\psi = \frac{\partial S}{\partial \psi} = \text{const},$$

because ψ is a cyclic co-ordinate,

In virtue of this equation and equation (2) we see that (6) is identical with (5).

We may formulate the equations (2) and (7) as follows : *not only the total moment of momentum p, but also its component p_ψ in the direction of the lines of force is an integral multiple of $h/2\pi$. The cosine of the angle of inclination of the moment of momentum to the direction of the lines of force is thus rational.*

For we immediately have, from (6), (7), (2), and (3),

$$\cos\alpha = \frac{p_\psi}{p} = \frac{n_\psi}{n_\phi} = \frac{n_\psi}{n_\psi + n_\theta} \quad . \quad . \quad . \quad (8)$$

Spatial quantising has no influence on the calculation of the energy of the orbits and of the consequent spectral inferences, so long as we restrict ourselves to the limiting case, " external force tends to zero." The two quantum numbers n_ψ and n_θ occur in the energy expression only as the sum $n_\phi = n_\psi + n_\theta$. Thus the energy expression and the spectral vibrations to be derived from it remain the same as for simple quantising in a plane.

It is on this account that the spatial Kepler problem is one degree more " degenerate " than the plane problem. Whereas we express it mechanically as a problem in three degrees of freedom by means of three co-ordinates, the energy expression involves only the quantum sum $n = n_\psi + n_\theta + n_r$. It is this particular circumstance of greatest degeneracy which makes our present treatment valuable as a preliminary step to the later wave-mechanical solution of the Kepler problem.

We consider successively the cases $n_\phi = 1, 2, 3, \ldots$, where, for reasons presently to be explained, we shall use for n_ϕ the abbreviation j (and not, as in the preceding section, $l + 1$). We wish to express by this changed notation that in every atom there is a quantity j (" inner quantum number ") which is a measure of the total moment of momentum, and which orientates itself in the magnetic field in the way in which, according to the above remarks, the moment of momentum p or its associated quantum number n_ϕ must orientate themselves.

In Figs. 29, *a*, *b*, *c* the direction of the lines of force is to be regarded as proceeding from above downwards, as in the preceding Figure.* The arrows represent the moment of momentum corresponding to our j. They are to be inclined to the direction of the lines of force in such a way that their projection on this direction in the unit scale of the Figure is integral. In Fig. 29*a* the unit scale is the radius itself, on account of $j = 1$; in Fig. 29*b* it is half the radius, since $j = 2$, and in Fig. 29*c* it is one-third of the radius, since $j = 3$. Hence, in Fig. 29*b* we divide the vertical radius into two, and in Fig. 29*c* into three, equal parts and then draw horizontal lines through the points of

* Figs. 29, *a*, *b*, *c* are taken from a paper by the author on the Zeeman effect of hydrogen, Physik. Zeits., **17**, 491 (1916) ; cf. also the paper by Debye, *ibid.*, p. 507, or Göttinger Nachr., June, 1916.

intersection as far as the circumference of the circle. The straight lines connecting these points of intersection with the centre give the theoretically possible orientations of the moment of momentum j. In view of the axial character of j we draw arrows in opposite directions.

Fig. 29*a*, $j = 1$. The moment of momentum sets itself either parallel or anti-parallel or perpendicular to the lines of force.

Fig. 29*b*, $j = 2$. Besides the parallel, anti-parallel, and perpendicular positions the position making an angle of 60° with the lines of force is also possible. The Figure shows this position to the right and to the left of the vertical. In space we may imagine these two positions to be connected by means of a circular cone described about the vertical.

Fig. 29*c*, $j = 3$. Besides the parallel, anti-parallel, and perpendicular positions, $\cos \alpha = \pm 1, 0$, we now also have the inclinations

$$\cos \alpha = \pm \tfrac{2}{3} \text{ and } \pm \tfrac{1}{3}.$$

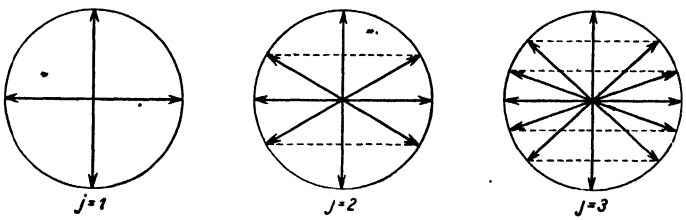


FIG. 29*a*. FIG. 29*b*. FIG. 29*c*.

Directional quantising in a magnetic field (regarded as proceeding from top to bottom). Possible positions of the total moment of momentum j for $j = 1, 2, 3$.

It would be logical to place at the beginning of these Figures the case $j = 0$. But in this case there is no position, since there is no moment of momentum to be placed in position.

On the other hand, it is illogical and yet, as we shall learn, necessary, to supplement our series of Figs. 29 by a second series of Figures in which j has *half-integral* values. If, from the preceding discussion, we retain the rule that the *difference* of the moments of momentum projected on the direction of the lines of force is to be *integral*, then we obtain the following Figures analogous to those which have just preceded :

Fig. 30*a*, $j = \frac{1}{2}$. Only the parallel and anti-parallel positions permissible.

Fig. 30*b*, $j = \frac{3}{2}$. In addition to the parallel and anti-parallel position, we also have those given by $\cos \alpha = \pm \frac{1}{3}$.

Fig. 30*c*, $j = \frac{5}{2}$. Besides the parallel and anti-parallel positions, the orientations $\cos \alpha = \pm \frac{1}{5}, \pm \frac{3}{5}$ are possible.

What is the position as regards the *empirical proof of spatial quantising?* We must state immediately that *au fond* every Zeeman photograph contains a proof of this kind, as we shall see in Chapter VI.

Without entering into details here, we may assert that the different components of a Zeeman pattern correspond to different positions of a magnetic moment in space, which results from the magnetic actions of the electrons in the atom. Since these components are discrete

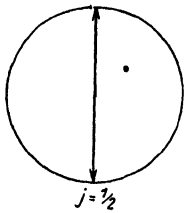


FIG. 30*a*.

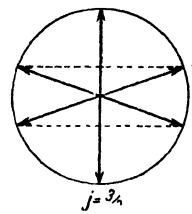


FIG. 30*b*.

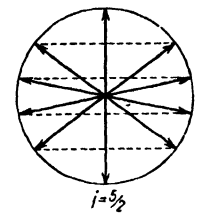


FIG. 30*c*.

Directional quantising in a magnetic field (regarded as proceeding from top to bottom). Possible positions of the total moment of momentum j for $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$.

and sharp, so also the positions of the magnetic moment and the corresponding orientations of the atom are sharply defined, that is, spatially quantised.

It is true that this proof is indirect. There is, however, a direct experimental proof, which has rightly caused a great stir, namely, the experiment of Stern and Gerlach.* The experimental arrangement is as follows (cf. the diagram of Fig. 31) : an evacuated tube contains a sample K of the substance to be examined (this was silver in the first experiments), which is then heated. It sends out " atomic rays " in all directions, that is, in this case atoms of silver, which have assumed a thermal velocity (several hundred metres per sec.) corresponding to the temperature of vaporisation. By the use of appropriate diaphragms B a sharp linear beam of atomic rays is cut out of the divergent beam. This linear beam passes through a magnetic field which is made as intense and non-homogeneous as possible, its lines of force, which run in the direction SN in the figure, being perpendicular to the direction of the atomic beam. The magnetic field deflects the atoms according

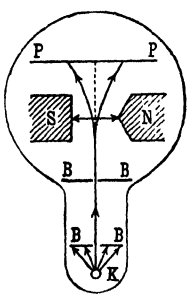


FIG. 31.—Experimental arrangement of the Stern-Gerlach experiment. A beam of atomic rays from the oven K, formed by the diaphragms B, passes through a non-homogeneous magnetic field NS, and strikes the plate P.

* We quote here only the most fundamental papers : O. Stern, Zeits. f. Phys., **7**, 249 (1921) ; W. Gerlach and O. Stern, *ibid.*, **8**, 110 (1921) ; **9**, 349 and 352 (1922). Since then the method has been elaborated in all directions in the " Untersuchungen zur Molekularstrahl-methode aus dem Institut für physikalische Chemie der Hamburgischen Universität " (Zeits. f. Phys., from 1922 up to the present time), and the number of experimental results obtained has been greatly increased. For the quantitative evaluation of the results see in particular No. 5 of these researches ; O. Stern, Zeits. f. Phys., **41**, 563 (1927).

to the inclination of their magnetic moment μ with respect to the magnetic field H with the force

$$\mu \frac{\partial H}{\partial s} \cos(\mu, H) \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Here $\frac{\partial H}{\partial s}$ gives a measure of the non-homogeneity of the field, that is, of the difference between the magnetic action on the positive and negative pole of the atomic magnet, and is equal to the increase of H in the direction of H. On a plate PP, which is placed in the path of the rays and is afterwards developed in some appropriate way, we therefore expect bullet marks to be made by the atoms as on a target: namely, a maximum density of distribution in the centre becoming continuously less as we proceed to the sides. But the true result of the experi-

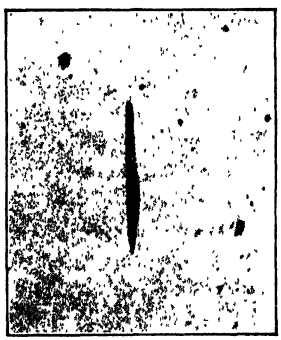


FIG. 32*a*.

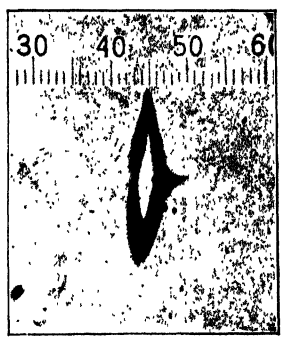


FIG. 32*b*.

Stern-Gerlach experiments with silver. Trace of the atomic rays on the sensitive plate—on the left, without a magnetic field; on the right, with a magnetic field.

ment with Ag-rays is shown in Fig. 32, magnified twenty times. On the left-hand side is the result without a magnetic field; on the right-hand side the field is on. The left-hand picture is the image of the diaphragms as marked out on the receiving plate PP by the atomic rays; we see a sharp image of the slit. The right-hand picture shows the deflection in the magnetic field; there is a band on each side, but *the middle is completely free of "bullets."* (The irregularity in the middle of the band on the right is due to the irregularity of the magnetic field at the right-hand pole of the magnet, which ends in an edge in order to produce a non-homogeneous field. The convergence of the band at the top and at the bottom signifies that the magnetic field decreases transversally, that is, perpendicularly to the plane of the diagram of Fig. 31.) How are we to interpret these two bands of the deflection picture? *Clearly they are due to the directional quantising of the silver atoms.* So soon as the atoms enter into the magnetic field the axes of

their magnetic moments orientate themselves either parallel or perpendicular to the lines of force. In the expression (9) $\cos(\mu, H)$ is either $+1$ or -1. There are no intermediate positions, and in particular no possibility of $\cos(\mu, H) = 0$. In Fig. 31 we have indicated the two positions of the silver atom and of its moment μ that are possible according to the quantum theory by arrows. The one arrow points precisely in the direction of the field SN, the other in precisely the opposite direction. In Fig. 33 we show the result of a new experiment with atomic rays of hydrogen.* The two parallel lines show the deflection in the magnetic field. The check photograph without a magnetic field was taken on the same plate which was simply rotated and displaced ; this gives the sharp oblique line on the right-hand side of the figure. A comparison of the picture with the preceding picture shows the advance in experimental technique that has been achieved in the meantime ; this is the more remarkable since the present subject of research, the hydrogen atoms, were more difficult to control and to be made to register a mark on the plate than the silver atoms. With regard to the theory the picture shows that the hydrogen atom—like the silver atom—sets itself either parallel or anti-parallel to the field, that is, in the sense of our Fig. 30*a*.

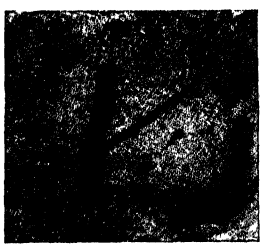


FIG. 33.—Stern-Gerlach experiment with hydrogen (according to Wrede). The two sloping parallel lines are obtained with a magnetic field ; the single oblique line without a magnetic field, the slit being rotated.

From the point of view of the theory hitherto put forward, this result is surprising. For we should expect rather a deflection picture of the character of Fig. 29*a*, that is, besides the two lateral bands a central band which is *not* deflected and which would correspond to the position perpendicular to the magnetic field. For by the theory so far developed the hydrogen atom should, in the ground state, have a moment of momentum $n_\phi = 1$, and it suggests itself at first sight to identify the moment of momentum j (which is the decisive factor for the position taken up) with n_ϕ. We noted on page 115, however, that according to wave-mechanics n_ϕ should be replaced by the number $l = n_\phi - 1$. But its value in the ground state would be $l = 0$, and this would lead to no definite position in the field at all if we identify j with l, and so have $j = 0$. The result of the experiment with the atomic rays, therefore, leads us to infer that there is a new sort of cause for the positions taken up, and that this cause leads to our scheme with $j = \frac{1}{2}$. This cause is, as we now know, the *spin of the electrons* (*Elektronen-Drall*, Goudsmit and Uhlenbeck), which has its roots ultimately in the relativistic scheme of physical events. We shall require

* E. Wrede, Zeits. f. Phys., **41**, 569 (1927).

the whole system of spectra to explain this most peculiar consequence of modern physics, and wave-mechanics to establish it logically. Here we must remain satisfied for the present with having found a first indication of electron-spin in the deflection picture, Fig. 33. At the same time we must note that the hydrogen atom—in its ground state and, as we may add, in its excited states—has not the single structure which we have hitherto assumed. Rather, it resembles the silver atom and is, like it, alkaline in its spectral character. We shall revert to this point frequently later.

We shall discuss a further consequence which Stern has deduced from these experiments. It concerns the magnitude of the magnetic moment μ which by (9) determines the amount of the deflection. To understand the significance of this inference we must make some remarks about some older work.

The view that every paramagnetic substance (i.e. susceptibility > 0) has a definite magnetic molecular moment is old established among physicists. It was developed in particular by Wilhelm Weber, and was rendered certain by Langevin's theory of the dependence of paramagnetism on temperature. During the last few decades P. Weiss * has been engaged in establishing, by means of a great number of detailed measurements, that this moment occurs not as an arbitrary quantity but as a *whole multiple of a certain elementary moment*, "**the magneton.**"

The assumption suggested itself to physicists that this elementary magnetic quantum was no new constant, but was probably connected with the elementary electric quantum of charge e and the quantum of action h. Let us endeavour to establish this connexion as simply as possible.

As we know, a magnetic moment is equivalent to an electric current; Weber's electromagnetic measure of current in C.G.S. units depends precisely on the fact that the current strength J multiplied by the area F of the enclosed surface around which the current flows is equal to the moment μ of the elementary magnet, which, placed at right angles to the plane of the current, produces the same magnetic field as the current

$$JF = \mu \quad . \quad . \quad . \quad . \quad . \quad (10)$$

If the current J is an "Ampère molecular current," produced by an electron revolving in an atom, then

$$J = \frac{e}{\tau},$$

where e is the electronic charge in electromagnetic units, τ = time of revolution of the electron, so that $\frac{1}{\tau}$ = number of times per second that the charge e traverses the "cross-section of the current."

* Summaries are given by P. Weiss, Phys. Zeits., **12**, 935 (1911), or Verh. d. D. Phys. Gesells., **13**, 718 (1911); R. H. Weber, Jahrb. f. Rad. v. Elektr., **12**, 74 (1915); B. Cabrera, J. de Chimie Physique (Guye), **16**, 442 (1918).

From (10) it follows that

$$\mu = e\frac{F}{\tau} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now the moment of momentum p of the revolving electron (cf. eqn. (17) on p. 113) is, generally,

$$p = 2m\frac{F}{\tau}.$$

So we obtain

$$\mu = \frac{ep}{2m} \quad . \quad . \quad . \quad . \quad . \quad (12)$$

But the moment of momentum is quantised so that we have here again to substitute instead of the moment of momentum quantum number n_ϕ of our elementary theory the number j*:

$$p = j\frac{h}{2\pi}.$$

Hence, by (12) the magnetic moment also becomes a quantised quantity which is expressed as a j-fold multiple † of an elementary quantum:

$$\mu = j\mu_1, \quad \mu_1 = \frac{e}{m}\frac{h}{4\pi} \quad . \quad . \quad . \quad (13)$$

Here μ_1 is the fundamental unit of magnetic moment of the quantum theory; it is the theoretical **magneton.** Instead of referring the fundamental unit of the magneton to the individual atom we prefer to refer it to the mol, that is, to L atoms (when L = Loschmidt's number per mol, or Avogadro's number; see p. 4), and we obtain as the macro-unit of magnetic moment the so-called **Bohr magneton**:

$$M_B = L\mu_1 = \frac{e}{m}\frac{h}{4\pi}L.$$

Inserting the known values of e/m, h and L, we obtain

$$M_B = 5564 \text{ gauss cm. per mol} \quad . \quad . \quad . \quad (14)$$

It is very remarkable that Weiss obtained from his measurements, particularly from those of the ferro-magnetic metals at the lowest temperatures, a smaller unit,—one nearly five times as small, namely,

$$M_W = 1123{\cdot}5 \text{ gauss cm. per mol} \quad . \quad . \quad (15)$$

* Even the form which thus results for p is not rigorously correct. For wave-mechanics shows that our j is, indeed, the quantum number to be ascribed to the total moment of momentum, but that for the absolute value of this total moment of momentum we must have $p = \sqrt{j(j+1)}\ h/2\pi$. Equation (13) is to be changed analogously to $\mu = \sqrt{j(j+1)}\ g\mu_1$. Concerning the factor g, cf. the following footnote.

† In Chapter VIII we shall see from the theory of the multiplet terms that a rational factor g has yet to be added on the right-hand side of (13). The above equation hence really holds only when $g = 1$ (singlet terms). Cf. also the remarks in Chapter VI, § 5, when the factor g is deduced for one-electron systems.

We shall endeavour to reconcile these apparently contradictory statements by using the idea of spatial quantising. At present we are interested in the Bohr magneton and not in the Weiss magneton.

Stern and Gerlach have shown by carefully measuring the magnetic field, its departure from homogeneity, and the deflection obtained on the photographic plate, Fig. 32*b*, that the magnetic moment of the silver atom is of the order of magnitude of our quantity μ_1; they estimate their experimental error to be only 10 per cent. *Hence the silver atom has in its ground state a magnetic moment of the magnitude of a Bohr magneton. The same value for* μ *follows from Fig.* 33 *for the hydrogen atom in the ground state.*

By means of their bold experimental arrangement, Stern and Gerlach have therefore not only demonstrated *ad oculos* the *spatial quantising of the atom in the magnetic field,* but they have also proved the *atomic nature of the magnetic moment, its quantum origin, and its relationship to the atomic structure of electricity.*

CHAPTER III

THE NATURAL SYSTEM OF ELEMENTS

§ 1. Small and Great Periods. Atomic Weights and Atomic Numbers

IN the face of the manifold of elements which were brought to light by the alchemists of the Middle Ages and by the research chemists of the eighteenth and nineteenth centuries, the human intellect has never quite lost the view that unity and order exist among them. The old postulate of natural philosophy that there must be a common basic substance in all matter recurred again and again, particularly in the form of Prout's hypothesis (1815), because only the fulfilment of this condition could give us hope that we should succeed in understanding fully chemical action.

This goal has assumed a more definite shape since the discovery of the natural or periodic system of the elements by Lothar Meyer and Mendelćeff about 1870. In this system, as is well known, the elements are written down in the order of increasing atomic weights, the series being broken off at appropriate points. Chemically related elements are written in the same vertical column, e.g. the alkalies, Li, Na, K, Rb, Cs, in the first column ; the halogens, F, Cl, Br, I, in Column VII ; since 1895 (Rayleigh and Ramsay) the inert gases He, Ne, A, Kr, X, Em, have become added as Column VIII (cf. Table 2).

In general, the number of the column is the same as the **oxygen-valency** of the elements contained in it. The valency increases by one for every step from left to right in the periodic system. On the other hand, a different kind of valency, the **hydrogen-valency**, increases in the periodic system from right to left ; this is particularly pronounced in the columns from VII to IV. As the oxygen-valency increases the electropositive character (basic nature) diminishes and passes over into the electronegative character (acidic nature).

In this mode of tabulation the system of elements seems, externally at least, to be built up of periods of eight. Before the discovery of the inert gases they were true " octaves " in the musical sense, i.e. periods of seven (Newlands, 1864). The structure in periods of eight is, however, only apparent, for the periodic system has not so simple a periodicity. At the beginning, for example, there is a period of only two elements (H and He). Then there follow two periods of eight, the two " small " periods of eight exactly corresponding elements. They are succeeded by

TABLE 4

	I	II	III	IV	V	VI	VII	VIII
1	1 H 1·0078							2 He 4·002
2	3 Li 6·940	4 Be 9·02	5 B 10·82	6 C 12·000	7 N 14·008	8 O 16·0000	9 F 19·00	10 Ne 20·18
3	11 Na 22·997	12 Mg 24·32	13 Al 26·97	14 Si 28·06	15 P 31·02	16 S 32·06	17 Cl 35·457	18 Ar 39·94
→ 4	19 K 39·104 29 Cu 63·57	20 Ca 40·07 30 Zn 65·38	21 Sc 45·10 31 Ga 69·72	22 Ti 47·90 32 Ge 72·60	23 V 50·95 33 As 74·96	24 Cr 52·01 34 Se 79·2	25 Mn 54·93 35 Br 79·916	26 Fe 27 Co 28 Ni 55·84 58·94 ↔ 58·69 36 Kr 82·9
5	37 Rb 85·45 47 Ag 107·880	38 Sr 87·63 48 Cd 112·41	39 Y 88·93 49 In 114·8	40 Zr 91·22 50 Sn 118·70	41 Nb 93·5 51 Sb 121·76	42 Mo 96·0 52 Te 127·5	43 Ma ↔ 53 I 126·93	44 Ru 45 Rh 46 Pd 101·7 102·9 106·7 54 Xe 130·2
6	55 Cs 132·81 79 Au 197·2	56 Ba 137·36 80 Hg 200·61	57 La 138·90 81 Tl 204·39	72 Hf 178·6 82 Pb 207·21	73 Ta 181·5 83 Bi 209·00	74 W 184·0 84 Po (210·0)	75 Re 188·7 85*	76 Os 77 Ir 78 Pt 190·9 193·1 195·23 86 Em 222
7	87*	88 Ra 225·97	89 Ac (227)	90 Th 232·12 ↔	91 Pa (231)	92 U 238·14		

Between 57 La and 72 Hf come the rare earths, as follows:—

58 Ce 140·13	59 Pr 140·92	60 Nd 144·27	61 Il	62 Sm 150·43	63 Eu 152·0	64 Gd 157·3
65 Tb 159·2	66 Dy 162·46	67 Ho 163·5	68 Er 167·64	69 Tu 169·4	70 Yb 173·5	71 Lu 175·0

The numbers preceding the symbols of the elements denote the "atomic numbers," the numbers below them denote the atomic weights. The latter are taken from the tables of the German Atomic Weight Commission of 1930.

two " great " periods of eighteen elements, which can be forced into the scheme of series of eight only by somewhat artificial reasoning. As a matter of fact the alkalies, halogens, inert gases, and altogether the elements which exhibit exactly corresponding chemical behaviour, follow one another after a further eighteen steps, and are thus separated in our scheme by an intermediate series. By writing the terms on the right or left side of the individual spaces we succeed in making only those elements that correspond exactly lie in a vertical line. The correspondence here implied is that which is connected with *atomic structure*, and which expresses itself particularly in the structure of spectral lines. From the *chemical point of view*, in which we are concerned with the behaviour of ions in compounds, we find it convenient to alter the distribution of elements among the sub-groups at some points, for example, in the third and fourth columns in the case of the lightest elements. It is to be noted, however, that the elements that lie consecutively in the same vertical column but are not written in an exact vertical line, are related in certain ways. For example, Cu and Ag are univalent just like the alkalies in the same column ; Zn and Cd are divalent like the alkaline earths, and so forth. This " secondary " relationship becomes weaker at the end of the horizontal series, particularly in Column VIII, in which we group with the inert gases the triads, Fe, Co, Ni, and Ru, Rh, Pd, constellations of elements that are interrelated among themselves, but are absolutely dissimilar from the inert gases. It is only by uniting these triads in one column that the number 18 of the great periods can be adapted to fit the double number 2 . 8 of the small periods.

The great periods are then followed by a very great period of thirty-two elements, which begins in the regular fashion with an alkali (Cs) and ends with an inert gas (Em). It, too, has its representative in Column VIII, a triad Os, Ir, Pt. But the whole series of rare earths (stretching from Ce to Lu), sixteen in number, will admit of no periodicity and can in no way be inserted in the Columns I to VIII ; they have had to be printed separately below. Written in this way, the period of thirty-two elements also appears distributed among the spaces of two horizontal series, whereby exactly corresponding elements, separated by a horizontal row, lie below the corresponding elements of the period of 18 ; thus W lies under Cr and Mo, Au under Ag, and so forth.

This greatest period is followed by a series of only six elements, which ends with the heaviest element, uranium. But it is quite admissible to imagine this series continued, say, to the number of thirty-two terms, and to assume that it is only due to reasons of radioactive decay that the later elements no longer exist.

The periodic numbers 2, 8, 18, 32, with which we are thus left, may finally be written in the following somewhat cabalistic form suggested by Rydberg :

$$2 = 2 \cdot 1^2, \quad 8 = 2 \cdot 2^2, \quad 18 = 2 \cdot 3^2, \quad 32 = 2 \cdot 4^2.$$

Various other suggestions have been put forward about the physical meaning of these numbers. For example, Bohr (Nature, 24th March, 1921) proposed the factors:

$$2 = 1 \cdot 2, \quad 8 = 2 \cdot 4, \quad 18 = 3 \cdot 6, \quad 32 = 4 \cdot 8.$$

We shall see later (pp. 154, 155) how Pauli's Principle confirms with the Rydberg scheme.

If we write down the natural system of the elements in the order of increasing atomic weights we find that at four points the natural order is transgressed. There is no doubt that we must write the inert gas Ar before the alkali K, although the atomic weight of the former is greater than that of the latter. Furthermore, Co must come before Ni and Te before I, in spite of the order of atomic weights. After the recent discovery of protoactinium we have the fourth exception, for we must set Th and Pa in the reverse order of their atomic weights. These necessary reversals of order have been indicated in the table by a double arrow. The method of X-ray analysis will remove these blemishes in the system and will restore the natural order of the elements. This method will show that the atomic weight is not the true regulative principle in the natural system, but that it is only a complicated function of the true "**atomic number**" (*Ordnungszahl*).

The true atomic number is, as we know (Chap. II, § 1), *the number of net positive units of charge in the nucleus*, or, what amounts to the same thing, *the number of electrons in the atom. It is equal to the atomic number*, that is, *to the number giving the position of the element in the natural system when the elements are arranged in the order appropriate to their chemical properties.* In our table we have inserted this number just before the symbol of each element.

On the basis of the periodic table physicists had been able, even earlier, to predict the existence of unknown elements, which were subsequently discovered. These were given the nationalistic names: Gallium (1875, Lecoq de Boisbaudran), Scandium (1879, Nilson), Germanium (1886, Winkler), Polonium (1898, Madame Curie), to which there have been added lately: Hafnium (Bohr, Coster, and Hevesy), Rhenium, Masurium (Noddack, Berg, and Tacke), and lastly Illinium (Hopkins, Harris, and Yntema). The first three had been predicted by Mendelejeff as eka-boron, eka-aluminium and eka-silicon, and their properties were accurately described. Nowadays—also by the method of X-rays—the number of gaps still present in the system has been found to be two only. These two have been marked by an asterisk in the table. According to their position in the table they are designated as eka-iodine and eka-caesium.

The atomic weights, with a regularity far exceeding the bounds set by the laws of probability, are integral numbers or very nearly so when referred to oxygen = 16. This integral property agrees with Prout's hypothesis (that elements are composed of hydrogen atoms). There

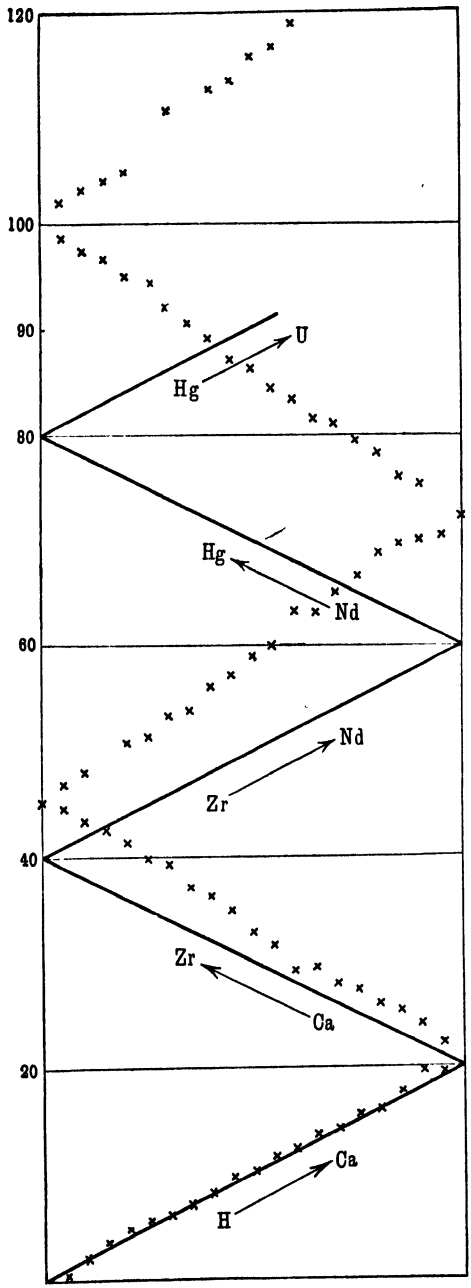


FIG. 34.

are certain exceptions (e.g. Cl=35·46, and Cu=63·57), but they are rare. We shall revert to these exceptions and to their elimination by F. W. Aston in the next section of this chapter. Whole numbers of the form, $4n$ and $4n + 3$, are particularly frequent, the former generally in even spaces, the latter in places where the atomic number is odd.

Thus, if we compare an element with the next but one element, we get for the difference of their atomic weights, as a rule, approximately four. Hence the average increase in the atomic weight as we pass from element to element is not one but two. *The atomic number of the element does not on the average coincide with the atomic weight, but with the half of the atomic weight.* This rule certainly holds only at the beginning of the system (as far as Ca); thence onwards systematic deviations occur in the sense that the semi-atomic weight increases more rapidly than the atomic number and exhibits a greater and greater difference (cf. Fig. 34).

For the sake of economising space we have marked off the atomic numbers (the abscissæ) alternately to the right and to the left after every twenty steps, so that the first branch of the line

corresponds to the elements from H to Ca, the second to those from Ca to Zr, and so forth. The ordinates represent for the one part the atomic numbers themselves (continuous line), for the other part half the atomic weights (crosses). We see that the latter, in the mean, increase to the same extent as the atomic numbers, but that with the exception of the lowest branch they lie above the corresponding points of the atomic numbers, the difference increasing as the atomic number increases. Thus our diagram gives us a picture of the above-mentioned complicated relationship between atomic weight and atomic number.

Concerning the arrangement of the periodic system in our table, it cannot fail to be recognised that it is in many ways arbitrary. We have already pointed out the arbitrary nature of the eight columns into which we could insert the great periods only by force, as it were. A further arbitrary adjustment consists in having placed the eighth column on the right, next to the seventh column. As is often done, we may place it as the 0th column in front of the first on the left. The 0th column would then contain the elements of " valency zero," that is the chemically inert gases. The whole theory of atomic structure, as we shall show in § 3 of the present chapter, points to the inert gases marking the end and the completion of a period, and not the beginning of a new period.

§ 2. The Laws of Radioactive Displacement and the Theory of Isotopes

The characteristic properties of the α-particle (its double charge, its great penetrative power, and so forth, cf. p. 17) have already served us as a direct and obvious confirmation of our fundamental views, namely, those on nuclei, nuclear charge, and atomic number (cf. §§ 3, 5). Radioactivity, however, can furnish us with still more information on this question.

Let us consider the genealogical tree of the radium family in Table 1 of page 53, and discuss the position of Ra itself. Since it was first isolated there has been no doubt that it belonged to the group of alkaline earths Ca, Sr, Ba. In particular, Ra is so closely related to Ba chemically, that, originally, it was difficult to separate them from one another ; the similarity in the spectra of the two is also perfect. On the other hand, radium emanation, in virtue of its chemically inert behaviour, beyond doubt belongs to the group of inert gases.

Now, *this mutual position of Ra and RaEm in the periodic system is just such as is demanded by our nuclear theory.* Ra disintegrates, producing RaEm and emitting α-radiation. The doubly charged positive α-particles comes out of the *nucleus of the Ra-atom* and thus diminishes its positive charge by two units, $2e$. Hence the atomic number of the resulting element must also be reduced by two, that is, the newly produced element must precede the Ra in the system of elements by *two places.* The nuclear mass becomes reduced simultaneously with the

nuclear charge, namely, by four units corresponding to the atomic weight of He. The atomic weight of Ra is 226·0. Radium emanation (also called radon and niton) must therefore have the atomic number $226 - 4 = 222$—which agrees with the results of experiment.

We generalise the remark just made about Ra and RaEm and enunciate the **first law of radioactive displacement** *thus. In every process of radioactive disintegration which is accompanied by the emission of α-rays (α-transformation) a product results, the atomic number of which in the periodic system is reduced by two units; the element moves two places to the left in the table. At the same time its atomic weight decreases by four units.*

Now what happens in the case of *β-transformations*, that is, of those radioactive processes during which β-rays are emitted? Does the β-ray electron in this case come out of the electronic shell of the element or out of its nucleus? In the former case the character of the element and its position in the periodic system would remain unaltered. We should have before us a process to which the term ionisation would have to be applied. But we know that β-transformations also cause new elements to be formed. Hence the β-emission, like the α-emission, must come *out of the nucleus.*

We must assume (this will be discussed in detail in § 6) that in a nucleus of atomic number Z there must be, in addition to the Z positive unit charges that determine this atomic number, other *positive* and *negative* charges which are mutually bound and which neutralise one another (cf. also the note on p. 63). Now if a negative unit charge (an electron) is thrown out of this neutral stock of charges, a positive unit of charge is free, that is, unbalanced by a negative charge. But then the nuclear charge must increase by one unit. Hence we get the **second law of radioactive displacement.** *In the case of β-transformations, the atomic number of the element undergoing change increases by one unit, and moves to the next position on the right in the periodic table. The diminution in the atomic weight in this process, however, is inappreciable on account of the small mass of the electron.*

In fact, the atomic weight does not become reduced at all if we take into account the fact that the atom which, owing to the β-transformation, has become positive, will soon neutralise itself by drawing to itself a free electron from without. Such free electrons, so we may assume, are always available in the interior of a metal, and in an atmosphere continually subject to radioactive radiations and hence ionised. Of course, the external electron just mentioned does not enter into the nucleus but into the electronic shell. In this way it completes the number of electrons that is properly due to the new element derived by the β-transformation. Hence the charging process of the β-transformation is followed by a *process of neutralisation. The small diminution of atomic weight that is initially caused by the loss of the β-electron is thus rectified again.*

After the α-transformation, too, a process of neutralisation will also take place. For the atom which has arisen through the α-emission will at first have two electrons more than the number corresponding to its nuclear charge. It will therefore give up two of its electrons to its surroundings, not, of course, in the form of β-radiation, but by way of balancing its charge without the generation of considerable kinetic energy. The decrease of atomic weight to the extent of four units, which corresponds to the α-emission, thus becomes slightly more marked owing to this additional loss.

It is of historical interest to note that Fajans * and Soddy † share equally the honour of having discovered these laws of displacement.‡ Soddy first enunciated the law of displacement for α-transformations. Fajans tested it on further material and added the law of displacement for β-transformations. He and, a little later, Soddy formulated both laws of displacement in the form which is now generally accepted as valid. A. S. Russell endeavoured to express the general law almost at the same time, but his formulation was not quite correct.

In our account we have read the laws of displacement directly out of the theory of nuclear structure. Historically, the state of affairs was of course different. When these laws were first enunciated this nuclear theory did not exist, nor was it possible at that time to arrange the radioactive products into the groups of the periodic system in all cases. It was rather the laws of displacement that have led to the present arrangement of the radioactive elements into the scheme, and at the same time they have given the theory of nuclear charges a sound foundation.

Table 5 shows on the one hand the distribution of the radio-elements in the periodic system, on the other, in the vertical columns, their distribution in the scale of atomic weights. The character of the radiation emitted is, as in the former table on p. 53, indicated by the letters, α, β prefixed to the symbol of the element under consideration.

Let us, for example, follow out the radium family, beginning with Ra and proceeding with the zig-zag step prescribed by the laws of displacement. We get from Ra (Column II, At. Wgt. 226) to RaEm (Column VIII, At. Wgt. 222) to RaA (Column VI, At. Wgt. 218), to RaB (Column IV, At. Wgt. 214) by successive α-transformations. Next, from RaB we get by a β-transformation to RaC (Column V, At. Wgt. 214). At RaC the interesting branching that was discussed earlier (on p. 53) takes place : by an α-transformation we get to RaC'' (Column III, At. Wgt. 210) and then by β-transformation to the long-lived RaD (Column IV, At. Wgt. 210) ; on the other hand, from RaC by a β-transformation to RaC' (Column VI, At. Wgt. 214)—to this transformation

* Habilitationsschrift Karlsruhe, 1912 ; Physik. Zeitschr., **14**, 131 and 136 (1913).

† *The Chemistry of the Radium Elements*, 1911 ; Chem. News, Vol. **107**, p. 97 (1913).

‡ The general law was being sought almost simultaneously by A. S. Russell (cf. Chem. News, Vol. **107**, p. 52), but his formulation was not quite correct.

TABLE 5

At. wt.	I	II	III	IV	V	VI	VII	VIII	At. wt.
206	—	—	—	Ra G	—	—	—	—	206
207	—	—	β Ac C″	**Pb**, Ac D	—	—	—	—	207
208	—	—	β Th C″	Th D	**Bi**	—	—	—	208
210	—	—	β Ra C″	β Ra D	β Ra E	α **Po**	—	—	210
211	—	—	—	β Ac B	$\alpha\beta$ Ac C	α Ac C′	—	—	211
212	—	—	—	β Th B	$\alpha\beta$ Th C	α Th C′	—	—	212
214	—	—	—	β Ra B	$\alpha\beta$ Ra C	α Ra C′	—	—	214
215	—	—	—	—	—	α Ac A	—	—	215
216	—	—	—	—	—	α Th A	—	—	216
218	—	—	—	—	—	α Ra A	—	—	218
219	—	—	—	—	—	—	—	α Ac-Em	219
220	—	—	—	—	—	—	—	α Th-Em	220
222	—	—	—	—	—	—	—	α **Ra-Em**	222
223	—	α Ac X	—	—	—	—	—	—	223
224	—	α Th X	—	—	—	—	—	—	224
226	—	$\alpha\beta$ **Ra**	—	—	—	—	—	—	226
227	—	—	β **Ac**	$\alpha\beta$ Ra Ac	—	—	—	—	227
228	—	β Ms Th_1	β Ms Th_2	$\alpha\beta$ Ra Th	—	—	—	—	228
230	—	—	—	α Io, β UY	—	—	—	—	230
231	—	—	—	—	α **Pa**	—	—	—	231
232	—	—	—	α **Th**	—	—	—	—	232
234	—	—	—	β UX_1	β UX_2, β UZ	α U II	—	—	234
238	—	—	—	—	—	α **U I**	—	—	238

we owe the emission of intense γ-rays by RaC—then by an α-transformation we likewise get to RaD. From RaD a two-fold β-transformation leads to RaE (Column V) and RaF (= Polonium, Column VI) in which the atomic weight 210 is retained. The position of polonium in the periodic system may, according to Marckwald, be verified by chemical methods. It is somewhat more electronegative than Bi (in the sense elucidated in § 1, p. 130) and this conforms with the position which has been assigned to it, namely, that immediately succeeding Bi. A final α-transformation changes polonium into RaG, also called radium lead (Column IV, At. Wgt. 206, which is less than the atomic weight of ordinary lead, 207·2). Radium lead is the final product of the radium series. The thorium and the actinium series also end at the same point of the periodic system, at thorium lead (ThD) and actinium lead (AcD).

We must next refer to the interesting complex of facts, to which the name **isotopes** is applied collectively. Isotope signifies " occupying the same position " ; isotopes are elements that occupy the same position in the periodic system. The totality of isotope elements in one compartment of the system is called a *pleiad*. In Table 5 every group composed of elements whose symbols lie vertically below one another form a pleiad of this kind. The pleiads of lead and polonium include no less than eight and seven members respectively. The individual members differ among themselves in atomic weight up to as many as eight units, but are yet so similar that they are usually considered, not as different elements, but as different species of the same element. *For isotopic elements cannot be separated from one another by chemical means at all and exhibit identical physical properties throughout.* The only means of separating them chemically or physically is that offered by the difference in the atomic weights which may manifest itself in a difference in their gravitational and inertial action.

The most convincing confirmation has been found for the theory of isotopes in the case of lead. When the atomic weights of lead isotopes of varying origin were compared with one another, it was shown that lead from radium minerals (RaG) has the atomic weight 206·0 and lead from thorium minerals has the atomic weight 207·9, whereas ordinary lead has an atomic weight 207·2.

On account of the interposition of isotopes the traditional framework of the periodic system must be extended. Since there are now several claimants to one space of the system, the scheme on one plane no longer gives a non-ambiguous allocation of the elements. It would be best to extend the scheme spatially. We imagine the isotopes to be placed behind one another in order of their longevity, say. The longest-lived element forms the chief representative of the pleiad in question and would stand furthest back in our spatial scheme, in the same vertical plane as the permanent elements which are not suspected of being radioactive. From this longest-lived element the series of

isotopes of decreasing longevity would then be successively arrayed outwards and upwards perpendicular to the plane scheme. Thus, in the two-dimensional table of elements, we should, to be more accurate, have to place U_I in the lowest space below uranium, whereas the isotope U_{II} would have to be placed in front of it (out in space). In the last place but one, protoactinium stands as the longest-lived element of its type (its stretch of life is about 32,000 years), whereas the element UX_2 (also called brevium) that has hitherto been installed there has a life of only 1·17 minutes and would thus have to be brought forward out of the table. Of the three emanations Ra-Em is the longest lived (3·825 days), and must therefore stand as the representative of the inert gases in the sixth period. In the former table the chief representatives of the types of corresponding elements were emphasised by being printed in dark type.

Through the discovery of isotopes *atomic weight has been displaced from its position of sovereignty by the nuclear charge.* We are acquainted with elements, for example, RaG and RaB, or Po and RaA, which differ in atomic weight by eight units and yet (as isotopes) they behave identically alike in chemical reactions. On the other hand, we know elements, for example, RaD and Po that behave chemically as differently as C and O, which belong, namely, to the fourth and sixth column of the periodic system, and yet they have the same atomic weight. Pairs of elements of the latter type are to be found in Table 5 in a horizontal line; pairs of elements of the former type occur vertically.

Not only among decaying elements but also *among permanent elements* there are isotopes. Nor do they occur as exceptions; indeed, they are the rule. Of the elements that have hitherto been investigated for signs of isotopy most have shown themselves to be multiform. Those that have been proved to be of one type * only are

H	He	Be	C	N	O	F
1·0078	4·002	9·02	12·000	14·008	16·0000	19·00
Na	Al	P	As	I	Cs	Bi
22·997	26·97	31·02	74·96	126·93	132·81	209·00

The following elements have been found to be multiple:

Li	B	Ne	Mg	Si	S	Cl
6·940	10·82	20·18	24·32	28·06	32·06	35·457
Ar	K	Ca	Fe	Ni	Cu	Zn
39·94	39·104	40·07	55·84	58·69	63·57	65·38
Se	Br	Kr	Rb	Sr	Zr	Ag
79·2	79·916	82·9	85·45	87·63	91·22	107·880
Cd	Sn	Sb	Te	Xe	Hg	Pb
112·41	118·70	121·76	127·5	130·2	200·61	207·21

* There are, however, extremely rare isotopes of O, C, and N.

We see that the atomic weights that have been printed below the symbols for the elements are in the case of the simple elements—in particular, of the lighter ones—almost exactly whole numbers ; on the other hand, they diverge considerably from integers in the case of elements that have been recognised as multiform. Further, the elementary constituents into which the latter may be resolved are here, as we shall see, exactly whole numbers, within the limits of error (except for the packing effect ; cf. § 6 of the present chapter).

We are indebted for this important knowledge to the work * of F. W. Aston, who, for his part, added a new link to the analysis of canal rays (" positive rays ") carried out by J. J. Thomson (cf. p. 66). In the canal-ray tube there are manifold fragments of matter, simply and multiply charged, atom-ions and molecule-ions. In an electrical field they are deflected by an amount proportional to their charge and inversely proportional to their mass. Hence in the case of two isotopes of the same charge and different mass the heavier constituent will be less deflected than the lighter. Furthermore, the amount of the deflection depends on the velocity that has been acquired by the particle in question. The advantage of Aston's method over Thomson's was gained by arranging behind the electrical field a magnetic field, the intensity and range of which was so chosen that all particles of the same mass were concentrated at one and the same spot : the photographs so obtained are called " mass-spectrograms."

The first result of Aston states : Neon consists of two isotopes of atomic weight 20·00 and 22·00, " neon " and " meta-neon." The atomic weight obtained by chemical means, 20·2, results from a mixture of both in a constant proportion.

The resolution of chlorine into two isotopes of atomic weight 35·0 and 3·70 is particularly impressive. The chemical atomic weight of chlorine, 35·46, which among the lighter elements is the first serious contradiction to the integral (whole number) character of the atomic weight, comes about owing to the fact that, as is shown from the photographic plate, the Cl_{35} is present in greater quantity than the Cl_{37} ; the proportion is 3 : 1. In addition to the spots of 35 and 37 we see in the mass spectrogram of the Cl-photographs also the spots 36 and 38 present in about equal proportions : these are to be interpreted as HCl_{35} and HCl_{37}. Then, again, there are spots 17·5 and 18·5 that represent doubly charged Cl_{35} and Cl_{37}. (In a spectrogram double the charge acts like half the mass.)

In the case of the inert gases krypton and xenon, not less than six and nine isotopes, respectively, have been disclosed, of which the atomic weights differ up to 8 units in the case of Kr, and 12 in that of Xe. In the case of Sn eleven isotopes were observed, in that of Zn and Hg there were seven for each. Hence we have pleiads here of the same number

* Phil. Mag., **39**, 449 and 611 (1920). See also *Isotopes*, F. W. Aston, 1922, Edward Arnold & Co., London.

as in the case of the radium elements (cf. Table 5). All elements of odd atomic number appear to have only 2 * isotopes, if they have any at all.

In the following Table 6 we follow Aston in attaching the letters *a*, *b*, *c*, . . . to the relative amount in which the corresponding species of element is represented in the "mixed element" (*a* denotes the strongest component, *b* the next strongest, and so forth).

Only atoms in the gaseous state can be examined by Aston's method. A series of non-volatile elements, for example, Mg, Zn, Ca, have been investigated by A. J. Dempster † by a canal ray method which differs from that used by Aston.

A more sensitive method than either of these and one which may also be used for very small quantities of isotopic admixtures is the method which uses spectral bands. In Chapter IX, § 2, we shall discuss the infra-red absorption spectrum of HCl, which brings out clearly the two isotopes Cl_{35} and Cl_{37}. But whereas in this case a known result is confirmed optically research on bands has disclosed new and entirely unexpected results in the case of oxygen, carbon, and nitrogen. Giaque and Johnston ‡ interpret certain weak lines in the atmospheric absorption bands of oxygen as a combination of O_{16} and O_{18}, and still weaker lines of the same spectrum have been ascribed by Babcock ‖ and Birge ¶ to a molecule which is formed from O_{16} and O_{17}. The rareness of the atomic species O_{17} and O_{18} is indicated in the weak intensity of the corresponding bands, the ratio of their frequency of occurrence (*Häufigkeitsverhältnis*) as compared with ordinary oxygen amounting to 1 : 1250 and 1 : 10,000 respectively. In the case of carbon an isotope of atomic weight 13 has been shown by Birge ** to be present in the C — C-bands (Swan spectrum)—as well as in the CO- and CN-bands (cyanogen bands)—and in this case, too, to so small an extent that it could not manifest itself directly in the mass spectrograph. According to researches by Naudé †† the N-isotope N_{15} is apparently indicated in the bands of NO.

In view of all these discoveries the traditional term "atomic weight" as used for the quantity which is familiar to the chemist is really no longer appropriate. The constant values of the latter must be interpreted as showing that the isotopes of the mixture came into existence before the earth's crust had solidified, in epochs in which their uniform commingling was possible and inevitable. This alone would explain why the chemist everywhere and at all times finds them occurring in the same proportions.

The striking characteristic of elementary atomic weights, that of

* F. W. Aston, Proc. Roy. Soc., **126**, 511 (1930).
† Phys. Rev., **11**, 316 (1918), and **17**, 427 (1921).
‡ Nature, **123**, 318 (1929). ‖ *Ibid.*, **123**, 813 (1929).
¶ *Ibid.*, **124**, 13 (1929). ** *Ibid.*, **124**, 182 (1929).
†† Phys. Rev., **34**, 1498 (1929). Besides the lines of $N_{15}O_{16}$ Naudé also finds those of the combinations with the rarer oxygen isotopes $N_{14}O_{17}$, $N_{14}O_{18}$.

TABLE 6

Li	B	Ne	Mg	Si	S	Cl	Ar	K	Ca	Fe	Ni	Cu
6b	10b	20a	24a	28a	32a	35a	36b	39a	40a	54a	58a	63a
7a	11a	21c	.25b	29b	33c	37b	40a	41b	44b	56b	60b	65b
		22b	26c	30c	34b							

Zn	Se	Br	Kr	Rb	Sr	Zr	Ag
64a	74f	79a	78f	85a	86b	90a	107a
65e	76c	81b	80e	87b	88a	92c	109b
66b	77e		82c			94d	
67d	78b		83d				
68c	80a		84a				
69g	82d		86b				
70f							

Cd	Sn	Sb	Te	Xe	Hg	Pb
110c	112i	121a	126b	124i	196g	206b
111e	114k	123b	128a	126h	198d	207c
112b	115l		130a	128g	199c	208a
113d	116c			129a	200b	
114a	117f			130f	201c	
116f	118b			131c	202a	
	119e			132b	204f	
	120a			134d		
	121h			136e		
	122g					
	124d					

being integral, restores *Prout's hypothesis* to its position of honour: according to this hypothesis, all atoms are supposed to be built up of hydrogen. The fact that hydrogen itself is simple has been proved not only by Aston but also by Stern and Volmer * by another method (fractionated diffusion of hydrogen and oxygen).

If, in accordance with the sense of Prout's hypothesis, H-nuclei are the real elementary "bricks" of which all gravitational matter is built up, it must cause surprise that in the radioactive transformations "H-rays" have never been observed. Why does not the hydrogen nucleus occur as a decay product of the higher elements just as well as the less simple He-nucleus? In the last section of this chapter we shall give reasons why *spontaneous* emission of protons does not occur. We shall here only remark, however, that in *artificially stimulated* disintegration, as first used successfully by Rutherford in the case of nitrogen, proton rays are actually produced. We shall also discuss the latter phenomenon in the last section.

§ 3. Peripheral and Central Properties of the Atom. Visible and X-ray Spectra. Configurations of the Inert Gases

In the representation of the periodic system given in the first paragraph we followed the example of Mendeléeff essentially, both in the setting out of the table and in giving valency the predominant position

* Ann. d. Phys., **59**, 225 (1919).

as the regulative principle for the various groups of elements. It remains now to develop the representation that Lothar Meyer gave the periodic system at the same time as Mendeléeff. Its crowning feat is the classical curve of atomic volumes, Fig. 35. As we know, atomic volume denotes the ratio

$$\frac{\text{atomic weight}}{\text{density}}.$$

This ratio has the dimensions of a volume (cm.^{3}); it denotes, however, not the volume of one atom, but of so many atoms as are contained in the number of grammes given by the atomic weight. Instead

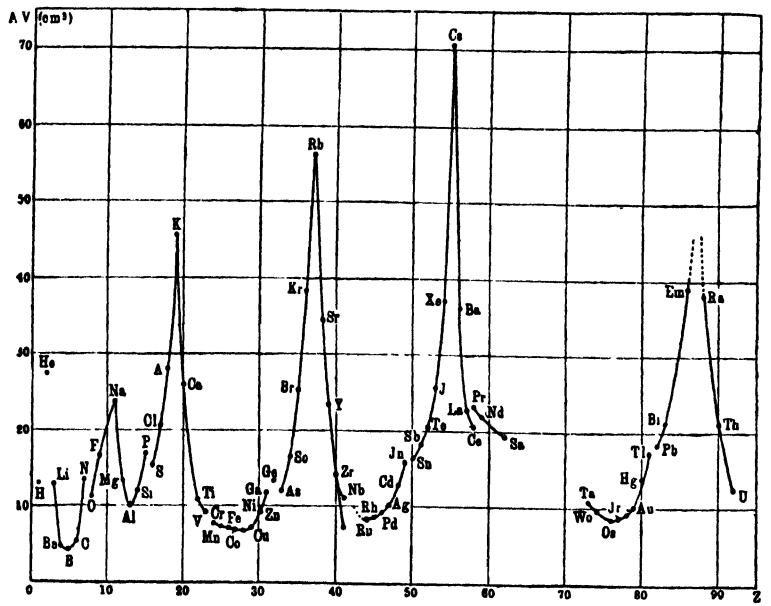


FIG. 35.—Curve of atomic volumes taken from one of the tables compiled by Stefan Meyer.* A distinct periodicity is exhibited.

of atomic volume we might say more correctly gramme-atom volume. We shall, however, retain the term that has been sanctioned by usage.

The atomic volume is, of course, defined only for the solid and liquid state. The gaseous state admits of no proper volume that is characteristic of a substance (unless we calculate such a volume from van der Waal's gas equation). In the case of the so-called permanent gases we must, therefore, in defining the atomic volume, derive the density from the liquid state. In the case of solids that occur in various allotropic modifications (diamond, graphite), we get several values.

We call attention to the following prominent features of the curve:

* *Elster and Geitel Festschrift* (Braunschweig, 1915), p. 152.

the steep maxima at the points occupied by the alkalies, the immediately following descending branches of the curve, the flat minimum in the middle of the period, the ascending branches before the next successive alkali, the likewise high ordinates of the points occupied by the inert gases, and particularly the similarity of appearance between the great periods of 18, 18, and 32 elements with the small periods of 8 and again 8 members; this similarity is such that in this representation of the periodic system there is no sign of a subdivision of the great periods into two small periods.

Later, a series of other properties were discovered which exhibited an analogous behaviour in their mode of dependence on the atomic

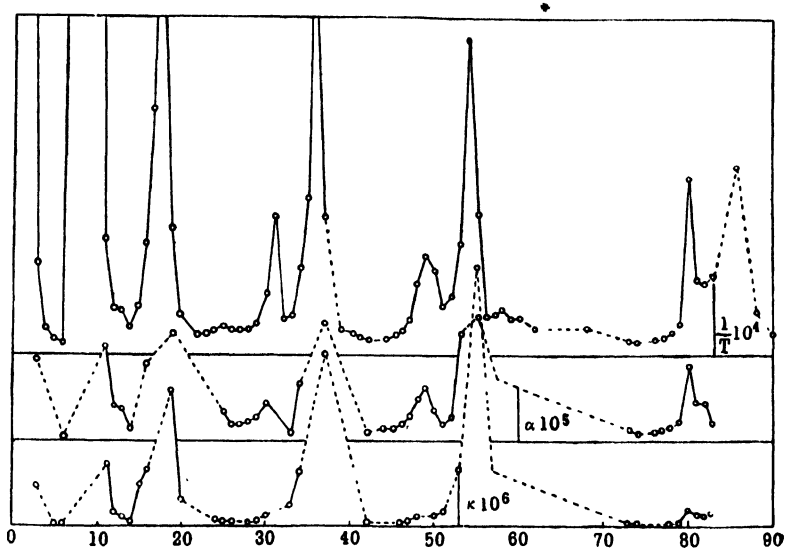


FIG. 36.—Further examples of periodic properties. Compressibility κ (bottom figure), coefficient of expansion α (middle figure), reciprocal melting-point 1/T (top figure) as ordinates, atomic numbers Z as abscissae.

weight (or atomic number, respectively). In Fig. 36 we exhibit as examples of such properties: the compressibility κ, the coefficient of expansion α, the reciprocal of the melting-point $\frac{1}{T}$ (as an inverse measure of the tendency of the element in question to be a solid); these are properties that concern not the filling of space itself as in the case of the atomic volume, but the alteration of the volume occupied owing to pressure and temperature changes. In a broad sense, these curves run parallel to those of the atomic volumes, but they seem a little less regular. In the curve of the reciprocal melting-points, the maxima are not at the alkalies but, as is easy to understand, at the inert gases, which show the least inclination towards becoming solids.

All these things concern a pronounced external property of the atom, namely, its claim on space. Its connexion with valency conditions and the structure of the periodic system in Lothar Meyer's curve shows that *chemical actions, too, depend on external properties of the atom.* In actual fact, they regulate the external relations of atoms to one another and themselves depend on the number and arrangement of the external electrons that determine the valency. Also the elastic properties of atoms, their thermal behaviour as shown by Dulong and Petit's law of specific heats and the electrical conductivity each give a curve analogous to that given by atomic volumes, and thereby prove that they too are *external properties of the atom.*

But also the phenomena that give rise to the emission of visible spectra occur at the periphery of the atom. The spectra of the alkalies exhibit an essentially similar structure in spite of their greatly different atomic numbers, Z = 3, 11, 19, 37, 55, and the consequent increase in complexity of the internal atomic structure. Only the peripheral arrangement of electrons in the series of alkalies is similar ; but this suffices to bring about an essential similarity in their visible spectra. The same correspondence exists between the spectra of the alkaline earths Mg, Ca, Sr, Ba, as well as between Zn, Cd, Hg. Almost in every case the *position of the element in its period* and *not* its position in the system as a whole (its atomic number) is the decisive factor. The latter (atomic number) gives only a slight sign of itself, in that the spectral lines are in general not simple lines but consist of two or three lines that belong together and are more or less close together in the spectrum. The differences between the frequencies of this " doublet " and " triplet " increase regularly with the atomic weight, as used to be stated, or, as we now say, with the atomic number or nuclear charge. But the part played by the nuclear charge in the optical spectra is but a minor one.

The position is different in the case of *X-ray spectra.* For them, the atomic number is the chief factor, in that from the atomic number of the element the corresponding X-ray line, and, conversely, from the X-ray spectrum the atomic number, can be determined uniquely. The frequency of a definite X-ray line, for example, the principal line of the K-series (cf. the next chapter), increases uniformly and continuously with the atomic number throughout the whole system of elements almost without showing a trace of periodicity. In this case it is not the position of the element within the period of the system but its *position in the system as a whole that is the all-important factor.*

Now, what does it signify that in X-ray spectra the atomic number of the element, its nuclear charge, exhibits itself so strikingly, whereas in the spectra of the visible region it hides itself ? This signifies that *the region in which the X-ray spectrum takes its origin is the innermost part of the atom, the immediate vicinity of the nucleus, and that, on the other hand, at the periphery of the atom, where the optical spectra are produced, the nuclear charge is screened off by the cloud of inner electrons*

or just shines faintly through them. It is owing to the fact that the X-ray spectra take their origin from the central region near the nucleus, where the forces are strongest and least modified, that their penetrative power and hardness is so great. In contrast with this, the visible spectra require for their excitation only small amounts of energy. At the surface of the atom the events occur on a moderate scale, but in the interior of the atom they become intensified to an extreme degree.

The nucleus and the innermost regions of the atom around it are not built up periodically but, in view of the intensity of the fields of force, their structure is a continuous growth in conformity with the continuous increase of the atomic number. The X-ray spectra reflect this systematic increase of growth and thereby lose all connexion with the periodic structure of the natural system. *Periodicity is an external, and not an internal, property of atomic structure.*

A general inference about the arrangement of the electrons about the nucleus may be drawn from observations concerning isotopes. *Two isotopes of an element cannot be separated by chemical means* (e.g. radium and mesothorium, thorium and radiothorium, or Cl_{35} and Cl_{37}); that is, the peripheral parts of their atoms are built up similarly, since it is these parts that are alone of account in chemical reactions. Moreover, *two isotopic elements have similar spectra* * *in the visible and the ultra-violet regions* (for example, thorium and ionium or mixtures of the two): this similarity also leads us to conclude that the arrangement of the external elements is very approximately the same. *But two isotopic elements have also the same X-ray spectra* (e.g. in the case of lead and RaG, according to Siegbahn and Stenström); hence they are also alike in the arrangement of the internal electrons. Hence the whole atomic structure is determined uniquely by the nuclear charge; given the same nuclear charge we get the same atomic structure, in spite of varying atomic weights; this applies, in particular, to the radioactive elements. As the decay continues and the nuclear charge alters, the new arrangement of the electrons that corresponds to the new nuclear charge is effected automatically. *The atomic structure is uniformly regulated, by electrical agency from within outwards as far as the periphery of the atom, by the magnitude of the nuclear charge.*

To describe the peripheral structure provisionally for the present, we picture to ourselves the progressive synthesis of the atoms in the order of the periodic system. At each step a new electron is added. In general the new electron attaches itself to the outside, as we may assume that in the interior of the atom there is no room for the immigration of additional electrons. As the number of external electrons increases, step by step, a limit is reached which, for reasons of stability, cannot be

* The similarity does not refer to the number and position of possible "satellites," cf. Chap. VIII. The latter are connected with the fine details of nuclear structure and may differ from one another in the case of isotopic atoms.

exceeded ; cf. § 4 of the present chapter. From that point onwards a new outer shell begins to form, the previous outermost shell contracting inwards. To picture this, we need only remember the rings of a tree in its yearly growth.

The alkalies are decidedly univalent and electropositive. There can be no doubt that we must assign to them in each period *one* outer electron in the outermost shell. The alkaline earths are divalent, the earths are trivalent ; to these must be ascribed, respectively, one, two, and three outer electrons (valency-electrons). In general we ascribe to the electropositive atoms at the beginning of each period just as many outer electrons as is expressed by their valency with respect to oxygen (cf. p. 130). *Electropositive character denotes readiness to part with electrons.* Now the electronegative elements are at the end of each period. *Electronegative character denotes readiness to take up electrons.* The electronegative atoms lack just as many electrons as they have hydrogen-valency ; fluorine wants one, oxygen two, nitrogen three. These electrons are not wanting in them for electrical neutralisation but for electromechanical stabilisation.

Between the electropositive elements following the end of a period and the electronegative elements preceding it there is situated in each case an inert gas. When the electropositive elements give up their valency-electrons, *they reduce their configuration to that of inert gases ;* whereas when the electronegative elements satisfy their valencies by taking up electrons, *they complete themselves as configurations of the inert gases.* Thus both parties strive towards this goal. Hence we must assume that the configuration of inert gases possesses a special degree of stability, and we see why in the progressive synthesis of the atoms in the natural system each period ends with an inert gas and that then a new shell begins.

The two small periods each contain eight elements. The inert gases neon and argon that stand at the end of these periods are thus entitled to eight electrons in the outer shell. We shall see that the other inert gases, also, as far as radium emanation are to be credited with eight outer electrons. Instead of " configuration of inert gases " we might just as well say " 8-shell." Helium with its two outer electrons is, of course, an exception.

The union of electropositive and electronegative elements denotes in the simplest cases the creation of one or more 8-shells. We call to mind HF, H_2O, NH_3. Fluorine, by taking from H the electron that it lacks, completes itself as an 8-shell ; in the same way, oxygen and nitrogen do likewise by depriving two or three hydrogen atoms of their electrons. In all cases the result is the neon configuration with attached hydrogen nuclei. Further, in the formation of NaCl two full 8-shells come about : the outer electron of Na emigrates to Cl ; Cl becomes raised to the argon type, and Na becomes lowered to the neon type. A corresponding argument holds for all the alkali halides. We may

represent this process by the somewhat unusual chemical formula

$$Na^+Cl^- = Ne_{11}A_{17}$$

which expresses that the positive Na-ion resembles a neon shell and that the negative Cl-ion resembles an argon shell, with the difference that the nuclear charge of the former is not 10 but 11, and that of the latter is not 18 but 17. In the case of divalent polar compounds two electrons pass from the electropositive to the electronegative component. For example, we find that with CaO two 8-shells form, the one, Ca^{++} being of the argon type, the other O^{--} being of the neon type; this may be expressed thus:

$$Ca^{++}O^{--} = A_{20}Ne_8.$$

Besides the tendency to the 8-configurations of the inert gases, we also find a tendency to the " 18-configurations " of the ions Cu^+, Ag^+, Au^+ in the compounds of the neighbouring atoms.

W. Kossel,* who revived Berzelius' theory, worked out fully this view of chemical action and tested it not only on the typically simple polar compounds, but also on Werner's complex compounds. He arrived at the result that in the case of all such compounds the directed single forces denoted by bonds in the old chemical schemes may be replaced by the electric forces of the ions, which are more intelligible physically. This view, of course, does not embrace non-polar bonds,† that is, those bonds for which no ions can be assumed, as in the case of, say, H_2, N_2, O_2; and, naturally, there are connecting transitions between the limiting conceptions polar and non-polar.

It has been held up as an objection to Kossel's line of reasoning, that, in the effort to trace chemical actions back to electrostatic forces alone, it has neglected the quintessence of the modern physics of the atom, namely, the quantum theory. The author is of the opinion that in Kossel's theory the quantum ingredient is represented by the fact that, going beyond Berzelius, Kossel takes the atomic volumes (better, the ionic volumes) into account whereby, for example, the decrease in the intensity of the polar union with increase of atomic size is explained according to Coulomb's law. In fact, the *size* of atoms is given, according to our modern view, merely by the extent of their peripheral electronic orbits, and these, in turn, are determined essentially by their quantum numbers.

This brings us for a moment back once again to the curve of atomic volumes, with which we started this section. The downward course of the curve at the beginning of each period may be made clear quite

* In his long paper, " Über Molekülbildung als Frage des Atombaues," Ann. d. Phys., **49**, 229 (1916). Cf. also " Über die physikalische Natur der Valenzkräfte," Naturwiss., **7**, 339 and 360 (1919), or the monograph, *Valenzkräfte und Röntgenspektren* (2nd ed., Springer, 1924).

† " Homeopolar " according to the nomenclature of R. Abegg, who prepared the way for Kossel's electrical theory. Instead of polar Abegg and Kossel use the term " heteropolar."

simply, if superficially, by the following consideration. In the case of a neutral atom of an alkali metal, an external electron is situated in the field of an atomic residue carrying a single positive charge. In the case of an atom of the alkaline earths, or of the earths, if they are electrically neutral, we have two or three outer electrons in the field of a doubly or trebly charged positive atomic residue. The increased attraction arising from this more highly charged atomic residue, which always outweighs the repulsion on the part of the other valency electrons, clearly effects a contraction of the dimensions of the orbit, as compared with the alkali atom, and so explains the decrease of the atomic volumes at the beginning of the periods. The ascending branches at the end of each period cannot be interpreted so readily.

§ 4. Introduction to the Theory of the Periodic System. Pauli's Principle

The theory of the periodic system is founded partly on the chemical system of arrangement and partly on spectroscopic facts. We touched on the former in the preceding section; we shall develop the latter in the following chapters. Hence in our present account of the theory of the periodic system we are forced to proceed somewhat dogmatically, and shall have to leave many empirical confirmations of spectroscopic origin till later. We commence by stating some general points of view which will be used as a basis for considerations given in the next section, which are more detailed.

1. Comparison with the States of the Hydrogen Atom

In the case of any arbitrary atom of atomic number Z we have Z electrons. We shall, as a first approximation, treat each of them as independent of the remainder. We may then compare it with the electron of the hydrogen atom,—in which case the nuclear charge of this hydrogen atom is to be set, not equal to 1, but to Z. Exactly as in the hydrogen atom we denote the state of the electron in question by means of certain quantum numbers. In describing the hydrogen-states in space we used the quantum numbers

$$n_r,\ n_\theta,\ n_\psi$$

(cf. p. 120), and called

$$n = n_r + n_\theta + n_\psi$$

the *principal quantum number*,

$$l = n_\theta + n_\psi - 1$$

the *azimuthal quantum number*. The latter takes the place of the quantum number

$$n_\phi = n_\theta + n_\psi$$

of the older theory (p. 115). Precisely as n_ψ was to signify the projection of n_ϕ on a favoured direction (magnetic axis), cf. page 121, so

in the sequel we shall use the projection of l on such a favoured direction and shall use m_l to signify the *magnetic quantum number*. The index l is to distinguish this number from an analogous quantity which will be introduced later and will be called m_s; m_l is a whole number, like n and l. From definition we then have, as in Fig. 29 of page 123,

$$-l \leqq m_l \leqq +l,$$

so that there are altogether $2l + 1$ different values of m_l for a given l.

The introduction of the *three* quantum numbers

$$n,\ l,\ m_l$$

in the case of the hydrogen electron or any selected electron of a complicated atom corresponds to the *three* degrees of freedom of the point-mass in particle mechanics. By adding to the three data n, l, m_l the above quantity m_s, we pass beyond the mechanics of the single point-mass and endow the electron with an axis ("spinning electron").

2. Principal Quantum Number and Shell Structure

We know that as we pass from one element in the periodic table up (in atomic number value) to the next, we find a new electron at each step. We also know that the electrons of an element distribute themselves over different shells.

As already hinted on page 116, we assign the values of the principal quantum number n to the individual shells of the atom. We speak of an innermost or K-shell; it consists of the electrons which have the value 1 for the principal quantum number. We call the next shell outwards the L-shell; it comprises the electrons for which $n = 2$. The complete scheme, so far as it is actually required in building up the elements, runs:

n	1	2	3	4	5	6	7
Shell . . .	K	L	M	N	O	P	Q

The conception and also the nomenclature of the successive atomic shells originate in the researches on X-ray spectra. The fact that steadily increasing values of the principal quantum number belong to the successive shells was suggested from the very beginning in the study of X-ray spectra and was confirmed by the discovery of L-doublets (cf. the next chapter, § 5). The beginning of a *new shell* in the periodic system at the same time denotes the beginning of a *new period*. But the allocation of the shells to the periods is not unique, as we shall see, and is complicated by various adjustments.

Our reason for giving the principal quantum number n the dominant position in distributing the electrons is that, as we know, the successive energy levels of hydrogen are distinguished by successive values of n. $n = 1$ denotes the ground state of hydrogen, the state of lowest energy. $n = 2$ is the next lowest energy state. Corresponding to this we have

that in any arbitrary atom the K-shell is the lowest in energy, the most stable, and the L-shell the next most stable, and so forth.

3. Azimuthal Quantum Number and Sub-Groups of the Shells

For a given principal quantum number n there are in general, in the case of the hydrogen atom, different types of orbits, according to the value of the azimuthal quantum number l, as illustrated in Figs. 26 and 27. We now assign to these different types of orbits different sub-groups of the shells in question; that is, we define subsidiary shells. Only the ground orbit, for which $n = 1$, is single. *Accordingly, the K-shell is also single.* Here l necessarily has the value zero. For $n = 2$ we had two types of orbits, which correspond to $l = 0$ and $l = 1$. *Accordingly, the L-shell divides into two sub-groups,* which we denote by

$$L_I \text{ and } L_{II} + L_{III}.$$

The reason for again dividing the second sub-group into L_{II} and L_{III} can be given only later when we deal with X-ray spectra. For the present we remark only that this distinction is connected with the spin of the electrons. The same applies to the sub-divisions in the successive later shells. For $n = 3$ we have drawn three types of orbits, which belonged to the values $l = 0, 1, 2$. *Hence the M-shell resolves into three sub-groups,* which we shall call

$$M_I, M_{II} + M_{III}, M_{IV} + M_V.$$

And so for the other shells. In the case of the N-shell we have four sub-groups, which we represent by the seven symbols,

$$N_I, N_{II} + N_{III}, N_{IV} + N_V, N_{VI} + N_{VII}.$$

They correspond, in order, to the values

$$l = 0, 1, 2, 3$$

of the azimuthal quantum number. Summarising, we may say that there are n sub-groups in the n^{th} shell, and that they are designated by $2n - 1$ symbols. In the case of hydrogen the different types of orbits do not differ at all as regards energy if n remains the same (degeneracy). This is not strictly true for a more complicated atom, but it is still correct to say that the energy-differences between the sub-groups, for example of the L-shell, are much smaller than the energy-difference between the K- and the L-shell, and so forth.

4. Magnetic Quantum Number and Multiplicity of the Sub-Groups. Introduction of the Spin Quantum Number

For a given l there are, as stated above, $2l + 1$ different possible values of the magnetic quantum number m_l. The states corresponding to the different values of m_l have, it is true, the same orbital type, and differ only in the different position of the orbit with respect to the axis

of reference chosen. But by characterising the states by means of their quantum numbers we treat such states of the same orbital type but differently orientated as being different. This will be so much more the case, since the wave-mechanical refinement of the orbital conception actually does lead here to different descriptions of the states (different proper functions). Every sub-group of the azimuthal quantum number l accordingly comprises $2l + 1$ states. Only the sub-groups belonging to $l = 0$, namely

$$K, L_1, M_1, N_1, \ldots,$$

are *simple*; for from $l = 0$ it necessarily follows that $m_l = 0$. On the other hand, the sub-groups that belong to $l = 1$, namely

$$L_{II} + L_{III}, M_{II} + M_{III}, N_{II} + N_{III}, \ldots$$

are *three-fold*, for here m_l can assume the values $+1, 0, -1$. In the same way the sub-groups for which $l = 2$, namely

$$M_{IV} + M_V, N_{IV} + N_V, \ldots$$

are *five-fold*, corresponding to the possible values $\pm 2, \pm 1, 0$ for m_l.

But the multiplicity which has been found in this way is not yet sufficient either for spectroscopic or for chemical purposes. *Each sub-group l comprises not $2l + 1$ but $2(2l + 1)$ states.* We express this in the language of quantum numbers by saying that the individual state of the electron is defined not by three, but by *four quantum numbers*. To the numbers n, l, m_l that have hitherto been used, we must add a *quantum number* m_s which is capable of having either of the values

$$m_s = \pm \tfrac{1}{2}.$$

This causes every state that has hitherto been simple to sub-divide into two different states, namely, those distinguished by the two values of m_s. In a certain graphical way the meaning of m_s is analogous to that of m_l. Whereas m_l defines the orientation of the revolving *motion in the orbit* with respect to a favoured axis, m_s denotes the orientation of the sense of rotation of the electron itself, namely, its "spin," which can set itself either parallel ($m_s = +\frac{1}{2}$) or anti-parallel ($m_s = -\frac{1}{2}$) to the favoured axis. For an empirical foundation of this interpretation we refer to the classical pictures of the *Stern-Gerlach effect* (see Figs. 32 and 33). The *two* deflections in the ground state of Ag and H, both of which signify a state with $l = 0$ (and hence also $m_l = 0$) are to be regarded as parallel and anti-parallel adjustments of the electron to the magnetic lines of force * and correspond to the two values $\pm \frac{1}{2}$ of the spin quantum number.

* The rigorous Dirac theory of the "rotating" electron formulates this somewhat differently; for our above "half-classical" model of the electron (no wave-mechanics being used) the description given in the text is logical and sufficient.

5. Pauli's Principle

We may now formulate rigorously and simply the fundamental principle of Pauli (Pauli's Exclusion Principle, the Pauli *Verbot*) * thus :

Inside an atom one and the same quantum state can be occupied only by one electron. The quantum state must be well defined, that is, it must be specified by its four quantum numbers n, l, m_l, m_s. In other words, *it is forbidden for any two electrons in the atom to have the same values for all the quantum numbers* n, l, m_l, m_s. The existence of one electron having certain definite values for these numbers excludes the existence of another electron having the *same* values for all four of these numbers.

The *empirical* confirmation of Pauli's principle is contained in the sum total of spectroscopic observation (occurrence or non-occurrence of quantum states in the visible and in the Röntgen region). A *theoretical* proof can be deduced neither from the older quantum theory nor from wave-mechanics. The principle must for the present be regarded as a point of view which becomes added to and regulates the quantum theory. But Pauli's principle may be expressed in a particularly simple and fundamental form by wave-mechanics (by the postulate of change of sign of the proper functions when any two electrons are exchanged). This will be demonstrated in Vol. II of the present work. For the present we must restrict ourselves to drawing the consequences of the principle for the periodic system, in particular for the completion of the shells and sub-groups. This is effected according to the following scheme :

Given	Number of Electrons
m_s, m_l, l, n	1
m_l, l, n	2
l, n	$2(2l+1)$
n	$2\sum_{0}^{n-1}(2l+1) = 2n^2$

The first line of this table is identical with the statement of Pauli's principle. The second uses the fact that m_s can have only the two values $\pm \frac{1}{2}$ (parallel or anti-parallel position). The third line adds the fact that m_l can assume the values $0, \pm 1, \ldots \pm l$ ($2l+1$ different positions). In this way we have found the maximum number of electrons that is possible, according to Pauli's principle, for the different sub-groups. We tabulate them as follows :

* W. Pauli, junr., " Über den Zusammenhang des Abschlusses der Elektronen," etc., Zeits. f. Phys., **31**, 765 (1925).

$l = 0$	K, L_I, M_I, N_I, . . .	$2 . 1 = 2$
1	$L_{II} + L_{III}$, $M_{II} + M_{III}$, $N_{II} + N_{III}$, . . .	$2 . 3 = 6$
2	$M_{IV} + M_V$, $N_{IV} + N_V$, . . .	$2 . 5 = 10$
3	$N_{VI} + N_{VII}$	$2 . 7 = 14$

The fourth row of the previous scheme is obtained by summing up the occupation numbers in the last scheme and gives us for the occupation numbers for the full shells

K-shell	$2 = 2 . 1^2$
L- ,,	$2 + 6 = 8 = 2 . 2^2$
M- ,,	$2 + 6 + 10 = 18 = 2 . 3^2$
N- ,,	$2 + 6 + 10 + 14 = 32 = 2 . 4^2$

These are, however, Rydberg's numbers for the lengths of the periods, which we called " cabalistic " in § 1 of this chapter. They are, as we see, a direct consequence of Pauli's principle (which is no less cabalistic).

It is to be remarked that historically E. C. Stoner * read off the numbers in the last table but one from regularities in the X-ray spectra a short time before Pauli. In contrast with Bohr, who sub-divided the Rydberg numbers provisionally into equal sub-groups,

$$8 = 4 + 4, \quad 18 = 6 + 6 + 6, \quad 32 = 8 + 8 + 8 + 8,$$

Stoner recognised the sub-division given in our last tabulation,

$$8 = 2 + 6, \quad 18 = 2 + 6 + 10, \quad 32 = 2 + 6 + 10 + 14.$$

We have here applied Pauli's principle only to the conditions in the individual *atom*. Its general character is, however, signalised by the fact that it holds for the totality of electrons that are united in an arbitrary *molecule*,—indeed, even for the far more comprehensive system of conduction electrons that belong to a *metal* of arbitrary extent. This raises in a more acute form the question which occurred in the case of the atom : How is it possible for the electrons to be aware of the quantum positions that are to be occupied so that they avoid transgressing the Pauli exclusion decree ? This question is certainly not capable of being answered from the corpuscular point of view. The wave-mechanical view tones down the paradoxical nature of the question, but by no means answers it completely.

§ 5. The Structure of the Elements in the Periodic System

We shall now describe how the elements are built up genetically, starting from hydrogen and ending at uranium. Alongside the real periodic system of the chemist we build up an ideal system such as is formed in the case of a highly charged nucleus (for example, $Z = 100$) by capturing 1, 2, 3 . . . electrons successively. Whereas in the case of

* Phil. Mag., 48, 719 (1924).

the real system of neutral atoms the nuclear charge grows concurrently with the successive number of electrons, in our ideal system we keep the nuclear charge fixed and allow only the number of electrons to grow larger. The real system gives us the peripheral properties of the atoms, which are of interest to the chemist and the spectroscopist in the visible region. The ideal system describes the interior of the atoms, and is of interest to the X-ray spectroscopist. The ideal system is simpler than the real system. By assuming a high nuclear charge we eliminate all questions involving stability, which play a part in the real system. In the ideal system, the electrons are bound in the order of shells and sub-shells; the binding energy can be read off directly from the X-ray spectra (cf. the section on absorption limits in Chap. IV). These spectra, therefore, also prove empirically that the regular succession of shells and sub-groups that we set up above,

$$K,\ L_I,\ L_{II} + L_{III},\ M_I,\ M_{II} + M_{III},\ M_{IV} + M_V,\ N_I,\ N_{II} + N_{III}, \ldots$$

is correct.

Before we describe the deviations from this ideal sequence that occur in the real system we shall interpose some historical remarks. In the front rank we find the name of Rydberg, who with visionary penetration had calculated out beforehand from very insufficient data the arithmetic relationships of the system and had obtained essentially correct results. The beginnings of the genetic view go back to works of Kossel (cf. the quotation on p. 149). In particular the position of the inert gases as mile-stones in the periodic system is emphasised. At the same time, and independently of Kossel, G. N. Lewis developed the idea of 8-shells, namely, in the geometrical form of cubes. The incomplete (*nicht-abgeschlossenen*) shells were first characterised by E. Ladenburg * as intermediate shells, and were brought into relationship with the paramagnetism of the associated ions. All these assumptions were systematically applied and elaborated in Bohr's theory of the periodic system † of 1921. In particular Bohr worked out the idea of the successive capture of the electrons, their binding energy, and the altered positions in the real and the ideal systems. Bohr's system was subjected to correction by Stoner (see quotation on p. 155). The final phase of the theory was achieved by Pauli's principle which fixed the completion of the shells by quantum numbers, in contradistinction to Bohr, who had hoped to be able to solve this problem by applying classical theory and the correspondence principle.

The attractive pictures with which Bohr had illustrated the theory of the periodic system are suppressed in the present edition of this book. Nevertheless, the orbital view still has a certain importance

* Naturwiss., 1920, Heft 1.

† Put forward in provisional form in a Copenhagen report of October, 1921, published as the third essay in "Drei Aufsätze über Spektren und Atombau," Sammlung Vieweg, Braunschweig 1922; further elaborated in the Ann. d. Phys., 71, 228 (1923).

even for the present-day view of wave-mechanics in so far as it is the carrier of the quantum numbers, as in the previous section. But it cannot be maintained beyond that point, as, for example, in postulating the symmetrical arrangement of orbits into stars or tetrahedra.

The hydrogen atom has been fully described in the preceding chapter. In the ground state the electron describes a *one-quantum* orbit about the nucleus ; this is shown in the first diagram of the Figs. 26 and 27. In the ground state of the helium atom both electrons taken alone describe a one-quantum orbit. All experimental results, particularly those involving the diamagnetism of the helium atom, agree in demanding that these orbits must form a symmetrical and stable configuration which must be closed in itself, and which endows helium with its character as an inert gas.

With helium the K-shell is completed. This shell retains 2 as the number of its electrons and also its closed character in all the subsequent elements. Pauli's principle, which demands the maximum number 2 for the K-shell, simultaneously guarantees that the shell will be closed, that is, completed. The spin moments of momentum of the two electrons compensate one another, since one $m_s = + \frac{1}{2}$, and the other $m_s = - \frac{1}{2}$. The spectroscopic character of the ground state of helium (parhelium-S-term, cf. Chap. VII, § 1) confirms this.

The L-shell begins with the third element Li, for which $Z = 3$, since Pauli's principle forbids the newly added electron to occupy a one-quantum orbit. The transition from a one-quantum orbit to two-quantum orbits is accompanied by a great increase in the orbital dimensions, namely, an increase in the ratio 1 : 4 if we calculate according to the simple model of the hydrogen atom. This explains the extremely great difference in the chemical behaviour of He and Li. Helium holds its electrons particularly tightly in paths which closely envelop the nucleus. Li readily parts with its external valency electron which can move out relatively far from the centre of the atom. Helium has the greatest ionisation potential (that is, the work necessary to detach an electron) of all elements for which this factor has been determined, whereas lithium, in agreement with its electropositive character, has a low value for this factor.

The same remark applies to all the alkalies. Since each stands at the beginning of a period, where the quantum number n increases by 1, their valency electron describes an orbit of relatively great dimensions, and may be removed with ease.

There are two kinds of 2-quantum states, corresponding to the sub-groups L_I, and $L_{II} + L_{III}$. The sub-group L_I presents itself first in the ideal system. There is spectroscopic confirmation that this actually occurs in the case of the Li atom. The so-called " principal series " in the lithium spectrum appears as absorption lines in unexcited lithium vapour. Thus the initial state of the lithium atom in this absorption process is the natural ground state of the lithium atom. We shall

characterise this initial state spectroscopically in Chapter VII, § 1, as an S-term. This implies, according to the general system of series, that we must ascribe to it the azimuthal quantum number $l = 0$. It may be proved rigorously by spectroscopic means that the valency electron of the lithium atom belongs to the sub-group L_I characterised by $l = 0$.

We arrive at the second element of the second period, beryllium, for which $Z = 4$. Be is divalent, like Mg, Ca, . . . ; so we also allocate the newly added electron to the L_I-shell. Pauli's principle ensures that this sub-shell becomes completed in the cases of Be and that it has no spin moment of momentum.

The third element, Boron, for which $Z = 5$, marks the beginning of the second sub-shell $L_{II} + L_{III}$. The three outer electrons (valency-electrons) of boron are thus dissimilar in kind : two belong to $l = 0$ (the L_I-shell), and one to $l = 1$. It is singular that also in the case of carbon ($Z = 6$) we must regard the four valencies as consisting of dissimilar pairs, which is contrary to the chemical fact of the carbon-tetrahedron ; two electrons belong to the L_I-shell, and are more tightly bound, the other two being more loosely bound and belonging to the $(L_{II} + L_{III})$-shell.

Proceeding to the end of the period, we arrive at the elements of more and more electronegative character. The significance of electronegative valency becomes clear when we advance to the inert gas type, neon, for which $Z = 10$. Here we have besides the two electrons of the K-shell, the $(2 + 6)$ electrons of the completed L-shell. We must picture to ourselves that the preceding elements, F, O, N strive to attain the completeness of the neon-shell, F by taking up one electron, O and N by drawing to themselves two and three electrons respectively.

We come to the third period of the system of elements and begin with Na for which $Z = 11$. A *3-quantum orbit* now presents itself, which marks the beginning of the *M-shell*. The fact that the valency electron of Na describes an orbit of the type $l = 0$ is inferred from spectroscopic data (from the " S-term " of the Na-spectrum) just as in the case of Li. In the case of sodium it is, in particular, the well-known D-line, the first term of the principal series which makes this conclusion incontrovertible. Hence the M-shell begins, as we must expect from the regular nature of the ideal system, with the sub-group M_I. This sub-group becomes completed in the next element Mg, for which $Z = 12$. As in the case of Be, we here have two valency electrons, whose spin moments of momentum compensate each other.

In the case of Al, for which $Z = 13$, the conditions are as for B. The last electron, the thirteenth, finds no room in the M_I-shell and enters the group of the $(M_{II} + M_{III})$-electrons. For Si, $Z = 14$, we have, as in the case of C (in spite of the chemical similarity of its valencies) two electrons in the group $(M_{II} + M_{III})$, and two others, more tightly bound, in the M_I-group. The third period closes with Ar, for

which $Z = 18$. The 8-shell, formed of $2 + 6$ electrons having the principal quantum number $n = 3$, is completed in such a way that the preceding electronegative elements balance their energies when they succeed, through capturing electrons, in completing themselves so as to achieve the symmetry of the argon atom.

The configuration of $2 + 6$ electronic orbits in the argon atom represents the "*provisional*" *but not the* "*final*" *completion of the M-shell.*

The qualitative similarity of the peripheral configuration of Ne and Ar will recur when we come to the higher inert gases Kr, Xe, Em.

We summarise all the above remarks in the following Table 7 ; it gives in a simple scheme the *distribution of electrons in the shells in the ground states for all the elements from H to Ar.*

From considerations of the ideal system, we should expect the next electron to become added to the M-shell, that is, to begin the ($M_{IV} + M_V$) group. But this is certainly not the case. Potassium, $Z = 19$, is univalent, with a pronounced tendency to part with its outer electron. Its configuration must resemble that of Li and Na. We must therefore begin a new shell, the N-shell, with K by putting its valency electron into a 4-quantum orbit. It can be proved spectroscopically that we are here dealing with an orbital type for which $l = 0$, that is, with the N_I-group.

K is followed by Ca, for which $Z = 20$. We here have two valency-electrons of equal value and of the same orbital type. The N_I-shell is completed when we arrive at Ca. Its premature appearance signifies the *first departure of the real from the ideal system.* To account for this deviation we can only follow Bohr and say that the capture of N_I-electrons (of orbital type 4_0) leads to a more stable configuration than the capture of ($M_{IV} + M_V$)-electrons (of orbital type 3_2). This is not, of course, a proper theoretical reason, but only a repetition of the state of affairs in another form. That this contrast of the ideal and the real system has a physical meaning may be shown very strikingly at just this point of the periodic table.

Let us consider the electronic configuration which consists of 19 electrons. An example of this is given by the neutral K-atom, $Z = 19$. Another example is given by the ionised Ca^+-atom, which has lost one of the 20 electrons which normally belong to it. We obtain spectroscopic information about the neutral K-atom from the *arc* spectrum of K, and about the ionised Ca^+-atom from the *spark* spectrum of Ca (the " first spark spectrum "). In both cases we find that the ground state is an " S-term " ; that is, it is characterised by $l = 0$. From this we conclude that the electron in question (the valency-electron in the case of K and the remaining one of the two valency electrons of Ca) belongs to the N_I-shell. As a third example of an electron configuration of 19 members we may take Sc^{++}, as a fourth Ti^{+++} (that is, doubly

TABLE 7

Shell symbol / Orbital type	K 1_0	L_I 2_0	$L_{II}+L_{III}$ 2_1	M_I 3_0	$M_{II}+M_{III}$ 3_1
1 H	1				
2 He	2				
3 Li	2	1			
4 Be	2	2			
5 B	2	2	1		
6 C	2	2	2		
7 N	2	2	3		
8 O	2	2	4		
9 F	2	2	5		
10 Ne	2	2	6		
11 Na	2	2	6	1	
12 Mg	2	2	6	2	
13 Al	2	2	6	2	1
14 Si	2	2	6	2	2
15 P	2	2	6	2	3
16 S	2	2	6	2	4
17 Cl	2	2	6	2	5
18 Ar	2	2	6	2	6

ionised scandium and trebly ionised titanium. Here * the " second " and " third " spark spectra, respectively inform us that the ground state belongs to $l = 2$ (" D-term " and not an " S-term "). But the shell $M_{IV} + M_V$ is characterised precisely by $l = 2$. We must therefore infer that the 19th electron enters in the case of Sc^{++}, Ti^{+++}, . . . into the still unoccupied ($M_{IV} + M_V$)-shell, whereas it prefers the N_I-shell in the case of K and Ca^+. Thus the increase of the nuclear charge from 19 (K) to 21 (Sc) just suffices to restore the manner of distribution of the ideal system and to avoid the premature filling of the N_I-shell in the real system. It should be mentioned that as early as 1921 Bohr had drawn the same conclusion from the spectra of K and Ca^+ by methods of extrapolation.

Hence we see that the occurrence of the N_I-shell in the case of K and Ca is only a superficial anomaly. In the case of Sc the higher nuclear charge 21 is already able to bind an electron, the 19th, into the ($M_{IV} + M_V$)-shell (orbital type 3_2). The other two electrons, namely, the 20th and the 21st, then attach themselves as parts of the N-shell to the outside of the M-shell, which is now modified and deviates from the argon shell.

With Sc we enter into a group of elements which have many interesting features, and which end in the iron-triad (Fe, Co, Ni). The otherwise

* R. C. Gibbs and H. E. White, Proc. Nat. Ac. Wash., **12**, 598 (1926).

regular advance in the valency factors here receives a check. Moreover, we here encounter the important paramagnetic properties (cf. the reference to Ladenburg on p. 156), not only in the case of neutral atoms but also in that of their ions ; in particular, we know doubly ionised atoms (for example, the ferro-ions, Fe^{++}) and triply ionised atoms (e.g. Fe^{+++}) ; the same applies to all the elements of this group. The magnetism of the ions means that the electron configuration is not neutralised magnetically, but has a resultant magnetic moment. We understand this immediately if we bear in mind that in the case of all these ions the (M_{IV} + M_V)-shell is incomplete, and is in process of being constructed. When we arrive at Ni, the end of the iron triad, we should in this way have 8 electrons more in the M-shell than in the case of Ar, that is, if the two electrons that lie in the N-shell in the case of Ca and Sc remain in this shell. Spectroscopic information proves that this is so with Ni, but that it does not hold for the element Cu which follows on Ni. The univalent character of Cu and its partial similarity to the alkalies shows that it has only one electron in the N-shell, the 29th electron, the last to be bound. Thus the two electrons which were valency electrons in the case of Ca and Sc have now migrated into the M-shell. In the case of Cu the M-shell consists not of 16 but of 16 + 2 = 18 electrons. This number 18 is the third in the series of periodic numbers 2, 8, 18, 32,— of page 155. *The complete M-shell becomes a reality for the first time in the case of the Cu^+-ion.*

In many respects the 18-shell of the Cu^+-ion is an analogous configuration to the 8-shell of the inert gases ; like the latter, it is completed and appears to be wonderfully stable. The elements that follow on Cu therefore add their superstructure to the 18-shell. But there is a difference in that the elements which precede Cu are not electronegative, namely, they do not complete themselves to an 18-shell. The configuration of Cu^+ (and likewise of Ag^+, Au^+) is striven after only one-sidedly, namely, from the side of the higher atomic numbers, but not from both sides, as in the case of the inert gas configurations.

We now come to the remaining elements of the fourth period, which now develop themselves on the outside of the M-shell in the normal manner as in the case of the small periods, and which leads to a provisional completion of the N-shell. Zn is the first to follow Cu ; it has two N_I-electrons, which finally complete the N_I-shell. With Ga we begin the construction of the (N_{II} + N_{III})-shell ; here we have an electron of orbital type $l = 1$ (a 4_1-orbit). In the case of Ge we have two such electrons, and so forth. The electronegative elements As, Se, Br follow with 3, 4, 5 electrons, respectively, of the same type, which strive to complete their number to that of the Kr configuration, and finally Kr itself with a normal 8-shell (two 4_0- and six 4_1-electrons).

We summarise what has been said of the fourth period in Table 8.

In the case of Cr the number of electrons in the ground state in the (M_{IV} + M_V)-shell jumps in an irregular manner from 3 to 5. The

TABLE 8

Shell symbol / Orbital type	K	L_I	$L_{II}+L_{III}$	M_I	$M_{II}+M_{III}$	$M_{IV}+M_V$	N_I	$N_{II}+N_{III}$
	1_0	2_0	2_1	3_0	3_1	3_2	4_0	4_1
19 K	2	2	6	2	6		1	
20 Ca	2	2	6	2	6		2	
21 Sc	2	2	6	2	6	1	2	
22 Ti	2	2	6	2	6	2	2	
23 V	2	2	6	2	6	3	2	
24 Cr	2	2	6	2	6	5	1	
25 Mn	2	2	6	2	6	5	2	
26 Fe	2	2	6	2	6	6	2	
27 Co	2	2	6	2	6	7	2	
28 Ni	2	2	6	2	6	8	2	
29 Cu	2	2	6	2	6	10	1	
30 Zn	2	2	6	2	6	10	2	
31 Ga	2	2	6	2	6	10	2	1
32 Ge	2	2	6	2	6	10	2	2
33 As	2	2	6	2	6	10	2	3
34 Se	2	2	6	2	6	10	2	4
35 Br	2	2	6	2	6	10	2	5
36 Kr	2	2	6	2	6	10	2	6

configuration of four 3_2- and two 4_0-electrons, which we here expect, is slightly less stable than that of five 3_2-electrons and one 4_0-electron (for further remarks on this point see Chap. VIII).

The fifth period which runs analogously to the fourth begins with the alkali Rb and ends with the inert gas Xe. First we find that the beginnings of the 5-quantum O-shell form about the incomplete N-shell, in the case of Rb with one valency electron in a 5_0-orbit, in that of Sr with two valency electrons in 5_0-orbits. So once again we have a deviation from the sequence of the ideal system, which would for its part demand the further construction of the N-shell. But even in the case of Y, the analogous element to Sc, the process of completing the N-shell begins. It is the 37th electron, similarly to the 19th in the case of Sc, which finds itself to be more stable in the N-shell than in the O-shell. On the other hand, the 38th and 39th electron of Y find their places in the O-shell. In the succeeding elements, as far as the palladium triad, the N-shell becomes filled up gradually, but not to its final and complete number which would amount to $2.2^4 = 32$, but only to the provisional stage of completion $2.3^2 = 18$. This stage is reached in this period by Pd. The spectrum of palladium teaches us that the normal state of Pd corresponds to a configuration of the ten 4_2-electrons. (Cf., however, the distribution in the homologous element Ni !) We find the same distribution in Ag^+, the analogous element to Cu^+ in the fourth period. From this point onwards all the available electrons are used to build up the O-shell, which becomes completed at Xe in the first stage as an 8-shell. It is unnecessary to add a special table for

these results, as it would come out, *mutatis mutandis*, very similarly to the preceding table.

We now come to the sixth period, the great period of 32 elements, which leads to the final completion of the N-shell and to the second stage of the completion of the O-shell, which at the same time, however, give the beginnings of the P-shell. Let us consider Table 9. In the case of Cs we have a 6_0-electron, in that of Ba we have two 6_0-electrons. We provisionally begin the P_I-shell and postpone the completion of the O-shell—again making a departure from the ideal order of sequence. In the case of the next element La, Z = 57, we find that as in Sc and Y an electron enters into the still empty (O_{IV} + O_V)-shell, here as a 5_2-electron. We might now conjecture that the filling up of this intermediate shell would be continued up to its next stage of completion. But in reality this process is once again temporarily suspended up to the Pt-triad, and the next element Ce begins the final stage of completing the N-shell. Ce brings us to the *group of the rare earths*, which through their stationary valency bear such striking testimony to the fact that the process of atomic construction does not now occur on the periphery of the atom, but in a layer which lies deeper. This deeper layer, the (N_{VI} + N_{VII})-shell is in a transition state in the whole group of the rare earths, and hence is not balanced out magnetically,—which accounts for the strong paramagnetic character of this group.

TABLE 9

Shell symbol	N_I	$N_{II}+N_{III}$	$N_{IV}+N_V$	$N_{VI}+N_{VII}$	O_I	$O_{II}+O_{III}$	$O_{IV}+O_V$	$O_{VI}+O_{VII}\cdots$	P_I	$P_{II}+P_{III}\cdots$
Orbital type	4_0	4_1	4_2	4_3	5_0	5_1	5_2	5_3	6_0	6_1
55 Cs .	2	6	10		2	6			1	
56 Ba .	2	6	10		2	6			2	
57 La .	2	6	10		2	6	1		2	
58 Ce .	2	6	10	1	2	6	1		2	
59 Pr .	2	6	10	2	2	6	1		2	
60 Nd .	2	6	10	3	2	6	1		2	
— — .	—	—	—	—	—	—	—		—	
71 Lu .	2	6	10	14	2	6	1		2	
72 Hf .	2	6	10	14	2	6	2		2	
73 Ta .	2	6	10	14	2	6	3		2	
74 W .	2	6	10	14	2	6	4		2	
— — .	—	—	—	—	—	—	—		—	
78 Pt .	2	6	10	14	2	6	8		2	

The number of elements of the rare earth type may now be specified theoretically; it is, according to Pauli's principle, equal to 2 (2*l* + 1) for *l* = 3, that is, 14. If we count from Ce, Z = 58, as the first of these elements, we arrive at Lu, Z = 71, as the last element of the group. *The element 72 is thus no longer to be expected to be a rare earth.*

This reflection on the part of Bohr led, as we know, to the discovery * of the element 72 by Coster and Hevesy, who gave it the name hafnium (Hf). When the N-shell has been completed at Z = 71 we arrive at Z = 72 in a manner fully analogous to that by which we arrived at Zr, Z = 40, and Ti, Z = 22. It has its place in the fourth column of the periodic system, where it also stands in our Table 4 of the periodic system ; this leads us to expect that it would occur naturally in association with Zr and possibly Ti. It was actually in zirconium minerals of different origin that Coster and Hevesy proved the existence of the new element by means of the X-ray method.

Hafnium recommences the filling up of the O-shell. In the case of Au the 18 O-shell is completed and provided with an outer valency electron. Thus Au^+ now represents the complete stage of development of the O-shell. Further development now occurs, as after Cu^+ and Ag^+, at the outside of the atom and leads to the 8 P-shell in the case of Em.

Lastly, we have in the incomplete seventh and last period the beginnings of the Q-shell and the beginning of the process of filling up the (P_{IV} + P_V)-group, but we do not even arrive at a provisional completion of this shell (cf. Table 10).

TABLE 10

Shell symbol	O_I	$O_{II}+O_{III}$	$O_{IV}+O_V$	$O_{VI}+O_{VII}$	$O_{VIII}+O_{IX}$	P_I	$P_{II}+P_{III}$	$P_{IV}+P_V$...	Q_I	$Q_{II}+Q_{III}$ ..
Orbital type	5_0	5_1	5_2	5_3	5_4	6_0	6_1	6_2	7_0	7_1
79 Au .	2	6	10			1				
80 Hg .	2	6	10			2				
81 Tl . .	2	6	10			2	1			
82 Pb .	2	6	10			2	2			
83 Bi . .	2	6	10			2	3			
— — . .	—	—	—			—	—			
86 Em .	2	6	10			2	6			
87 * . .	2	6	10			2	6		1	
88 Ra .	2	6	10			2	6		2	
89 Ac .	2	6	10			2	6	1	2	
90 Th .	2	6	10			2	6	2	2	
91 Pa .	2	6	10			2	6	3	2	
92 U . .	2	6	10			2	6	4	2	

On the whole, then, we are able to give a complete and unforced account of the facts of chemical constitution, which is brought out particularly well by the properties of hafnium in a very striking manner. Conclusive proof is, however, given by the numerous spectroscopic facts which we shall adduce later.

* The claims of Urbain to have discovered and named this element seem devoid of foundation.

§ 6. Some Remarks about Nuclear Physics

There is no doubt that the radioactive nuclei contain helium nuclei and electrons, which they emit as α- and β-rays. Prout's hypothesis and its confirmation by Aston's researches on isotopes demand still further that *all* atomic nuclei must ultimately be built up from protons and electrons. In the case of the helium nuclei themselves this necessarily leads to the assumption that it consists of four H-nuclei which are bound together by two electrons.

In general, we may say that a nucleus of atomic weight A and atomic number Z must contain, in all,

$$K = A - Z \quad . \quad . \quad . \quad . \quad . \quad (1)$$

electrons. For A (which, following Aston, we assume to be integral) denotes the number of hydrogen nuclei and hence also the total number of positive charges ; Z is the value of the positive charge which acts outwards. The difference between these two charges must be compensated by the nuclear electrons.

In the case of the light elements in particular we find that atomic weights of the form $A = 4n$ occur with atomic numbers $Z = 2n$, for example, in the case of C, O, Mg, Si, S, Ca and so forth. This points to possible sub-nuclear units of the same composition as α-particles. For when $A = 4n$ and $Z = 2n$ we get by (1) that $K = 2n$, and hence is not greater than is necessary to bind together each of the n He-nuclei. But presumably we need not imagine this union of protons and electrons to be so tight as regards the energy involved as is encountered outside the nuclei in the case of real α-particles. Otherwise no energy would remain for binding the α-particles themselves together.

The excess Δ of half the atomic weight above the atomic number which we studied superficially in Fig. 34 and which is equal to zero in the case of the elements $A = 4n$, $Z = 2n$, shows that there are nuclear electrons present in these cases, which are not built into the He-nuclei.

We shall calculate this generally not only for atomic weights of the form $4n$, but also for those of the form $4n + \alpha$ (where $\alpha = 1, 2$ or 3). Let x be the number of He-nuclei ; y and z the number of electrons, and H-nuclei, respectively, which are not combined in the form of He-nuclei. Then we clearly have

$$A = 4x + z$$
$$Z = 2x + z - y.$$

Thus
$$\Delta = \frac{A}{2} - Z = y - \frac{z}{2},$$

or
$$y = \Delta + \frac{z}{2} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The number y of electrons not built into the He-nuclei is thus *at least* equal to the excess Δ. Hence, according to Fig. 34 the number

y increases systematically with the atomic number, but in such a way that y remains small compared with the number of α-particles contained in the nucleus.

From this we may make an inference about the probability and number of α- and β-emissions in the case of the radioactive elements. Let us imagine a diagram in which atomic weight A (as ordinates) is plotted against nuclear charge Z (as abscissæ) and form a band-like region which characterises the stable nuclei, that is nuclei in which a concentration of α- and β-particles exists which is favourable to the maintenance of the nuclei. The middle course of this band approximately follows the straight line $A = 2Z$ with the upward deviation shown in Fig. 34. Now β-radiation displaces the nucleus parallel to the axis of abscissæ to the right by one unit. Hence we see that after a small number of β-emissions the nucleus will have travelled through the band of stability. On the other hand, α-emission denotes the displacement of the nucleus parallel to the straight line $A = 2Z$ (diminution of A by 4 units and Z by 2 units), so that with continued α-emissions the nucleus will have appreciably changed its position with regard to the band of stability only after several such processes. If the band of stability were to run exactly parallel to the straight line $A = 2Z$, the nucleus would never leave the band of stability at all through α-emissions. In reality a small number of β-emissions is necessary to restore the stability impaired by α-emission. In this way the general character of the decay schemes of page 53—several α-emissions and only a few β-emissions—is in agreement with our argument. The fact that the β-emissions almost always occur in pairs may perhaps be brought into relationship with the spin of the electrons, which may favour the balancing of electrons in pairs in the nucleus. Experiments have taught us that the second β-emission follows the first in a shorter time than the first follows the preceding α-emission. This may be interpreted by stating that the nucleus with complete pairs of electrons is more stable than a nucleus which has an electron which is not balanced. L. Meitner * has endeavoured to explain the occurrence of β-emissions in pairs by means of a special hypothesis (α'-particles which are previously present in the nucleus and are not bound). But after our above remarks it seems that this argument is unnecessary.

These speculations entered upon an entirely new phase after Rutherford † had succeeded in 1919 in artificially disintegrating the nuclei of the lighter elements, in the first place, nitrogen. On that occasion, the H-nuclei were shown for the first time also to be elementary constituents of the nuclear structure, and were studied quantitatively.

Rutherford used α-rays from RaC ; their velocity is $2 \cdot 10^9$ cm./sec.,

* Zeits. f. Physik., **4**, 146 (1921).

† Phil. Mag., **37**, 537, 562, 571, 581 (1919) ; Rutherford and Chadwick, *ibid.*, **42**, 89 (1921) ; **44**, 417 (1922).

their range 7 cms. ; that is, in air at atmospheric pressure they excite scintillations in a luminescent screen (ZnS-screen) at distances less than 7 cms., but not at greater distances. Such α-rays represent the most powerful concentration of energy available to us at the present time. When they encounter hydrogen molecules or bodies containing water, they release H-nuclei as very fast " H-rays." The range of these secondary H-rays is, corresponding to their smaller mass, greater than that of the primary α-rays, namely, 28 cms. in air. Hence they can easily be distinguished from the α-rays by means of the fluorescent screen. The nature of these rays was later examined very carefully by G. Stetter * by accurate measurements of a simultaneous magnetic and electric deflection (determination of e/m_H with an accuracy of 1 per cent.).

But H-rays could be proved to exist not only in gases containing hydrogen but also in air free of water vapour. Considerably more scintillations occurred in pure nitrogen than in a mixture of nitrogen and oxygen. This led experimenters to conclude that the *H-rays originate in the nitrogen nucleus.* Thus for the first time an atom had been artificially transmuted and the dream of the alchemists had become a reality.

In addition to nitrogen, Rutherford also succeeded in disintegrating the following atoms by means of α-rays from RaC :

	B	F	Na	Al	P
Z =	3	9	11	13	15
A =	10 ; 11	19	23	27	31

The scintillation method was also used in these cases. Going still further Kirsch and Petterson † have found that Be (Z = 4) and Mg (Z = 12) and Si (Z = 14) also yield H-rays.

In the case of Al and P scintillation observations gave surprisingly great ranges (for Al the maximum range was 90 cms.), although these great ranges occurred only quite exceptionally. The mean range is much smaller. If, as we are led to assume, we are also dealing with H-rays in the case of these great ranges, their initial energy would be up to 36 per cent. greater than the energy of the exciting α-rays. (If the carriers were of greater mass, it is clear that a still greater value would result for the energy.) Here we have a first indication of the possibility of releasing the internal energy of the nuclei and achieving over 100 per cent. output ; that is, if 100 calories of energy of α-radiation are expended then *more* than 100 calories of kinetic energy of H-rays are gained if we calculate the nuclear disintegration in terms equivalent to the energy of the α-radiation.

By using indirect methods of observation (the fluorescent screen in this case not being in the prolongation of the incident rays, but laterally situated) it was found possible to add further elements to the list

* Zeits. f. Physik., **34**, 158 (1925).

† *Veröffenthchungen des Radiuminstituts*, Wien, 1923.

of atoms that could be disintegrated, in particular also atoms of the type $A = 4n$, $Z = 2n$, which Rutherford originally believed could not be disintegrated. Experiments carried out partly in Vienna and partly in Cambridge showed that all elements between fluorine and calcium could be disintegrated by means of α-rays from RaC. In this sequence of elements the range of the H-rays from elements of even atomic number is always less than that of H-rays from elements of odd atomic number. This may be regarded as an indication that the nuclei of even atomic number are more stable than those of odd atomic number.

Originally there was some uncertainty as to what became of the N-atom which had been disintegrated. The readiest suggestion was to assume a transition to C, two protons being emitted. We nowadays, know, however, from the beautiful cloud-track photographs of P. M. S. Blackett * that the α-particle is taken up by the nitrogen nucleus, an H-ray being emitted :

$$N_{14} + \alpha = O_{17} + H.$$

Hence in this case there is actually no disintegration of matter but a building up by the acquisition of new matter ! This result had already been predicted theoretically a little earlier by Kirsch † on the basis of observations of the velocity of H-rays produced by α-rays of different ranges. The spectroscopic proof of the existence of O_{17} which has been obtained in the meantime (cf. p. 142) has given strong support to this view.

We revert to the simplest problem of nuclear structure, that of helium (cf. the beginning of this section). The atomic weight of He apparently suggests that it is not built up from four H-nuclei. According to the most exact measurements, the atomic weight of H is 1·0078 and that of He is 4·002. In associating themselves into He the four H-nuclei would therefore suffer a *defect in mass* which, calculated for the gramme-atom of He, comes out as

$$\Delta m = 4 \,.\, 1{\cdot}0078 - 4{\cdot}002 = 0{\cdot}029 \quad . \quad . \quad . \quad (3)$$

The mass of the two electrons which become added to the four H-nuclei increases this number by unity in the last decimal place.

But this defect in mass is only *apparently* a contradiction to the idea of the construction of the He-nucleus, from four H-nuclei. In reality it explains the great *stability* of the He-nucleus in a very satisfactory manner.

As early as 1900 Lorentz deduced from the point of view of the electromagnetic theory that the mass of a system of positive and negative charges lying close together must be smaller than the sum of the individual masses of these charges. The theory of relativity has given a solid foundation to this result, and has generalised it. As we

* Proc. Roy. Soc., **107**, 349 (1925). † Phys. Zeits., **26**, 457 (1925).

saw in Chapter I, § 7, mass and energy are linked together by the formula $E = mc^2$. Hence, if any system loses energy (say by emission) it suffers a defect in mass. Conversely, from a defect in mass Δm we can deduce a loss of energy ΔE of value

$$\Delta E = c^2 \Delta m \quad . \quad . \quad . \quad . \quad (4)$$

Accordingly, we may assume that the four H-nuclei, when they combine to form an He-nucleus with the agency of the two binding electrons, give off the energy determined by (4). Such an emission of energy is familiar to us from atomic chemical reactions. There we call it, when measured in heat units, the " heat of combination " or " heat tone " (Wärmetönung), and call a reaction " exothermic " when it occurs with the emission of energy. We shall apply this idea and this terminology to our nuclear reaction. By (3) and (4) the emission of energy amounts to

$$\Delta E = c^2 \Delta m = 0{\cdot}03c^2 \quad . \quad . \quad . \quad . \quad (5)$$

per gramme-atom of He.

This at the same time determines the work that must be expended to separate each He-nucleus of the gramme-atom into its four H-nuclei, and hence furnishes us with a measure for the stability of the He-nucleus. This amount of work is so great that we are unable to produce it by our physical methods. Let us compare it, for example, with the energy which is available in the motion of the α-particle of RaC. Since the velocity in this case is $v = 2 \cdot 10^9 = \frac{2}{30}c$, this energy amounts to

$$\tfrac{1}{2} m_{He} v^2 = 2 m_H (\tfrac{2}{30})^2 c^2 = \tfrac{8}{900} c^2 = 0{\cdot}009c^2.$$

It is three times smaller than the energy (5) which has been calculated on the same basis, that is, for the gramme atom.

By dividing ΔE by the mechanical equivalent of heat in kilogramme-calories ($= 4{\cdot}19 \cdot 10^{10}$ ergs) we may then speak, as in chemical reactions between atoms, of the heat of formation Q of our nuclear reaction,

$$Q = \frac{0{\cdot}03c^2}{4{\cdot}19 \cdot 10^{10}} = 6{\cdot}4 \cdot 10^8 \text{ kilogramme-calories} \quad . \quad . \quad (6)$$

This quantity of energy is enormous. As a basis of comparison we quote the fact that the heat of formation in ordinary chemical processes is of the order of 100 kilogramme-calorie. Thus our He-nuclear combination is more stable than ordinary chemical compounds in the ratio $6{\cdot}4 \cdot 10^8 : 10^2$. Hence, whereas heat motion alone is often sufficient to break up chemical compounds the energy of the fastest α-rays does not suffice to break up the nuclear " compound."

We see from this remarkably general reflection, which requires no particular idea of nuclear constitution but only the trustworthy " Principle of the Conservation of Energy," that the stability of the He-nucleus is, in effect, secured, and that to destroy it by the means at present available appears out of the question. In conjunction with

Rutherford's experiments it therefore follows from this that not only are the helium elements of structure that are struck very stable, but also the impinging α-particles. It is true that our reflections on stability are bound up with the assumption that the He-nucleus would dissociate directly into four H-nuclei. In the event of incomplete disintegration, for example, if a single H-nucleus were to be split off or were to be taken up in the manner of the nitrogen reaction $N_{14} \rightarrow O_{17}$, no assertion can be made about the energy of the resultant product, and therefore we can say nothing about the stability.

We generalise this for other nuclei and restrict ourselves, of course, to nuclei of atomic elements of a single kind, disregarding mixtures of isotopes. Whereas the atomic weights rounded off to whole number values give us information about the number of protons concerned in the construction of the nucleus in question (for example, four in the case of He), the deviations of the atomic weights from whole numbers give us information about the finer structure of the nucleus. We are indebted to Aston for the empirical foundation of our argument, namely the exact mass-spectroscopic knowledge of the atomic weights of the elements, and we shall in the first place follow his account. Aston * refers the atomic weights as usual to $0 = 16{\cdot}000$ and divides the deviation from the integral values so defined by the number of protons concerned in the construction of the nucleus, that is, by the atomic weight rounded off to a whole number. He calls the number obtained in this way the "packing effect per proton." There is, however, the difficulty that in the meantime it has been shown that oxygen is not a simple element but that there are also atoms of O_{18} and O_{17}, even if only in vanishingly small quantities, and this has somewhat displaced the physical foundation used for calculating the packing effects and, indeed, for determining atomic weights in general.

Fig. 37 shows Aston's packing effect, multiplied by 10^4, as a function of the number of protons. Oxygen, as it should, has the packing effect zero. The value of the ordinate of He is in round numbers,

$$\frac{4{\cdot}002 - 4}{4} \cdot 10^4 = 5.$$

Beyond oxygen the packing effect becomes negative and later becomes positive again only when we reach Hg and Pb. The most striking feature of this celebrated curve is its branching into two directions for small numbers of protons; the lower branch passes through the atomic weights of the form $4n$, the higher branch passes through the remaining atomic weights. Otherwise the curve runs smoothly and exhibits no relationship to the periodic system of the elements.

Let us now inquire how we are to define the packing effect in the

* Proc. Roy. Soc., **115**, 487 (1927).

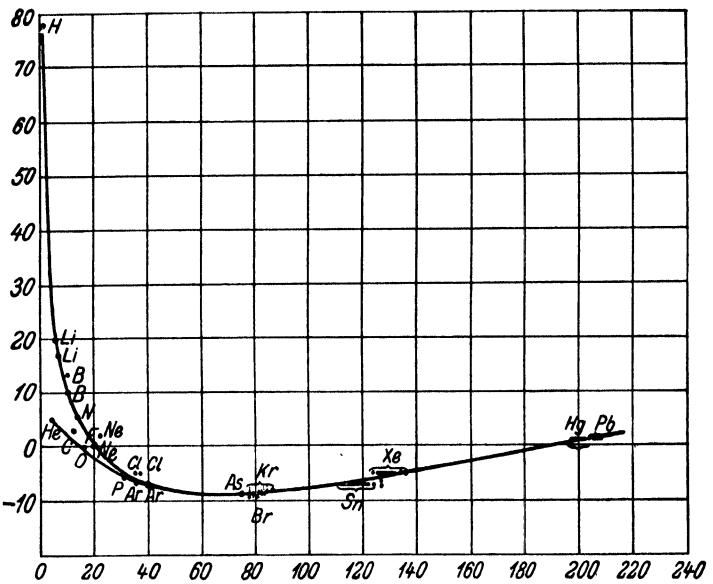
sense of our analysis of the He-nucleus. In this analysis we calculated in equation (3) that

$$\Delta m = 4 \,.\, 1{\cdot}0078 - 4{\cdot}002 \quad . \quad . \quad . \quad (7)$$

If we divide throughout by the factor 1·0078, we obtain

$$D = 4 - \frac{4{\cdot}002}{1{\cdot}0078} \quad . \quad . \quad . \quad . \quad (8)$$

which is the *defect in mass referred to* $\dot{H} = 1$; for the second term on the right-hand side of (8) is equal to the atomic weight referred



* Fig. 37.—Packing effect per proton, referred to O = 16·0000, according to J. W. Aston.

to H = 1, and the first term is equal to the number of protons or the atomic weight in round numbers.

What we have here said about the He-nucleus applies generally. If A_{16} is the atomic weight referred to O = 16, if

$$A_1 = \frac{A_{16}}{1{\cdot}0078} \quad . \quad . \quad . \quad . \quad (9a)$$

is the atomic weight referred to H = 1, if M is A_{16} in round numbers, and if

$$D = M - A_1, \quad . \quad . \quad . \quad . \quad (9b)$$

then

$$\Delta m = D \,.\, 1{\cdot}0078 \quad . \quad . \quad . \quad . \quad (9c)$$

* See note at end of chapter.

gives the true packing effect.* Stefan Meyer † has plotted the curve for D/M with M as the abscissa (see Fig. 38, where the numbers on the ordinate axis denote D . 10^3/M). Fig. 38 exhibits two essential differences as compared with Aston's curve in Fig. 37 : (1) there is no reason for making the curve resolve into two branches for small numbers of protons ; (2) the curve is not smooth, rather it shows peaks and valleys which are at first not well marked and then become less prominent, and which appear to indicate a relationship with the periodic system.

This method of presentation seems to us to be preferable to that of Aston since it corresponds better with our measure of stability Δm than the latter. We might also, as we did in the case of helium, add the mass of the nuclear electrons (A − Z in number, by eqn. (1)) to the mass of the nuclear protons, but this would not alter the course of the curve appreciably. The connexion between stability of the

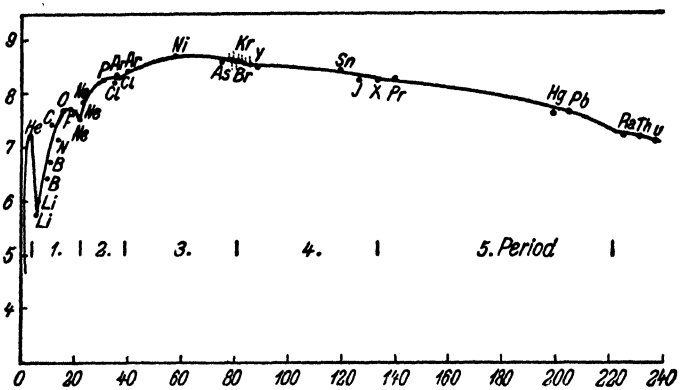


FIG. 38.—Packing effect per proton, referred to H = 1, according to Stefan Meyer. The ordinate scale gives the value of D/M . 10^3 ; abscissae = M = number of protons.

nucleus and periodicity of the atomic envelope which emerges from Fig. 38 is very surprising.

As in all questions of stability we must be clear as to what states are to be compared in forming a measure of stability. In our case it is obviously the state in which the nucleus is considered completely resolved into its primary components, protons and electrons. This was emphasised above in the case of the helium nucleus. Just as there so here our D/M is proportional to the " heat of formation " generated when the nucleus is built up from its primary components.

But if we are concerned with only a partial resolution of the nucleus, only individual protons or electrons being dismembered, the states to

* The same definition is used as a basis by H. Pettersson in his discussion of the stability and disintegrative tendency of nuclei ; cf. Arkiv. f. Mat., Astr. och Fys., **21** A, 1 (1928).

† Wiener Ber., **138**, 431 (1929).

be compared are now different; for we have simply to use in our calculations the atomic weights of the initial element and of the disintegrated product, including the emitted corpuscles. We illustrate this by giving two examples, one being an imagined disintegration accompanied by the emission of an H-ray, the other being an actual case of disintegration caused by the emission of an α-ray.

Let us first compare Ar_{36} ($Z = 18$) with Cl_{35} ($Z = 17$). Ar_{36} contains in its nucleus 36 protons and 18 electrons; Cl_{35} has 35 protons and likewise 18 electrons. In each case, according to measurements made by Aston,* the A_{16} is equal to 35·976 and 34·983, respectively. The difference between these two members, namely, 0·993, is less than 1·0078, which is the A_{16} of H. Thus the one H-nucleus is so firmly embedded in A_{36} that its release (the transition from A_{36} to Cl_{35}, with the emission of H^+) required the energy $(1{\cdot}0078 - 0{\cdot}993)\,c^2$ to be expended per gramme-atom. Consequently it is impossible for spontaneous emission of H^+ to occur in this case. The same may be proved of any two elements of the periodic system, which differ to the extent of only one proton (or of a proton + an electron), so long as their atomic weights are sufficiently well known. We thus see from our comparison of the atomic weights why no spontaneous emission of H-rays occurs when the elements decay.

If, however, we compare two elements with each other, which differ by one or more in the number of helium nuclei, we can find examples where spontaneous decay is possible. Let us consider U_{238} ($Z = 92$) and uranium lead (RaG_{206}, $Z = 82$); † they differ by 32 protons and 22 electrons, or, expressed in helium nuclei, by 8 helium nuclei and 6 electrons (in addition to the 16 electrons contained in the 8 helium nuclei). The latter constitution is also to be deduced from the uranium line of decay on p. 53. The A_{16} of these 8 He-nuclei is $8 \cdot 4{\cdot}002 = 32{\cdot}016$ (the electrons affect only the third decimal place and may therefore be neglected). On the other hand the A_{16} of U amounts to 238·14 and that of RaG to 206·0, so that the difference in the atomic weights is 32·14. It is greater than the weight of the 8 He-nuclei. From this we may conclude that the decay is *spontaneous;* that is, it may occur without the agency of external energy. On the other hand we may easily convince ourselves that the transition U → RaG *cannot* occur *spontaneously* with the emission of separate protons and electrons (32 and 22, respectively).

Recapitulating, we say:

The ejection of helium nuclei (He^{++}) that is, the emission of α-rays is possible at certain places in the periodic table, but not the ejection of H-nuclei, that is, protons.

* Aston, *loc. cit.*

† We choose the example because, although it suffers from the defect that we do not know these atomic weights exactly, it illustrates a form of decay which actually occurs in nature. We believe that our conclusions will not be essentially affected by an exact knowledge of the atomic weights.

Connected with the stability of the nuclei there is the question of the *frequency of occurrence of the elements*. It is very remarkable that 99 per cent. of the earth's crust (also of meteorites) is formed of elements of atomic numbers $\leqq 26$ (iron). The most prevalent element is O, followed by Fe. Even C occurs in a relatively small amount. Moreover, it is remarkable that the frequency of occurrence *decreases* within any column of the periodic table as the atomic weight *increases*. It is also a surprising fact that all common elements have *even* atomic numbers (Fe 26, O 8). We must refer the reader for further details on this subject and on that of frequency of occurrence generally to the researches of Harkins.* The variation of frequency is shown particularly strikingly in the group of rare earths : in spite of their great similarity and the difficulty of separating them they are not uniformly mixed ; rather the earths of even atomic number always occur a little more frequently than those of odd atomic number.† The same law holds generally for the elements that are represented in the solar spectrum by Fraunhofer lines.‡ There are, of course, no theoretical points of view available at all at present which might give an answer to these questions. We must also mention the following rule which appears to point to the construction of nuclei from already formed α-particles : there are no stable nuclei of odd atomic number and of atomic weight $4n$ (Fajans).

Certain observations of the scattering of α-particles lead us to infer that the structure of nuclei is not rigid but is mobile in itself. For in the distribution of scattered α-particles certain deviations are found to occur from the law of probability which is to be expected in the case where the nucleus is spherically symmetrical and where Coulomb's law is assumed to hold without modification. Rutherford and his colleagues were inclined to assume that in the close vicinity of the nucleus the Coulomb repulsion of the α-particle becomes replaced by an attraction. But H. Pettersson || showed that this hypothesis is unnecessary. and that it can be replaced by the simpler assumption that the positive and negative charges are capable of being displaced to the periphery of the nucleus in such a way that under the influence of the incident α-particle the negative charges become pushed towards the direction of the α-particle and the positive charges in the opposite direction. In this manner the nucleus becomes polarised and so loses its spherical symmetry ; the dipole induced in the nucleus exerts an attractive force on the approaching α-particle. The same idea has

* For example, "Evolution of Elements," Amer. Chem. Soc., **39**, 856 (1917). A graphical representation of the frequency of distribution is given in *Science*, 1917.

† V. M. Goldschmidt, "Geo-chemical Laws of Distribution of the Elements," Norske Vid. Akad. I, 1925-27, Oslo. It is based on the well-known occurrence of the elements in Sweden (Ytterby).

‡ H. N. Russell, Astrophys. Journ., **70**, 11 (1929).

|| Arkiv. f. Mat., Astr. och Fys., **19** B, Nr. 2 (1925).

been worked out quantitatively by Debye and Hardmeier and has been shown to agree with the facts in order of magnitude.*

Just as the spectral lines in the visible and X-ray region reflect most perfectly the structure of the atomic envelope, so we may expect the most trustworthy information on the structure of nuclei to be given by the emitted γ-rays. The γ-rays are, like the X-rays that come from the atomic shells, essentially monochromatic. This is the general result at which L. Meitner has arrived after a detailed study of the radioactive sequences and of their γ-emissions. Moreover, it is found that γ-radiations are emitted, not by the decaying, but by the already decayed nucleus, namely, in that the γ-emission presumably originates in the process of rearranging the nuclear constituents, which has become necessary through the decay. The question suggests itself as to whether the rearrangement occurs in a change of position of an electron or of a proton or α-particle. W. Kuhn † believes that the latter case is that which actually occurs, as he shows that the γ-rays may be assigned on the classical theory to the vibrations of heavy masses, protons or α-particles, but not of β-particles.

In general the monochromatic character of γ-rays shows that the energy-levels of the nucleus, whose differences are the frequencies of the γ-rays, form a *discontinuous series*. We are compelled to conjecture that these energy-levels are determined by *quantum laws*. The indications of periodicities in the curve which exhibits the packing effects, Fig. 38, leads to the same suggestion. Hence we infer that *the construction of the nuclei from elementary constituents is probably effected according to the same laws, namely those of the quantum theory, as the construction of atoms from electrons and nuclei.*‡

NOTE.—It has been pointed out to the author that the Figs. 37 and 38 for the packing effect differ only in the manner of presentation and not in their content. The packing effect as given by Aston is equal to 0·0078 minus the packing effect as given by Stefan Meyer; that is, the values are complementary. Meyer used later and more accurate values for the atomic weights, so that his curves exhibit some finer details.

* Phys. Zeits., **27**, 196 (1926); **28**, 181 (1927); cf. also the wave-mechanical treatment by Th. Sexl, Naturwiss., **18**, 247 (1930) and G. Beck, Zeits. f. Physik., **62**, 350 (1930).

† Zeits. f. Physik., Vols. 43 and 44, 1927.

‡ See Translator's note, p. 596.

CHAPTER IV

X-RAY SPECTRA

§ 1. Laue's Discovery *

IN our introductory note on Röntgen or X-rays (Chap. I, § 5) we saw that Röntgen radiation is a *radiation of transverse* waves. We spoke of the *wave-length* and of the *spectrum of X-ray radiation*, both in the case of the *characteristic radiation*, which is the part that is characteristic of the material composing the anti-cathode, corresponding to the free vibrations of the electrons of the anti-cathode, and in that of the *impulse radiation*, which is the part that is characteristic of the voltage of the X-ray tube, corresponding to forced radiation of the electrons of the cathode rays. Assuming the results of experiment, we described the spectrum of the *characteristic radiation* as a *line spectrum*, that is, as a discrete sequence of individual wave-lengths, and the spectrum of *impulse radiation* as a *continuous spectrum* which stretches from long wave-lengths over a region of maximum intensity to a sharply defined edge of short wave-length. In both cases the wave-length (the dominant wave-length, the region of greatest intensity) is an inverse measure of the *hardness*, a direct measure of the *softness*, of X-rays.

How are the wave-lengths of X-rays measured? The general properties of X-rays, compared with those of visible light, show that their wave-lengths must be very much smaller than optical wave-lengths. In optics the best method of measuring wave-lengths, and the only method that leads to absolute determination of them, is that founded on *diffraction*.

As early as 1895 Röntgen himself had made tentative diffraction experiments with his X-rays, but the result was negative. Results by other experimenters, which were claimed to be positive, were later proved to be due to optical illusions, half-shadow effects arising from the scattering of the secondary radiation. Accurate diffraction photographs were first obtained in 1900 by Haga and Wind, who used

* Laue has given a comprehensive account of his discovery in "Jahrbuch für Radioaktivität und Elektronik," **11**, 308 (1914). Its application to crystal analysis is described in the books, *X-Rays and Crystal Structure*, by W. H. Bragg, London, 1924 (Bell), and *Kristalle und Röntgenstrahlen*, by P. P. Ewald Springer, Berlin, 1923.

a slit that was placed perpendicular to the course of the ray; the jaws of the slit were not, as is usual, parallel to one another, but met at the lower end, so that its opening, which had a width of several μ at the upper end, became reduced to several $\mu\mu$ at the lower end. The diffraction effect was to manifest itself in a broadening of the dark band of the negative at the lower end of the slit. These photographs were repeated with greater refinement by Walter * and Pohl. The plates were worked out by the author, after P. P. Koch † (of Hamburg) had measured them out photometrically with great care by his own method. From a photograph taken with hard Röntgen radiation the dominant wave-length ("width of impulse," as it was called at that time) was found by calculation to be $\lambda \cong 4 \cdot 10^{-9}$ cms. Contrast with this the wave-length of yellow light, which is $6 \cdot 10^{-5}$ cms.

Only a year after these results were made known, this determination of wave-lengths was to be surpassed in accuracy and certainty in an undreamt-of manner by Laue's discovery.

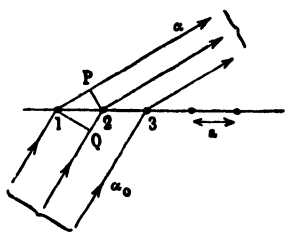


FIG. 39.—Diffraction at a line grating.

In optics, the diffraction grating is more effective than the diffraction slit, both as regards the intensity of its light and its resolving power. The action of the diffraction grating depends on the regular succession of the lines of the grating, the distance between which we shall call the "grating constant" a. The width of the form of these lines have no influence on the angle of diffraction and are only of secondary importance even for the distribution of intensity among the spectra of various orders.

The theory of the diffraction grating is one of the most familiar branches of the wave-theory of optics. Nevertheless, to lay bare the root of Laue's discovery, we must here set out some of its essentials.

In Fig. 39 we exhibit a section of the grating; 1, 2, 3, . . . are the traces of the lines of the grating; the distances $(1, 2) = (2, 3) = \ldots$ are equal to the grating constant a. Let the incident beam of rays have the direction cosine α_0 with the line 1, 2, 3, . . ., the direction cosine of the emergent beam with respect to the same line 1, 2, 3, . . . being α. (α_0 and α are simultaneously the sines of the angles of incidence and emergence.) Using Huyghen's Principle, let us imagine rays starting out from each grating line in all directions. Thus, for the present, we may regard α as any arbitrary angle whatsoever. In

* We anticipate later remarks by stating that in 1924 B. Walter, using monochromatic X-rays (CuKα-line) obtained definite diffraction fringes at a fine slit, and that A. Larsson in his Dissertation (Upsala, 1929) includes extraordinarily beautiful diffraction pictures, which, in the sharpness and number of the maxima and minima are quite as good as those obtained with ordinary light.

† P. P. Koch, Ann. d. Phys., **38**, 507 (1912).

the figure the case of *transmitted* light is pictured. By folding the diffracted rays in the figure about the axis 1, 2, 3, . . ., we get the case of light reflected by diffraction.

The theory of the diffraction grating is contained in the equation

$$a(\alpha - \alpha_0) = h\lambda \quad . \quad . \quad . \quad . \quad (1)$$

In (1) the left-hand side denotes the difference in length of path between the ray, for example, that goes through aperture 1 and that which goes through aperture 2 (and, generally, the difference of path between any such ray and its neighbours). For $a\alpha = 1P$ is the difference of path between the diffracted rays through 1 and 2, and likewise $a\alpha_0$ is the difference between the lengths of path of the incident rays through 2 and 1. Thus our equation demands that the path-difference in the whole course of the rays be equal to a wave-length, or a multiple of the wave-length (that is, h must be an integer). In this case we get an amplification of intensity through interference, that is, a diffraction maximum. We get diffraction minima, that is, a neutralisation of intensity by choosing $h =$ ½, or $h =$ an integer + ½.

In the first place, equation (1) shows that the diffraction grating is a *spectral apparatus*, inasmuch as it gives for each wave-length λ a definite angle of diffraction. Hence incident white light is analysed into its spectral components. Again, red is more strongly diffracted than blue. For $h = 1$, we get a *spectrum of the first order ;* for $h = 2$, we get one of the *second order*, and so forth. Corresponding to the case $h = 0$ is *direct light*, which is not resolved spectrally. On the other side of the direct ray spectra of the first, second, . . . order also occur, namely, for $h = -1$, $h = -2$, and so forth. The separation of the colours (the *dispersion*) is double as great for a spectrum of the second order as for one of the first order, and so forth. Further, equation (1) tells us that the *grating constant* a must be greater than λ, but not *too much greater*. For if $a < \lambda$, we should have $h\frac{\lambda}{a} > 1$, and hence $h\frac{\lambda}{a}$ could not be equal to $\alpha - \alpha_0$, as is demanded by (1) (since $\alpha - \alpha_0$, being the difference between two cosines, is < 1). If, on the other hand, $a \gg \lambda$, then $\alpha - \alpha_0$ will become very small for moderate values of h, and the spectra of first, second, . . . order, if caught on a screen, would lie very close to the direct light ; the dispersion would be insufficient and the grating would fail to be of use as a spectral apparatus. In the case of Rowland gratings, which are of perfect construction, $\frac{a}{\lambda}$ amounts to less than 10 units.

Besides the grating constant a, a decisive feature for the excellence of a grating is the number of lines N of the grating. It conditions not only the brightness of the diffraction spectra, as is immediately apparent, but also the **resolving power** of the grating, that is, the power

to separate and make measurable spectral lines whose wave-lengths differ only slightly from one another. The resolving power is given directly by the number of lines N.

From the simple line-grating we pass on to the **crossed grating,** or **lattice.** Every one knows the beautiful diffraction spectra that are presented to the eye when we look at a distant source of light through finely woven gauze. We shall confine our attention in particular to a quadratic system of fine apertures ; that is, we suppose the threads of the web or network to run at right angles to one another and suppose them to be comparatively thick, so that the intermediate spaces that let through the light may be regarded as mere points. The distance between each two neighbouring apertures is to be called the " lattice constant " a. In Fig. 40 we take two rows of such apertures as our x- and y-axis ; we draw a z-axis perpendicular to both. We cannot picture the course of the beam for the incident and diffracted rays since their paths lie in space. Nevertheless we may, exactly as in Fig. 39, let α_0, β_0 be the direction cosines of the incident ray with respect to the x- and y-axis, respectively ; let α, β be those of the diffracted ray. In the diffracted ray the contributions of all apertures are to strengthen one another additively as a result of the interference. For example, let us consider the contributions of 1 and 2. If they strengthen one another then

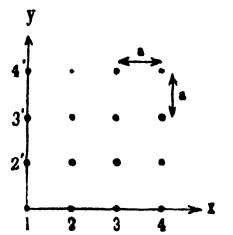


FIG. 40.—Crossed grating (plane-lattice) : regular arrangement of the diffracting apertures.

$$a(\alpha - \alpha_0) = h_1\lambda \quad . \quad . \quad (2)$$

where h_1 = an integer. In the same way the contributions of 1 and 2′ are to act additively through interference. To assure this, we must have

$$a(\beta - \beta_0) = h_2\lambda \quad . \quad . \quad . \quad . \quad (2')$$

where h_2 = an integer. This equation, too, may be read off from Fig. 40, if we project the distance between 1 and 2′ on the incident and the diffracted ray. But if 1 acts together with 2 and 2′ to produce increase of brightness as a result of the interference, then every opening acts in the same sense, since, then, the difference of path between each two openings is equal to a whole number of wave-lengths.

Likewise the lattice (crossed grating) resolves the incident light into its spectral components. For, from equations (2) and (2′), if h_1 and h_2 are given, there is defined for each λ a different direction (α, β) of the diffracted rays. We construct the path of this ray as follows. We describe about the x-axis of Fig. 40 a cone such that the cosine of its angle of aperture is equal to the direction cosine α, as obtained from equation (2). In the same way we describe about the y-axis a cone which is similarly determined by the direction cosine

β given by (2′). These cones intersect in the ray whose position we require (as well as in the ray that is symmetrical to the latter with respect to the xy-plane, the lattice acting, so to speak, as a reflecting plane). Our construction holds for a definite wave-length λ. For a new λ the apertures of the cones must be altered to accord with (2) and (2′), and thus we get a new direction for the diffracted ray. Hence, for given values of h_1 and h_2 we obtain a *spectrum* which corresponds to the two *order numbers* h_1, h_2, and by varying h_1, h_2 we get a *two-fold manifold of spectra*. Each of these spectra repeats the complete series of spectral colours from red (on the outside) to violet (on the inside), with the exception of the spectrum (0, 0), the continuation of the incident ray, which is not analysed in this special case. The spectra (1, 0), (2, 0), (3, 0) . . . lie in the plane through the incident ray and the x-axis ; the spectra (0, 1), (0, 2), (0, 3) . . . lie in the plane through the incident ray and the y-axis. The spectra (1, 1), (2, 2), (3, 3) . . ., further, are situated in the plane through the incident ray and the bisectors of the angle between the x-axis and the y-axis, and so forth for the other spectra. Besides the spectra $(+ h_1, + h_2)$, there are, allotted to the other quadrants of the xy-plane, spectra $(+ h_1, - h_2)$, $(- h_1, + h_2)$, and $(- h_1, - h_2)$. *As in the case of the line-grating we must have* $a > \lambda$ *but we cannot allow* $a \gg \lambda$.

From the crossed grating or plane-lattice we pass on to consider the case of a **space-lattice**, for example, a cubical space-lattice. We may imagine that there is added to the quadratic system of openings of Fig. 40 a whole system of similar systems placed one behind another at equal distances a. For this purpose we prefer to talk, not of " apertures," but of " **lattice-points**," which act as " **diffraction centres** " or as " scattering points." Thus we have a cubical system of lattice-points, of which each two neighbours are separated by a distance equal to the lattice constant a along the direction of each axis, x, y, z. We allow light to fall into the system of lattice-points in the direction $\alpha_0\beta_0\gamma_0$ (these being the direction cosines with respect to the three axes, respectively). At each of our lattice-points a fraction of the incident light will be diffracted or scattered in all directions, for example, in the direction $\alpha\beta\gamma$. At a great distance from our space-lattice the waves that emerge in the direction $\alpha\beta\gamma$ from each lattice-point form a homogeneous ray, namely, the ray $\alpha\beta\gamma$ diffracted by our space-lattice. (In order that this ray might form without obstruction in all directions, it was necessary to replace the idea of " diffraction apertures " by that of " diffraction centres," otherwise the formation of the diffracted ray would be impeded by the diffracting screens that we should have to assume between the diffraction apertures.)

The diffracted ray $\alpha\beta\gamma$, however, is appreciably bright only when the contributions of all the lattice-points act together in the same phase in producing it. For this it is necessary that the path-difference of the rays from neighbouring lattice-points be a whole number of

wave-lengths. Thus we arrive at *three conditions*, one for the direction of x (that is, for two neighbours that are at a distance a from one another in the direction of x), one for the y-direction, and one for the z-direction :

$$a(\alpha - \alpha_0) = h_1\lambda \quad . \quad . \quad . \quad . \quad (3)$$
$$\alpha(\beta - \beta_0) = h_2\lambda \quad . \quad . \quad . \quad . \quad (3')$$
$$\alpha(\gamma - \gamma_0) = h_3\lambda \quad . \quad . \quad . \quad . \quad (3'')$$

When these conditions are fulfilled, the effect of interference is to amplify the intensity, and indeed, not only of that due to two neighbours but generally, to that due to any two of our lattice-points, since for them the path-difference is a whole multiple of the difference of path for two neighbours. The rays thus intensified as a result of interfcrence from all the lattice-points are, furthermore, the only ones that are appreciably bright. For, in the case of a sufficiently great number of lattice-points (N_1, N_2, N_3 in the three co-ordinate directions), rays that are intensified through the combined action of only a fraction of these lattice-points (for example, only the lattice-points, N_1 and N_2) would appear infinitely faint compared with those discussed above.

Equations (3) comprises the essential features of the theory of the space-lattice. We read from them that : *every interference ray is characterised by three whole numbers* (h_1, h_2, h_3), *the* **order numbers** *of the interference phenomenon in question.* We may not, however, as before, speak of a *spectrum* of the order (h_1, h_2, h_3). The light that is diffracted by the space-lattice no longer contains all the wave-lengths in juxtaposition, as happens in the case of the crossed grating or plane-lattice ; it is, on the contrary, *monochromatic light.*

For, from equations (3) it follows that

$$\alpha = \alpha_0 + h_1\frac{\lambda}{a}, \quad \beta = \beta_0 + h_2\frac{\lambda}{a}, \quad \gamma = \gamma_0 + h_3\frac{\lambda}{a} \quad . \quad (4)$$

Moreover, we have the relation between the direction cosines :

$$\alpha^2 + \beta^2 + \gamma^2 = 1, \quad \text{and likewise} \quad \alpha_0^2 + \beta_0^2 + \gamma_0^2 = 1. \quad . \quad (5)$$

By squaring each member of (4) and then summing, using (5), we get

$$1 = 1 + 2(h_1\alpha_0 + h_2\beta_0 + h_3\gamma_0)\frac{\lambda}{a} + (h_1^2 + h_2^2 + h_3^2)\frac{\lambda^2}{a^2}$$

and hence,

$$\lambda = -\,2\frac{a(h_1\alpha_0 + h_2\beta_0 + h_3\gamma_0)}{h_1^2 + h_2^2 + h_3^2} \quad . \quad . \quad . \quad (6)$$

Thus the wave-length that can be diffracted in the interference ray of order (h_1, h_2, h_3) is fully determined for a given direction of incidence. We illustrate this by a conical construction analogous to that which we have already used in the case of the plane-lattice. About the x-, y-, z-axis in turn we describe cones whose angular apertures have cosines such as are demanded by equations (4). Two of these will intersect,

whereas the third will not, in general, pass through a line of intersection of the other two. But the latter condition is absolutely necessary if the amplification produced by interference is to reach full strength. Hence, for an arbitrarily chosen λ, there will, in general, be no diffracted ray. By altering λ we also alter, according to (4), the conical apertures continuously. If we proceed in this way we shall succeed, at a certain value of λ, in making all three cones have a common line of intersection. This is the interference ray $(\alpha\beta\gamma)$; the corresponding wave-length is that which was calculated in (6).

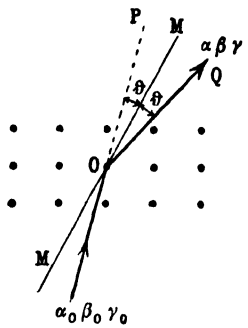


FIG. 41.—Diffraction at a space-lattice.

From equations (3) we shall straightway make a further deduction. For this purpose we introduce the following symbols (cf. Fig. 41): 2θ is to denote the angle between the incident and the diffracted ray, that is, θ is the angle which the incident or the diffracted makes with the middle plane MM between both. We then have

$$\cos 2\theta = \alpha\alpha_0 + \beta\beta_0 + \gamma\gamma_0 \quad . \quad (7)$$

By squaring each member of (3), then summing and using (5) and (7), we get

$$(\alpha - \alpha_0)^2 + (\beta - \beta_0)^2 + (\gamma - \gamma_0)^2 = 2 - 2\cos 2\theta = 4\sin^2\theta = (h_1^2 + h_2^2 + h_3^2)\frac{\lambda^2}{a^2}. \quad (8)$$

Taking the square root, we get

$$\sin\theta = \frac{\lambda}{2a}\sqrt{h_1^2 + h_2^2 + h_3^2} \quad . \quad . \quad . \quad (9)$$

We shall find that this equation will be of fundamental importance in § 2.

In the region of optics our space-lattice is only a fiction, a model which we have conceived so as to generalise the scheme of diffraction as presented by ordinary diffraction gratings. The art of the mechanic and of the weaver are of no avail for producing such space-lattices. In the realm of Röntgen radiation, the position is different. It was Laue's brilliant idea to recognise that the space-structure of crystals is just as happily adapted to the wave-length of Röntgen radiation, as the structure of a Rowland grating is adapted to the wave-length of ordinary light, that is, that we can take directly out of the hands of Nature the diffraction apparatus necessary for Röntgen rays, in the form of one of her masterpieces, a crystal of regular growth.

It was a favourite idea of mineralogists and mathematicians (Hauy, Bravais, Frankenheim, Sohnke, Fedorow, Schönflies) to account for the regular shape and structure of crystals by the regular arrangement

of their elements of structure, of their molecules or atoms. According to this, a lattice of the cubical type would have to be ascribed to a crystal of the regular or cubical system. If we determine the lattice constant a of such a crystal from the density of the crystal and the mass of the atoms composing it (as we shall do at the end of § 2 of this chapter for the case of rock-salt), we find that a is of the order of magnitude 10^{-8} (for example, $a = 5{\cdot}6 \,.\, 10^{-8}$ in the case of NaCl). On the other hand, we saw at the beginning of this section that the wave-length of Röntgen rays is to be placed between the orders of magnitude 10^{-8} and 10^{-9} cms. ($4 \,.\, 10^{-9}$ for a hard tube, according to a rough calculation based on the diffraction). We assert then that *the lattice constant a of the crystal is greater than the wave-length λ of the Röntgen rays, but not very great in comparison with them.* Thus a and λ are related to one another in just the way that we found above to be necessary if a diffraction apparatus is to be effective. We can read the same condition out of equation (9); if $\frac{\lambda}{a}$ is a proper fraction that is not too small, we get for the angle of diffraction 2θ, a possible and not too small value. The atoms that compose our space-lattice are directly effective as lattice-points. We encountered in Chapter I, § 5, their property of forming diffraction (or scattering) centres for Röntgen rays; there we saw that their scattering is proportional to the number of electrons Z contained in them.

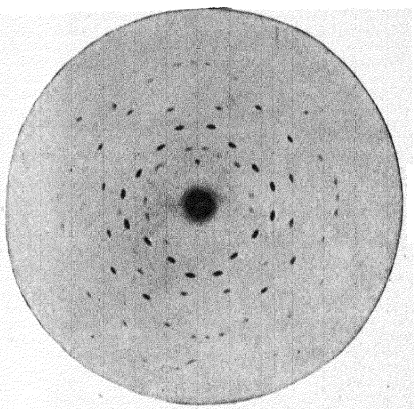


Fig. 42. - Diffraction of "white" Röntgen light at the crystal lattice of ZnS. The crystal is cut parallel to the cube face, and the incident light is perpendicular to the crystal surface. The photographic plate is at a distance of 3·5 cms. from the crystal. Note the four-fold symmetry of the diffraction pattern.

Figs. 42, 43, 44 are reproductions of some of the famous photographs taken by Laue, Friedrich, and Knipping early in 1912. The experiment was arranged very simply. By means of lead guides (screens with holes), a fine beam was separated out of the light from an X-ray bulb. This beam fell on a crystal plate—in the plates reproduced these were of zinc blende, ZnS—about 0·5 mm. thick, 5 mm. wide and long,—which was mounted on a spectrometer table, and capable of being accurately adjusted with it. When the incident "primary" ray traverses the crystal plate, secondary "interference" rays are deflected out of it owing to diffraction by the atomic lattices of the crystal. These interference rays emerge from the crystal as a widely

divergent beam of many members. Several centimetres behind the crystal is the photographic plate. On it there is traced, besides the primary ray (greatly magnified owing to irradiation), the track of the beam of interference rays. In the first photographs the time of exposure was many hours; the tube was run with about 3 milliamps. and 60 kilovolts. The plate and the crystal were protected by being surrounded by lead.

In Figs. 42 and 43 the crystal plate was cut parallel to the face of the cube and placed at right angles to the incident ray, with the difference that in Fig. 42 the photographic plate was 3·5 cms. from the crystal, whereas in Fig. 43 the distance was only 1 cm. Thus Fig. 43 is a section through the same interference beam as Fig. 42, but greatly

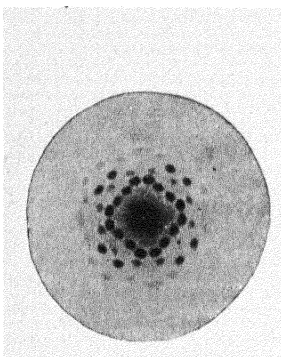


FIG. 43.—Photograph taken as in Fig. 42, but with the photographic plate only 1 cm. away from the crystal.

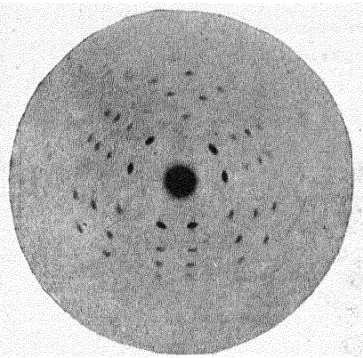


FIG. 44.—Diffraction of "white" Rontgen light at the crystal lattice of ZnS. The crystal is cut perpendicular to a space diagonal of the cubic lattice, and the incident light is perpendicular to the crystal surface. Three-fold symmetry of the diffraction pattern.

compressed and reduced in size. In Fig. 42 as well as in Fig. 43 the primary ray travelled in the direction of the four-fold axis of symmetry (edge of the cube). Correspondingly, the respective diffraction pictures are of four-fold symmetry. They have four planes of symmetry, two parallel to the edges, two parallel to the diagonals of the cube face. Every spot that lies on one of these planes of symmetry in the picture occurs four times, whereas every other spot occurs eight times. Each such group of related spots that again arises from itself by rotation and reflection shows the *same intensity* and is marked on the plate by the same *wave-length*. If the photographic plate and our retina were sensitive to the imaginary colour of Röntgen rays, we should see each such group of points shining forth in one pure colour and each two different groups of points in general emitting different colours. For example, there belong to the two particularly strongly pronounced

8-groups of spots in Figs. 42 and 43, the fractional numbers

$$\frac{\lambda}{a} = \frac{2}{27} \text{ and } \frac{\lambda}{a} = \frac{2}{35} \text{ respectively.}$$

Since the lattice constant for zinc blende is found to be

$$a = 5{\cdot}43 \,.\, 10^{-8} \text{ cm.},$$

we get the corresponding wave-lengths as

$$\lambda = 4{\cdot}02 \,.\, 10^{-9} \text{ cm.} \quad \text{and} \quad \lambda = 3{\cdot}11 \,.\, 10^{-9} \text{ cm.}$$

In Fig. 44, the crystal plate was cut perpendicular to a space diagonal of the cube, which represents a triply symmetrical axis for the substance of the crystal. The primary Röntgen radiation again fell perpendicularly on the plate, and thus traversed the crystal in the direction of one of its *three-fold* axes. Corresponding to this, Fig. 44 is of three-fold symmetry: it possesses three planes of symmetry inclined to one another at an angle of 120°. In general, each spot occurs six times, but in a particular position on one of these planes of symmetry it occurs three times. Each 3- or 6-group of spots, respectively, is produced by the same wave-length. For example, in the case of the very prominent 6-group of spots we have

$$\frac{\lambda}{a} = \frac{2}{19\sqrt{3}}, \quad \lambda = 3{\cdot}30 \,.\, 10^{-9} \text{ cm.}$$

The wave-lengths that are singled out in this way by the crystal structure and are diffracted to definite points of the photographic plate are all contained in the primary bundle of rays, just as the colours of the rainbow are contained in the white light of the sun. In Laue's method the *continuous* spectrum is used to produce the interference picture. This continuous spectrum, however, is not, as in the case of the line-grating or plane lattice (crossed grating), mapped out completely, but certain individual wave-lengths (more accurately, several narrow regions of wave-lengths) that are appropriate for the crystal structure are selected from the continuous manifold of the spectrum and made prominent. The prominence of certain wave-lengths in the interference picture is partly due to the fact that they are particularly strongly represented in the primary spectrum (the region of maximum intensity of the continuous spectrum), and partly due to the fact that the photographic plate reacts particularly strongly to them (selective sensitivity of the silver bromide). Laue's method tells us nothing of the *line-spectrum*, of which the discrete wave-lengths are not in general adapted to the crystal structure. Since the line-spectrum, as the characteristic radiation of the atoms of the anti-cathode, is particularly important for the study of atomic structure, we shall not require to draw further from Laue's original method. Of course the spectrometric methods that we shall discuss in the sequel will differ from Laue's method only in the mode of arrangement, not

in the root idea. This idea, of using the crystal as an analyser for Röntgen rays, is as essential to them as to the original method.

So far we have given Laue's theory for the case of the regular system with the lattice constant a. How this is to be extended to the other systems of crystals suggests itself to us immediately. In the case of the rhombic system, which is built upon three mutually perpendicular axes, it is only necessary to replace the quantity a in equation (3) by the lattice constants, a, b, c in the directions of the three axes respectively. We then get in place of equation (6)

$$\lambda = -2\frac{\frac{h_1}{a}\alpha_0 + \frac{h_2}{b}\beta_0 + \frac{h_3}{c}\cdot\gamma_0}{\frac{h_1^2}{a^2} + \frac{h_2^2}{b^2} + \frac{h_3^2}{c^2}} \quad . \quad . \quad . \quad (10)$$

In the same way, equation (9) now becomes

$$\sin\theta = \frac{\lambda}{2}\sqrt{\frac{h_1^2}{a^2} + \frac{h_2^2}{b^2} + \frac{h_3^2}{c^2}} \quad . \quad . \quad . \quad (11)$$

The case of the tetragonal system is given by setting $b = a$. In the remaining crystal systems, in which the axes of the lattice are in general inclined towards one another (oblique), the *direction angles* of the crystal axes appear in the corresponding formulæ, besides the *lengths of the edges.*

The roads of research opened up by Laue's discovery branch off in two directions. In the one case *we measure out the Röntgen spectrum of a given tube and of an anti-cathode of given material in terms of the lattice constants of a suitably chosen crystal.* In the other case, we *measure out the structure of a given crystal in terms of a suitably chosen wave-length of a Röntgen ray.*

The results of the first line of investigation form the content of the present chapter. For the results of the second line of research consult, for example, the book by Ewald mentioned at the beginning of this chapter.

The experimental methods of X-ray spectroscopy were first summarised by M. Siegbahn, " Spectroscopy of X-rays " (O.U.P.). More recent results up to the present time are contained in the account by A. Lindh, " Röntgenspektroskopie," Vol. 24, 2, of the Handbuch der Experimentalphysik (Wien-Harms).

§ 2. Methods of Measuring Wave-lengths

Whereas in the first section we have discussed the diffraction by lattices exclusively from Laue's point of view, we shall now pass on to that of W. H. and W. L. Bragg. For this purpose, we prove the following theorems :—

1. The median plane MM between the incident ray ($\alpha_0\beta_0\gamma_0$) and the

diffracted ray ($\alpha\beta\gamma$) is a *net plane* of the crystal, that is, a plane that cuts an infinite net of points out of the crystal lattice, and may therefore be regarded as a possible crystallographic boundary surface.

2. The diffracted rays may be regarded as being generated by a reflection at this net plane.

In proving 1, we restrict ourselves, as in the first section, to the regular system.

In Fig. 41, above, let the distances

$$OP = OQ = 1.$$

If we choose O as the origin of a rectangular system of co-ordinates, which coincides with the crystal axes, then the co-ordinates

$$\text{of P are } \alpha_0\beta_0\gamma_0, \quad \text{and} \quad \text{of Q are } \alpha\beta\gamma.$$

Let the co-ordinates of any point M in the median plane be x, y, z. The median plane is the geometrical locus of equal distances, PM = QM. Thus its equation is

$$(x - \alpha_0)^2 + (y - \beta_0)^2 + (z - \gamma_0)^2 = (x - \alpha)^2 + (y - \beta)^2 + (z - \gamma)^2$$

or, after reduction,

$$(\alpha - \alpha_0)x + (\beta - \beta_0)y + (\gamma - \gamma_0)z = 0.$$

If we insert into this the interference conditions (3) of § 1, we get

$$h_1x + h_2y + h_3z = 0 \quad . \quad . \quad . \quad . \quad (1)$$

Let n be some common divisor of the order numbers h_1, h_2, h_3, that is

$$h_1 = nh_1^*, \quad h_2 = nh_2^*, \quad h_3 = nh_3^* \quad . \quad . \quad . \quad (2)$$

whereby h_1^*, h_2^*, h_3 have no common factor. Equation (1) then states that a plane that is parallel to MM has intercepts on the crystallographic axes that are inversely proportional to the integers h_1^*, h_2^*, h_3^*, which are prime to one another. The numbers h_1^*, h_2^*, h_3^* are called the *indices of the surface* MM. The fundamental law of crystallography, the "law of rational indices" states that every surface that has integral indices is a possible surface of a crystal. (As in the case of all physical laws in which rational ratios occur, rational indices denote such as are representable by the ratios of *small* integers.) From the point of view of the lattice idea, this law is self-evident. It states nothing else than that every boundary surface of a crystal is occupied by a full net of lattice-points.

We have thus seen that *the median plane* MM *between the incident and the diffracted ray is a net plane of the crystal: the order numbers* h_1, h_2, h_3 *of the interference phenomenon determine simultaneously the indices* h_1^*, h_2^*, h_3^* *of this net plane.*

The incident and the diffracted ray make equal angles with this plane, namely, the angle θ in Fig. 41. Thus there is nothing to prevent

us from interpreting the phenomenon of diffraction as a reflection at this net plane. This is, however, *not surface reflection*, but *space reflection*. On the one hand, it is not necessary for the reflecting net plane of the crystal to be a bounding plane of it : the reflection takes place just as well at the inner virtual crystal planes as at the external real ones. On the other hand, the whole system of parallel net planes reflects concurrently with the individual plane MM. As we saw in the first section, all lattice-points on which the primary ray impinges contribute to the interference phenomenon. Thus *the reflected intensity is derived from the interior of the crystal.*

But, further, we are here dealing not with *a general reflection of all wave-lengths*, but with a *selective reflection of certain favoured wave-lengths*. " White light " is not reflected back as white light, as occurs in optics, but reappears " coloured." Whereas all other wave-lengths remain appreciably united in the primary ray, and traverse the crystal in a straight line, certain wave-lengths, of appropriate length for the lattice structure, are selected by the reflection. This selective colour of interference rays has already been met with in the first section. We shall now deduce it again from the standpoint of reflection.

Let OA, OQ be the incident and reflected rays at the lattice-point A, and let PC, CR be the incident and reflected rays at the lattice-point C, which is situated in the plane parallel and adjacent to MM. The difference between the lengths of path of both sets of rays is found by dropping from A the perpendiculars AB and AD on to PC and CR. The difference of path is, if d denotes the distance AC between the net planes,

$$\mathrm{BC} + \mathrm{CD} = 2d \sin \theta.$$

This must be a whole multiple of λ if the two reflected rays AQ and CR are to be in phase and are to strengthen one another by interference. This gives us the fundamental relation

$$2d \sin \theta = n\lambda \quad . \quad . \quad . \quad . \quad (3)$$

According to Darwin and Ewald, Bragg's calculation is to be corrected to

$$2d_n \sin \theta = n\lambda, \quad d_n = \frac{d}{1 - \frac{k}{n^2} \frac{d^2}{\lambda^2}}$$

where k depends on the tightness with which the electrons are bound. Cf. the summary given by Ewald in Vol. 24 of the Handbuch der Physik (Geiger-Scheel) ; for the experimental confirmation see A. Larsson, *Zeits. f. Physik.*, **35**, 401 (1926) ; **41**, 507 (1927), and M. Siegbahn, *Journ. de Phys.*, **6**, 228 (1925).

But in deriving this relation we have made an unnecessary specialisation. It is not necessary for the two lattice-points A and C, in Fig. 45, which are being compared to lie directly behind one another, that

is, on the same normal to MM as we found it convenient to assume for the sake of simplicity in the figure. Rather, we may displace the point C arbitrarily in its net plane to C′. The path of the rays P′C′R′ (dotted in Fig. 45) clearly has the same optical length as the path PCR, provided that the two points PP′ and RR′ are assumed, in particular, to lie on a wave plane through the incident and reflected ray, respectively. This is shown clearly in Fig. 46, in which the points RR′ are placed still more specially, namely, symmetrically to PP′ with respect to the plane of symmetry SS there drawn ; this has no effect on the phase-difference at R and R′. We see that the optical paths PCR and R′C′P′ are images of one another. If the two rays incident at P and P′ are in phase, then also the two reflected rays at R and R′ will be in phase. But then it follows from Fig. 45 that in it, too, there is the same difference of path between the reflected rays C′R′ and AQ as between CR and AQ, namely, the difference $n\lambda$; the former strengthen one another by interference just as much as the latter.

In fact, generally, any two lattice-points of the crystal, no matter whether they lie on two neighbouring net planes or on two net planes

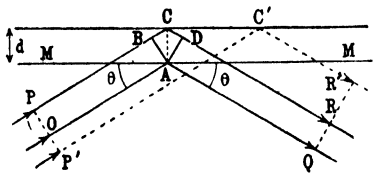


Fig. 45.

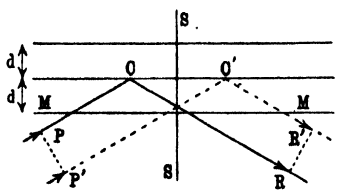


Fig. 46.

Diagrammatic illustrations of the Bragg relation $2d \sin \theta = n\lambda$. Reflection at the lattice planes of a crystal.

that are distant from one another by various multiples of d, no matter whether they lie in the plane of incidence (that of the page) or not, will strengthen one another by interference, provided only that the wave-length and the angle of incidence are related to one another by the condition postulated in (3). It is not even necessary for the points CC′ . . . to be arranged in lattice form, that is, equidistantly, within their net plane. What is important for reflection at the system of planes MM is merely the regular sequence of these planes, not the regular sequence of points within a plane of the system. The latter factor comes into account only when we wish to change the reflection plane, that is, when the crystal, besides reflecting from the system of planes MM, is also to reflect from other net planes running through the crystal. For this, that is, for the existence of further net planes and for their action by interference, the necessary condition is that the lattice-points be regularly arranged in the first system of net planes.

In optics we are familiar with the process of O. Wiener, in which,

by means of stationary waves, silver particles are precipitated in parallel equidistant planes in a layer of silver chloride. The silver particles succeed each other irregularly within each plane, but the planes succeed each other regularly at a distance equal to half that between two crests of the stationary light, that is, equal to half the wave-length of the monochromatic light used. These strata of Wiener have been used, as we know, in Lippmann's process of photography in natural colours. Here we have the case assumed above of a regularly stratified system of planes, which, for their part, are irregularly occupied by silver granules. In interpreting such phenomena our equation (3) played a part,* long before its importance in the realm of Rontgen rays could be surmised in any way.

Of course this equation must be identical with the formulæ (9) and (11) found in § 1 for the wave-length. In fact, on the view that the quantities h_1^*, h_2^*, h_3^* are surface indices we see by the simple geometrical consideration that the distance d between two successive planes of the group parallel to MM is given in the cubic and the rhombic system, respectively, by

$$\frac{1}{d} = \frac{1}{a}\sqrt{h_1^{*2} + h_2^{*2} + h_3^{*2}}, \qquad \frac{1}{d} = \sqrt{\frac{h_1^{*2}}{a^2} + \frac{h_2^{*2}}{b^2} + \frac{h_3^{*2}}{c^2}} \quad . \quad (4)$$

If, taking account of (2), we introduce these values into (9) and (11) of the first section, both these equations resolve into our present equation (3). We see from the method by which it has now been derived, that it is not confined to the case of the regular system but is generally valid. The meaning, too, of the integral number n introduced in equation (2) (it is the greatest common factor of the order numbers h_1, h_2, h_3 of the interference effect) is now also intelligible physically: n denotes the order number of the reflection phenomenon, that is, the number of wave-lengths by which each reflected ray differs from its neighbouring rays that are reflected from the next or the preceding net plane.

For a given angle of reflection θ and given distance d between the net planes, equation (3) determines one and only one quite definite wave-length, λ_1 of the first order (for $n = 1$) that is capable of reflection, and likewise one of the second, third, . . . order, $\lambda_2 = \frac{\lambda_1}{2}$, $\lambda_3 = \frac{\lambda_1}{3}$, . . . (for $n = 2, 3 \ldots$). Hence if we wish to reflect the whole spectrum from one and the same crystal face, for example, in the first order, then θ must be made variable. For the short-wave side of the spectrum, θ is to be chosen small, for the long-wave side it must be chosen correspondingly great. This goal has been reached in various ways experimentally. On account of its historical importance we shall discuss chiefly the *method of the revolving crystal*, with which W. H. and W. L.

* In the theory of W. Zenker. Cf. his *Lehrbuch der Photochromie*, Berlin, 1868.

Bragg * achieved such striking success, namely in the two directions characterised on page 186, the analysis of X-rays by crystals and the analysis of crystal structure by X-rays.

Fig. 47 gives a schematic horizontal section of the arrangement of apparatus for the method of revolving crystals. At the top the Röntgen tube is indicated by its cathode K and its anti-cathode A. The slit S_1 in a lead plate singles out from the rays emitted from the focus of the anti-cathode a narrow beam of rays. S_2 is a second small slit of lead, which serves to limit the pencil of rays still further. This beam then falls on the crystal Kr, which is set up on a table T, carrying vernier divisions, in such a way that the front reflecting net plane of the crystal (for example, a cleavage plane of rock-salt) passes through the vertical axis of rotation O of the vernier table. The latter is slowly turned about the axis O within a certain range of angles. All wave-lengths of a certain range of wave-lengths then impinge on the table successively at the necessary angle of incidence θ (or "glancing angle") and are separated spectrally by the reflection. They delineate themselves sharply on the photographic film FF, which is best fixed (see below) along the circle S_1PP_1 that passes through S_1; for a small range of angles, it may also be replaced by the plane photographic plate P'P'. Now, P_1 is the point on the film, at which is marked the primary radiation of the Röntgen tube that has traversed the crystal without reflection; there follow consecutively on the film the shortest wave-lengths contained in the primary beam of X-rays, and then the longer ones. The longest wave-length which, according to equation (3), may be reflected by a crystal with a given distance d between the net planes is $\lambda = 2d$; the corresponding angle $\theta = \frac{\pi}{2}$. The trace of the wave-length on the film would coincide with S_1. It is obvious that this maximum wave-length can be reflected only in the first order ($n = 1$).

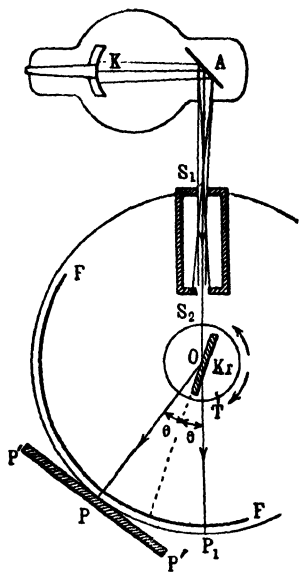


FIG. 47. — Rotating crystal method used with Röntgen rays.

Of course a variable angle of incidence of the rays can also be obtained without rotating the crystal if we use a diverging or a converging

* They used the ionisation method (see below). Maurice De Broglie first used the revolving crystal method for taking photographs.

beam of rays. In the latter case the slit which marks off the beam may be replaced by a metal edge which is brought near to the crystal surface (Seemann's method).*

In the case of *hard rays* a difficulty arises owing to their great penetrating power in that the exact position of the system of reflecting layers is uncertain and this renders it impossible to measure accurately the angle of incidence. Instead of reflected light we therefore use in this case *transmitted* X-rays, which are reflected at the inner net planes of the crystal. The slit must then be adjusted *behind* the crystal plate. This arrangement was first used by Rutherford and Andrade † for analysing γ-rays.

Another difficulty in the case of very hard rays consists in the fact that for them the angle θ, by (3), becomes very small, so that the accuracy is reduced. In the case of very small values of λ/d we have almost grazing incidence with respect to the reflecting net-plane. We may circumvent this difficulty by observing in a higher order (cf. the factor n in eqn. (3)) and by using as small a distance d between the net-planes as possible. Changing the crystal does not, however, alter d by much. Whereas for rock-salt the lattice-constant is $a = 2d = 5{\cdot}63 \cdot 10^{-8}$, for the crystal of smallest known lattice-constant, namely, diamond, the value is $a = 3{\cdot}55 \cdot 10^{-8}$. It is more effective to pass from a crystal face (for example, of cube face 100) to one with higher indices (for example, of octahedral face 111), which, by eqn. (4) makes d smaller (in the ratio $\sqrt{3} : 1$). Both these devices (proceeding to higher order of reflection and faces with higher indices) lead to a diminution of intensity.

If very soft rays, which are strongly absorbed in several centimetres of air at atmospheric pressure, are to be photographed, the whole course of the rays must lie *in vacuo*. This requirement leads to the construction of vacuum spectrographs, which have been developed by Siegbahn along the lines of Moseley. The whole apparatus (see Fig. 47) from the circle S_1PP_1 up to and including the plate $P'P'$ has for this reason been enclosed in a brass case connected with an air-pump. The X-ray tube is also to be considered in this figure as connected with this brass case by a tube S_1 that may be evacuated.

Further difficulties are also raised here by the lattice-constant of the crystal. Now the fundamental equation (3) demands for the case where $n = 1$ (observation in the first order, to which we may restrict ourselves if the rays are very soft),

$$2d > \lambda \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Accordingly rock-salt ($2d = 5{\cdot}63 \cdot 10^{-8}$) may be used only as far as wave-lengths not exceeding $\lambda = 5$Å. Gypsum and mica, however,

* H. Seemann, Ann. d. Phys., **49**, 470 (1916), and Phys. Zeits., **18**, 242 (1917). See also Seemann and Friedrich, *ibid.*, **20**, 55 (1919).

† Rutherford and Andrade, Phil. Mag., **28**, 263 (1914).

supply us with good crystals with considerably greater values for the lattice constant. (This corresponds with the rule, which is self-evident, that very easy cleavage is usually associated with a large value of the lattice constant for the net planes in question.) A step towards crystals of still finer reticulation was first taken by Siegbahn and Thoraeus,* who used palmitic acid, for which $2d = 70{\cdot}98$ Å, as the reflecting crystal.

We now proceed to discuss two other methods of X-ray spectroscopy, the first being the ionisation method of W. H. Bragg. In it the photographic plate or film is replaced by an ionisation chamber, that is, by a vessel that is filled with a (preferably heavy) gas, which receives the reflected radiation at P (Fig. 47). The gaseous content becomes conducting (ionised) in proportion to the radiation absorbed; the conductivity is measured by electrometers. The ionisation chamber must be turned, step by step, along the circle P_1PS of Fig. 47 to the same extent as the crystal is turned forward, step by step, when we pass from one wave-length of the spectrum to another that is neighbouring to it. Thus, in this case, the spectrum is represented not by a continuous distribution of darkened spots, but by a discontinuous succession of electrometer deflections. The method has its advantage in measuring the intensities in the X-ray spectrum as, through the use of electrometers, it is specially sensitive and allows quantitative comparisons (on account of the approximate proportionality between X-ray intensity and ionisation).

Secondly, in the method of crystal powders, devised by Debye and Scherrer, the various angles of incidence that are requisite for the various wave-lengths of the spectrum are furnished by the natural lack of order in the crystal powder. The same method has been developed in America by A. W. Hull. It is a typical example of the inevitableness of scientific development that, in spite of the blockade due to the war, the same idea sprang up almost simultaneously in Germany and America. A narrow pencil of Röntgen rays falls into a little tube which is filled with a micro-crystalline powder, and strikes one and the same crystal face in all possible orientations. For each wave-length there are crystal faces inclined at the correct angles, and indeed in all positions around the direction of the incident ray. Hence, the reflected radiation forms for each wave-length a cone about the incident ray. A circularly cylindrical film placed axially in position, will be darkened by the reflected radiation at its curve of intersection with this cone. If the primary ray travels along horizontally, the mantle (sheet) of the cylindrical film is placed vertically. The arrangement is particularly simple and has already been of great service in crystal analysis, since most minerals occur more often in the powder form, so-called amorphous form, than in that of

* Cf. Journ. Opt. Soc. Amer., B, 235 (1926).

well-grown crystals; if necessary, the fineness of the granules may be increased artificially.

We now give an indication of the power of X-ray spectroscopy by reproducing some photographs of historic importance. Fig. 48 represents one of the first really successful X-ray photographs; it was taken by E. Wagner in 1917 by means of a platinum anti-cathode and a rotating crystal of rock-salt.* The wave-lengths increase from left to right. On the less exposed right side of the figure the characteristic lines of platinum (so-called L-series, denoted by $\alpha\beta\gamma\delta$) stand out very conspicuously as straight lines, accompanied by several weaker lines of iridium, which is related to platinum, and several mercury lines. On the left side of the figure, which was exposed to the reflected rays more often owing to the manner of adjustment of the crystal, and was therefore darkened relatively more than the background of the right side of the picture, we see the *continuous spectrum* depicted as a fairly uniformly darkened field. The intensity of the darkness decreases at the point marked *d* ("bromine band," cf. § 7 of this chapter) in a strikingly sudden way towards the right, owing to the selective sensitivity of the photographic layer of silver bromide for X-rays. Hence we here have documentary evidence of the two components of X-rays, repeatedly mentioned above, namely, the continuous spectrum (impulse radiation) and the line-spectrum.

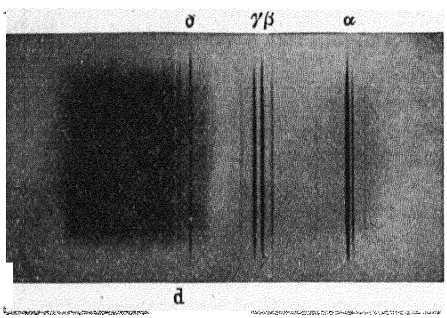


FIG. 48.—Characteristic Röntgen spectrum of Pt (L-series, α, β, γ, δ) taken with a rotating crystal of NaCl. The strong selective absorption of the bromine (K-absorption limit) in the light sensitive layer of the photographic plate begins at *d*. Wave-lengths increase towards the right.

The next picture is one of a series of systematic photographs by means of which W. H. and W. L. Bragg have unravelled the structure of rock-salt (Fig. 49). The source of radiation was a tube with a rhodium anti-cathode. This gives, in addition to a weak continuous spectrum, two lines, in particular, one, the more intense but softer α-line, and the other, the weaker but harder β-line of the so-called K-series. The cube face of rock-salt served as the reflecting crystal face. The intensity of reflection was measured by the ionisation method. The ordinates of the figure are thus electrometer deflections giving the intensity of the ionisation current; the abscissæ denote

* Phys. Zeits., **18**, 405 (1917).

the angles 2θ (cf. Fig. 47), through which the ionisation chamber must be turned so as to be able to receive the reflected intensity under consideration in turn. The figure shows the two lines α and β in three different positions. The difference between the lines, which gives a measure of the spectroscopic resolution, increases with the order-number of the reflection; at the same time, however, the intensity of the lines rapidly decreases (the amount of this decrease depends not only on the general conditions of the diffraction, but also on the particular structure of the crystal used). Both facts, increase of resolution and decrease of intensity, have already been emphasised above. The sharpness of the lines, compared with the preceding photograph, is by no means great in this ionisation picture.

We give as our third picture a photograph,* taken by Debye and Scherrer, of very finely powdered LiF. The source of radiation, a tube with a Cu-anti-cathode, again emits, in particular, two characteristic wave-lengths, the α- and the β-lines of the K-series, the former being a little more intense than the latter. The dark lines of

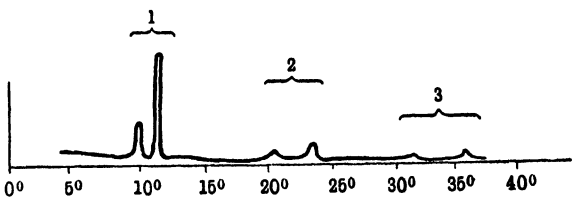


FIG. 49.—Characteristic Rontgen spectrum of Rh ($K\alpha\beta$) obtained with an ionisation chamber. The numbers 1, 2, 3 denote the 1st, 2nd and 3rd orders of reflection at the crystal face (cube face of NaCl).

the photograph are produced by these two wave-lengths, whereas the continuous spectrum of the Cu tube has produced no appreciable darkening. These dark lines are, as we remarked above, the intersections of the film with the circular cones that start out from the crystal powder, and are described about the direction axis of the incident X-ray pencil. In the middle of the picture the lines of darkness are straight, because the circular cone that is described about the primary ray becomes a plane when its angle of aperture is 90°, and it therefore intersects the film in a straight line. Towards the right and the left ends of the picture (emergent and incident directions of the primary ray) the curvature of the lines of intersection increases. The very dark lines correspond throughout to the α-line of Cu, likewise the moderately dark ones; the weak lines correspond to the β-line, in the main. The α-radiation and likewise the β-radiation gives us not only one, but several dark images, because it is reflected appreciably at several faces of the micro-crystals (octahedral, dodecahedral,

* Taken from the Göttinger Nachrichten of the year 1916.

cubic face, and, indeed, not only in the first order, but also in the second, third, and fourth orders), whereby these faces must in each case have the appropriate orientation towards the incident Röntgen light.

But we must now follow the purpose stated in the title of this section—the *measurement* of the wave-length of Röntgen rays. This depends, as is clear from equation (3) and from Laue's own fundamental idea, on a comparison of the wave-length sought with the dimensions of the crystal lattice, in particular, with the distance d between the net planes.

Let us return to the method of the revolving crystal and assume that a number of lines are photographed very distinctly and sharply on the film FF of Fig. 47. The distance of an individual line from the primary ray gives us the angle 2θ directly (cf. Fig. 47). From this we calculate θ and sin θ. Thus, so long as d is known, λ can also be given directly from (3).

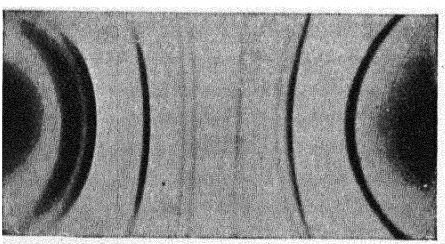


FIG. 50.—Debye-Scherrer-photograph obtained with powdered LiF. Characteristic Röntgen spectrum of Cu ($K\alpha\beta$).

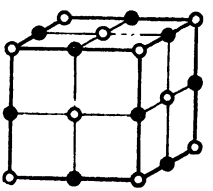


FIG. 51.—Crystal model of rock salt. Cubic lattice.

It only remains for us to describe how d is found.* The earliest precise measurements were made by using a piece of rock-crystal cleaved along the cube faces. The structural skeleton of the NaCl crystal is shown in Fig. 51. We have a simple cube lattice whose points are occupied alternately by Na- and Cl-atoms (more correctly, Na^+- and Cl^--ions). The distance between the net planes which comes into question here is $d = a/2$, that is, it is equal to half the edge of the cube in which the Na-ions and the Cl-ions are arranged. If we imagine a cube d^3 described about each Na- and Cl-ion as centre, then these cubes completely fill the crystal. Hence, in the space $2d^3$ there will be a mass $m_{Na} + m_{Cl}$. This mass amounts to

$$(23{\cdot}00 + 35{\cdot}46)m_H = \frac{58{\cdot}46}{L} = \frac{58{\cdot}46}{6{\cdot}06} \cdot 10^{-23},$$

that is, the sum of the atomic weights of Na and Cl multiplied by the mass m_H of the hydrogen atom, or, more accurately, with the recip-

* Cf. the detailed discussion by E. Wagner, Ann. d. Phys., **49**, 625 (1916).

rocal of L, Loschmidt's number per mol, the value of which we get from Fig. 1B on page 7.

We get in this way, for the density of mass of rock-salt,

$$\rho = \frac{58{\cdot}46}{6{\cdot}06\,.\,2d^3}\,.\,10^{-23}.$$

This density of mass is, on the other hand, known from direct observation, or can be determined experimentally for the crystal of rock-salt used in each particular case. A very exact measurement by Röntgen gives

$$\rho = 2{\cdot}164.$$

By comparing the two values of ρ we find

$$d = \sqrt[3]{\frac{58{\cdot}46\,.\,10^{-23}}{2\,.\,2{\cdot}164\,.\,6{\cdot}06}} = 2{\cdot}814 \text{ Å} = 2814 \text{ X-units},$$

where, following Siegbahn, we have introduced the unit

$$1 \text{ X-unit} = {}_{1\,0\,0\,0}^{1} \text{ Å}.$$

The greatest uncertainty in the numbers used is contained in the value of the Loschmidt (or Avogadro) number, and amounts to at most 1 per cent.; the possible error in the lattice-constant d hence becomes less than $\frac{1}{3}$ per cent.

The value $d = 2{\cdot}814$ Å was used as the basis for the first wave-length determinations by Moseley in 1913. Seigbahn adopted the convention of taking 2814·00 X-units as his basis; all measurements obtained in Siegbahn's laboratory are referred to this value. In practical respects, however, fluorspar is superior to rock-salt on account of the nature of its cleavage planes and its small coefficient of expansion. Precision measurements are therefore performed wherever possible with fluorspar; the lattice-constant of fluorspar, referred to the d of rock-salt, amounts at 18° C. to 3029·04 X-units.

The methods so far discussed give a *relative* wave-length measurement, which depends on an exact knowledge of the value of d for a normal crystal. Since the appearance of a fundamental paper by Compton and Doan * in 1925 it has become possible to make an *absolute* measurement of wave-lengths in the manner used in measuring lattices optically. All that is necessary is an ordinary ruled grating on reflecting metal or glass, which need not even have a very small lattice-constant (for example, 50 lines to the millimetre).

How does this harmonise with our assertion in § 1, according to which the lattice-constant must not be great compared with the wave-length? The explanation is that in these experiments *extremely small angles of incidence* are used. For the lattice equation (1) in § 1 shows directly that a may be increased in proportion as $\alpha - \alpha_0$ is

* A. H. Compton and R. L. Doan, Proc. Nat. Ac., **11**, 598 (1925).

diminished. Moreover, in the new method it is not selective but *total reflection* that is used, and this implies a considerable gain in intensity and sharpness of the lines. The phenomenon of total reflection, which occurs when a ray passes from a denser to a less dense medium (glass into air), is, of course, well known in the optical region. In the X-ray region air or a vacuum is the "denser" and glass or metal the "less dense" medium. We saw in note 1 that in scattering processes ordinary and X-ray light behaved in opposite respects. Whereas in the optical region we could neglect ω in comparison with ω_0 (the frequency of the light in comparison with the natural or "proper" frequency of the scattering atoms), in the X-ray region we had to neglect ω_0 in comparison with ω. Hence in eqn. (2) of note 1 the characteristic denominator reverses its sign. But the same denominator also occurs in the dispersion formula and here determines the deviation of the refractive index from 1. Whereas the refractive index of ordinary light is greater than unity in passing from air to glass, the refractive index of X-ray light becomes *less than* 1 although only by a very small amount. Hence total reflection can occur in this transition, *but only when the angles are extremely small.*

In the meantime this method has been perfected to an extraordinary degree, both in Upsala by Bäcklin (Dissertation, 1928) and in Chicago by Bearden (Nat. Ac., 1929); it yields X-ray lines of irreproachable definition and resolution as far as the tenth order. From such photographs the wave-length λ of the X-ray line in question can be determined absolutely by using the lattice-constant a. On the other hand, by comparing the λ-values so obtained with those obtained by reflections from crystals we can determine the lattice-constant d of the crystals. For fluorspar, for example, Bäcklin obtained the value

$$d = 3033 \text{ X-units},$$

which is not inconsiderably greater than that given above.

But this involves a further correction in Loschmidt's number and consequently also in the value for the elementary charge e. According to Bäcklin or Bearden, Millikan's value $e = 4{\cdot}774 \,.\, 10^{-10}$ (cf. p. 15) would have to be increased to

$$e = 4{\cdot}793 \,.\, 10^{-10} \text{ or } 4{\cdot}804 \,.\, 10^{-10} \text{ respectively.}$$

Judgment about the sources of error involved in the new method must be suspended for the present. Hence for the present we shall retain the values given in Chapter I for the fundamental constants e, m, L and so forth. We consider it only right, however, to point out that possibly a more accurate determination of those constants will be possible as a result of absolute lattice measurements of the wave-lengths of X-rays.

§ 3. Survey of the K-, L-, and M-series and the Corresponding Limits of Excitation

We now enter into a region of physical research which was founded only in 1913 and which, in spite of the unfavourable conditions of the intervening years, has already been developed so far that to-day its structure is exposed to our gaze with greater clearness of detail than the regions which have been explored much longer and from which the new researches have borrowed their aims and methods. It is in fact true that the *spectroscopy of Röntgen rays* shows in many ways simpler and more satisfactory results than the illimitable *spectroscopy of the visible region.*

The reason for this striking fact was touched on in § 3 of the preceding chapter: the X-rays came from the inner part of the atom where the electrons, owing to the influence of the unweakened nuclear charge, obey simple laws: visible spectra start out from the periphery of the atom, where the electrons accumulate and the nuclear charge loses its regulative power. A further reason must be added: right from the outset X-ray spectroscopy had the new atomic theory of Bohr (1913) to guide it and direct it, whereas optical spectroscopy was for decades without theoretical guidance and had first to generate from within, as it were, the facts on which the atomic theory could be founded.

Let us first cast a glance at our knowledge of Röntgen radiation before Laue's discovery, that is at the *characteristic radiation of the elements.* Barkla, whose works are almost the only ones that come into account for this question, showed that every element, on to which cathode rays or X-rays are allowed to fall, emits characteristic primary or secondary Röntgen rays of quite definite hardness. The hardness was measured by noting the coefficient of absorption of the radiation in the case of, say, aluminium. The simplicity of the law of absorption led to the conclusion that characteristic X-rays must to a great extent be *homogeneous.* Moreover, it was found that there is a simple relation between the hardness of radiation and the atomic weight of the element emitting it. The hardness increases (that is, the absorption decreases) as the atomic weight increases. In the case of compounds, the characteristic radiation emitted was found to be the sum of the characteristic radiations of the elements constituting the compound. This proved that the characteristic part of the Röntgen radiation was a fundamental property of the atom and that it was conditioned by the atomic weight.

Barkla succeeded in showing the existence of two series of characteristic radiation, which he called the K-*series* and the L-*series.* He observed the K-series of rays in the case of the lighter metals (as far as Ag) and the L-series in that of heavy metals (e.g. Au, Pt). The extrapolation of the observed L-rays for the case of the light elements

made it evident that they would be so soft that, with the means at that time available, their presence could not be detected. On the other hand, the extrapolation of the K-radiation in the direction of the heavy metals showed that in their case the K-radiation would have to be so hard that it could not be excited by the X-ray tubes that were available at that time. For it is a general law of the excitation of a characteristic radiation that the *exciting radiation must be harder than that which is excited.* This law of excitation pointed to an analogy in the realm of optics, namely to *Stoke's rule for light produced by fluorescence.* If a fluorescent substance is to be made to fluoresce, the incident light must in general be of shorter wave-length than that of the light emitted by fluorescence. In this case, too, then, the exciting light must be " harder " than that which is excited. Hence Barkla also called characteristic X-rays *fluorescence rays,* thus characterising their origin fittingly. Just as the fluorescence light is determined by the nature of the fluorescent body and is different in nature from the exciting light, so the fluorescence X-ray light is determined by the structure of the emitting atom, independently of the constitution of the exciting radiation, provided that the latter is sufficiently hard.

After Laue's discovery all these relations became incomparably more certain and definite. The qualitative measurement of hardness by means of *absorption* was replaced by the quantitative measurement of *wave-length,* which was free from all arbitrariness. The *homogeneity* of the characteristic radiation was on the one hand sharpened and on the other limited. The spectroscopic resolution of the characteristic radiation disclosed a spectrum of sharp lines, of which each, taken alone, represents Röntgen light of very great homogeneity, but the totality of which signifies an emission of light of a certain degree of heterogeneity. The general dependence of the hardness on the atomic weight could now, after the arbitrary mode of measurement by absorption had been replaced by the natural method of measuring wave-lengths, and after, thanks to Bohr's theory, the somewhat indefinite atomic weight had been replaced by the simpler quantity, atomic number, be expressed as a *simple numerical law between wave-length and atomic number.* It also became possible to express *the condition of excitation* quantitatively. When the exciting radiation was resolved spectroscopically, it was seen by how much its short-wave end had to exceed the excited radiation in hardness, in the sense of Stoke's rule. Finally, it was found possible to add to the two characteristic emissions denoted K- and L-radiation by Barkla two other radiations, appropriately called M-, N- and O-radiation.

We next give a general graphical survey of the wave-lengths of K-, L-, and M-radiation, which is derived from an account given by M. Siegbahn and R. Thoraeus (Fig. 52). We mark off the wave-lengths horizontally, whereas, starting from the top, we measure off vertically the increasing atomic numbers of the elements emitting these

wave-lengths. The horizontal line thus signifies in a certain sense the extent of the spectrum in question, and the vertical direction, in steps of 3 units at a time, the sequence of the natural system of the elements. The K-radiation is the hardest of the three types of rays ; it has been observed for cases ranging from the lightest elements, for which even the K-radiation is already extraordinarily soft, to cases for which the rays are extremely hard. Still softer than the L-radiation there is the M-radiation, which has so far been observed only in the case of heavy elements, and even then special precautions (vacuum spectrograph, cf. p. 192) were rendered necessary. The N-radiation is again softer and has been observed only in the case of the heaviest elements.

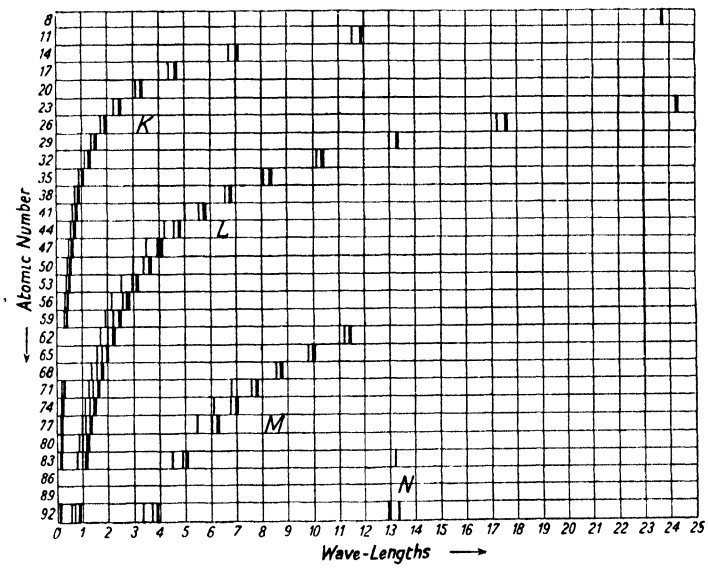


FIG. 52.

Each of these kinds of rays consists, as the figure indicates, of several lines and each increases regularly in hardness as the atomic number increases.

We follow this survey of the experimental results by the theoretical picture to which they have led. This picture is based entirely on the atomic model, consisting of the positive nucleus as the central body and the electron shells surrounding it, which, anticipating Barkla's nomenclature, we called K-, L-, and M- shell in the preceding chapter. For the present we shall consider these shells, as was originally done, as uniform so far as the energy-content of each is concerned ; that is, we shall disregard the sub-division of the shells into various sub-groups.

We shall now describe (*a*) the phenomenon of excitation, (*b*) the

process of emission for the K-, L-, M-radiation according to the plan of W. Kossel,* whose views seem to be more and more confirmed by the facts.

To excite K-radiation, an electron must be removed from the innermost shell, the K-ring, and transferred to the periphery of the atom. If the excitation occurs through the agency of cathode rays, it is easy to imagine that the tearing-off of the " K-electron " is effected by the impact of a cathode-ray particle that has penetrated into the atom. To detach the K-electron, a certain energy, lifting power, is necessary. The energy of the impinging cathode ray must be at least as great as this lifting energy. This sets a definite limit to the excitation necesary to produce the K-radiation, that is, there is a lower limit to the necessary hardness of the cathode rays. If the excitation is effected not by cathode rays but by primary Röntgen radiation, then we must demand for the corresponding minimum of its hardness that its $h\nu$ value (cf. Chap. I, § 6) is at least as great as the lifting power required to do the work of transference.

To *excite the* L-*radiation*, it is necessary to remove an electron from the L-shell to an outer position. The lifting work necessary is less than the corresponding work for the same atom in the case of a K-electron. Hence, for the L-electron, the necessary hardness of the exciting cathode rays or Röntgen rays is less. In Fig. 53 the process of excitation is represented diagrammatically by the arrows that point from within outwards. They bear the signs K-Gr. (K-*Grenze* = K-limit), L-Gr. (L-limit), and so forth.

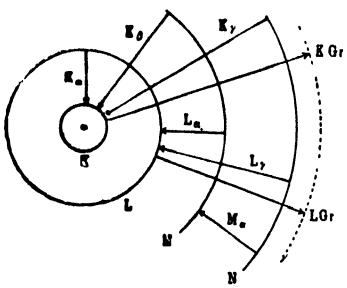


FIG. 53.—Diagrammatic representation of the excitation and emission of Röntgen series (K-, L-, M-series).

Through the excitation the atom is prepared for the subsequent *process of emission*. When the K-electron has been torn out, the K-shell strives to complete itself again. The missing electron may be furnished by either the L-shell or the M-shell, or some other. Whereas the process of excitation was accompanied by a gain of energy (work of lifting, absorption of energy), the converse process takes place with the loss of energy (energy of falling, emission). We assume that this appears in the form of energy of radiation, and that it is emitted as monochromatic radiation, that is, as radiation of *one* wave-length, in each case. According as the missing electron, however, returns to the K-ring from the L-, M-, or N-shell, the energy set free will be

* W. Kossel, Verh. d. Deutschen Physikal. Gesellsch., 1914, pp. 899 and 953; 1916, p. 339.

different in amount : correspondingly there will be various possible K-radiations, each of which is represented by a definite wave-length. We talk of the Kα-line (transition from the L- to the K-shell), of the Kβ-line (transition from the M- to the K-shell), of the Kγ-line (transition from the N- to the K-shell). The lines Kα, Kβ, Kγ together constitute the K-*series*. Kβ is *harder* than Kα, and Kγ is harder than Kβ on account of the successive increase in the energy of falling that is available. On the other hand, Kα is *more intense* than Kβ, and Kβ is *more intense* than Kγ owing to the fact that the probability of the occurrence of the transition becomes successively smaller. It seems very plausible to suppose that the replacement of the missing electron is effected more often by the neighbouring shell than by the next or some later shell. In Fig. 53 these electronic transitions are represented by the arrows that point inwards to the nucleus ; they are distinguished, in so far as they belong to the emission of K-lines, by the symbols Kα, Kβ, Kγ.

Whereas all electronic jumps that end in the K-shell belong to the K-series, all these that end in the L-shell belong to the *lines of the* L-*series*. If a place in the L-shell has become vacant owing to a preceding excitation, the L-shell seeks to restore its full complement of electrons at the expense of the M- or the N-shell, and so forth. The energy that is hereby set free again appears as monochromatic radiation. We speak of the Lα-line (transition from the M- to the L-shell), of the Lγ-line (jump from the N- to the L-shell), and so forth. Lγ is harder and less intense than the Lα-line for reasons analogous to those given above. Concerning the naming of these arrows it must be remarked that there are also *lines* Lβ and Lδ, which, however, like a series of further lines of the L-series, have not yet been successfully fitted into our provisional scheme. The following sections will deal further with this circumstance.

Finally, electronic transitions that end in the M-shell, furnish differences of energy that correspond to emissions of lines of the M-series. In our figure this series is represented by only one line, Mα, corresponding to the transition from the N- into the M-shell. In reality, it, too, consists of several lines.

In several absorption experiments with light substances (water, aluminium, paper) Barkla believed in 1917 that he had detected signs of a radiation still harder than K-radiation ; he called it " J-radiation." Repeated tests by other observers have, however, not been able to confirm the existence of this radiation. Nor has the theory a place for such radiation, so that we must regard K-radiation as the hardest possible radiation ; this is expressed in our figure.

In succession to Fig. 53 we give Fig. 54 as a still more schematic illustration of the process of emission of Röntgen rays. This diagram has an advantage in that it takes more account of the quantitative aspect of the phenomenon. In it we visualise the various shells not

by their relative positions in the atom but by their relative energy-differences. Thus we draw a succession of *energy-steps* such that the difference of height between two steps gives the energy that is liberated when an electron drops from the higher to the lower step (orbit). The lowest step bears the sign K, the next L, and so forth. The energy-level of the nucleus is to be considered at $-\infty$. The highest dotted limit of the steps corresponds to the periphery of the atom. If we consider the energy-levels of the hydrogen atom to the first degree of approximation, that is, disregarding the interaction between the atomic electrons and considering only their energy in the nuclear field, then we must set down the position of the n-quantum step below the highest level at a distance proportional to $\frac{1}{n^2}$ (cf. p. 87). Accordingly we make the height of the steps in the figure decrease, from

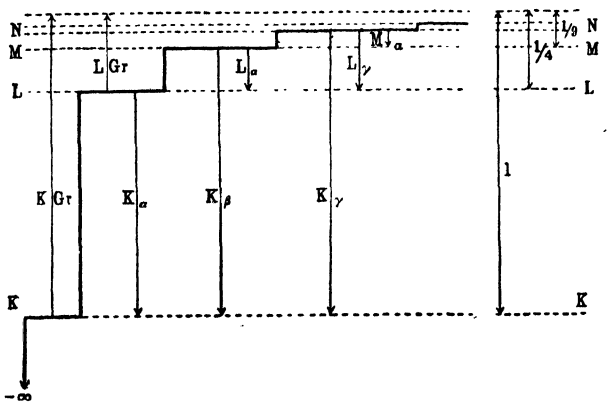


FIG. 54.—Diagrammatic representation of the energy levels of a Röntgen spectrum.

the bottom upwards, in the manner indicated by the differences of height 1, $\frac{1}{4}$, $\frac{1}{9}$, . . . written at the side (on the right). Moreover, we again draw the arrows Kα, Kβ, . . ., Lα . . . that correspond to the various possibilities of energy-emission, and the arrows K-Gr, L-Gr, which correspond to the various kinds of energy-absorption.

This theoretical diagram enables us to understand at once the general laws for the hardness of Röntgen lines that came into evidence in Fig. 52. For according to the fundamental quantum relation $h\nu = W_1 - W_2$ the lengths of the arrows in our figure denote directly the frequency of the associated emission lines and absorption limits.

Hence it follows: *for one and the same atom the* K*-series is harder than the* L*-series which, in turn, is harder than the* M*-series.* Within the K-series *the hardness increases from* Kα *beyond* Kβ to Kγ, but in ever-decreasing steps, and finally arrives approximately at the hardness of the K-limit. The same holds for the L-series, and likewise for the

others. But further, the available differences of energy depend essentially on the amount of the nuclear charge. The greater the nuclear charge (and hence the atomic number of the element), the more intense is the electric field around the nucleus. The energy steps become greater as Z increases (roughly, in proportion to Z^2, as in the case of the hydrogen-like atom, eqn. (13), on p. 87). But this means that the *hardness increases for every line with every step forward in the natural system of elements.*

But Fig. 54 also enables us to recognise a further principle. If we use K, L, M, . . . to denote directly the works of excitation (or ionisation) divided by h, which are necessary to remove an electron from the K-, L-, M- . . . shell, we clearly have *

$$\left.\begin{array}{lll} K\alpha = K - L, & K\beta = K - M, & K\gamma = K - N, \ldots \\ & L\alpha = L - M, & L\gamma = L - N, \ldots \\ & & M\alpha = M - N, \ldots \end{array}\right\} \quad (1)$$

These equations denote the first step towards representing X-ray spectra by means of *terms*, which we shall give in its final form in § 7 of the present chapter. At the same time they show how Ritz's Combination Principle (cf. Chap. II, § 2) is applied to X-ray spectra.

From the equations (1) we obtain, by eliminating the limits K-, L-, M-, . . ., the *combination relations* between the emission lines, which were first set up by Kossel, namely,

$$\left.\begin{array}{lll} K\beta = K\alpha + L\alpha \ldots & \text{from the first and second columns of eqns. (1)} & \\ K\gamma = K\alpha + L\gamma \ldots & \text{,, first and third} & \text{,,} \\ L\gamma = L\alpha + M\alpha \ldots & \text{,, second and third} & \text{,,} \\ K\gamma = K\beta + M\alpha \ldots & \text{,, second and third} & \text{,,} \end{array}\right\} \quad (2)$$

The relationships may obviously also be read off the figure directly without the use of the equations (1). It is highly suggestive that the equations (2) hold only approximately and not exactly. This is not due to the combination principle not being accurately true but to our idea of the energy-levels of the different shells, as hitherto represented, being still too inaccurate, and that the L- and M-shells have to be *sub-divided.* A hint to this effect is also given by the two lines $L\beta$ and $L\delta$ of the L-series which were mentioned on page 203. The succeeding sections serve to describe the refinement of the levels-scheme in this sense.

* If these equations are to hold directly in wave-numbers (cm^{-1}) we must divide the works of excitation not by h but by hc. Cf. p. 71. In the sequel we shall assume that this has been done.

§ 4. The K-series. Its Bearing on the Periodic System of Elements

Following in the footsteps of Barkla, Moseley * was the first to bring the emission of the Röntgen lines into relationship with the scheme of the natural system. His first photographs (1913) dealt with the K-series of the elements between Ca, Z = 20, and Cu, Z = 29, inclusive.

Let us at once look at a now famous figure in Moseley's paper. The photographs have here been pasted above each other successively so that positions vertically below one another denote equal wave-lengths. The wave-lengths increase as we pass from the left to the right. We learn from Fig. 55 :

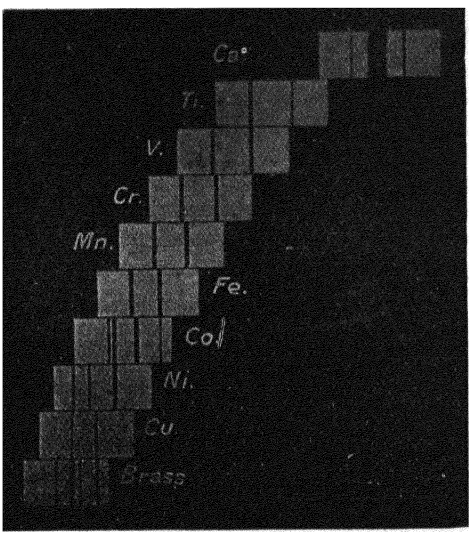


Fig. 55.—Moseley diagram of the K-series from Ca (Z = 20) to Cu (Z = 29). Wave-lengths increase towards the right. Equal wave-lengths are arranged under one another.

1. As the atomic number increases, corresponding lines in the spectra move regularly and successively towards the region of smaller wave-lengths. **The hardness of the lines increases as Z increases.** This is already known to us from the previous section and holds not only for the K-series but also, as Fig. 52 shows, for the L- and M-series.

2. In the case of each element, two lines occur : they are *the more intense but softer line* Kα *and the less intense but harder line* Kβ, which we have already met under the same names in the preceding paragraph. The faint line Kγ that was also mentioned earlier is not distinguishable from the Kβ, and appears only when refined spectroscopic methods are applied.

3. The X-ray spectra are a pure property of the atom, and, indeed, an *additive property*. The last picture of the series, which represents brass, that is, an alloy of Cu and Zn, accordingly exhibits the same

* H. G. J. Moseley, "The High Frequency Spectra of the Elements," Phil. Mag., **26**, 1024 (1913) ; **27**, 703 (1914). Moseley's apparatus is still preserved in the Electrical Laboratory, Oxford, where he carried out these researches under the supervision of Professor J. S. Townsend.—(Transl.)

lines as the preceding element Cu and the following element Zn (not shown in our figure). Further, we observe in the case of Co, which it is difficult to separate from Ni and Fe (first triad of the periodic system), besides the α- and β-line of Co also less intense images of the α-lines of Fe and Ni.

4. The order of Co and Ni in the periodic system is rectified by this result of X-ray analysis. Whereas, according to the values of the atomic weights, Ni should precede Co (at. wgts. being 58·68 and 58·97 respectively), we had to write Co before Ni in the chemical scheme of Table 4, page 131. The X-rays are not deceived by the atomic weight and so they confirm the true order Co, Ni. *Not the atomic weight, but the atomic number governs the Röntgen spectra.*

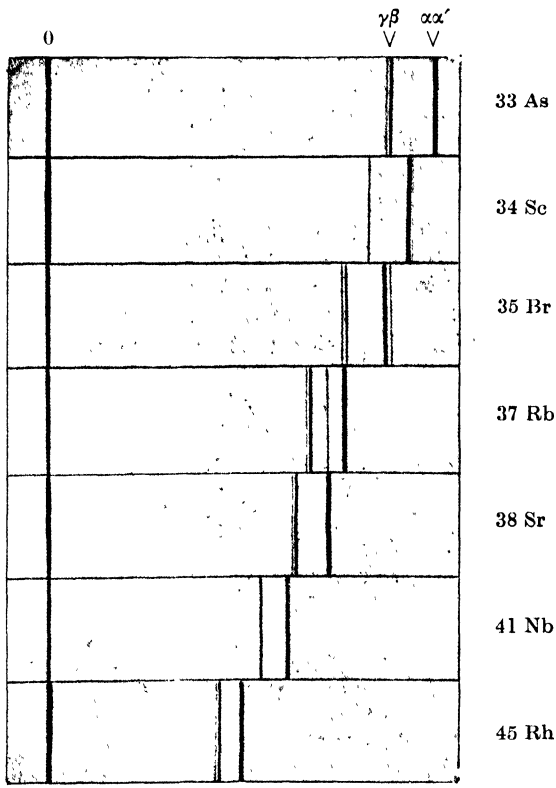


FIG. 56.—Rotating crystal photographs of the K-series between As (Z = 33) and Rh (Z = 45).

The same is true of the order of Te and I and this is likewise established properly by Röntgen analysis (cf. Fig. 57). As Rutherford incidentally remarks, the original problem that Moseley was trying to solve when he set about his experiment was to determine whether it was not the nuclear charge, instead of the atomic weight, that decided the nature and the hardness of the characteristic Röntgen radiation.

5. Since the discovery of the periodic system, particular interest was centred on the presence of gaps and the prediction of new elements in the system (cf. p. 133). In Moseley's figure, the rare element scandium is missing between Ca and Ti. Its absence is betrayed by too great a leap between the elements Ca and Ti that succeed one another

in the figure. The regular increase (that was emphasised in 1) in the hardness as Z increases reveals infallibly every gap in the system. Whereas we are here concerned with the well-known element Sc, we shall in Fig. 57 recognise a gap of this sort at Z = 43, which points to the element Masurium which was only recently discovered, the discovery being made by means of X-rays. The previous gaps Z = 61 and 75 have also been filled by the X-ray method, whereas the two places Z = 85, Z = 87 are still shown to be gaps by the same method.

Partly to continue Moseley's figure in the direction of increasing atomic numbers and partly to bring into evidence the advances that have been made in photographing Röntgen rays, we give as our next illustration Fig. 56, by Siegbahn : it represents the elements from As, Z = 33, to Rh, Z = 45. In this case the spectra have been taken by the method of the revolving crystal ; as a result, the lines are sharper than in Moseley's case and more completely separated. Besides the second most intense line Kβ, we see here also the *faint line* Kγ (to the left, and hence harder than Kβ), the origin of which we know from the preceding section. Further, we see that the most intense line Kα has been resolved into the doublet (α, α') (α' is to the right of α, and hence is softer). Besides these lines, the zero mark (on the extreme left) has been photographed ; it is made by the undiffracted primary radiation.

The same remarks apply to this figure as to the former ; the hardness increases for each line as the atomic number increases ; the Sr-line adulterates the Rb-spectrum ; gaps occur in the succession of the elements, exhibited by irregularly great differences in the hardness, namely, between Br, Z = 35, and Rb, Z = 37, the inert gas Kr, Z = 36, is missing.

We first give a short survey of the different nomenclatures and the origin and intensity of the K-lines.

TABLE 11.

Sommerfeld	Siegbahn	Origin	Intensity
α'	α_2	$L_{II} \rightarrow K$	50
α	α_1	$L_{III} \rightarrow K$	100
β'	β_3	$M_{II} \rightarrow K$	35
β	β_1	$M_{III} \rightarrow K$	
γ	β_2	$N_{III} \rightarrow K$	15

The lines are arranged in order of increasing hardness. In Siegbahn's notation two groups of lines are distinguished, the soft α-lines and the harder β-lines ; he numbers the lines in both groups according to their intensity. A number of fainter lines that occur only in the case of the lowest atomic numbers, and that are to bear the names α_3, α_4, α_5, α_6, according to Siegbahn, are not included

in our list. We shall revert to this in § 7. The intensity data have been borrowed from Siegbahn's book (referred to on p. 186) and denote ratios.

The data about the origin of the lines correspond to the representation of terms in eqn. (1) of the preceding section and supplement this scheme in the sense of the sub-division of the energy-steps there set out. For this reason we have provided the symbols of the L-, M-, and N-shell with indices, whose general scheme we shall discuss in § 6 of the present chapter. The lines $\alpha'\alpha$, $\beta'\beta$ have been bracketed together to denote that they form with each other the doublet differences $L_{III} - L_{II}$ and $M_{III} - M_{II}$, which we shall discuss in the next section.

We now give a list of the wave-lengths of the principal lines of the K-series, using in general X-units (cf. p. 197); $1\ X = 10^{-11}$ cm. $= 10^{-3}$ Å. We shall keep to the measurements obtained in Seigbahn's Institute, except in the case of Ma, for which we give Berg and Tacke's measurements. Finally we add in the last column but one the wave-lengths of the absorption limits (K-limit) as given by the measurements of Leide (Dissertation, Lund, 1925), so that we have now collected the most important data relating to wave-lengths of the K-series in one table. We shall give a detailed discussion of the absorption limits in § 6.

At the beginning of the table the lines $\alpha\alpha'$ have not yet been separated. While the gaps in the table are obviously accidental (for example, the inert gases are absent) the γ-line seems to find its natural limit in the neighbourhood of Ti, $Z = 22$; we shall revert to this in § 7 in conjunction with the interesting questions of the successive building up of the shells.

From the wave-lengths λ we pass on to their reciprocal values, the wave-numbers ν; to arrive at un-named numbers of a convenient order of magnitude we divide the ν's by the Rydberg constant (eqn. (16) on p. 89). In this way we obtain the columns 2 to 5 in Table 13. We set next to them in columns 6 and 7 the differences between the ν/R's for the lines α and α' and the value of $\sqrt{\nu/R}$ for the line Kα (at the head of the table we have denoted these columns briefly by $\alpha - \alpha'$ and $\sqrt{\alpha}$).

The column $\alpha - \alpha'$ will occupy us in the next section. We shall first fix our attention on the last column but one. It forms an arithmetic series; that is, there is a steady increase from element to element. At the beginning of the table the increase is regular, later it increases a little. The same would hold for $\sqrt{\beta}$. We also read this out of Fig. 57, which expresses the values of $\sqrt{\nu/R}$ as a function of the atomic number, in the manner of Siegbahn. The α-lines and the β-lines (the two central lines of the figure) increase regularly in a linear manner except for a slight curvature in the case of the greater Z's;

Table 12

Wave-lengths of the K-series in X-units

Z	α′	α	β	γ	K-Limit	Z
8 O	23·73 (Å.-U.)		—	—	—	8 O
9 F	18·30 ,,		—	—	—	9 F
11 Na	11883·6		11591	—	—	11 Na
12 Mg	9867·75		9534·5	—	—	12 Mg
13 Al	8319·40		7940·5	—	—	13 Al
14 Si	7109·17		6739·3	—	—	14 Si
15 P	6141·71		5789·0	—	—	15 P
16 S	5363·75	5360·90	5021·3	—	—	16 S
17 Cl	4721·36	4718·21	4394·6	—	—	17 Cl
19 K	3737·06	3733·68	3446·80	—	—	19 K
20 Ca	3354·95	3351·69	3083·43	—	—	20 Ca
21 Sc	3028·40	3025·03	2773·94	—	—	21 Sc
22 Ti	2746·81	2743·17	2508·98	2493·7	—	22 Ti
23 V	2502·13	2498·35	2279·72	2264·6	—	23 V
24 Cr	2288·907	2285·033	2080·586	2066·71	—	24 Cr
25 Mn	2101·489	2097·506	1906·195	1893·27	—	25 Mn
26 Fe	1936·012	1932·076	1753·013	1740·80	—	26 Fe
27 Co	1789·187	1785·287	1617·436	1605·62	—	27 Co
28 Ni	1658·353	1654·503	1497·045	1485·61	—	28 Ni
29 Cu	1541·16	1537·26	1389·33	1378·0	1377·65	29 Cu
30 Zn	1435·87	1432·06	1292·60	1280·97	1280·8	30 Zn
32 Ge	1255·21	1251·30	1126·74	1114·62	—	32 Ge
33 As	1177·40	1173·43	1055·18	1042·93	1042·63	33 As
34 Se	1106·43	1102·42	990·25	977·90	977·73	34 Se
35 Br	1041·60	1037·56	930·84	918·26	918·09	35 Br
37 Rb	927·72	923·60	827·03	814·84	814·10	37 Rb
38 Sr	877·54	873·37	781·53	769·19	768·37	38 Sr
39 Yt	831·19	827·01	739·31	726·92	—	39 Yt
40 Zr	788·50	784·29	700·47	688·34	687·38	40 Zr
41 Nb	748·82	744·57	664·49	652·55	651·58	41 Nb
42 Mo	712·105	707·831	630·978 *	619·698	618·48	42 Mo
43 Ma	0·675 (Å)	0·672 (Å)	0·601 (Å)	—	—	43 Ma
44 Ru	646·15	641·81	571·43	560·48	—	44 Ru
45 Rh	616·371	612·023	544·491 *	533·957	533·03	45 Rh
46 Pd	588·632	584·266	519·471 *	509·181	507·95	46 Pd
47 Ag	562·669	558·277	496·009 *	486·030	484·80	47 Ag
48 Cd	538·29	533·86	474·29	464·39	463·13	48 Cd
49 In	515·46	511·03	453·72	444·08	442·98	49 In
50 Sn	494·016	489·572	434·297 *	424·992	423·94	50 Sn
51 Sb	473·87	469·31	416·23	407·10	406·09	51 Sb
52 Te	454·91	450·37	399·26	390·37	389·24	52 Te
53 I	437·03	432·49	383·29	374·71	373·44	53 I
55 Cs	404·11	399·59	—	—	344·07	55 Cs
56 Ba	388·99	384·43	—	—	330·70	56 Ba
57 La	374·66	370·04	—	—	318·14	57 La
58 Ce	361·10	356·47	—	—	306·26	58 Ce
60 Nd	335·95	331·25	—	—	284·58	60 Nd
62 Sm	313·02	308·33	—	—	—	62 Sm
63 Eu	302·65	297·90	—	—	—	63 Eu
64 Gd	292·61	287·82	—	—	—	64 Gd
65 Tb	282·86	278·20	—	—	—	65 Tb
66 Dy	273·75	269·03	—	—	—	66 Dy
67 Ho	264·99	260·30	—	—	222·64	67 Ho
68 Er	256·64	251·97	—	—	—	68 Er
70 Yb	240·98	236·28	—	—	—	70 Yb
74 W	213·52	208·85	184·36	179·40	—	74 W
77 Ir	195·8	—	168·4	—	—	77 Ir
78 Pt	190·10	185·28	163·4	158·2	—	78 Pt

* In the case of these elements β' has been separated from β whereas for the other elements our wave-length data for β denote the unresolved complex of lines $\beta + \beta'$. We have

$\beta' - \beta = 0{\cdot}565$ X-units for Mo, Z = 42 $\quad \beta' - \beta = 0{\cdot}638$ X-units for Ag, Z = 47
$= 0{\cdot}602$,, ,, Rh, Z = 45 $\quad = 0{\cdot}650$,, ,, Sn, Z = 50
$= 0{\cdot}619$,, ,, Pd, Z = 46

TABLE 13

ν/R-values of the K-series

Z	α'	α	β	γ	$\alpha - \alpha'$	$\sqrt{\alpha}$*	Z
8 O	38·40		—	—	—	6·197	8 O
9 F	49·80		—	—	—	7·057	9 F
11 Na	76·68		78·62	—	—	8·757	11 Na
12 Mg	92·34		95·57	—	—	9·609	12 Mg
13 Al	109·53		114·76	—	—	10·465	13 Al
14 Si	128·18		135·21	—	—	11·321	14 Si
15 P	148·37		157·41	—	—	12·176	15 P
16 S	169·89	169·98	181·48	—	0·09	13·037	16 S
17 Cl	193·01	193·14	207·36	—	0·13	13·897	17 Cl
19 K	243·84	244·07	264·38	—	0·23	15·623	19 K
20 Ca	271·61	271·88	295·51	—	0·27	16·488	20 Ca
21 Sc	300·90	301·24	328·51	—	0·34	17·356	21 Sc
22 Ti	331·75	332·20	363·20	365·42	0·45	18·226	22 Ti
23 V	364·19	364·75	399·72	402·40	0·56	19·097	23 V
24 Cr	398·124	398·799	437·987	440·93	0·675	19·9700	24 Cr
25 Mn	433·631	434·454	478·057	481·32	0·823	20·8436	25 Mn
26 Fe	470·694	471·653	519·831	523·48	0·959	21·7176	26 Fe
27 Co	509·321	510·433	563·404	567·55	1·112	22·5928	27 Co
28 Ni	549·503	550·781	608·712	613·40	1·278	23·4687	28 Ni
29 Cu	591·27	592·79	655·91	661·30	1·52	24·347	29 Cu
30 Zn	634·65	636·34	704·99	711·39	1·69	25·226	30 Zn
32 Ge	725·99	728·26	808·56	817·56	2·27	26·986	32 Ge
33 As	773·96	776·59	863·61	873·78	2·63	27·867	33 As
34 Se	823·62	826·61	920·24	931·86	2·99	28·751	34 Se
35 Br	874·88	878·28	978·98	992·39	3·40	29·636	35 Br
37 Rb	982·27	986·65	1101·9	1118·3	4·38	31·411	37 Rb
38 Sr	1038·4	1043·4	1166·0	1184·7	5·0	32·302	38 Sr
39 Yt	1096·4	1101·9	1232·6	1253·6	5·5	33·195	39 Yt
40 Zr	1155·7	1161·9	1300·9	1323·8	6·2	34·087	40 Zr
41 Nb	1216·9	1223·9	1371·4	1396·5	7·0	34·948	41 Nb
42 Mo	1279·692	1287·420	1444·227 †	1470·515	7·728	35·8807	42 Mo
44 Ru	1410·3	1419·9	1594·7	1625·9	9·6	37·681	44 Ru
45 Rh	1478·44	1488·95	1673·63 †	1706·64	10·51	38·5869	45 Rh
46 Pd	1548·12	1559·68	1754·22 †	1789·64	11·56	39·493	46 Pd
47 Ag	1619·55	1632·29	1837·20 †	1874·96	12·74	40·402	47 Ag
48 Cd	1692·9	1707·0	1921·3	1962·2	14·1	41·315	48 Cd
49 In	1767·9	1783·2	2008·4	2252·0	15·3	42·227	49 In
50 Sn	1844·62	1861·36	2098·27 †	2144·21	16·74	43·144	50 Sn
51 Sb	1923·0	1941·7	2189·3	2238·4	18·7	44·064	51 Sb
52 Te	2003·2	2023·4	2282·4	2334·4	20·2	44·982	52 Te
53 I	2085·2	2107·0	2377·5	2432·0	21·8	45·902	53 I
55 Cs	2255·0	2280·5	—	—	25·5	47·755	55 Cs
56 Ba	2342·5	2370·4	—	—	27·9	48·687	56 Ba
57 La	2432·3	2462·6	—	—	30·3	49·625	57 La
58 Ce	2523·6	2556·3	—	—	32·7	50·560	58 Ce
60 Nd	2712·5	2751·0	—	—	39·5	52·450	60 Nd
62 Sm	2911·2	2955·5	—	—	44·3	54·365	62 Sm
63 Eu	3011·1	3059·1	—	—	48·0	55·309	63 Eu
64 Gd	3114·3	3166·1	—	—	51·8	56·268	64 Gd
65 Tb	3221·6	3275·6	—	—	54·0	57·233	65 Tb
66 Dy	3328·8	3387·2	—	—	58·4	58·200	66 Dy
67 Ho	3438·9	3500·8	—	—	61·9	59·168	67 Ho
68 Er	3550·8	3616·6	—	—	65·8	60·138	68 Er
70 Yb	3781·5	3856·7	—	—	75·2	62·103	70 Yb
74 W	4267·8	4363·3	4942·9	5072·5	95·5	65·327	74 W
77 Ir	4654	—	5411	—	—	68·21	77 Ir
78 Pt	4793	4918	5577	5760	128	69·23	78 Pt

* Between 8 O and 15 P inclusive, α and α' are not separated; only at 16 S do we find our $\sqrt{\alpha}$-values to be the $\sqrt{\nu/R}$'s of the α-lines.

† Here β' and β are separated (cf. Table 12, p. 210) (ν/R)$_{\beta'}$ has the values: 42 Mo 1442·935, 45 Rh 1671·77, 46 Pd 1752·13, 47 Ag 1834·84, 50 Sn 2095·13.

the neighbouring lines α' and γ (the two outermost lines) follow them in their course.

In Fig. 57 our earlier statements about the behaviour of X-ray spectra and their relationship to the natural system of elements are shown particularly clearly. We see the regular increase of hardness with atomic number, which is linear in our present method of representation. There is as yet no sign of the periodicity of the elements. We interpreted this earlier as meaning that only the peripheral parts of the atom are constructed in a periodic way and that the energy

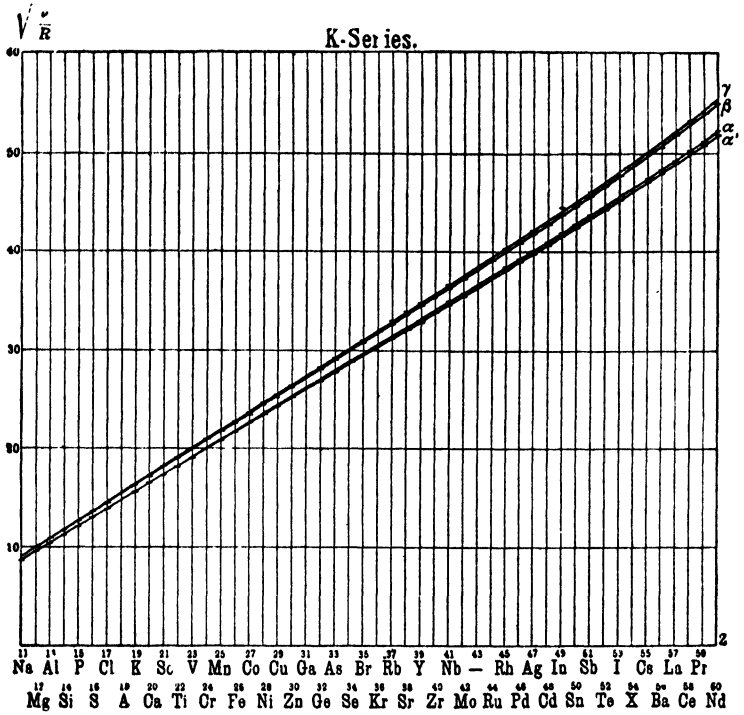


FIG. 57.—$\sqrt{\nu/R}$ of the K-series lines a (very nearly) linear function of the nuclear charge Z.

ratios in the interior of the atom increase regularly with the nuclear charge.

This method of representation gains in certainty when we draw inferences about the possible gaps in the system of elements. If the figure had been drawn without account being taken of the gap which was present earlier at Z = 43 (masurium), a discontinuity would have manifested itself at the point in question in the course of the graph and this would at once have called attention to the missing element. Also note the sequence Te, I (Z = 52 and 53), which is

established beyond doubt in our diagram and which agrees with the requirements of the chemical scheme (I in the seventh vertical column, below F, Cl and Br).

It is also interesting to note the magnitude of the increase of $\sqrt{\alpha}$ in Table 13, that is, the change in $\sqrt{\nu/R}$ in the Kα-line as we pass from one element to the next. It amounts to about

$$0{\cdot}86 = \sqrt{\tfrac{3}{4}}.$$

Consequently we may for the present express the linear gradient in Fig. 57 by the following formula :

$$\sqrt{\frac{\nu}{R}} = \sqrt{\tfrac{3}{4}}(Z - s).$$

It follows also from the graph that the constant s which has here been introduced and which we shall call the " screening constant," must be nearly equal to 1. In this way we arrive at the following expression, already developed by Moseley, for the wave-number of the Kα-line :

$$\frac{\nu}{R} = \tfrac{3}{4}(Z - 1)^2 = (Z - 1)^2(1 - \tfrac{1}{4}) = (Z - 1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) \quad . \quad (2)$$

This formula exhibits a far-reaching analogy with Balmer's expression for the hydrogen series given in Chapter II ; in comparison with the formula (15) on page 89 we find that the only difference is that now the full nuclear number Z does not occur and that it is reduced by the amount $s \sim 1$. As the name " screening-constant " signifies, this has to be interpreted as meaning that in the interior of atoms that are different from the hydrogen type—and it is with such that we are here concerned—the presence of negative electronic charges near the nucleus reduces the action of the positive nuclear charge.

From the point of view of the theory as accepted at the present time we can no longer regard Moseley's equation (2) as exact. A complete expression for the Kα-line for all atomic numbers Z would also have to explain the slight curvature of the graph in Fig. 57 on the basis of the " relativity corrections " which are to be discussed in Chapter V ; nor can we rest satisfied with the above approximate determination of the constant s. But above all the form of eqn. (2) has been chosen too narrow from the point of view of the Combination Principle. According to this principle Kα must be represented as the difference of two terms which in eqn. (1) of page 205 we denoted by K and L. There is no basis for assuming the screening constant s as having the same value in both terms, as is done in Moseley's formula. Rather, it is plausible from the outset that the screening in the case of the K-term will be smaller than in the case of the L-term, because in the latter the two electrons of the K-shell have a screening effect to the full extent of their charges and the other electrons of the L-shell

will also contribute to the screening, whereas for the K-term essentially only the K-electrons come into consideration with a part of their charge. Hence a rational expression for the Kα-line must not start from the specialised Moseley formula (2) but from the Combination Principle and the general formula (1) on page 205. Nevertheless it will be a cause of wonder for all time that when Moseley first made quantitative measurements in the realm of X-rays he at the same time took the first decisive step in interpreting theoretically the high frequency spectra.

§ 5. The L-series. Doublet Relationships

The L-series is constructed in a more complicated way than the K-series, as is shown, in the first place, by its lines being present in greater number. A survey of the different nomenclatures and the origin and approximate intensities of the principal lines is given in Table 14; besides the lines here set out there are several weaker lines to which we shall refer in § 7. A reproduction of the L-series of platinum has already been given (Fig. 48, § 2).

TABLE 14

Sommerfeld	Siegbahn	Origin	Intensity
α′	α_2	$M_{IV} \rightarrow L_{III}$	1
α	α_1	$M_V \rightarrow L_{III}$	10
β	β_1	$M_{IV} \rightarrow L_{II}$	8
γ′	—	$N_{IV} \rightarrow L_{III}$	0
γ	β_2	$N_V \rightarrow L_{III}$	6
δ	γ_1	$N_{IV} \rightarrow L_{II}$	4
ζ′	—	$O_{IV} \rightarrow L_{III}$	3
ζ	β_5	$O_V \rightarrow L_{III}$	
θ	γ_6	$O_{IV} \rightarrow L_{II}$	2
ϵ	l	$M_I \rightarrow L_{III}$	3
η	η	$M_I \rightarrow L_{II}$	1
φ′	β_4	$M_{II} \rightarrow L_I$	2
φ	β_3	$M_{III} \rightarrow L_I$	3
χ′	γ_2	$N_{II} \rightarrow L_I$	1
χ	γ_3	$N_{III} \rightarrow L_I$	1
ψ′	—	$O_{II} \rightarrow L_I$	1
ψ	γ_4	$O_{III} \rightarrow L_I$	

Our nomenclature agrees with that of Moseley, so far as his lines reach (he had measured and named only the lines α, β, γ, δ, ψ), and is intended to extend it systematically by following on with the successive letters at the end and the beginning of the Greek alphabet. Siegbahn's nomenclature is at present in general use and has some practical advantages; it distinguishes three groups of lines which may be approximately separated in hardness, namely a soft α-group, a medium β-group and a harder γ-group, the degree of hardness and softness of course changing from element to element as the atomic

number changes. Siegbahn numbers the lines within each group according to their intensity. The intensities are understood in the relative sense and relate to the heavy elements; they claim to give only average estimates.

In contrast with the first two columns the third column gives a *rational* nomenclature to the lines. It is not much more cumbersome than the two other methods and is free from arbitrariness. It therefore seems to be destined to supersede both Siegbahn's and the author's nomenclature. The position of affairs here is similar to that in the spectroscopy of the visible region. The arbitrary names given to the absorption lines by Fraunhofer are not much used nowadays; rather, it has been found necessary to characterise each line by its series relationships (cf. Chap. VII). Correspondingly we say in the X-ray region, instead of $K\alpha$, $L\beta$, . . ., $L_{III} \rightarrow K$, $M_{IV} \rightarrow L_{II}$, . . . or $K - L_{III}$, $L_{II} - M_{IV}$, ... It must be admitted that this nomenclature presupposes that we have finally succeeded in interpreting the lines. Until this has been achieved we shall have to make use of Siegbahn's notation for experimental purposes and to our own notation of the Moseley type for theoretical considerations.

The order of the lines in Table 14 does not correspond throughout with the order of the hardness of the lines; α is certainly always softer than β and γ softer than δ, but β is not softer than γ in the case of all elements. The softest line in the case of all elements is ϵ (discovered by Siegbahn and denoted by l). The lines β, γ, and ψ overlap in numerous places. Further peculiarities can be read off from Fig. 59.

Concerning the origin of the lines the following details are expressed in Table 14: the line $L\alpha$ corresponds, as already shown in Fig. 53 and 54 to the transition of an electron from the M- to the L-shell, the line $L\gamma$ to the transition from the N- to the L-shell. But it now becomes necessary to sub-divide these shells still further. Even in Table 11 of the preceding section we distinguish two L-shells, L_{II} and L_{III}. It now becomes necessary to assume still another shell, the third, namely L_I. In the case of the M-shell we have to distinguish five such steps, which we denote by M_I, M_{II}, . . . M_V. The N-shell is analogous and must be divided into seven steps. The experimental reasons for this sub-division are left over for discussion in the next section.

As the brackets in the first column of Table 14 (to the right of the notation for the lines) indicate, the pairs of lines ($\alpha'\beta$), ($\gamma'\delta$), ($\zeta'\theta$), ($\epsilon\eta$) belong together and form doublets. We call them **L-doublets**; they are denoted by successive letters of the Greek alphabet. Their characteristic feature is: both lines of an L-doublet have the **same initial level**; the softer line ends in the L_{III}**-level**, the harder line in the L_{II}**-level.**

We shall call the pairs of lines ($\alpha'\alpha$) and ($\phi'\phi$) **M-doublets** because the lines associated together in them have the *same L-level as final*

level but different M-levels as initial levels. For a corresponding reason the pairs of lines ($\gamma'\gamma$) and ($\chi'\chi$) are called **N-doublets.** We are led to conjecture that the lines ζ and ψ are, analogously, unresolved pairs of lines which we call O-doublets. The M-, N- and O-doublets have been indicated as such by brackets on the left of the symbols in Table 14. The symbol for the softer doublet line is distinguished from that for the harder line only by an accent. In contrast with the L-doublet we find that in the case of the M-doublet ($\alpha'\alpha$) and the N-doublet ($\gamma'\gamma$) the softer component is the weaker component. In the case of the doublets ($\phi'\phi$), ($\chi'\chi$) and ($\psi'\psi$) which have the same final level L_I (letters taken from the end of the Greek alphabet), the softer component of the doublet is only inappreciably if at all weaker than the harder component.

In Table 15 we give the measurements of Siegbahn and Thoraeus for the L-lines of the lighter elements V 23 to Br 35, in terms of Ångström units. That the lines $\alpha\alpha'$ could not be separated is not surprising. It is noteworthy that the lines γ and δ, which come from the N-shell (cf. Table 14) are not yet represented. The reason for this is clearly that the N-shell in the case of these elements is either incompletely developed or not at all. A series of weak companions, that are observed here, are omitted (cf. § 7).

TABLE 15

Wave-lengths of the L*-series of the lighter elements (in* Å.U.)

Z	α', α	β	ϵ	η	$\phi'\phi$	Z
23 V	24·2	—	—	—	—	23 V
24 Cr	21·53	21·19	—	—	—	24 Cr
25 Mn	19·39	19·04	—	—	—	25 Mn
26 Fe	17·58	17·22	20·12	19·65	15·61	26 Fe
27 Co	15·94	15·62	18·20	17·77	—	27 Co
28 Ni	14·528	14·235	16·55	16·17	13·14	28 Ni
29 Cu	13·308	13·029	15·19	14·83	12·10	29 Cu
30 Zn	12·224	11·958	13·95	13·61	11·16	30 Zn
32 Ge	10·414	10·152	11·920	11·585	—	32 Ge
33 As	9·650	9·394	11·047	10·710	8·911	33 As
34 Se	8·971	8·717	10·271	9·234	—	34 Se
35 Br	8·357	8·108	9·563	9·939	—	35 Br

Millikan and Bowen * have launched into the region of extremely soft X-rays ; not, however, from the direction of X-rays but from that of ultra-violet spectra. They did not make their observations with a crystal lattice but with an artificial ruled grating, the construction of which had to be specially developed, and with a highly condensed

* Astrophys. Journ., **52,** 47 and 286 (1920) ; **53,** 150 (1921) ; Phil. Mag., VII, **4,** 561 (1927).

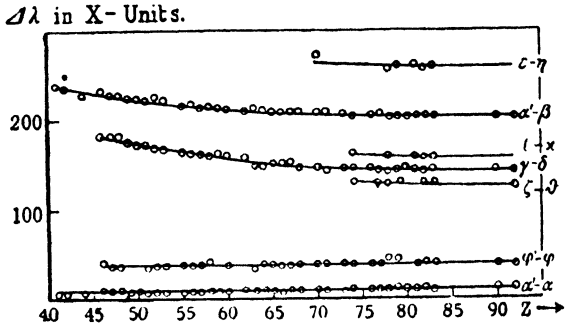


FIG. 58.—Approximate constancy of $\Delta\lambda$ for the L-doublets.

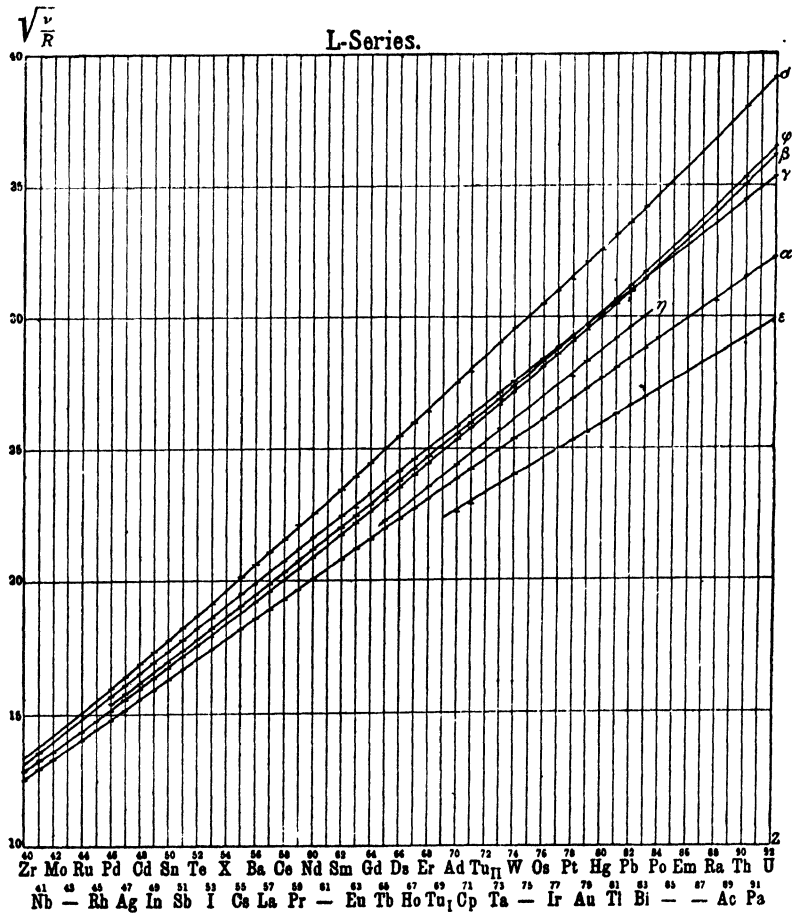


FIG. 59.—Regular course of the $\sqrt{\nu/R}$ values for the L-series. $\sqrt{\nu/R}$ is a very nearly linear function of Z.

TABLE 16. *Wave-lengths of the*

Z	α′	α	β	γ	δ	ζ	θ	ε
37 Rb	—	7302·7	7060·4	—	—	—	—	—
38 Sr	—	6847·8	6609·2	—	—	—	—	7821
39 Yt	—	6434·9	6198·4	—	—	—	—	—
40 Zr	—	6055·9	5822·8	5573·4	5373·0	—	—	6898
41 Nb	5717	5711·3	5479·6	5225·3	5024·1	—	—	6509
42 Mo	5400	5394·3	5165·8	4909·2	4711·1	—	—	—
44 Ru	4838·67	4835·67	4611·00	4361·9	4172·82	—	—	—
45 Rh	4595·56	4587·78	4364·00	4122·1	3935·7	—	—	5207·0
46 Pd	4366·60	4358·50	4137·30	3900·7	3716·36	—	—	4939·6
47 Ag	4153·82	4145·64	3926·64	3693·83	3514·85	—	—	4697·6
48 Cd	3956·36	3947·82	3730·08	3506·4	3328·00	—	—	4471·3
49 In	3772·42	3763·67	3547·83	3331·2	3155·29	—	—	4259·3
50 Sn	3601·08	3592·18	3377·92	3167·9	2994·93	—	—	4063·3
51 Sb	3440·75	3431·77	3218·36	3016·6	2845·07	—	—	3880·3
52 Te	3291·00	3281·99	3069·97	2876·1	2706·47	—	—	3710·1
53 I	3150·87	3141·66	2930·93	2746·08	2577·48	—	—	—
55 Cs	2895·60	2886·10	2677·84	2506·4	2342·52	—	—	—
56 Ba	2779·02	2769·64	2562·24	2399·3	2236·60	—	—	3128·7
57 La	2668·93	2659·68	2453·30	2298·0	2137·20	—	—	3000
58 Ce	2565·11	2556·00	2351·00	2204·1	2044·33	—	—	—
59 Pr	2467·63	2457·70	2253·90	2114·8	1956·81	—	—	2778·1
60 Nd	2375·63	2365·31	2162·21	2031·4	1873·83	—	—	2670·3
62 Sm	2205·68	2195·01	1993·57	1878·1	1723·09	—	—	2477·0
63 Eu	2127·33	2116·33	1916·31	1808·2	1654·3	—	—	2390·3
64 Gd	2052·62	2041·93	1842·46	1741·9	1558·63	—	—	2307·1
65 Tb	1982·31	1971·49	1772·68	1679·0	1526·6	—	—	2229·0
66 Dy	1915·64	1904·60	1706·58	1619·8	1469·27	—	—	2154·0
67 Ho	1852·06	1840·98	1643·52	1563·7	1414·2	—	—	2082·1
68 Er	1791·40	1780·40	1583·44	1510·6	1362·3	—	—	2015·1
69 Tu	1733·9	1722·8	1526·8	1460·2	1312·7	—	—	1951·1
70 Yb	1678·9	1667·79	1472·5	1412·8	1264·8	—	—	1890·0
71 Lu	1626·36	1615·51	1420·7	1367·2	1220·3	—	—	1831·8
72 Hf	1577·04	1566·07	1371·1	1323·5	1176·5	—	—	1777·4
73 Ta	1529·8	1518·85	1324·23	1281·90	1135·58	1250·6	1110·0	1724·2
74 W	1484·38	1473·36	1279·17	1242·03	1096·30	1212·5	1072·0	1675·0
75 Re	—	1429·88	1236·04	1204·1	—	—	—	—
76 Os	1398·2	1388·16	1194·59	1168·38	1022·47	1140	—	—
77 Ir	1359·8	1348·47	1155·40	1132·97	988·76	1103·0	963·6	—
78 Pt	1321·55	1310·33	1117·58	1099·74	955·99	1070·1	931·7	1497·23
79 Au	1285·02	1273·77	1081·28	1068·01	924·61	1038·2	901·25	1456·54
80 Hg	1249·7	1238·63	1046·52	1037·70	894·6	1007·8	—	1418·3
81 Tl	1216·03	1204·93	1012·99	1008·22	865·71	978·3	841·7	—
82 Pb	1183·52	1172·58	980·83	979·90	838·01	949·52	813·70	1346·62
83 Bi	1153·3	1141·50	950·02	953·24	811·43	922·3	787·4	1312·95
90 Th	965·24	954·05	763·56	791·92	651·76	762·59	630·1	1112·41
92 U	920·14	908·74	718·51	753·07	613·59	724·13	592·6	1064·77

" vacuum spark." The L-series is followed from Al (Z = 13) downwards to its entrance into the optical spectrum of Li (Z = 3).

Table 16 contains precision measurements (given in X-units) for the heavy elements ; only the lines which are more important for the method of classification are tabulated. Here we see a first characteristic feature of our doublets. We calculate the differences $\Delta\lambda$ of

L-*series* (*in* X-*units*)

η	ϕ'	ϕ	χ'	χ	ψ	L_I	L_{II}	L_{III}	Z
8029·0	6802·8	6769·9	6028·2		—	5985·4	—	6841·3	37 Rb
7505	6385·5	6349·9	5629·4		—	5571·4	6162·1	6362·0	38 Sr
—	6001·9	5967·9	—		—	5221·6	5737·3	5944·4	39 Yt
6593·1	5652·7	5618·2	4941·2		—	4857·4	5365·9	5561·0	40 Zr
6195	5331·4	5295·9	4639		—	4571·7	—	5212·1	41 Nb
5835	5035·8	5000·2	4361·3		—	4289·7	4712·0	4904·2	42 Mo
—	4512·6	4476·4	3887·9		—	—	4164·8	4357·7	44 Ru
4911·2	4277·8	4241·3	3677·0		—	3620·8	3931·5	4118·4	45 Rh
4650·2	4062·3	4025·7	3480·9		—	—	—	—	46 Pd
4410·1	3861·1	3824·45	3299·7		—	3244·8	3506·2	3693·0	47 Ag
4187·5	3674·25	3636·42	3131·6		—	3070·9	3321·8	3495·3	48 Cd
3976·1	3499·0	3461·9	2973·6		2919·1	2919·4	3139·5	3315·5	49 In
3781·8	3336·3	3298·9	3827·3		2771·3	2769·6	2972·3	3149·3	50 Sn
3599·6	3184·3	3145·14	2688·9		2633·6	2631·7	2821·9	2990·7	51 Sb
—	3040·0	3001·3	2564·9		2505·7	2503·9	2679·3	2845·7	52 Te
—	2906	2867	—	—	—	2383·9	2547·5	2713·9	53 I
2983·3	2660·5	2622·93	2232·2	2227·0	2169·1	—	2307·5	2467·4	55 Cs
2857·1	2549·8	2511·0	2134·0	2129·5	2071·5	2062·0	2199·3	2356·8	56 Ba
2734	2443·8	2405·3	2041·6	2036·5	1978·7	1968·9	2098·9	2253·7	57 La
2614·7	2344·2	2305·9	1955·9	1950·9	1895·2	1885·6	2006·7	2159·7	58 Ce
2507	2250·1	2212·4	1875·0	1869·9	1815·3	1807·1	1920·1	2072·8	59 Pr
2404·2	2162·2	2122·2	1797·4	1792·5	1740·8	1731·7	1839·1	1990·7	60 Nd
2214	1996·4	1958·0	1655·9	1651·7	1603·3	1595·4	1699·1	1840·8	62 Sm
—	1922·1	1882·7	1593·9	1587·7	—	1533·3	1622·8	1771·7	63 Eu
—	1849·3	1810·9	1531·0	1525·9	1481·8	1474·0	1558·7	1706·2	64 Gd
—	1781·4	1742·5	1473·8	1468·3	1423·9	1418·1	1498·1	1645·3	65 Tb
1892·2	1716·7	1677·7	1420·3	1413·9	1371·4	1364·8	1441·4	1587·0	66 Dy
1822·0	1655·3	1616·0	1367·7	1361·3	1319·7	1314·6	1386·9	1532·2	67 Ho
1754·8	1596·4	1557·9	1318·4	1311·8	1273·2	1266·0	1334·9	1479·6	68·Er
1692·3	1541·2	1502·3	1271·2	1265·3	1226·4	1219·6	1284·9	1429·9	69 Tu
1631·0	1488·2	1449·4	1225·6	1219·8	1182·0	1176·5	1239·2	1382·4	70 Yb
1573·8	1437·2	1398·2	1183·2	1177·5	1141·0	1136·2	1194·5	1337·7	71 Lu
1519·7	1389·3	1349·7	1141·3	1135·6	1100·1	1095·3	1151·5	1293·0	72 Hf
1465·5	1343·1	1304·1	1102·9	1097·1	1062·4	1057	1110·2	1251·7	73 Ta
1418·1	1298·79	1259·92	1065·88	1059·87	1025·8	1020·5	1071·3	1211·6	74 W
—	—	—	—	—	—	—	—	—	75 Re
—	1215·0	1177·2	—	—	—	—	—	—	76 Os
—	1176·4	1137·9	963·6	956·6	—	—	—	—	77 Ir
1240·1	1139·8	1099·50	931·7	925·6	895·0	—	—	—	78 Pt
1199·5	1104·4	—	901·25	895·68	866·3	—	—	—	79 Au
1161·9	1068·6	1030·1	869·5		834·8	—	—	—	80 Hg
1125	1037·1	997·8	844·7	837·9	810·0	—	—	—	81 Tl
1090·2	1004·69	966·02	818·2	813·70	783·6	—	—	—	82 Pb
1057	975·4	935·7	792·9	787·4	761	—	—	—	83 Bi
—	789	752·1	—	—	—	—	—	—	90 Th
802·9	745·4	708·4	604·4	597·0	—	—	—	—	92 U

the wave-lengths of two associated doublet lines in each case. We then find that for the whole series of elements associated doublet lines have *very nearly equal wave-length differences* $\Delta\lambda$. Expressed more accurately, we bracket together as doublets such lines and only such lines as have nearly *equal distances between their wave-lengths.*

Let us consider Fig. 58. Here we have tabulated in the first place

TABLE 17.

Z	α′	α	β	γ	δ	ζ	θ
37 Rb	—	124·79	129·07	—	—	—	—
38 Sr	—	133·07	137·88	—	—	—	—
39 Yt	—	141·61	147·02	—	—	—	—
40 Zr	—	150·48	156·50	163·50	169·60	—	—
41 Nb	159·4	159·56	166·30	174·40	181·38	—	—
42 Mo	168·7	168·93	176·40	185·62	193·43	—	—
44 Ru	188·14	188·45	197·63	208·92	218·38	—	—
45 Rh	198·29	198·63	208·82	221·07	231·54	—	—
46 Pd	208·69	209·08	220·26	233·62	245·20	—	—
47 Ag	219·38	219·81	232·07	246·70	259·26	—	—
48 Cd	230·33	230·83	244·30	259·89	273·82	—	—
49 In	241·56	242·12	256·85	273·56	288·81	—	—
50 Sn	253·05	253·68	269·77	287·66	304·27	—	—
51 Sb	264·85	265·54	283·15	302·09	320·30	—	—
52 Te	276·83	277·66	296·83	316·84	336·70	—	—
53 I	289·21	290·05	310·91	331·87	353·55	—	—
55 Cs	314·71	315·74	340·30	363·58	389·01	—	—
56 Ba	327·91	329·02	355·65	379·81	407·44	—	—
57 La	341·44	342·62	371·45	396·55	426·38	—	—
58 Ce	355·26	356·52	387·31	413·44	445·75	—	—
59 Pr	369·29	370·78	404·31	430·90	465·69	—	—
60 Nd	383·59	385·26	421·45	448·59	486·31	—	—
62 Sm	413·15	415·16	457·10	485·21	528·86	—	—
63 Eu	428·36	430·59	475·53	503·97	550·85	—	—
64 Gd	443·95	446·28	494·59	523·15	573·62	—	—
65 Tb	459·70	462·22	514·06	542·75	596·93	—	—
66 Dy	475·70	478·46	533·94	562·58	620·04	—	—
67 Ho	492·03	494·99	554·46	582·77	644·37	—	—
68 Er	508·69	511·83	575·50	603·25	668·92	—	—
69 Tu	525·57	528·93	596·84	624·10	694·23	—	—
70 Yb	542·78	546·39	618·86	645·01	720·49	—	—
71 Lu	560·31	564·08	641·42	666·55	746·76	—	—
72 Hf	577·84	581·89	664·60	688·51	774·55	—	—
73 Ta	595·69	599·97	688·15	710·88	802·47	728·65	820·98
74 W	613·90	618·50	712·39	733·70	831·22	751·56	850·07
75 Re	—	637·305	737·249	756·81	—	—	—
76 Os	651·75	656·45	762·83	780·58	891·25	799·6	—
77 Ir	670·17	675·78	788·70	804·32	921·63	826·18	945·6
78 Pt	689·55	695·45	815·40	828·63	953·22	851·57	978·07
79 Au	709·15	715·41	842·77	853·24	985·57	877·70	1011·12
80 Hg	729·19	735·71	877·76	878·16	1018·64	904·22	—
81 Tl	749·39	756·29	899·59	903·84	1052·62	931·4	1082·6
82 Pb	769·96	777·15	929·08	929·98	1087·42	959·72	1119·97
83 Bi	790·20	798·31	959·22	955·97	1123·04	987·98	1157·5
90 Th	944·08	955·16	1193·45	1150·71	1398·16	1194·94	1446·2
92 U	990·37	1002·78	1268·28	1210·07	1485·15	1258·43	1537·7

our L-doublets $(\epsilon\eta)$, $(\alpha'\beta)$, $(\gamma'\delta)$, $\zeta\theta$. The curve $\epsilon - \eta$ lies highest, the curve $\alpha' - \beta$ below it, and so forth in the order of sequence of the hardness of the pairs of lines. But within each curve the $\Delta\lambda$'s are nearly constant for the whole range from Z = 40 to Z = 92 (along the x-axis), with a slight drop as we pass from lower to higher atomic numbers. The $\Delta\lambda$'s of our M-doublets $(\alpha'\alpha)$ and $(\phi'\phi)$ are at the lower end of the figure still more constant.

ν/R-values of the L*-series*

ε	η	φ′	φ	χ′	χ	ψ	Z
—	113·50	133·96	134·61	151·17		—	37 Rb
116·5	121·4	142·71	143·51	161·88		—	38 Sr
—	—	151·83	152·70	—		—	39 Yt
132·1	138·22	161·21	162·20	184·42		—	40 Zr
140·0	147·1	170·93	172·07	196·4		—	41 Nb
—	156·1	180·96	182·25	208·94		—	42 Mo
—	—	201·94	203·57	234·39		—	44 Ru
175·01	185·55	213·02	214·86	247·83		—	45 Rh
184·48	195·96	224·32	226·36	261·79		—	46 Pd
193·99	206·63	236·01	238·27	276·17		—	47 Ag
203·80	217·62	248·02	250·59	290·99		—	48 Cd
213·95	229·19	260·44	263·22	306·45		312·17	49 In
224·27	240·96	273·14	276·23	322·31		328·82	50 Sn
234·85	253·16	286·18	289·74	338·90		346·02	51 Sb
245·62	—	299·76	303·63	355·26		363·68	52 Te
—	—	313·5	317·8	—	—	—	53 I
—	305·46	342·52	347·42	408·24	409·19	420·11	55 Cs
291·26	318·95	357·39	362·91	427·02	427·93	439·91	56 Ba
303·7	333·3	372·89	378·86	446·35	447·45	460·54	57 La
—	348·52	388·73	395·19	465·91	467·10	480·83	58 Ce
328·02	363·4	404·99	411·89	486·01	487·34	501·99	59 Pr
341·26	379·03	421·44	429·40	506·99	508·38	523·48	60 Nd
367·89	411·5	456·46	465·41	550·32	551·72	568·37	62 Sm
381·24	—	474·10	484·02	571·72	573·96	—	63 Eu
394·99	—	492·76	503·21	595·21	597·20	614·98	64 Gd
408·82	—	511·55	522·97	618·31	620·63	639·98	65 Tb
423·06	481·59	530·83	543·17	641·60	644·51	664·48	66 Dy
437·67	500·15	550·52	563·90	666·28	669·41	690·5	67 Ho
452·22	519·30	570·83	584·93	691·19	694·67	715·73	68 Er
467·05	538·49	591·26	606·60	716·83	720·22	743·03	69 Tu
482·15	558·72	612·33	628·72	743·53	747·07	770·96	70 Yb
497·47	579·01	634·06	651·75	770·17	773·90	798·59	71 Lu
512·70	599·66	655·91	675·20	798·46	802·48	827·68	72 Hf
528·50	621·83	678·50	698·78	826·26	830·65	857·74	73 Ta
544·05	642·60	701·63	723·27	854·94	859·80	888·35	74 W
—	—	—	—	—	—	—	75 Re
—	—	748·25	774·08	—	—	—	76 Os
—	—	774·62	800·82	945·6	952·6	—	77 Ir
608·64	734·82	799·52	828·80	978·07	984·52	1018·17	78 Pt
625·63	759·97	825·15	—	1011·12	1017·41	1051·8	79 Au
642·50	784·29	852·77	884·6	1048·0	—	1091·6	80 Hg
—	810·3	878·64	913·2	1078·8	1087·5	1125·0	81 Tl
676·70	835·90	907·01	943·3	1113·8	1119·9	1162·8	82 Pb
694·07	862·3	934·22	973·8	1149·2	1157·5	1196·8	83 Bi
819·19	—	1155·0	1211·6	—	—	—	90 Th
855·84	1134·9	1222·5	1286·2	1507·8	1526·4	—	92 U

We pass from the values of the λ's to the values of ν/R and first exhibit a graphical representation (Fig. 59) of the values of $\sqrt{\nu/R}$, similar to that of Fig. 57. To prevent confusion in the figure we show only the lines α, β, γ, δ, ϵ, η, ϕ. We have again plotted the atomic numbers along the x-axis. In this case, too, the course of the graphs is essentially *straight*, which indicates that ν increases approximately in proportion to Z^2. The deviations from linearity are, however,

more marked than before, particularly in the case of the line δ; they are connected with the "relativity correction" mentioned on page 213. Moreover, we see in the figure the overlapping which was referred to earlier and which was absent in the case of the K-series: the line β cuts the line γ at Pb, Z = 82; beyond 82 it is harder than γ, below 82 it is softer than γ. Moreover ϕ and γ cut at Pt, Z = 78. From this we see that the relationships between the lines are not as simple and rigorous here as in the case of the lines of the K-series.

In Table 17 we exhibit the ν/R-values corresponding to the precision measurements of Table 16. This brings to light a new relationship characteristic of doublets. We calculate the differences $\Delta\nu/R$ but not now for the same doublet of *different* elements but for *different* L-*doublets of the same element;* these L-doublets have, within the limit of error, the same *wave-number difference* $\Delta\nu/R$:

$$\beta - \alpha' = \delta - \gamma = \theta - \zeta = \eta - \epsilon.$$

These values of $\beta - \alpha'$, $\delta - \gamma$, and so forth have been inserted in Table 18; inspection will show that they agree appreciably; it will also be found that the values of $\beta - \alpha$ deviate appreciably more from the other doublet differences than those of $\beta - \alpha'$. In this way we establish that the β-line, the second strongest line of the L-series, does not form the characteristic doublet difference with α, the strongest line, but with its weak satellite α'. We may add that the same phenomenon will also be found later to occur in the visible region (cf. Chap. VIII), where we deal with the so-called "composite doublets": in this case, too, the weak satellite of the principal line and not the principal line itself forms the doublet with a second line.

The γ-line also has a weak satellite, which we have denoted by γ' in Table 14. To be accurate we must measure the doublet difference not between δ and γ but between δ and γ'. But since γ' is separated from γ only in the case of a few elements * we have inserted $\delta - \gamma$ in the above equations instead of the more exact $\delta - \gamma'$. The same holds for $\theta - \zeta$, which should really be replaced by $\theta - \zeta'$ (cf. Table 14). In the fourth-, third- and second-to-last column of Table 18 we have noted down the M- and N-doublets $\alpha - \alpha'$, $\phi - \phi'$, $\chi - \chi'$. They are related neither among themselves nor to the L-doublet separation.

In the last column of Table 18 we have given the fourth roots of the characteristic L-doublet difference $\Delta\nu/R = \beta - \alpha'$. These form, as we easily see, an arithmetic series. As Z increases the numbers in this row increase by a constant amount of about 0·043. The particular point of this fact which we have here established empirically will be dealt with at the end of the section. The fourth roots of the M- and N-doublet-separations also increase linearly with Z.

The law of constant wave-number differences is now immediately

* Allison, Phys. Rev., **34**, 176 (1929).

TABLE 18

$\Delta\nu$/R-values of the L-series

Z.	$\beta-\alpha$.	$\beta-\alpha'$.	$\delta-\gamma$.	$\theta-\zeta$.	$\eta-\epsilon$.	$L_{II}-L_{III}$.	$\alpha-\alpha'$.	$\phi-\phi'$.	$\chi-\chi'$.	$\sqrt[4]{\beta-\alpha'}$.
37 Rb	4·28	—	—	—	—	—	—	0·65	—	—
38 Sr	4·81	—	—	—	4·9	4·64	—	0·80	—	—
39 Yt	5·41	—	—	—	—	5·54	—	0·87	—	—
40 Zr	6·02	—	6·10	—	6·1	5·96	—	0·99	—	—
41 Nb	6·74	6·90	6·98	—	7·1	—	0·16	1·14	—	1·622
42 Mo	7·47	7·7	7·81	—	—	7·58	0·2	1·29	—	1·666
44 Ru	9·18	9·49	9·46	—	—	9·58	0·31	1·63	—	1·755
45 Rh	10·19	10·53	10·47	—	10·54	10·52	0·34	1·84	—	1·802
46 Pd	11·18	11·57	11·58	—	11·48	11·65	0·39	2·04	—	1·849
47 Ag	12·26	12·69	12·56	—	12·64	12·93	0·43	2·26	—	1·887
48 Cd	13·47	13·97	13·93	—	13·82	13·91	0·50	2·57	—	1·933
49 In	14·73	15·29	15·25	—	15·24	15·41	0·56	2·78	—	1·977
50 Sn	16·09	16·72	16·61	—	16·69	17·23	0·63	3·09	—	2·022
51 Sb	17·61	18·30	18·21	—	18·31	18·2	0·69	3·56	—	2·068
52 Te	19·17	20·00	19·86	—	—	19·9	0·83	3·87	—	2·115
53 I	20·86	21·70	21·68	—	—	21·9	0·84	4·3	—	2·158
55 Cs	24·56	25·59	25·43	—	—	26·9	1·03	4·90	0·95	2·249
56 Ba	26·63	27·74	27·63	—	27·69	28·00	1·11	5·52	0·91	2·294
57 La	28·83	30·01	29·83	—	29·6	29·4	1·18	5·97	1·10	2·341
58 Ce	30·79	32·05	32·31	—	—	32·5	1·26	6·46	1·19	2·379
59 Pr	33·53	35·02	34·79	—	35·4	35·24	1·49	6·90	1·33	2·433
60 Nd	36·19	37·86	37·72	—	37·77	38·04	1·67	7·96	1·39	2·481
62 Sm	41·94	43·95	43·65	—	43·6	43·9	2·01	8·95	1·40	2·575
63 Eu	44·94	47·17	46·88	—	—	47·1	2·23	9·92	2·24	2·621
64 Gd	48·31	50·64	50·47	—	—	50·56	2·33	10·45	1·99	2·668
65 Tb	51·84	54·36	54·18	—	—	—	2·52	11·42	2·32	2·715
66 Dy	55·48	58·24	57·46	—	58·53	58·01	2·76	12·34	2·91	2·763
67 Ho	59·47	62·43	61·60	—	62·48	—	2·96	13·38	3·13	2·811
68 Er	63·67	66·81	65·67	—	67·08	66·77	3·14	14·10	3·48	2·859
69 Tu	67·91	71·27	70·13	—	71·44	71·92	3·36	15·34	3·39	2·912
70 Yb	72·47	76·08	75·48	—	76·57	74·50	3·61	16·39	3·54	2·953
71 Lu	77·34	81·11	80·24	—	81·54	81·63	3·77	17·69	3·73	3·001
72 Hf	82·71	86·76	86·04	—	86·90	86·60	4·05	19·29	4·02	3·052
73 Ta	88·18	92·46	91·59	92·33	93·33	92·3	4·28	20·28	4·39	3·101
74 W	93·89	98·49	97·52	98·51	98·55	98·71	4·60	21·64	4·86	3·150
75 Re	99·944	104·84	103·76	105·29	104·88	—	—	—	—	3·200
76 Os	106·38	111·08	110·67	—	—	111·9	4·70	25·83	—	3·246
77 Ir	112·92	118·53	117·31	119·42	—	118·6	5·61	26·20	7·0	3·286
78 Pt	119·95	125·85	124·59	126·50	126·18	126·3	5·90	29·28	6·45	3·349
79 Au	127·36	133·62	132·33	133·42	134·34	133·6	6·26	—	6·29	3·400
80 Hg	135·05	141·57	140·48	—	141·79	142·2	6·52	31·8	—	3·449
81 Tl	143·30	150·20	148·78	151·2	—	150·7	6·90	34·6	8·7	3·501
82 Pb	151·93	159·12	157·44	160·25	159·20	161·0	7·19	36·3	6·1	3·552
83 Bi	160·91	169·02	167·07	169·52	168·23	168·7	8·11	39·6	8·3	3·711
90 Th	238·29	249·37	247·45	251·26	—	250·0	11·08	56·6	—	3·974
92 U	265·50	277·91	275·08	279·27	279·1	276·6	12·41	63·7	18·6	4·083

clear if we call to mind the assumptions which we made in Table 14 about the origin of the lines; according to them two associated L-doublet lines should differ only in their final levels (L_{II} or L_{III}). Hence their wave-number differences become independent of the initial level of the transition in question and are represented by the fixed distance between the levels of the L_{II} and the L_{III}-shell.

But the electron cannot only pass from a higher level to the L_{III}-, L_{II}-shells, but it can also pass from the L_{II}-level to the lower K-level. Now in general the transition $L \rightarrow K$ denoted the line $K\alpha$. We now see that this line must be a *doublet* and we understand the origin of the line $K\alpha'$, which has already been hinted at in Table 11 on page 208 and which is explained in greater detail in Fig. 60. (For the description of the upper part of this figure see p. 226.) It is clear that the *doublet interval* $(\alpha'\alpha)$ *in the* K-*series must be equal to the doublet interval* $(\alpha'\beta)$ *in the* L-*series* and hence also equal to the remaining L-doublets $(\gamma'\delta)$, $(\epsilon\eta)$, $(\zeta\theta)$, all of them being measured of course as ν's or ν/R's. Actually, this interval is determined in all cases by the difference of energy between the L_{II} and the L_{III} levels of our figure. On the other hand, the interval between the lines $L\alpha$ and $L\beta$, which do not form a true L-doublet, is, when measured in wave-numbers, less than

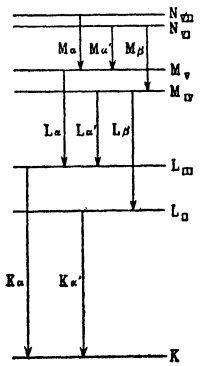


FIG. 60.—Diagrammatic representation of the origin of the most important K-, L- and M-lines.

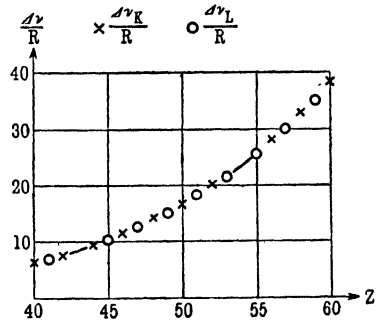


FIG. 61.—$\Delta\nu_K/R$ ($K\alpha\alpha'$, L-doublet of the K-series) and $\Delta\nu_L/R$ (L-doublet of the L-series) plotted between Zr (Z = 40) and Nd (Z = 60).

($L_{II}L_{III}$). With reference to the intensities we may note that the line $K\alpha'$ which starts from the energy-level L_{II} is weaker than the line $K\alpha$ which starts from the L_{III}-level, just as the line $L\beta$ which stretches to the L_{II}-level is weaker than the line $L\alpha$ which ends in the L_{III}-level. Hence as regards intensity $K\alpha'$ corresponds to the line $L\beta$ and $K\alpha$ to the line $L\alpha$. But with respect to hardness the relationship is reversed, as a glance at Fig. 60 shows ; this is because the L_{II}- and L_{III}-level respectively form the initial level for the K-lines but the final level for the L-series. Hence there is the following characteristic difference between the K- and the L-series ; *in the* K-*series the weaker* α'*-line is softer than the principal line* α (smaller interval in the figure), *whereas in the* L-*series the weaker* β*-line is harder than the principal line* α *or* α' (longer arrow).

This qualitative theoretical deduction agrees fully with the observed facts. Moreover, even the quantitative deduction of the

equality of the doublet ($\alpha'\alpha$) in the K-series with the "L-doublet" in the L-series is completely confirmed by the measurements.

We show this in Fig. 61. It contains all the elements (from Z = 40 to Z = 60) for which the measurements of the K-series and those of the L-series overlap. The values of $\Delta\nu_K/R$, indicated by $\times$, are formed in accordance with Table 13 as the difference between the ν/R-values for Kα and Kα'; the values of $\Delta\nu_L/R$, represented by $\circ$, are taken from the fifth to last column of Table 18. To prevent confusion in the figure we have plotted the points $\Delta\nu_K/R$, $\Delta\nu_L/R$ alternately. For one and the same element the two points would fully coincide on the scale of our diagram.

From Table 12 we see that the K-doublet, or more correctly the L-doublet of the K-series, also obeys the law of approximately constant difference in wave-lengths. Actually the wave-length difference of K($\alpha'\alpha$) is uniformly equal to about 4 or 5 x-units throughout the whole series of elements.

We shall close these general considerations with some preliminary remarks leading up to the quantitative theory of X-ray doublets.

In dealing with Table 18 we remarked earlier that $\sqrt[4]{\Delta\nu/R}$ of the L-series increases by 0·043 for each unit increase of the atomic number. Hence we have a linear equation of the form

$$\sqrt[4]{\frac{\Delta\nu}{R}} = 0{\cdot}043(Z - s) \quad . \quad . \quad . \quad . \quad (1)$$

and we easily see from the last column of Table 18 that $s \sim 3{\cdot}5$.

If we raise each side to the fourth power and, for convenience, take out the factor 2^4 in the denominator, we obtain

$$\frac{\Delta\nu}{R} = \frac{5{\cdot}3 \,.\, 10^{-5}}{2^4}(Z - 3{\cdot}5)^4 \quad . \quad . \quad . \quad (2)$$

This law leads us far into the mechanics of the interior of the atom, as we shall see in Chapter V. *Whereas according to Moseley the wave-numbers advance as the square of the atomic numbers, the differences in the wave-numbers of the doublet components are proportional to the fourth power of the atomic number.* This not only holds, as shown here, for the L-doublets, but also for all analogous doublets, for example, for the M-doublet ($\alpha'\alpha$) of the L-series. In the latter case we have only to replace the denominator 2^4 by $2{\cdot}3^4$ and the number 3·5 by a greater number which is to be empirically determined. The law that $\Delta\lambda$ is very nearly constant for all such doublets now follows directly from eqn. (1) and Moseley's law. For we have

$$\lambda = \frac{1}{\nu}, \quad |\Delta\lambda| = \frac{\Delta\nu}{\nu^2}.$$

Since $\Delta\lambda$ is here the quotient of a biquadratic and the square of a quadratic function of Z, it becomes appreciably independent of Z, particularly for greater values of Z.

We append a few remarks about the M-series; for the results of observation and the manner in which they have been sifted we refer the reader to the article by Lindh quoted on page 186.

The two strongest lines of the M-series are called $M\alpha$, $M\beta$. On the side of the softer rays $M\alpha$ has a weak satellite $M\alpha'$. The origin of these lines is: $M\alpha = N_{VII} \rightarrow M_V$, $M\alpha' = N_{VI} \rightarrow M_V$, $M\beta = N_{VI} \rightarrow M_{IV}$. But, particularly in the case of the heavier elements, we know of another sequence of lines of the M-series, which correspond to the transitions $N \rightarrow M$ or $O \rightarrow M$.

To explain the mutual relationship between the L- and the M-series we find the following remark by R. Swinne * of particular interest: *The difference $\beta - \alpha'$ in the* M*-series is equal to the difference $\alpha - \alpha'$ in the* L*-series. Hence we find the same relationship between the* M- *and the* L*-series as previously between the* L- *and the* K*-series* (cf. Fig. 60). Our notation is chosen so that it also exhibits this relationship explicitly. For we have

$$(\alpha'\beta)_M = (\alpha'\alpha)_L$$

fully analogously to

$$(\alpha'\beta)_L = (\alpha'\alpha)_K.$$

And, as we see from Fig. 60, the same characteristic inversion of hardness and intensity occurs in this case as above between the corresponding lines in the L- and the K-series: *whereas in the* M*-series the weaker line β lies on the harder side of α, in the* L*-series the weaker line α' lies on the softer side of the principal line α.*

Besides the "M-doublet" $(\alpha'\beta) = (M_V, M_{IV})$ there also occurs at various points of the M-series a second M-doublet, namely (M_{III}, M_{II}), which discloses its character of "regular doublet," like the L-doublet, by having a constant value for $\Delta\lambda$ in the series of elements and also the same value for $\Delta\nu$ for lines of one and the same element.

Isolated observations have also been made of the N- and the O-series, in particular by Hjalmar for the elements U, Th, Bi.

§ 6. Excitation and Absorption Limits. Regularities in the Absorption Coefficients

We must now deal more fully with the process of excitation of X-ray series which we have already described briefly in § 3. We there spoke of the *excitation limit* of the K-lines and understood this as standing for the minimum energy, which cathode rays must have

* Physik. Zeits., **17**, 485 (bottom), 1916. Swinne here compares the doublets $(\alpha'\alpha)_L$ and $(\alpha\beta)_M$. It was remarked by the author in Zeits. f. Phys., **1**, 135 (1920), that it is more exact and more logical to replace $(\alpha\beta)_M$ by $(\alpha'\beta)_M$.

to remove an electron from the K-shell to the periphery of the atom. In Fig. 54 this excitation limit of the K-series was represented by an energy-level which is higher than the energy-steps for Kα or Kβ or even Kγ. If we assign a wave-number K to it in accordance with the $h\nu$ law,* we have in comparison with the wave-numbers of the emission lines :

$$K > K\gamma > K\beta > K\alpha.$$

Hence the excitation limit measured in this way is the *series* limit to which the K-lines tend (cf. the dotted line in Fig. 54). This observation leads to several consequences. Let us make the potential V of a cathode ray tube increase to the value $eV_\alpha = hcK\alpha$ and inquire when the line Kα, characteristic for the anti-cathode material of the tube, is first emitted. It does not yet occur when the potential is V_α. We increase the potential to V_β ; neither Kβ nor Kα is yet emitted. Rather, we have to increase the potential up to the excitation limit $eV = hcK$ or beyond this value, and then we find that Kα, Kβ, Kγ appear simultaneously. This was confirmed experimentally by some careful experiments by Webster.† We follow E. Wagner in calling the difference between the wave-numbers K and Kα the Stokes transition (*Sprung*) for the line Kα and so link up with Barkla's term for the characteristic radiation, namely "*fluorescent radiation.*" The Stokes transition for Kβ is smaller than that for Kα, and for Kγ it is almost vanishingly small. Stokes' rule for visible fluorescence is confirmed almost without exception in the X-ray region. In the visible region where the conditions are simpler than in the X-ray region, apparent exceptions to Stokes' rule also occur occasionally.

The circumstances that surround the excitation of the L-series are still more interesting. In Fig. 54 we exhibited the excitation limit for the lines α, γ, . . . of the L-series. We shall give it the more accurate name L_{III}-limit. Regarded as a wave-number it gives us the series limit for the lines αγεζ, that is

$$L_{III} > L\zeta > L\gamma > L\alpha > L\epsilon.$$

In Fig. 60 we drew the energy-level L_{II} lower than the energy-level L_{III} ; the lines βδηθ that end in this level are harder than the doublet lines αγεζ assigned to them. To excite them it is necessary to raise an electron from the level L_{II} to the surface of the atom. The energy required for this is greater than that required for the L_{III}-level. The wave-number L_{II} defined by the $h\nu$-relationship becomes the series limit for the second doublet lines :

$$L_{II} > L\theta > L\delta > L\beta > L\eta.$$

* To be calculated from the excitation energy by dividing it by hc (cf. Note 1 on p. 205).

† Phys. Rev., **7**, 599 (1916).

Thus we have a *doublet of excitation limits for the* L*-series.* The assertion that the interval $L_{II} - L_{III}$ between these excitation limits for every element is equal to the L-doublet $\Delta\nu_L$ studied in the preceding section will shortly receive support from direct measurements.

We again infer: to excite the line $L\alpha$ it is not sufficient to apply the cathode ray energy equivalent to $L\alpha$; rather, it is necessary to raise the potential to the value given by $eV = hc\lambda_{III}$, and then all the lines $\alpha, \gamma, \epsilon, \zeta, \ldots$ of the L-series appear simultaneously, but not the line $\beta, \delta, \eta, \theta, \ldots$. *To excite the latter the cathode ray energy must be increased to the second excitation limit.* For energies between the first and the second excitation limit only the softer line of each L-doublet is produced. Precisely as in the K-series the excitation limit K coincides appreciably with the hardest K-line γ, so in the L-series the limits L_{III} and L_{II} coincide appreciably with the lines ζ and θ of the hardest doublet.

But there is still a third energy-level L_I below L_{II}, in which the lines $\phi\phi'$, $\chi\chi'$, $\psi\psi'$ end. These lines do not yet occur when the second excitation limit has been exceeded. The potential V has then to increase still further to a *third excitation limit*, given by the equation $eV = hcL_I$. Only then does the L-series become fully developed. We then have

$$L_I > L\psi > L\psi' > L\chi > L\chi' > L\phi > L\phi'.$$

All these assertions have been fully confirmed by careful measurements performed by Webster and Clark,* and Hoyt,† for Pt and W. In the case of W the three excitation limits are

L_{III}-limit	V = 10·2 kilo-volts.
L_{II}-limit	V = 11·6 ,,
L_I-limit	V = 12·0 ,,

By adjusting the potential to values around these figures it was possible to observe the appearance or disappearance of these lines, and their changes of intensity, partly by photographic means and partly by the method of the ionisation chamber. Hoyt regards the allocation of the following lines to the three given limits as beyond dispute:

L_{III}-limit	$\epsilon\alpha'\alpha\gamma\zeta$
L_{II}-limit	$\eta\beta\delta$
L_I-limit	$\phi'\phi\psi$

But what happens at the excitation limits to the incident energy E of the cathode rays? It is used to drive the K- or the L-electron to the periphery of the atom and hence becomes *absorbed.* On the other hand, what happens if we drive the electron out by means of

* D. L. Webster and H. Clark, Proc. Nat. Acad., **3**, 181 (1917); D. L. Webster, *ibid.*, **6**, 26 (1920). Cf. also the introductory paper by M. de Broglie, Journ. de Phys., **6**, 161 (1916).

† F. C. Hoyt, Proc. Nat. Acad., **6**, 639 (1920).

primary X-rays ? Its $h\nu$ becomes weakened by the same amount as the energy of the cathode rays.

But this means : *the excitation limits show themselves in the continuous X-ray spectrum as absorption limits.*

We shall give an illustrative example. Let the primary Röntgen radiation be that of a tube of about 40 kilovolts tension, that is, it is to have a continuous spectrum which is to extend to wave-lengths of 300 X-units (cf. p. 41). Let the matter receiving the radiation be a silver leaf. In the case of Ag (cf. Table 12, column second to end) the excitation voltage of the K-series is at the wave-length $\lambda_K = 485$ X-units. The softer portions of the incident spectrally resolved continuous spectrum $\lambda > \lambda_K$ are only slightly weakened as they undergo only a general absorption, which, moreover, decreases as the hardness increases. At $\lambda = \lambda_K$ a strong selective absorption suddenly occurs. This persists also for $\lambda < \lambda_K$ up to the limit of the continuous spectrum ; it gradually becomes less, corresponding to the uniform decrease of the absorptive power with the increase of hardness.

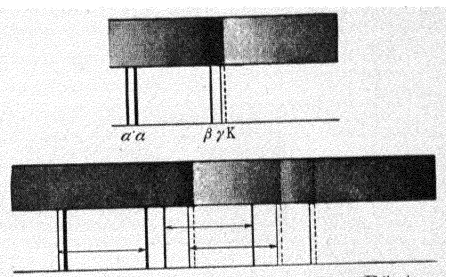


FIG. 62.– Absorption of continuous Röntgen light in a Ag-foil (below) and a Au-foil (below). The light which passes through the foil falls on a photographic plate, and the upper bands in the figure are diagrammatic representations of the pictures so obtained. Below them is shown the K-series of Ag and the L-series of Au. Strong selective absorption by the foil (small darkening of the plate by the light passing through) is exhibited at the excitation limits of the K- and L-series.

Fig. 62 exhibits these conditions as they appear on a photographic plate placed directly behind the Ag-leaf.* At the left half of the upper band, for $\lambda > \lambda_K$, the absorption is weak, that is the darkening of the plate is intense, and indeed the more intense the longer the wave-length, that is, it increases towards the left. At $\lambda = \lambda_K$ the selective absorption of the silver in the leaf comes into action. On the right side of the band the photographic plate is thus strongly screened by the Ag-leaf. We have at first a region of little darkening and then, as the hardness of the rays increases, a slow increase of the darkening, corresponding to a slow increase in the transparency of the Ag-leaf.

Similar results are found for the L-series. Let the matter through which the radiation is transmitted be, for example, a gold leaf. In

* We here disregard altogether the specific action of silver in the photographic layer, which partly reverses the action of the absorbing silver leaf. This action is illustrated in Fig. 63.

the case of Au the three L-absorption or excitation limits L_I, L_{II}, L_{III} are at $\lambda_{L_I} = 861$, $\lambda_{L_{II}} = 899$, $\lambda_{L_{III}} = 1038$ X-units.

Accordingly, a photographic plate which is placed behind the Au-leaf and of which the darkening is shown in Fig. 62 (lower half), exhibits intense darkening to the left of the first limit L_{III}; immediately to the right of this it appears very bright, on account of the selective absorption in the Au-leaf. The darkening increases slowly towards the light till it decreases suddenly at the second limit L_{II}, though less suddenly than at the limit L_{III}; at the third limit L_I a third weak brightening follows. With increasing hardness the darkening beyond L_I increases continuously.

Concerning Fig. 62, we have yet to remark that, towards the left in the upper part of the figure, the L-absorption limits, towards the right in the lower part of the figure the K-absorption limit, may be imagined to be added, but at a considerable distance away.

After the schematic Fig. 62 we consider in Fig. 63 a spectrum

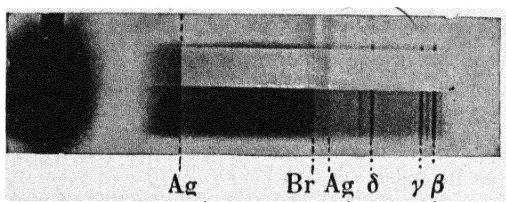


FIG. 63.—Rotating crystal photograph of the Röntgen spectrum of a W anticathode (L-series, β, γ, δ) in which the continuous spectrum of the anticathode forms a background. The spectrum was partly screened by an Al sheet 1·4 mm. thick (upper part of the figure). The Br-Ag layer of the photographic plate shows strong selective absorption of the Rontgen light: the first order K-limit of Ag is shown on the left and the second order on the right, the Br K-limit being in the middle. The Br limit is completely extinguished by the Al sheet, but not so the Ag limit.

that was photographed by E. Wagner * and J. Brentano, of a tungsten anticathode; in the lower part no absorbing layer was interposed, whereas in the upper part the radiation had been made to pass through an aluminium plate 1·4 mm. thick. The big spot on the left is the over-exposed point of intersection of the primary radiation with the photographic plate. A revolving crystal has spread out the wave-lengths in increasing order towards the right, that is, in the opposite direction to that in the schematic Fig. 62. At the right end of the lower part of the figure we see the comparatively soft L-lines of the tungsten anticathode marked out with extraordinary clearness on the weakly tinted background, which represents the continuous spectrum of the anticathode. The lines α and α' were too distant to be taken on the plate. The photographed lines are successively counted from

* Ann. d. Phys., **46**, 868 (1915). Cf. also the introductory papers by M. de Broglie, C.R., **157** (1913); **158** (1914).

right to left, ϕ', β, ϕ, γ, δ, χ; the three most intense lines β, γ, and δ have been made recognisable as such in the margin. In the upper part of the figure the softer L-lines and, for the greater part, also the continuous background has been extinguished by absorption in the aluminium sheet. If we follow the continuous spectrum towards the left, in the lower part of the figure, we come across several striking sharply defined absorption edges that here (namely, in the scale of wave-lengths) extend towards the left with decreasing darkening. What do these absorption edges in the lower part of the figure denote, in view of the fact that no absorbing medium intervenes ? They are due to the *photographic silver bromide layer*. The intense band on the left is the K-absorption edge of Ag and it is repeated in the weak band furthest to the right; the extended band between these is the K-absorption band of Br. Corresponding to its position in the natural system (Br, Z = 35; Ag, Z = 47) the Br-band is softer than the Ag-band. The former is entirely extinguished by the Al-sheet, whereas the latter is *not* absorbed either in the second order or in the first. Of course, actually, the Ag-band reflected in the second order has the same wave-length as that in the first order. This explains the circumstance, which at first sight seems paradoxical, that the Br-band is weakened more in its passage through the absorbing Al than the Ag-band of the second order, which, according to its position in the figure, seems softer, but which is in reality much harder. To conclude the description of this instructive figure we have now only to mention that the photographic darkening is dependent on the quantity of the absorbed energy. That is why the plate becomes dark, particularly where the wave-lengths absorbed selectively by the Ag or the Br strike it. The AgBr layer acts simultaneously as an absorber and as an indication of the absorbed energy, and its increased absorption is indicated by increased darkening. A bolometric or an ionisation measurement of the radiation transmitted by the AgBr layer would, on the other hand, indicate increased absorption by exhibiting a lessening of the energy.

The data concerning the absorption limits has been given for the K-series in Table 12 and for the L-series in Table 16.

The representation of the absorption edges in Table 16 by Roman numerals (I, II, III, . . . in the order of increasing wave-lengths) was introduced by Bohr and Coster. In contrast to this in the earlier editions of this book a representation by means of double suffixes was recommended which gave the theoretical quantum meaning of the energy steps concerned. The relation between the two methods of notation is to be seen in Table 19. We have re-introduced the earlier notation because of the fact that the multiplicity of the edges does arise from the combination of two quantum numbers (which we nowadays denote by l and j, following the terminology of optical spectra). Moreover, the rational definition of j (in Röntgen spectra

TABLE 19.

	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	O_I	O_{II}	O_{III}	O_{IV}	O_V	P_I	P_{II}	P_{III}
Present		L_{11}	L_{21}	L_{22}	M_{11}	M_{21}	M_{22}	M_{32}	M_{33}	N_{11}	N_{21}	N_{22}	N_{32}	N_{33}	N_{43}	N_{44}	O_{11}	O_{21}	O_{22}	O_{32}	O_{33}	P_{11}	P_{21}	P_{23}
Previous	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V	N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	O_I	O_{II}	O_{III}	O_{IV}	O_V	P_I	P_{II}	P_{III}

as in all doublet spectra) is not integral but half-integral; and the rational normalisation of l is in the case of wave mechanics one unit smaller than in the older theories. We should, therefore, have to write $L_{0,\,1/2}$, $L_{1,\,1/2}$, $L_{1,\,3/2}$ instead of L_{11}, L_{21}, L_{22}. This would be inconvenient, especially for the purpose of general term notation. We have consequently adopted the use of the suffixes I, II, III. . . .

From Tables 12 we see that the K-limits lie hard by the line Kγ, and, indeed, in accordance with Stokes' law they are displaced a little towards the direction of shorter wave-lengths, by about ½ per cent., as Duane and Stenström have proved for W by means of precision measurements.* The same remark follows from Table 16 with regard to the L-edges, and the lines Lζ, Lθ, and Lψ. But Table 18 also shows that *the absorption doublets of the* L*-series coincide, within the limits of error, with the emission doublets.* The significance of this fact in the atomic model becomes particularly clear in the light of Fig. 60: the absorption doublet is given as the difference in the energy-levels by the energy-step between the L_I- and the L_{II}-level, in the same way as the emission doublet is given as the energy drop in passing to the new energy-level.

It is to be regarded as an outstanding achievement of the spectroscopy of X-rays that also the M-absorption limits have been fixed completely at least in the case of the heaviest elements. In the cases of U and Th, Stenström found three, and Coster five different limits, that is just as many as we found it necessary to assume in the scheme of L-lines of emission to explain their existence. There seems no likelihood at the present time of showing the existence of the seven N-limits spectroscopically.† Even in the case of the absorption limits of the M-series the experimental difficulties are extremely great: it is necessary to use a vacuum spectrograph and the absorbing metallic salts have to be used in exceedingly minute quantities, such as are taken up in solution by tissue paper.

Hitherto we have dealt only with the *position* of the absorption limits. Concerning the *amount of the absorption* we mentioned merely its general decrease as the wave-length decreased and its sudden increase in passing the absorption edge. The amount of the absorption is measured numerically by the **absorption coefficient** μ. This is defined by the statement that for homogeneous radiation the rela-

* Proc. Nat. Acad., **6**, 477 (1920).

† They have been observed by H. Robinson, Proc. Roy. Soc., **104**, 455 (1923), who used a refinement of the magnetic method.

tive decrease of intensity in the passage through a layer of depth d is $e^{-\mu d}$. From the absorption coefficient μ, we pass on to the *true absorption coefficient* $\bar{\mu}$ in which the loss due to the coefficient of scattering s (cf. Chap. I, p. 30) has been subtracted ; and from this again, if we divide it by the number of atoms per cubic centimeter, to the *true absorption coefficient per atom*, which we shall call μ_{At}. In the following discussion we shall give the corresponding coefficient * for the gramme-atom, which becomes $L\mu_{At}$, where L is Loschmidt's number, as this gives us a more convenient order of magnitude. According to very accurate measurements by Richtmeyer, Allen and others, which have been exhaustively discussed by B. Walter,† the following relation holds between $L\mu_{At}$ and the wave-length λ of the absorbed radiation and the atomic number Z of the absorbing element for the short wave side of the K absorption-limit (λ expressed in cms.) :

$$L\mu_{At} = 136 \cdot 10^{-4} \cdot Z^4\lambda^3 \text{ for } \lambda < \lambda_K ; \quad . \quad . \quad . \quad (1)$$

on the long wave side of the absorption edge $L\mu_{At}$ depends on λ in the same way, namely λ^3, but the Z exponent becomes modified :

$$L\mu_{At} = 5{\cdot}29 \cdot 10^{-4} \cdot Z^{4{\cdot}3}\lambda^3 \text{ for } \lambda > \lambda_K \quad . \quad . \quad (2)$$

The Z^4-law in eqn. (1) was discovered by Bragg and Peirce.‡

We arrive at the expressions (1) and (2) if we plot the logarithms of the measured values of the absorption coefficients as ordinates and the logarithms of the wave-lengths or the atomic numbers as abscissæ. The points thus obtained lie in segments of straight lines, from the position and slope of which we may determine the factors and exponentials of eqns. (1) and (2). The rather unprepossessing fractional form of the exponent 4·3 for $\lambda > \lambda_K$ shows that we are here dealing with a purely empirical expression.

In this way we get for the dependence of $\log \mu$ on $\log \lambda$ the characteristic picture of Fig. 64. Suppose we are dealing, for example, with Ag, at first in the vicinity of the K-absorption edge, $\lambda_K = 485$ X-units. If we start from the less hard rays ($\lambda > \lambda_K$, at the right end of the continuous line in the figure), $\log \mu$ decreases uniformly as $\log \lambda$ decreases, as far as $\lambda = \lambda_K$. At the latter point, on account of the excitation of the characteristic radiation of Ag, increased absorption begins ; the absorption coefficient suddenly jumps up, and, indeed, to a value seven times as great as that before the jump ; to this there corresponds in the logarithmic representation a jump of the amount $\log 7 = 0{\cdot}84$. After the jump the uniform decrease of the absorption recommences as the absorbed radiation increases in hardness ; the

* The value μ/ρ usually given denotes the absorption per unit of mass, that is, per gramme. Hence our $L\mu_{At}$ becomes equal to $A\mu/\rho$, where A is the atomic weight.

† Fortschritte auf dem Gebiete der Röntgenstrahlen, **35**, 927 and 1308 (1927).

‡ Phil. Mag., **28**, 626 (1914).

logarithmic value of the decrease as before the jump being again determined by the exponent 3 of λ in equation (1). If, on the other hand we go towards the right into the dotted region (which is not corroborated by measurements in the case of Ag), we arrive at the L-absorption limits. Our figure has been drawn with dotted lines here because it does not correctly depict the height of the sequence of lines in comparison with the K-edge; corresponding to the gap in the x-axis the sequence of lines for the L-edge should in reality be raised. The course is here similar to that for the K-absorption limit: there are sudden jumps, the graph having a parallel course before and after the jump. In the figure three such jumps, of decreasing intensity, have been inserted, corresponding to the three absorption limits L_I, L_{II}, L_{III}.

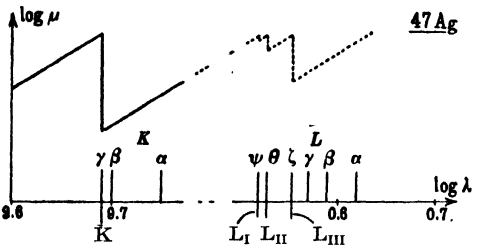


FIG. 64.—The logarithm of the absorption coefficient μ of Röntgen radiation is a discontinuous linear function of the logarithm of the wave-length λ. Illustrated diagrammatically for Ag.

Concerning the rise of the absorption at the limit in question, it is not quite sharp and sudden as was previously believed and as it appears in Fig. 64. Moreover, the limit often has a certain structure. Stenström showed this for the M-limits, G. Hertz for the L-limits, and Fricke for the K-limits of the lightest elements. Fig. 65 shows the K-limit of sulphur, according to H. Fricke,* as a photometric record of the darkening of the plate. The abscissæ are wave-numbers (increasing towards the right). Great values of the ordinates denote good transmission, that is, little darkening of the plate measured photometrically and corresponding strong absorption in the absorption film placed in front of the plate. The photograph for the case of sulphur shows a precipitous but nevertheless steady rise of the absorption between k and K. The distance kK amounts to about 5 X-units and is a measure, so to speak, of the breadth of the K-edge. But the two absorption maxima behind K, called A and B in the figure, are still more remarkable. (The small zig-zags are due to the granules of the photographic plate.)

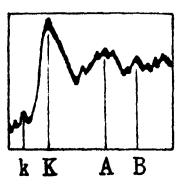


FIG. 65.—Structure of a Röntgen absorption edge (K for sulphur) according to Fricke.

Kossel † accounts for the successive maxima as follows: The principal limit K corresponds to the energy which is necessary to

* Phys. Rev., **16**, 202 (1920).

† Zeits. f. Physik, **1**, 124 (1920).

transfer an electron from the K-shell into the first unoccupied orbit * of the atom ; the following maxima A, B belong to transitions of a K-electron to orbits of the atom that lie still further outside. The amounts of energy required for this are of course greater than the strongest limit denoted by K ; hence the maxima A, B, . . . lie on the side of the greater wave-numbers. From Kossel's view it follows that the distance of these maxima from one another and from K, when measured in wave-numbers, should be of the order of magnitude of the Rydberg constant R, which is confirmed by the figure. Hence it follows, too, that the phenomenon of a band-structure can be observed only in the case of very soft bands, and hence (for K-absorption) only in the case of the lightest elements. The successive maxima at the absorption edges in the region of harder rays come close together, when measured in wave-numbers.

This brings us to the fundamental question : how is it that the visible spectral lines may be observed in emission and absorption but that the X-ray lines appear only in emission ? The reason for this, again according to Kossel, is to be found in the contrast between the interior and the exterior of the atom. In the interior of the atom the shells are *occupied* by electrons ; the electron which is to be raised from the interior finds no place free, in accordance with Pauli's principle, and hence must be taken as far as the periphery of the atom or beyond. Hence in the X-ray region absorption lines appear only in association with absorption edges, in transitions that lead the electron beyond the periphery of the atom into the exterior of the atom which is unoccupied by electrons. In the visible region, on the other hand, the transitions occur generally between *unoccupied* quantum states in the *exterior* regions of the atom. The same line can occur in absorption and emission, according to the direction of the transition.

Since the structure of the outer atomic shells depends on the chemical activity of the atom (or ion), R. Swinne † and W. Kossel ‡ surmised as early as 1916 that the position of edges depended on the valency state of the element. This dependence has since been found in many cases, particularly for the K-edges of the elements between Si 14 and Co 27 and for the L-edges of I, Sn, Sb. The behaviour of Cl and S is especially characteristic. According to Lindh, Stelling and others they exhibit three different edges according as the compounds contain univalent, pentavalent or heptavalent chlorine, or divalent, tetravalent or hexavalent sulphur.

Not only in the case of absorption lines but also in the case of emission lines it has been possible to show a slight dependence on the

* The fact that it is really the first unoccupied orbit that corresponds to the most rapid increase of absorption, is proved for certain L- and M-limits of heavy atoms very accurately by A. Sandström, Zeits. f. Physik, **66**, 784 (1930).

† Phys. Zeits., **17**, 487 (1916). ‡ Verh. d. D. Phys. Ges., **18**, 339 (1916).

nature of the chemical bond. For example, in the lighter elements a fine-structure of the Kβ-line occurs, which varies with the nature of the bond, and also a displacement of the doublet K$\alpha\alpha'$. We see, then, that we must modify our remark on page 206 that the emission of X-rays is a purely atomic property. It is true, however, that this is due to a fineness of detail which manifests itself only when the measurements are extremely precise.

Finally, we shall make a little digression into the region of *medical Röntgen photographs*. These are, as we know, whether received on a fluorescent screen or on the photographic plate, *shadow pictures*. They are thus concerned only with the transmissive or the absorptive power of the object through which the rays pass. The human body is essentially composed of the elements H, C, N, O, P, Ca (for which Z = 1, 6, 7, 8, 15, 20). Now the atomic absorption increases, as we saw, approximately in proportion to the fourth power of the atomic number, and the absorption of a compound of a mixture or of an aqueous solution is composed of the additive absorptions of its constituents. Thus to know the absorption of bone-substance $Ca_3(PO_4)_2$, we have only to superpose the absorptions of Ca, P, and O, whereby each is to be counted the number of times it occurs in the formula (thus, 3, 2, and 8), and to find the relative absorption of the bones with respect to the surrounding tissues, we have to compare them with the absorptions of H_2O, which is easily the preponderant constituent of the tissues. In this way we get

$$\frac{3 \cdot 20^4 + 2 \cdot 15^4 + 8 \cdot 8^4}{2 + 8^4} \sim 3\left(\frac{5}{2}\right)^4 + 2\left(\frac{15}{8}\right)^4 + 8.$$

As we see from this, the amount for Ca considerably outweighs even that for P; the fluorescent screen counts, so to speak, only the Ca-atoms. But if a lead bullet (Pb, Z = 82) is lodged in the bone, its absorption exceeds that of the bone to an extraordinary degree. The excellent contrast effect produced by a solution of bismuth that has been introduced into the stomach or the intestine is due to this; for its atomic number is 83. The concentration of the bismuth solution need not even be high; on account of the ten times higher atomic number of bismuth compared with oxygen, a Bi-atom acts about as strongly as 10,000 O-atoms and 1 grm. of Bi acts about as strongly as 1 kilogrm. of water. The same explanation holds for the surprisingly strong absorptive action of iodine preparations that are photographed, for example, as iodoform in the bandages; for iodine has the atomic number 53.

But the dependence of the absorption on the wave-length and its jump at the absorption edge also comes into account for the medical use of Röntgen rays. For it is on this fact that one of the commonest hardness-gauges, that of Wehnelt, and the associated Wehnelt scale is founded (or Benoist's hardness-gauge, which is based on the same

principle). Its construction is familiar : an aluminium wedge is placed alongside a silver plate of uniform thickness. We read off that position of the aluminium wedge at which it absorbs just as strongly as the silver plate, so that equal brightness is caused in the fluorescent screen. Whereas Ag absorbs the harder rays for which $\lambda < 485$ X-units relatively more than the softer rays (cf. Fig. 62), in the case of Al we obtain no discontinuity in the absorption coefficient in the spectral region accessible to the technical X-ray tubes because even the K-edge of Al lies at such soft wave-lengths that it does not come into question practically. Therefore, in the transition from soft to harder rays, the point of equal brightness moves along the scale in the direction of the thicker end of the Al-wedge, as then the Ag-absorption begins for a greater part of the mixed rays and so the same thickness of silver becomes equivalent to a greater thickness of the aluminium wedge.

This may suffice to show that in the medical application of X-rays the more refined results of physical research, in particular those concerning the absorption laws, come into account.

§ 7. General System of X-ray Spectra. Tables of Terms. Selection Rules. X-ray Spark Spectra. Relationships with the Periodic System.

We discussed the excitation- and absorption-limits after the emission lines because this conforms with the historical order of development. From the point of view of system we might equally well have reversed the order. The energy conditions of the atom express themselves most clearly in the absorption limits. They represent directly the amounts of energy through the manifold combination of which the emission lines arise.

The relationship between absorption limits and emission lines in the X-ray region is the same as that between the " terms " and the wave-numbers of the lines in the visible region. We repeat what has already been said on page 72 : *the goal of spectroscopy is the atomic states and their energy-values.* The observation of spectral lines is only a means of obtaining the values of the terms. Accordingly, in this section we first develop as complete as possible a *Table of X-ray terms.**

We must first make a remark of fundamental importance. Hitherto we have spoken of the energy-steps on which the individual electron is situated before and after the emission or before and after the excitation. We shall now adopt a more correct point of view. *In*

* This was done for the first time in the third German edition of the present volume, 1922, p. 630 ; a little later the table of Bohr and Coster, Zeits. f. Physik, **12**, 350 (1924), appeared which had been supplemented by new data. For the present we find it best to take the term table of Lindh, *loc. cit.*, pp. 228-231, which has been further supplemented.

Terms of the X-ray spectra

Z	K	L_I	L_{II}	L_{III}	M_I	M_{II}	M_{III}	M_{IV}	M_V
12 Mg	95·8	—	3·5		—	—		—	
13 Al	114·7	—	5·2		—	—		—	
15 P	157·8	—	9·9		—	0·8		—	
16 S	181·9	—	11·8		—	0·3		—	
17 Cl	207·8	—	14·8	14·7	—	0·4		—	
19 K	265·6	—	21·4	21·2	—	0·9		—	
20 Ca	297·4	—	25·9	25·6	—	2·0		—	
21 Sc	331·2	—	30·3	30·0	—	2·7		—	
22 Ti	365·8	—	32·6	32·2	—	2·2		—	
23 V	402·7	—	38·2	37·6	—	2·6		—	
24 Cr	441·2	—	43·1	42·4	—	3·6		0·1	
25 Mn	481·8	—	48·2	47·3	—	3·7		0·3	
26 Fe	524·0	—	53·4	52·4	7·1	4·2		0·6	
27 Co	568·2	—	59·0	57·8	7·7	4·7		0·7	
28 Ni	614·1	—	64·7	63·4	8·3	5·4		0·7	
29 Cu	661·6	—	70·3	68·8	8·8	5·7		0·4	
30 Zn	711·7	—	77·1	75·4	10·1	6·8		0·9	
33 As	874·0	—	100·0	97·4	14·9	10·4		3·0	
34 Se	932·0	—	108·4	105·4	16·7	11·6		3·8	
35 Br	992·6	—	117·7	114·3	19·0	13·5		5·2	
37 Rb	1119·4	152·1	137·1	132·7	23·6	18·1	17·5	7·9	
38 Sr	1186·0	163·5	147·6	142·6	26·2	20·8	20·0	9·5	
40 Zr	1325·7	187·0	170·0	163·8	31·8	25·8	24·8	13·4	
41 Nb	1398·5	199·2	181·6	174·6	34·5	28·3	27·1	15·2	15·0
42 Mo	1473·4	212·1	193·7	185·9	37·6	31·4	29·8	17·2	17·0
45 Rh	1709·6	251·5	231·2	220·7	45·6	38·5	36·6	22·4	22·1
46 Pd	1794·0	267·1	245·7	234·1	49·7	42·9	40·7	25·4	25·0
47 Ag	1879·7	282·0	260·1	247·2	53·4	46·0	43·6	27·8	27·4
48 Cd	1967·6	296·9	274·7	260·6	57·0	48·8	46·1	30·3	29·8
49 In	2057·2	312·0	289·3	274·0	60·1	51·8	48·8	32·4	31·9
50 Sn	—	329·4	306·3	289·5	65·3	56·2	53·1	36·5	35·9
51 Sb	2241·7	346·1	323·6	305·3	70·4	60·0	56·4	40·4	39·7
52 Te	2345·0	364·1	340·3	320·1	74·5	64·4	60·5	43·2	42·4
53 I	2448·3	382·6	357·6	336·0	79·2	69·1	64·8	46·8	45·9
55 Cs	2649·1	421·8	394·9	369·3	89·8	79·3	74·4	54·6	53·6
56 Ba	2756·4	441·9	414·3	386·7	95·4	84·6	79·0	58·8	57·6
57 La	—	462·9	434·2	404·4	100·7	90·0	84·0	62·9	61·7
58 Ce	2972·2	483·3	454·1	421·9	106·2	94·6	88·1	66·7	65·4
59 Pr	3093·3	504·3	474·6	439·6	111·6	99·3	92·4	70·3	68·9
60 Nd	3214·2	526·2	495·5	457·8	116·5	104·8	96·8	74·2	72·5
62 Sm	3457·0	571·2	538·9	495·0	127·1	114·7	105·8	81·9	79·9
63 Eu	3583·4	594·3	561·5	514·4	133·1	120·2	110·3	86·0	83·8
64 Gd	3711·9	618·2	584·6	533·9	139·0	125·5	115·0	90·0	87·7
65 Tb	—	642·6	608·3	553·9	145·0	131·0	119·6	94·2	91·6
66 Dy	3972·5	667·7	632·2	574·2	151·2	136·9	124·5	98·5	95·8
67 Ho	4115·9	693·2	657·1	594·7	157·1	142·7	129·3	102·7	99·8
68 Er	—	719·6	682·6	615·9	163·6	148·8	134·7	107·2	104·0
69 Tu	—	746·8	708·8	637·3	170·3	155·5	140·2	111·7	108·4
70 Yb	—	774·6	735·4	659·2	177·1	162·2	145·8	116·4	112·8
71 Lu	—	802·6	762·9	681·2	183·8	168·6	150·9	120·9	117·2
72 Hf	—	832·0	791·3	704·5	191·8	175·9	156·9	126·6	122·6
73 Ta	—	862·2	820·8	728·0	199·5	183·2	162·9	132·2	127·8
74 W	5113·8	893·0	850·6	752·1	208·1	191·3	169·8	138·3	133·7
78 Pt	5764·0	1026·8	978·7	852·0	243·4	227·3	198·0	162·3	156·4
79 Au	5940·4	1060·2	1014·4	878·5	252·9	235·1	202·8	169·3	163·0
80 Hg	6115·9	1094·6	1048·6	906·1	—	—	—	—	—
81 Tl	6289·0	1132·4	1084·2	933·2	273·9	253·8	219·2	184·0	176·8
82 Pb	6463·0	1169·3	1121·9	960·5	283·8	262·3	226·0	190·5	183·0
83 Bi	6646·7	1207·9	1159·4	990·0	295·9	273·6	234·0	199·4	191·4
90 Th	8073·5	1509·7	1451·5	1200·6	381·6	354·4	298·0	256·6	244·9
92 U	8477·0	1603·5	1543·1	1264·3	408·9	382·1	317·2	274·0	261·0

in Rydberg frequency units

N_I	N_{II}	N_{III}	N_{IV}	N_V	N_{VI}	N_{VII}	O_I	O_{II}, O_{III}	O_{IV}, O_V	Z
—	—	—	—	—	—	—	—	—	—	12 Mg
—	—	—	—	—	—	—	—	—	—	13 Al
—	—	—	—	—	—	—	—	—	—	15 P
—	—	—	—	—	—	—	—	—	—	16 S
—	—	—	—	—	—	—	—	—	—	17 Cl
—	—	—	—	—	—	—	—	—	—	19 K
—	—	—	—	—	—	—	—	—	—	20 Ca
—	—	—	—	—	—	—	—	—	—	21 Sc
—	—	—	—	—	—	—	—	—	—	22 Ti
—	—	—	—	—	—	—	—	—	—	23 V
—	—	—	—	—	—	—	—	—	—	24 Cr
—	—	—	—	—	—	—	—	—	—	25 Mn
—	—	—	—	—	—	—	—	—	—	26 Fe
—	—	—	—	—	—	—	—	—	—	27 Co
—	—	—	—	—	—	—	—	—	—	28 Ni
—	—	—	—	—	—	—	—	—	—	29 Cu
—	—	—	—	—	—	—	—	—	—	30 Zn
—	—	0·2	—	—	—	—	—	—	—	33 As
—	—	0·2	—	—	—	—	—	—	—	34 Se
—	—	0·2	—	—	—	—	—	—	—	35 Br
1·9	0·9	1·1	—	—	—	—	—	—	—	37 Rb
2·5	1·6	1·3	—	—	—	—	—	—	—	38 Sr
3·7	2·6	1·9	0·4	0·3	—	—	—	—	—	40 Zr
4·1	2·9	2·0	0·2	0·2	—	—	—	—	—	41 Nb
4·6	3·2	2·9	0·3	0·3	—	—	—	—	—	42 Mo
5·3	3·7	3·5	—	—	—	—	—	—	—	45 Rh
6·7	5·3	5·0	0·5	0·5	—	—	—	—	—	46 Pd
7·3	5·8	4·9	0·8	0·5	—	—	—	—	—	47 Ag
8·0	5·9	5·3	0·9	0·7	—	—	—	—	—	48 Cd
8·2	5·5	5·2	0·5	0·4	—	—	—	—	—	49 In
10·2	7·1		2·0	1·9	—	—	0·2	0·6	—	50 Sn
12·1	7·2		3·3	3·2	—	—	0·8	0·1	—	51 Sb
12·7	8·9		3·6	3·2	—	—	—	0·5	—	52 Te
14·0	9·4		4·1	4·1	—	—	—	0·7	—	53 I
17·1	13·6	12·6	5·9	5·7	—	—	1·9	1·7	—	55 Cs
18·8	14·9	14·0	6·9	6·9	—	—	3·1	2·0	—	56 Ba
20·5	16·5	15·4	7·8	7·8	—	—	3·0	2·3	—	57 La
21·7	17·4	16·2	8·4	8·5	—	—	3·2	2·5	—	58 Ce
22·7	18·3	16·9	8·9	8·7	—	—	3·1	2·3	—	59 Pr
23·7	19·2	17·8	9·2	9·2	—	—	3·1	2·7	—	60 Nd
25·9	20·9	19·5	10·0	9·8	—	—	3·1	2·8	—	62 Sm
27·2	22·6	20·4	10·7	10·4	—	—	3·6	2·9	—	63 Eu
28·6	23·0	21·0	11·0	10·8	—	—	4·0	3·3	—	64 Gd
29·4	24·3	22·0	11·4	11·1	—	—	3·5	2·6	—	65 Tb
31·0	26·1	23·2	12·2	11·6	0·8	—	3·1	3·2	—	66 Dy
31·8	26·9	23·8	12·8	12·0	0·8	0·2	—	2·7	—	67 Ho
33·1	28·4	24·9	13·7	12·6	0·9	0·3	3·9	3·9	—	68 Er
34·4	30·0	26·6	14·5	13·2	0·9	0·4	—	3·8	—	69 Tu
36·2	31·0	27·5	14·9	14·2	0·9	0·6	—	3·6	—	70 Yb
36·9	32·5	28·7	16·1	14·7	1·0	0·7	4·2	4·0	—	71 Lu
40·0	34·0	29·8	16·8	16·0	1·6	1·4	4·8	4·3	—	72 Hf
41·2	35·3	30·9	17·8	16·6	2·2	1·9	4·7	4·4	—	73 Ta
44·1	38·0	33·0	18·8	18·4	2·9	2·8	5·7	5·2	—	74 W
52·5	48·7	42·3	24·5	23·2	5·2		7·1	8·6	0·4	78 Pt
58·0	49·1	42·8	26·4	25·0	6·4		7·8	8·3	0·8	79 Au
—	—	—	—	—	—	—	—	—	—	80 Hg
63·7	53·6	44·9	30·6	29·0	10·0	9·6	10·6	7·4	1·7	81 Tl
66·0	55·4	49·3	32·2	30·5	10·8	10·3	10·3	6·4	0·8	82 Pb
71·0	58·7	50·3	35·7	33·7	13·6	13·0	—	11·0	2·0	83 Bi
97·8	—	—	51·2	48·7	24·8	24·1	—	—	5·7	90 Th
106·6	95·7	77·1	56·3	53·6	28·4	27·6	26·2	15·4	5·8	92 U

the inter-changes of energy it is not the individual electron but the whole atom that is involved. Every process of excitation means an addition of energy to the atom owing to the work of ionisation, whole or part, that is done. The energy of the ionised atom is greater than that of the neutral atom, the more so the more tightly the ejected electron was bound. If we agree to set the energy of the neutral atom equal to zero, the energy of the ionised atom becomes equal to h times the vibration number of the absorption edge in question. The associated wave-number, that is the "Röntgen or X-ray term" corresponding to the absorption edge, thus measures the energy-content of the atom in a definite state of ionisation, compared with the energy of the neutral atom.

Every assertion about the origin of an emission line contains a perfectly definite numerical statement about a relationship between the wave-number of an emission line and two absorption edges. If, for example, we describe the origin of Kα by the symbol $L_{III} \rightarrow K$, we imply that the following equation between the wave-number ν of Kα and the wave-numbers of the limits K and L_{III} is exactly fulfilled:

$$\nu = K - L_{III} \quad . \quad . \quad . \quad . \quad (1)$$

From our present point of view this equation signifies the following state of affairs. First the atom is ionised in the K-shell. If the electron passes from the L_{III}-shell to the K-shell with the emission of Kα, an electron in the L_{III}-shell is wanting in the atom in its final state. Thus the energy-content of the atom in the final state is the same as if the atom had been primarily ionised in the L_{III}-shell. Thus eqn. (1) expresses an energy relationship between the wave-number of Kα and the energy-contents (terms) of two atomic states.

We are fully convinced that all such relationships demanded by the theory hold absolutely rigorously. Empirical confirmation can of course be obtained only in those special cases where, besides the emission lines, also the absorption edges have been measured with sufficient accuracy. The precision measurement of the edges is restricted by their fine-structure. According to the maximum to which one adjusts, different values of the wave-number are obtained. An exact test for the L-series has been undertaken by Coster * for the elements Bi, Th, U, for which besides the L-edges also the M-edges are accessible.

In setting up the table of terms our procedure is to postulate that all the relationships between lines and edges, which the theory (cf., for example, the column with the heading "origin" in our Tables 11 and 14) demands, hold quite accurately, and that inaccurately measured edges are corrected in this sense and new ones become added if, as in the case of the N-edges, they are too soft to be measured.

* Zeits. f. Physik, **6**, 195 (1921).

In contrast with the visible spectra, for which the number of series terms is immeasurably great, we have the advantage in the case of the X-ray spectra that the number of the terms is small and the complete list of terms of all the elements does not occupy much more than two pages. For there are only $1 + 3 + 5 + 7 + 5 + 3 = 24$ limits, of which, moreover, a fair number are wanting in the case of the lighter elements ; thus the number of term magnitudes for all the 92 elements taken together is less than 24.92. These term magnitudes are fixed characteristics of the atom.

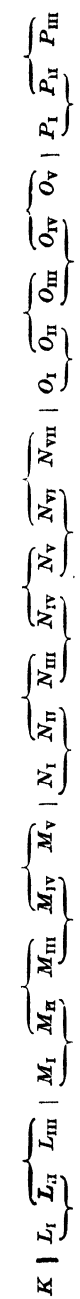
To accompany the tabular survey of Table 20 we add the graphs of Fig. 66. We have drawn this figure in the same way as the earlier figures of this chapter, in which the K-level was placed at the bottom. We might also have followed Bohr and Coster in choosing the reversed position, since according to the beginning of this section the energy of the whole atom is greatest when the K-shell is ionised and since it decreases, for example, when during the emission of Kα the K-shell becomes filled and the L-shell is left ionised. In such a method of representation the energy-levels would represent the *positive* energies of the whole atom. In our method of representation they denote *negative* energies. *The double arrows* drawn in the figure are to indicate that, on the one hand, we may consider the energy of the *whole* atom, in which case the arrow is to be taken in the upward direction, or, on the other hand, we may localise the process in the chief carrier in the transformation of energy and from this point of view the arrow must be taken in the downward direction.

The figure is to be regarded purely diagrammatically. For example, within each shell the levels are drawn equi-distant, whereas in reality the level-differences are very different. Likewise the decrease due to transitions to the external shells is much more marked in reality than as shown in the figure. In cases where, such as in the M- and the N-shell, the arrows occur without letters, the lines in question are to be expected theoretically but have partly not been found and partly not been provided by us with special symbols. Several of the line-symbols added in the figure (for example, β', γ' in the K-series, $\iota\kappa\lambda\mu$ in the L-series) are sufficiently defined through the scheme of levels itself.

This scheme is supported by a great series of combination-relations between the emission lines. Fig. 60, which depicts such relations is actually only a section of our now more comprehensive figure. Here we shall touch only on those combination-relations which have played a particular part in setting up the scheme as a whole.

The Kβ-line comes into question in the first place. According to the original Kossel relations the following relation should actually hold in wave-numbers (see eqn. (2) at the end of § 3) :

$$K\beta = K\alpha + L\alpha \quad . \quad . \quad . \quad . \quad (2)$$



The author endeavoured to establish in 1916 * whether the equation holds exactly in this form and found that it did not.

We actually obtain from the precise explanation of the lines in question in Fig. 66

$$K\beta = K - M_{III}, \quad K\alpha = K - L_{III}, \quad L\alpha = L_{III} - M_V,$$

that the correct form of the relation (2) is

$$K\beta = K\alpha + L\alpha + (M_V - M_{III}) \quad . \quad . \quad (3)$$

Secondly, we must name two relations which led Smekal † to allocate the lines $L\phi$ and $L\phi'$ correctly :

$$\left.\begin{aligned} K\beta &= K\alpha + L\phi + (L_I - L_{III}) \\ K\beta - K\beta' &= L\phi - L\phi' \end{aligned}\right\} \quad . \quad . \quad (4)$$

The line $K\beta' = M_{II} \rightarrow K$ which occurs here (see our scheme of levels) is a weaker satellite of $K\beta$ which has, however, been found only in the case of a few elements ; in the case of Rh it was first observed by de Broglie.‡

By comparing the results with the measurements of the M-edges Coster ‖ then established the interpretation of the L-M-combinations by showing that the following relations hold between the L-lines and the M-edges :

$$\left.\begin{aligned} L\phi - L\phi' &= M_{II} - M_{III} \\ L\alpha - L\epsilon &= M_I - M_V \end{aligned}\right\} \quad . \quad . \quad . \quad (5)$$

Almost more convincing than these numerical details the regular structure of the whole scheme of levels itself furnishes the best evidence for its logical conception. To make this clear we must introduce two terms, for the introduction of which we shall not give the reason until we arrive at Chapter V, namely : " regular or relativistic doublets " and " irregular or screening doublets."

We have already learned at the end of § 5 the characteristic way in which the difference in the edges $L_{II} - L_{III}$ (the L-doublet there investigated) depends on the atomic number Z ; this dependence is explained by the theory of relativity and represents the type of the *regular doublet.* In addition we have in the L-series the edge-difference $L_I - L_{II}$, which exhibits a different but no less characteristic dependence on Z, which has been elucidated by G. Hertz (cf. Chap. V, § 5). This depend-

* Ann. d. Phys., **51**, 125 (1916). Remark at the end.

† Zeits. f. Physik, **5**, 91 (1921). This paper and the paper by Coster mentioned just below were of fundamental importance for setting up the scheme of levels. They prove that the L-shell is subdivided three times, and the M-shell five times.

‡ Comptes Rendus, **170**, 1053, 1245 (1920).

‖ Zeits. f. Physik, **5**, 139 (1921).

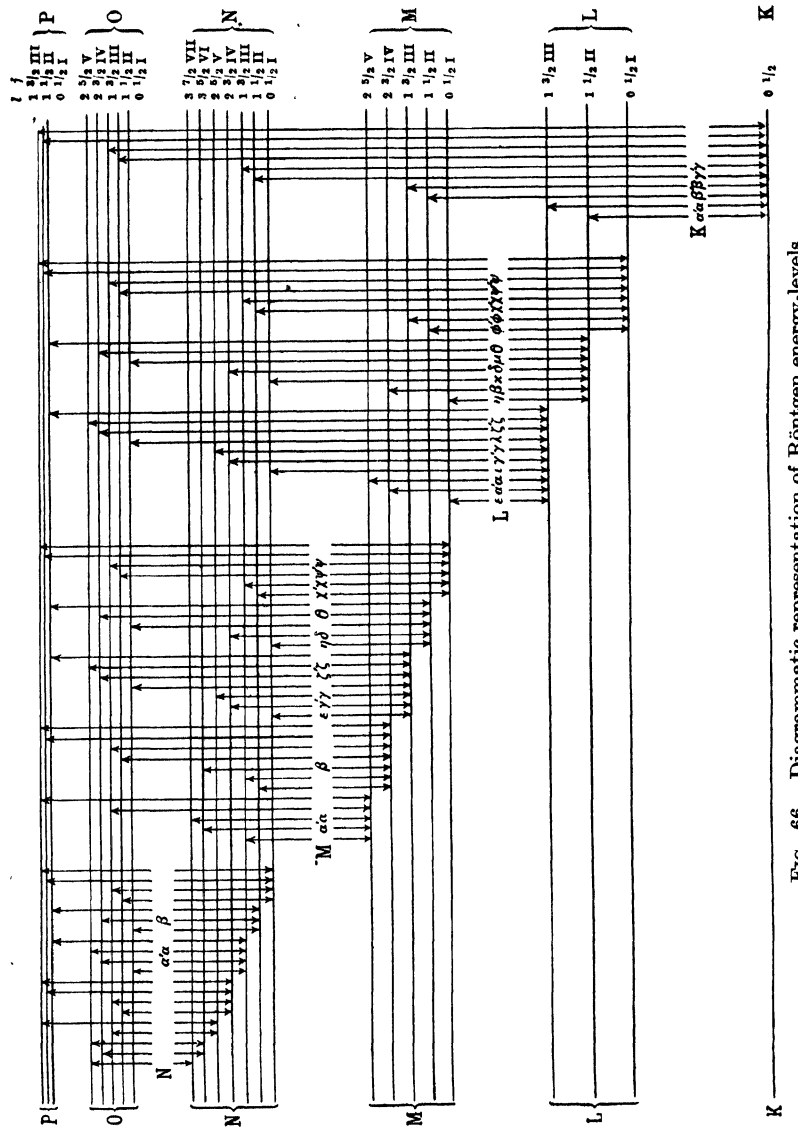


Fig. 66.—Diagrammatic representation of Röntgen energy-levels.

ence points to a difference in the "screening constants" and represents the type of the irregular doublet.

But these two types do not only present themselves in the L-shell but also in all the subsequent shells, and, in fact, in regular alternation as shown in the above scheme.

The brackets *over* the symbols denote *regular doublets*, those under

the symbols *irregular doublets ;* both are characterised by a definite analytical law as a function of the atomic number.

We have now to show how the energy-levels characterised in this way combine with each other. To accomplish this we must assign " quantum numbers " to them. We do this in the manner found to be expedient when dealing with the analogously constructed doublet-spectra of the alkalies. For we distinguish between three quantum numbers :

$$n, l, j.$$

1. The principal quantum number n increases step by step, as we know from §§ 4 and 5 of the preceding chapter, in the successive shells : for we have

	$n=1$	2	3	4	5	6	
in the	K-	L-	M-	N-	O-	P-	shell.

This quantum number is *not* restricted by a selection principle.*

2. The azimuthal quantum number l assumes the values

$$l = 0, 1, 2, \ldots n-1 \quad . \quad . \quad . \quad . \quad (6)$$

within each shell, if it is fully developed. The allocation of these numbers to the sub-divisions of the shells (*Unterschalen*) may be seen from the following scheme :

$l=0$	K,	L_I,	M_I,	N_I . . .
$l=1$		$L_{II} + L_{III}$,	$M_{II} + M_{III}$,	$N_{II} + N_{III}$ . . .
$l=2$			$M_{IV} + M_V$,	$N_{IV} + N_V$ . . .
$l=3$				$N_{VI} + N_{VII}$ . . .

The following selection rule holds :

$$\Delta l = -1, \quad \text{or} \quad \Delta l = +1. \quad . \quad . \quad . \quad (7)$$

3. The introduction of the " inner " quantum number j is rendered necessary by the electron spin (cf. p. 153). In every shell we have to ascribe to it the values :

$$j = l \pm \tfrac{1}{2} \quad \left\{\begin{matrix}\text{minimum value } j = \tfrac{1}{2} \\ \text{maximum value } j = n - \tfrac{1}{2}\end{matrix}\right\} \quad . \quad . \quad (8)$$

* It has occasionally been conjectured that a special decree exists which forbids transitions within one and the same shell, that is, for $\Delta n = 0$; the ground given is as follows : Coster [Phil. Mag., **43**, 1070 (1922), Part 2, § 10] has looked in vain for the line L_I-L_{III}, which would in the case of tungsten lie in the region of the M-series, and would not contradict the other selection principles. Cf. also Hjalmar, Zeits. f. Physik, **15**, 65 (1923), in particular p. 89. But the absence of such lines can be accounted for without a special decree on the ground that their transition-probabilities are very small. Cf. Pauling and Goudsmit, " Structure of Line Spectra," McGraw-Hill, New York, 1930, pp. 178, 179.

The allocation to the sub-divisions of the shells is seen in the following schemes :

$j = \frac{1}{2}$	K,	$L_I + L_{II}$,	$M_I + M_{II}$,	$N_I + N_{II}$ . . .
$j = \frac{3}{2}$		L_{III},	$M_{III} + M_{IV}$,	$N_{III} + N_{IV}$ . . .
$j = \frac{5}{2}$			M_V	$N_V + N_{VI}$ . . .
$j = \frac{7}{2}$				N_{VII} . . .

The selection rule in this case is

$$\Delta j = -1, \quad \Delta j = 0 \quad \text{or} \quad \Delta j = +1. \qquad . \qquad . \qquad (9)$$

In Fig. 66 the energy-levels are shown with their corresponding l-and j-values. By combining our rules (7) and (9) we obtain *all* lines drawn in Fig. 66 and *only* these lines. This was shown simultaneously by Wentzel * and Coster.†

Not only is it possible to predict the occurrence of lines but also their *intensity* generally. For this purpose we supplement our selection rules so as to have qualitative *intensity rules*. Although, like the former, the latter appear at present as empirical postulates, this does not reduce their regulative power. To give a theoretical basis for them would require extensive calculations of a preliminary kind and would lead us into Dirac's theory of the spinning electron.

We postulate : *those transitions are strong in which* l *and* j *change in the same sense ; the transitions are the weaker, the more the change in direction of* l *and* j *is different*. To this we must add : a transition in the decreasing sense $l \to l - 1$ is, *ceteris paribus*, *stronger* than a transition in the increasing sense $l \to l + 1$. We shall find that the same rule holds in the case of multiplet spectra in the visible region (Chap. VIII) as a qualitative intensity rule, and moreover in their case the rule will first find its full application, for in X-ray spectra (and doublet spectra in general) the case of oppositely directed transitions (*ungleichsinnige Übergänge*), for example, $\Delta l = -1$, $\Delta j = +1$, does not occur at all, because it would lead to a final state in which $j - l$ would be two units greater than in the initial state. But this is forbidden since the difference between j and l, by (8) must always amount to $\pm \frac{1}{2}$. Consequently, in the case of X-ray spectra we have in addition to the strong similarly directed transitions only such weak transitions as have $\Delta j = 0$.

The application to the K-series is very simple : here the strong lines, α, β, γ belong to the transitions $\Delta l = \Delta j = -1$, the weaker satellites, α', β', γ' (which are half as strong) belong to the transitions $\Delta l = -1$, $\Delta j = 0$.

The conditions become more manifold in the case of the L-series.

* Zeits. f. Phys., **6**, 84 (1921).

† *Ibid.*, **6**, 185 (1921). The scheme suggested by Coster deviates only in formal respects from that of Wentzel in that Coster originally endeavoured to do with only one quantum number (l or k) ; later Coster and Bohr also decided to introduce the second quantum number (our present j).

The strongest transitions M → L, namely Lα and Lβ, belong to $\Delta l = \Delta j = -1$ (cf. Fig. 66); likewise the strongest transitions N → L, namely Lγ and Lδ. The weaker satellites α′, γ′ correspond to the transition $\Delta l = -1$, $\Delta j = 0$, whereas β and δ can have no such satellites, in accordance with the relationship just mentioned between j and l. Let us now consider the pair ϵ, $M_I \rightarrow L_{III}$, and η, $M_I \rightarrow L_{II}$. In the case of ϵ we have $\Delta l = +1$, $\Delta j = +1$, in the case of η we have $\Delta l = +1$, $\Delta j = 0$. Hence ϵ is stronger than (about twice as strong as) η. The fact that this pair, taken absolutely, is much weaker than, for example, the pair α, β, is to be explained by the circumstance that ϵ, η belong to $\Delta l = +1$ (*increasing sense*) whereas α, β belong to $\Delta l = -1$ (*decreasing sense*). The same as holds for ϵ, η also holds for the still weaker pairs of lines iκ, λμ (cf. Fig. 66); the same as holds for α, β also holds for φφ′, χχ′ and so forth ($\Delta l = -1$, $\Delta j = -1$ for φ, χ . . .; $\Delta l = -1$, $\Delta j = 0$ for φ′, χ′, . . .). The same selection and intensity rules hold for the M- and N-series, but we shall not enter into them here.

Our selection rules are not absolutely binding; but wherever an exception appears to occur, the line in question proves to be particularly weak, so that it can be photographed only after a very long exposure; in Fig. 66 such lines were not included, nor in our Tables 12 and 16, pages 210 and 218, and so forth. These exceptions include the interesting line * $L_I \rightarrow K$, which has been separated by Duane and Stenström in the third and fourth order from the closely adjacent line $K\alpha' = L_{II} \rightarrow K$ by the ionisation method in the case of tungsten. For the transition $L_I \rightarrow K$ we have $\Delta l = 0$, which contradicts the rule of selection (7). Occasionally there are also transitions $\Delta l = -2$, which are characterised by going preferably with the transition $\Delta j = -2$, than with $\Delta j = -1$. The fact that the selection rules break down in strong external fields is analogous to what happens in the visible region (cf. Chap. VI). It suggests itself to us that in the case of the X-ray spectra, too, the occurrence of forbidden lines is to be traced back to the action of strong internal atomic fields. We might even be led to conjecture that it is possible quite generally to obtain signs of otherwise forbidden lines by making the exposures long enough.

But there are also lines which refuse to be fitted into the diagram of levels altogether. They generally occur as satellites of strong lines, mostly on the hard, but sometimes also on the soft side. We quote as an example in the K-series of the lightest elements the line α_3, α_4, discovered by Siegbahn and Stenström in 1916, which is weak compared with Kα but intense compared with the other satellites; also the satellites α_5, α_6, shown to exist by Hjalmar in 1920, for which the inequalities hold:

$$K\alpha < \alpha_3 < \alpha_4 < \alpha_5 < \alpha_6.$$

* Contrary to this interpretation, Wentzel regards this line as a "spark line" (see below). Wentzel, Zeits. f. Physik, **31**, 451 (1925).

The Kβ-line also has short-wave satellites. In the L-series we know of both short- and long-wave satellites, the latter occurring in elements for which the initial level of the principal line is incompletely developed (Coster and Druyvesteyn *).

Wentzel † has proposed a remarkable theory for the short-wave satellites, which was described in some detail in the fourth German edition of the present volume. This theory interpreted the satellites in question as " spark spectra of the X-ray spectrum." As remarked in Chapter II, § 2, we take spark lines in the optical spectrum to stand for lines emitted by the *ionised* atoms. To excite ordinary X-ray lines single ionisation is already necessary ; to excite the " spark lines " of the X-ray spectrum Wentzel considers that *double or multiple ionisation is necessary.*

It was possible to confirm this theory in several points in the case of the short-wave satellites of the K-series,‡ but some objections have also manifested themselves. The double or multiple ionisation of an atom is a process which is improbable in itself. The excitation potential necessary to effect it is considerably higher than that required for single ionisation. It has, indeed, been shown experimentally that the short-wave satellites actually appear at first at higher potentials than the principal lines, but the potentials are not in general as high as is to be expected from Wentzel's theory. The interpretation also becomes considerably more complicated for another reason which Wentzel || himself first recognised : whereas the ordinary X-ray spectra have a doublet character the X-ray spark spectra should have singulet or triplet structure or in the case of higher ionisation, multiple structure in general. The excitation limits which are then to be decisive for the emission of X-ray spark lines not only become different from the ordinary or " arc " lines but also far more numerous. The number of possible combinations increases correspondingly. Wentzel expects no fewer than twenty-four lines in the case of double ionisation, whether of the K- or L-shell or in the case of simultaneous ionisation of the K- and L-shell ¶ (K^2- L^2- or KL-terms ; formerly only two such combinations were enumerated, which were allocated to the lines α_3 and α_4).

A view which differs from that of Wentzel has been proposed and supported by Richtmyer.** He, too, assumes as a condition for the appearance of satellites a double ionisation, the one occurring in

* Zeits. f. Physik, **40**, 765 (1927).

† Ann. d. Phys., **60**, 437 (1921) ; **73**, 647 (1923).

‡ T. Wetterblad, Zeits. f. Physik, **42**, 611 (1927). The particular point involved is the equality of the wave-number difference $\alpha_2 - \alpha_4$ of an element with the wave-number difference $\alpha_3 - \alpha_1$ of the next successive element.

|| Zeits. f. Physik, **31**, 445 (1925) ; **34**, 730 (1925).

¶ M. J. Druyvesteyn, Dissertation, Groningen, 1928 (" Das Röntgen-spektrum zweiter Art ") confirms Wentzel's views in the main.

** K. F. Richtmyer, Phil. Mag., **6**, 64 (1928) ; and Phys. Rev., **34**, 574 (1929).

an inner shell, the other in an outer shell, the latter being produced, say, by an electron ejected from the inner shell with an excess of velocity. In the case of the K- or L-satellites the inner shell would be the K- or L- shell respectively, the outer the M- or N-shell respectively. The satellite is supposed to arise through a *double transition* (*Doppelsprung*) in that both gaps are filled up by an electron in each case from a shell lying further outside, in which process the $h\nu$'s of these two transitions become added to the $h\nu$ of the emitted satellite. Such double transitions are known to occur in the visible spectrum, in fact lead to particularly characteristic and strong groups of lines (for example, the pp'-lines of the doublet- and triplet-spectra, cf. Chap. VII, § 7). A kind of Moseley's law holds for the difference $\Delta\nu$ between the wave-number of the satellites and that of its " parent line " (that is, the " diagram line " which corresponds to the filling of the inner shell alone) : for we have that $\sqrt{\Delta\nu}$ is a linear function of the atomic number. This law has been well confirmed experimentally by Richtmyer for the short-wave satellites of Kα, as well as for those of Lα, Lβ, Lγ, in particular in the case of those elements whose M- or N-shell is incomplete, that is, where the external gap above demanded is present of itself. The difficulty of the high excitation potential mentioned above as necessary for Wentzel's explanation becomes superfluous in Richtmyer's * theory : the excitation-potential need be but little greater than that of the parent-line (experimentally it was between 20 per cent. and 30 per cent.).

We now return to the true diagram lines and consider their presence or absence in connection with the theory of the periodic system.

We have pointed out repeatedly that the number of sub-divisions of the levels increases as far as the N-shell and then again decreases. If it were to increase still further, thus, if the O-shell were to be nine-fold instead of five-fold, more lines would have to occur in the M-series, according to the selection rules, than have actually been observed. This may be regarded as a first test of Bohr's theory of the periodic system.

We shall now look for further signs of this theory in the whole region of X-ray spectra. They will emerge, to speak quite generally, from the circumstance that certain lines decrease in intensity, when we pass from the heavier to the lighter elements, in proportion as the quantum state of the initial level is no longer realised by the atomic structure.

Let us first consider the levels P_{II} and P_{III} ; they drop out between U 92 and Tl 81. Actually the line $P_{III} \rightarrow N_I$ has been observed not only for U 92, Th 90, but also for Bi 83 ; the transitions $P_{III} \rightarrow M_I$, $P_{III} \rightarrow M_V$ are so far known only for U 92 and Th 90. It is remark-

* In the meantime the theory has received considerable support from the exact investigation of the line CuKα_3, cf. J. W. M. Du Mond and A. Hoyt, Phys. Rev., **36**, 799 (1930).

able that in the L-series certain lines suddenly appear between Ho 67 and Ce 58 which must be allocated to the transitions $P_{II,\ III} \rightarrow L_I$. According to our Table 9, page 163, we have that in the case of these elements only the P_I-shell is occupied by two electrons (at most). Thus the lines just mentioned correspond to transitions to L_I from energy-levels not yet occupied (virtual). At anyrate no lines starting from the P-levels have been observed in the case of elements which, according to our view, have no electrons at all in the P-shell. We shall get to know two examples of combinations with unoccupied levels, but in each case they are levels which belong to shells in which at least one electron is present.

The next energy-level that fades away in the periodic system is O_{IV} or O_V. Whereas, according to Table 9, in the case of Pt 78 this level is occupied by eight electrons, in the case of Hf 72 it is occupied only by 2 and after that only by one electron. In the same region of the periodic system, the lines $L\zeta$, $O_V \rightarrow L_{III}$ and $L\theta$, $O_{IV} \rightarrow L_{II}$ exhibit a marked decrease in intensity; below Ta 73 no more lines have been observed, which would correspond to combinations with these two levels O_{IV}, O_V.

The energy-levels $N_{VI} + N_{VII}$ cease in the region of the rare earths (from Hf 72 down to Ce 58); Ce has only one electron in this shell. Actually, combinations of these levels have been shown to occur only as far as Dy 66.

The energy-levels that next fade out are, in order, $O_{II} + O_{III}$, $N_{IV} + N_V$, O_I. It is in agreement with the fading out of $O_{II} + O_{III}$ at In 49 that the line $L\psi$, $O_{III} \rightarrow L_I$ here finally ceases. The level O_I, which is represented in the observations only by the weak lines $L\lambda = O_I \rightarrow L_{III}$ and $L\mu = O_I \rightarrow L_{II}$ of the L-series should cease, according to theory at Rb 37. $L\lambda$ was last observed at In 49 and $L\mu$ at Ba 56. The fading out of $N_{IV} + N_V$, which we expect at Y 39, may be tested by means of the strong lines $L\gamma$, $N_V \rightarrow L_{III}$ and $L\delta$, $N_{IV} \rightarrow L_{II}$. They have been proved to occur as far as Zr 40.

The lines of the K-series are particularly serviceable for further investigation; we shall use lines of the L-series only where, on account of the selection rules, lines of the K-series are no longer available. Let us consider $N_{II} + N_{III}$, that is, the lines $K\gamma$, γ'; the stronger of the two $K\gamma$'s arises in the transition $N_{III} \rightarrow K$. According to theory the level N_{III} should occur for the last time at Ga 31. Hence our experience with the L-series would lead us to expect that $K\gamma$ is strong as far as As 33 and cannot be followed far beyond Ga 31. Actually, however, the $K\gamma$-line * has been shown to exist as far as K 19, that is, as far as the element, in which electrons occur in the N-shell at all. From this we must infer that not only the energy-levels actually occupied by electrons but also, as in the visible spectrum, virtual levels

* E. Bäcklin, M. Siegbahn and R. Thoraeus, Phil. Mag., **49**, 513, 1320 (1925).

may serve as initial states for the X-ray lines. In admitting this we somewhat weaken the strength of our argument. Accordingly we shall regard observations about the fading-out of X-ray lines as being instructive for a theory of the structure of the atoms in broad outline but not as binding in details.

The last levels to disappear are, in order, N_I, $M_{IV} + M_V$, $M_{II} + M_{III}$, M_I, $L_{II} + L_{III}$, L_I. N_I can combine only with L_{II} and L_{III}; according to Fig. 66 $N_I \to L_{II} = L\kappa$, $N_I \to L_{III} = L\iota$. Both lines are weak and known only as far as Rb 37; theoretically they should last occur at K 19. The levels M_{IV}, M_V reach as far as Sc 21; but here, too, as in the case of N_I, combinations with K are not possible normally, but we certainly have the lines $M_V \to L_{III} = L\alpha$ and $M_{IV} \to L_{III} = L\alpha'$, which have been measured as far as V 23, and the line $M_{IV} \to L_{II} = L\beta$, which is known as far as Cr 24. The levels M_{II}, M_{III} should cease at Al 13; in reality the line $M_{III} \to K = K\beta$ only ends at Na 11, that is, at the first element which has an electron in the M-shell. $K\beta$ behaves similarly to $K\gamma$. It is known with certainty that $K\beta$ does not exist below Na 11. We cannot say anything about the vanishing of M_I, because here again only combinations with L_{II}, L_{III} are possible and the L-series is not known as far as the critical region (Na 11). L_{II} and L_{III} give with K the combinations $L_{II} \to K = K\alpha'$ and $L_{III} \to K = K\alpha$. We should expect them as far as B 5, or after our experiences with $K\beta$ and $K\gamma$ perhaps as far as Li 3, where the L-shell begins. Measurements of $K\alpha$ * are available as far as B 5. Finally, L_I gives no lines with K, so that we cannot follow its disappearance with the X-rays.

As a result of our last reflections we must once again state that we here have on the whole a convincing confirmation of the theory of the periodic system developed in the preceding chapter. Our ultimate result as regards the content of the present section is, however, far more positive: it has been completely and finally possible to arrange the whole material of observation in X-ray spectroscopy into a term- and level-scheme. This scheme is strengthened by innumerable combination relationships and governed by very simple selection rules.

* J. Thibaud and A. Soltan, Comptes Rendus, **185**, 642 (1927); Journ. de phys. et le Radium, **8**, 484 (1927); A. Dauvillier, *ibid.*, **8**, 1 (1927).

CHAPTER V

THEORY OF FINE STRUCTURE

§ 1. Relativistic Kepler Motion

WE shall refrain here from giving a special introduction * to the theory of relativity such as was given in the earlier editions of the present volume ; in the first place because the theory of relativity has become common property to all readers of science and, secondly, because the few results which we shall require—and they come only from the " special " and not from the " general " theory —have already been met with in Chapter I. These results were as follows :

1. The variation of mass with velocity (cf. p. 20) :

$$m = \frac{m_0}{\sqrt{1-\beta^2}}. \quad . \quad . \quad . \quad . \quad (1)$$

2. The inertia of energy (cf. p. 44). By defining the kinetic energy as the excess of the energy of the moving body above that of the body at rest and by expressing these energies by means of the corresponding masses m and m_0, we obtain

$$\mathrm{E}_{kin} = c^2(m - m_0) = c^2 m_0\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) \quad . \quad . \quad (2)$$

The expression $m_0 v^2/2$ of classical mechanics results from (2), as it must, by expanding in ascending powers of β to a first approximation, that is, for the limit $c \to \infty$.

We first treat the relativistic Kepler problem in an elementary way but then proceed as in Chapter II, § 7, to use the general " Hamiltonian method," which is remarkably suited to the nature of our problem. Let the nuclear charge be Ze, and the charge on the electron $-e$. We shall leave out of account the relative motion of the nucleus and shall take the nucleus as the origin of a polar co-ordinate system r, ϕ.

* The fundamental papers have been collected in the volume *The Principle of Relativity*, by Lorentz, Einstein, Minkowski (Methuen). Easy accounts are given in *The Theory of Relativity*, Einstein (Methuen) ; *Einstein's Theory of Relativity*, Born (Methuen). See also W. Pauli, *Enzykl. d. math. Wiss*, Vol. V, art. 19, Leipzig (Teubner) ; *Space, Time, Matter*, Weyl (Methuen).

The differential equations of relativistic mechanics state, exactly like classical mechanics (cf. p. 77): change of impulse or momentum is proportional to the external force. In the present case the external force is the Coulombian attraction emanating from the nucleus. The *impulse* or *momentum* is mv. We resolve it with respect to the co-ordinates r and ϕ into the two *momentum components* :*

$$p_r = m\dot{r}, \quad p_\phi = mr^2\dot{\phi}. \quad . \quad . \quad . \quad . \quad (3)$$

They differ from the impulse or momentum co-ordinates obtained in the non-relativistic treatment (eqn. (4) on p. 110) only in now having the mass m variable. Instead of starting from the differential equations of the problem we prefer to start from their first integrals, the *law of areas* and the *energy law*.

The law of areas states, as in classical mechanics, that the moment of the momentum about the centre of force, that is, our impulse component p_ϕ is constant :

$$p_\phi = p = \text{const.} \quad . \quad . \quad . \quad . \quad (4)$$

In the energy law the kinetic energy is given by eqn. (2) ; the potential energy is the same as in the classical treatment, namely $-\frac{Ze^2}{r}$. Hence the energy equation † runs

$$\mathrm{E}_{kin} + \mathrm{E}_{pot} = m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) - \frac{Ze^2}{r} = \mathrm{W}$$

or

$$\frac{1}{\sqrt{1-\beta^2}} = 1 + \frac{\mathrm{W} + Ze^2/r}{m_0c^2} \quad . \quad . \quad . \quad . \quad (5)$$

Now, in view of eqn. (3) we have

$$\beta^2 = \frac{v^2}{c^2} = \frac{1}{c^2}(\dot{r}^2 + r^2\dot{\phi}^2) = \frac{1}{c^2m^2}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right)$$

or, on account of (1),

$$\frac{\beta^2}{1-\beta^2} = \frac{1}{c^2m_0^2}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right)$$

$$\frac{1}{1-\beta^2} = 1 + \frac{1}{c^2m_0^2}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right).$$

* The momenta canonically conjugate to the co-ordinates q are to be defined relativistically as derivatives with respect to the q's, not of the kinetic energy, but of a " kinetic potential " $\mathrm{F} = -m_0c^2\sqrt{1-\beta^2} + \text{const.}$

† Here the rest-energy m_0c^2 has not been included in E_{pot}. Hence the energy constant W here has clearly the early significance (cf., for example, Chap. II): energy without rest-energy. In Note 6 we shall include the rest-energy in our calculations ; there the energy-constant E is related to W by the equation

$$\mathrm{E} = \mathrm{W} + m_0c^2.$$

Substituted in eqn. (5) this gives

$$1 + \frac{1}{c^2 m_0^2}\left(p_r^2 + \frac{1}{r^2}p_\phi^2\right) = \left(1 + \frac{W + Ze^2/r}{m_0 c^2}\right)^2 \quad . \quad . \quad (6)$$

By eqn. (3),

$$\frac{p_r}{p_\phi} = \frac{m\dot{r}}{mr^2\dot{\phi}} = \frac{1}{r^2}\frac{dr}{d\phi} = -\frac{ds}{d\phi} \quad . \quad . \quad . \quad (7)$$

where we have set

$$s = \frac{1}{r} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Taking $p_\phi^2 = p^2$ out of the brackets in eqn. (6) we have

$$1 + \frac{p^2}{m_0^2 c^2}\left[\left(\frac{ds}{d\phi}\right)^2 + s^2\right] = \left(1 + \frac{W + Ze^2 s}{m_0 c^2}\right)^2 \quad . \quad . \quad (9)$$

It is convenient to differentiate this equation with respect to ϕ:

$$p^2\left(\frac{d^2s}{d\phi^2} + s\right)\frac{ds}{d\phi} = m_0 Ze^2\left\{1 + \frac{1}{m_0 c^2}(W + Ze^2 s)\right\}\frac{ds}{d\phi}.$$

By cancelling $ds/d\phi$ on both sides and taking over the terms in s to the left-hand side, we obtain the following *linear* differential equation for s:

$$\frac{d^2s}{d\phi^2} + \gamma^2(s - C) = 0 \quad . \quad . \quad . \quad . \quad (10)$$

Here we have used the abbreviations

$$\gamma^2 = 1 - \frac{Z^2e^4}{p^2c^2} \quad . \quad . \quad . \quad . \quad . \quad (10a)$$

$$C = \frac{m_0 Ze^2}{p^2\gamma^2}\left(1 + \frac{W}{m_0 c^2}\right) \quad . \quad . \quad . \quad (10b)$$

The general integral of (10) is

$$s = A\cos\gamma\phi + B\sin\gamma\phi + C \quad . \quad . \quad . \quad (11)$$

where A and B are the integration constants. We count the angle ϕ in such a way that $\phi = 0$ corresponds to the perihelion of the orbit, that is, to the value $r = r_{min}$, $s = s_{max}$. We then have for $\phi = 0$

$$\frac{ds}{d\phi} = 0 \quad \text{and, by (11),} \quad B = 0.$$

Equation (11) then becomes

$$s = \frac{1}{r} = C + A\cos\gamma\phi \quad . \quad . \quad . \quad (12)$$

The equation (12) differs from the non-relativistic form of the orbital equation only in having the factor γ in the argument of the cosine. By (10*a*) this argument has the significance

$$\gamma^2 = 1 - \frac{p_0^2}{p^2} \quad . \quad . \quad . \quad . \quad (13a)$$

where p_0 denotes the abbreviation

$$p_0 = \frac{Ze^2}{c} \quad . \quad . \quad . \quad . \quad (13b)$$

and has the same dimensions as p. For $c = \infty$ we find that $p_0 = 0$ and $\gamma = 1$, so that our eqn. (12) becomes the equation which represents the ordinary Kepler ellipse. In reality, on account of the high value of c we see that in all the cases that come into question p_0 *is small compared with* p and γ *is very little less than* 1.

The form of the relativistic Kepler orbit has been drawn in Fig. 67. Here O is the fixed focus at which the nucleus is situated, P is the initial position of the perihelion. Let $\phi = 0$ be the straight line OP; the orbit then reaches its perihelion next, not when $\phi = 2\pi$, but when $\gamma\phi = 2\pi$, that is, when

$$\phi = \frac{2\pi}{\gamma} > 2\pi.$$

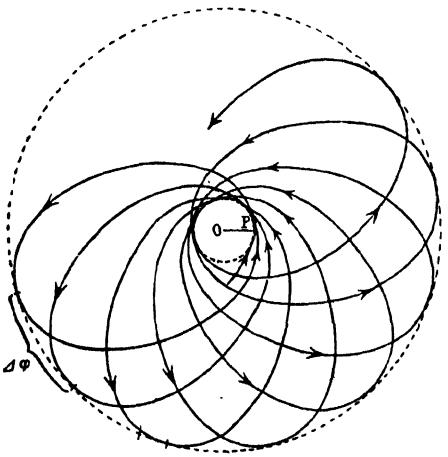


FIG. 67.—Relativistic Kepler motion. The perihelion and aphelion move in two concentric circles round the nucleus at 0.

The motion of the perihelion occurs in the same sense in which the orbit is being described and has the angular value

$$\Delta\phi = \frac{2\pi}{\gamma} - 2\pi \; . \quad (14)$$

If we refer the motion to a polar co-ordinate system which participates in the motion of the perihelion, namely to the system

$$r = r, \psi = \gamma\phi \quad . \quad . \quad . \quad . \quad (15)$$

then we again have an ordinary closed ellipse. In Fig. 67 we have also inserted, as dotted circles, the geometrical loci of the successive perihelia and aphelia, the outer and inner envelopes of the orbit.

The motion of the perihelion of the relativistic Kepler ellipse invites us to make a digression into the field of astronomy. As we know, Mercury, in disobedience to Newton's law, exhibits an advance of the perihelion which, according to Newcomb,* amounts to 43″ per century. Can this anomaly be explained in the light of formula (14) above? In the first place it is clear that our relativistic motion of the perihelion would manifest itself most readily in the case of Mercury, the planet nearest the sun. For this motion becomes more

* A later calculation by Newcomb gave 41″. Both numbers are discussed critically by E. Grossmann, Zeits. f. Physik, **5**, 280 (1921).

pronounced as γ decreases, and γ decreases with p. But the planet nearest the sun has the smallest areal constant p of all the planets. Calculation shows, however, that our relativistic motion of the perihelion is nevertheless far too small. In the case of Mercury it would amount to only 7″ per century. It was only when Einstein widened his special theory of relativity and proposed his general theory of relativity, which included gravitation, that he was able to give a theoretical explanation of the observed motion of Mercury's perihelion. In this way he found that for Mercury the theoretical value came out accurately as 43″ per century!

We now proceed to deal with the quantum conditions and the calculation of the energy. This is best done by referring to Hamilton's general method with which we treated the non-relativistic Kepler-ellipse in Chapter II, § 7. Instead of the momenta we introduce the action function S by means of

$$p_r = \frac{\partial S}{\partial r}, \quad p_\phi = \frac{\partial S}{\partial \phi} \quad . \quad . \quad . \quad . \quad (16)$$

Eqn. (6) then becomes the *Hamilton-Jacobi differential equation of the relativistic Kepler problem*

$$\left(\frac{\partial S}{\partial r}\right)^2 + \frac{1}{r^2}\left(\frac{\partial S}{\partial \phi}\right)^2 = 2m_0 W + \frac{2m_0 Ze^2}{r} + \frac{1}{c^2}\left(W + \frac{Ze^2}{r}\right)^2 . \quad (17)$$

The last term on the right-hand side is the supplementary relativity term, which distinguishes this equation from eqn. (5) on page 110.

Equation (17) admits separation in the co-ordinates r and ϕ. Since ϕ is cyclic the law of areas holds

$$\frac{\partial S}{\partial \phi} = \text{const.} = p \quad . \quad . \quad . \quad . \quad (18)$$

The azimuthal quantum condition demands that

$$J_\phi = \int_0^{2\pi} p_\phi d\phi = \int_0^{2\pi} \frac{\partial S}{\partial \phi} d\phi = n_\phi h \; . \quad . \quad . \quad (19)$$

where n_ϕ is a positive integer, *the azimuthal quantum number*. On account of (18) we have

$$2\pi p = n_\phi h \quad \text{or} \quad \frac{\partial S}{\partial \phi} = \frac{n_\phi h}{2\pi}.$$

Hence eqn. (17) becomes

$$\frac{\partial S}{\partial r} = \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}} \quad . \quad . \quad . \quad (20)$$

where

$$\left.\begin{aligned} A &= 2m_0 W + \frac{W^2}{c^2} = m_0{}^2 c^2 \left\{\left(1 + \frac{W}{m_0 c^2}\right)^2 - 1\right\} \\ B &= m_0 Ze^2 + \frac{Ze^2 W}{c^2} = m_0 Ze^2 \left(1 + \frac{W}{m_0 c^2}\right) \\ C &= -\frac{n_\phi^2 h^2}{4\pi^2} + \frac{Z^2 e^4}{c^2} = -\frac{n_\phi^2 h^2}{4\pi^2}\left[1 - \frac{\alpha^2}{n_\phi^2} Z^2\right] \end{aligned}\right\} \quad . \quad (21)$$

In the last expression, C, we have used the abbreviation

$$\alpha = \frac{2\pi e^2}{hc} \quad . \quad . \quad . \quad . \quad . \quad (22)$$

already introduced in eqn. (8) on page 86. α is called the **fine-structure constant.** It is a *pure number* which has the approximate (or exact ?) value $\frac{1}{137}$.

The radial quantum condition demands

$$J_r = \oint p_r dr = \oint \frac{\partial S}{\partial r} dr = n_r h. \quad . \quad . \quad . \quad (23)$$

Here n_r is a positive integer, namely the *radial quantum number.* On account of (20), (23) becomes

$$\oint \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}}\, dr = n_r h.$$

This condition differs neither in form nor in content from that of Chapter II, § 7, eqns. (10) and (11), and hence gives

$$-2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}}\right) = n_r h. \quad . \quad . \quad . \quad (24)$$

But on account of the present meaning (21) of A, B, C we have

$$-2\pi i\sqrt{C} = -n_\phi h\sqrt{1 - \frac{\alpha^2}{n_\phi^2}Z^2}$$

$$\frac{B}{\sqrt{A}} = \frac{Ze^2}{c}\left\{1 - \left(1 + \frac{W}{m_0c^2}\right)^{-2}\right\}^{-\frac{1}{2}}.$$

Hence eqn. (24) becomes

$$\frac{2\pi iZe^2}{c}\left\{1 - \left(1 + \frac{W}{m_0c^2}\right)^{-2}\right\}^{-\frac{1}{2}} = \left[n_r + \sqrt{n_\phi^2 - \alpha^2Z^2}\right]h \quad . \quad (25)$$

Dividing by h we get $i\alpha Z$ in front of the bracket; squaring we obtain

$$1 - \left(1 + \frac{W}{m_0c^2}\right)^{-2} = -\frac{\alpha^2Z^2}{\left[n_r + \sqrt{n_\phi^2 - \alpha^2Z^2}\right]^2}$$

$$1 + \frac{W}{m_0c^2} = \left\{1 + \frac{\alpha^2Z^2}{\left[n_r + \sqrt{n_\phi^2 - \alpha^2Z^2}\right]^2}\right\}^{-\frac{1}{2}} \quad . \quad . \quad (26)$$

We can now write down immediately the *general relativistic formula for all hydrogen-like series* by adducing only Bohr's fundamental equation

$$h\nu = W_1 - W_2$$

(where W_1 = energy of the initial orbit of the hydrogen electron and W_2 = energy of the final orbit). We then obtain

$$\frac{\nu}{R} = \frac{2}{\alpha^2}\left[\left\{1 + \frac{\alpha^2 Z^2}{\left[n_r + \sqrt{n_\phi^2 - \alpha^2 Z^2}\right]^2}\right\}_1^{-\frac{1}{2}} - \left\{1 + \frac{\alpha^2 Z^2}{\left[n_r + \sqrt{n_\phi^2 - \alpha^2 Z^2}\right]^2}\right\}_2^{-\frac{1}{2}}\right] \quad (27)$$

The indices 1 and 2 attached to the bottom of the brackets } signify that for n_r and n_ϕ we must insert the values corresponding to the initial and final states respectively. Z is equal to 1, 2, 3, . . . for H, He^+, Li^{++}, . . .

Since the right-hand side of (27) has zero dimensions R is expressible in the same form as ν. Hence we may, according to requirements express ν and R simultaneously either in wave-numbers (cf. p. 70) or in vibration numbers (frequencies).

It is only necessary to add a note about the constants that multiply the square bracket in our way of writing eqn. (27). From eqn. (26) we first obtain

$$\nu = \frac{m_0 c^2}{h}\left[\ \ldots\ \right] \quad . \quad . \quad . \quad . \quad (28)$$

for which we wrote in eqn. (27),

$$\nu = \frac{2R}{\alpha^2}\left[\ \ldots\ \right] \quad . \quad . \quad . \quad . \quad (28a)$$

We see at once from the significance of R in sec.$^{-1}$

$$R = R_\infty = \frac{2\pi^2 m_0 e^4}{h^3}, \quad \alpha = \frac{2\pi e^2}{hc}$$

that the two factors in (28) and (28*a*) are identical. The fact that we here calculate with R_∞ is connected with the circumstance that we have disregarded the relative motion of the nucleus in this section. To take this into account subsequently (cf. also note 2 on p. 259) we shall continue to take R as standing for R_H (in the case of He the value is R_{He}, cf. Chap. II, § 5).

Our present spectral formula no longer depends only on the quantum sum $n_r + n_\phi$ as was the case in the earlier spectral formula (14) on page 112. Hence it follows that *the lines having the same principal quantum number earlier now become separated by relativity.* This separation depends on the correction term which carries the small factor $\alpha^2 = 5{\cdot}3 \,.\, 10^{-5}$. For this reason the separation is only slight and can be shown to exist only by the most refined means of experimental spectroscopy. The lines that were formerly described as coincident now split up into a *narrow complex of lines.* The individual

component lines of the complex determine, through their intervals of separation and intensities, the **fine-structure** of the configuration.

The above-calculated *energy-levels* and the line-complexes to be derived from them also retain their validity in wave-mechanics. The way in which wave-mechanics derives them is not only far less picturesque (*anschaulich*) but also much more laborious than the way described above. Hence it was necessary to carry out the calculation as far as possible according to the method of the older quantum theory; the inferences drawn can then later be taken over directly into wave-mechanics.

§ 2. General Inferences. Line-separations and Relativity Corrections

To make the final formula (27) of the preceding section more convenient for purposes of calculation we expand it in powers of the small quantity α^2. If Z is not a large number (H, He^+) it is sufficient to retain the first two powers of α^2. This is so in the case of the *visible* and *ultra-violet spectra*. If Z is a great number the third and the fourth power of α^2 must also be taken into consideration. This is so in the case of X-ray spectra. For extremely great values of Z (U, Th, . . .) it may even be convenient not to expand α^2 at all but to use the complete formula (27).

For the *visible spectra* the calculation therefore becomes simple. If we denote the denominator that occurs in eqn. (27), § 1, generally by S, then

$$S = n_r + \sqrt{n_\phi^2 - (\alpha Z)^2} = n_r + n_\phi - \frac{1}{2n_\phi}(\alpha Z)^2 + \ldots \quad (1)$$

and we obtain

$$\left\{1 + \frac{(\alpha Z)^2}{S^2}\right\}^{-\frac{1}{2}} = 1 - \frac{1}{2}\frac{(\alpha Z)^2}{S^2} + \frac{3}{8}\frac{(\alpha Z)^4}{S^4} - \ldots \quad (2)$$

Further we obtain to a sufficient degree of approximation, with $n = n_r + n_\phi$,

$$\left.\begin{aligned} \frac{1}{S^2} &= \left[n - \frac{1}{2n_\phi}(\alpha Z)^2 + \ldots\right]^{-2} = \frac{1}{n^2}\left[1 + \frac{1}{nn_\phi}(\alpha Z)^2 + \ldots\right] \\ \frac{1}{S^4} &= \frac{1}{n^4}[1 + \ldots] \end{aligned}\right\} \quad (3)$$

Substituted in (2) this gives

$$\left\{1 + \frac{(\alpha Z)^2}{S^2}\right\}^{-\frac{1}{2}} = 1 - \frac{1}{2}\frac{(\alpha Z)^2}{n^2} - \frac{1}{2}\frac{(\alpha Z)^4}{n^4}\left(\frac{n}{n_\phi} - \frac{3}{4}\right) + \ldots \quad (4)$$

If we substitute this expansion in eqn. (27) of the preceding section the first term 1 of the two expansions cancels in the difference, and we may divide out the factor $2/\alpha^2$, which stands in front of the bracket. The wave-number ν then appears as the difference between a *first*

positive term dependent on the quantum numbers of the *final orbit* and a *second negative term* dependent on the quantum numbers of the *initial orbit*. By using the same symbol ν for the terms as for the emitted wave-number we obtain

$$\nu = \nu_1 - \nu_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\nu_i = RZ^2\left\{\frac{1}{n^2} + \frac{\alpha^2}{n^4}Z^2\left(\frac{n}{n_\phi} - \frac{3}{4}\right) + \ldots\right\}, \; i = 1, \; 2 \quad . \quad (6)$$

The first term on the right-hand side agrees with the term representation for the hydrogen-like lines in the second chapter and depends only on the principal quantum number n. The second term expresses the influence of relativity. For the states * $n = n_\phi$ it is

$$\frac{1}{4}\frac{\alpha^2 R}{n^4}Z^4.$$

Compared with the Balmer formula it effects an increase in the value of the terms. We call this part the *general relativity correction.* In the case of the first term of the Balmer series ($Z = 1$, $n = 2$) it bears the following ratio to the whole term :

$$\frac{\alpha^2}{16} = 3 \cdot 10^{-6}.$$

On the other hand, relativity causes a special increase in the case of the states $n > n_\phi$, which depends on n *and* n_ϕ *individually and increases with decreasing* n_ϕ. *Calculated relatively to the states* $n = n_\phi$ *its value is*

$$\left(\frac{n}{n_\phi} - 1\right)\frac{\alpha^2 R}{n^4}Z^4.$$

We call this part the *separation* (*Aufspaltung*) *of the term ;* it is the foundation of the *fine-structure of the lines.*† For the first term of the Balmer series and the only state that comes into consideration here, $n \neq n_\phi$ ($n = 2$, $n_\phi = 1$), this separation bears the following ratio to the whole term :

$$\frac{\alpha^2}{4} = 1{\cdot}3 \cdot 10^{-5}.$$

* The states $n = n_\phi$ clearly denote " circular orbits " in the sense of the old orbital ideas ($n_r = 0$), whereas the states $n > n_\phi$ denote " elliptic orbits " ($n_r > 0$). We avoid these expressions now because these old orbital ideas can be allocated uniquely to the wave-mechanical states only with respect to energy, not with respect to quantum numbers, cf. § 4 of the present chapter, p. 280.

† C. G. Darwin has performed the same calculation, taking into account rigorously the relative motion of the nucleus [Phil. Mag., **39**, 537 (1920)]. He finds that the nuclear motion manifests itself not only in the Rydberg constant, but also in a small additive correction term of the order of magnitude $\alpha^2 m/M$ (m = electronic mass, M = atomic mass), which is inappreciable practically. The fine-structure remains quite unaffected by it.

For the purposes of X-ray spectroscopy we must now carry the accuracy of the calculation further. In place of (1), (2), and (3) we must then write

$$S = n_r + n_\phi - \frac{\alpha^2 Z^2}{2n_\phi} - \frac{\alpha^4 Z^4}{8n_\phi^3} - \frac{\alpha^6 Z^6}{16 n_\phi^5} - \ldots \quad (1a)$$

$$\left\{1 + \frac{(\alpha Z)^2}{S^2}\right\}^{-\frac{1}{2}} = 1 - \frac{1}{2}\frac{(\alpha Z)^2}{S^2} + \frac{3}{8}\frac{(\alpha Z)^4}{S^4} - \frac{5}{16}\frac{(\alpha Z)^6}{S^6} + \frac{35}{128}\frac{(\alpha Z)^8}{S^8} + \ldots \quad (2a)$$

and to a sufficient degree of approximation in each case :

$$\left.\begin{aligned}
\frac{1}{S^2} &= \frac{1}{n^2}\left[1 + \frac{1}{nn_\phi}(\alpha Z)^2 + \frac{n + 3n_\phi}{4n^2 n_\phi^3}(\alpha Z)^4 + \frac{n^2 + 3nn_\phi + 4n_\phi^2}{8n^3 n_\phi^5}(\alpha Z)^6 + \ldots\right] \\
\frac{1}{S^4} &= \frac{1}{n^4}\left[1 + \frac{2}{nn_\phi}(\alpha Z)^2 + \frac{n + 5n_\phi}{2n^2 n_\phi^3}(\alpha Z)^4 + \ldots\right] \\
\frac{1}{S^6} &= \frac{1}{n^6}\left[1 + \frac{3}{nn_\phi}(\alpha Z)^2 + \ldots\right] \\
\frac{1}{S^8} &= \frac{1}{n^8}\left[1 + \ldots\right]
\end{aligned}\right\} \quad (3a)$$

If we substitute (3a) in (2a) we obtain (after cancelling 1 and multiplying by $-2R/\alpha^2$) as the complete expression for the term :

$$\begin{aligned}
\nu_i = RZ^2\Big\{&\frac{1}{n^2} + \frac{\alpha^2}{n^4}Z^2\left(\frac{n}{n_\phi} - \frac{3}{4}\right) \\
&+ \frac{\alpha^4}{n^6}Z^4\left[\frac{1}{4}\left(\frac{n}{n_\phi}\right)^3 + \frac{3}{4}\left(\frac{n}{n_\phi}\right)^2 - \frac{3}{2}\frac{n}{n_\phi} + \frac{5}{8}\right] \\
&+ \frac{\alpha^6}{n^8}Z^6\left[\frac{1}{8}\left(\frac{n}{n_\phi}\right)^5 + \frac{3}{8}\left(\frac{n}{n_\phi}\right)^4 + \frac{1}{8}\left(\frac{n}{n_\phi}\right)^3 - \frac{15}{8}\left(\frac{n}{n_\phi}\right)^2 + \frac{15}{8}\frac{n}{n_\phi} - \frac{35}{64}\right] + \ldots\Big\}, \; i = 1, 2
\end{aligned} \quad (6a)$$

We shall use this expression in § 4 ; the expression (6) is sufficient for the next problems, which lie in the visible region. We are concerned with the *separation* of the different series terms. A survey of the types of separation is given in Fig. 68. The distance between the lines gives the difference in the term-values and also the difference in the vibration numbers of the spectral lines which are formed from these term-values. The numbers attached to the distances between the lines denote ratios and are explained by the equations (8a), (9a), and (10). The types which stand vertically below one another are not directly comparable in size, having been reduced to equal distances

for the extreme components, whereas in reality these distances decrease rapidly on account of the increasing denominator, 2^4, 3^4, 4^4. . . .

$n = 1$, $n_\phi = 1$.

The value $n_\phi = 0$ is to be excluded here as in the non-relativistic case (cf. p. 115); *the series term is simple.*

$n = 2$, $n_\phi = 2$ or 1.

The series term is double. The difference between the sub-levels (*Teilniveaux*) corresponds spectroscopically, according to eqn. (6), to *a doublet-line with the difference in vibration numbers:*

$$\Delta\nu = \frac{R\alpha^2}{2^4}Z^4. \quad . \quad . \quad (7)$$

$n = 3$, $n_\phi = 3$ or 2 or 1.

The series term is three-fold. The corresponding term-values $n_\phi = 3$, 2, 1 increase successively. By eqn. (6) the successive term differences are:

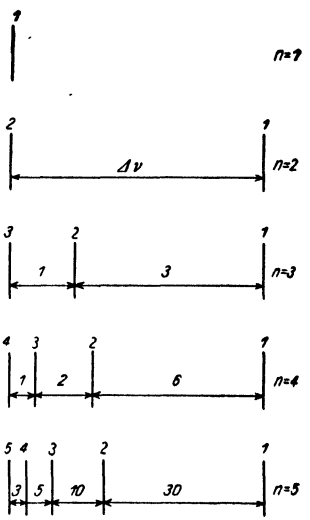


FIG. 68.—Relative separation of the hydrogen terms, n, $n\phi$ according to the relativistic term formulæ (6). The numbers written against the individual lines denote the respective values of n_ϕ.

$$\left.\begin{aligned}\text{Term-difference between } n_\phi = 3 \text{ and } n_\phi = 2 &= \frac{R\alpha^2Z^4}{3^4}\left(\frac{3}{2} - \frac{3}{3}\right)\\ \text{Term-difference between } n_\phi = 2 \text{ and } n_\phi = 1 &= \frac{R\alpha^2Z^4}{3^4}\left(\frac{3}{1} - \frac{3}{2}\right)\end{aligned}\right\} \quad (8)$$

Corresponding to them we have the differences in vibration-numbers of a *triplet with the relative distances between the lines*:

$$\Delta\nu_1 : \Delta\nu_2 = 1 : 3 \quad . \quad . \quad . \quad . \quad (8a)$$

$n = 4$, $n_\phi = 4, 3, 2, 1$.

The series term is four-fold. By eqn. (6) the successive term differences come out as:

$$\left.\begin{aligned}\text{Term-difference between } n_\phi = 4 \text{ and } n_\phi = 3 &= \frac{R\alpha^2Z^4}{4^4}\left(\frac{4}{3} - \frac{4}{4}\right)\\ \text{Term-difference between } n_\phi = 3 \text{ and } n_\phi = 2 &= \frac{R\alpha^2Z^4}{4^4}\left(\frac{4}{2} - \frac{4}{3}\right)\\ \text{Term-difference between } n_\phi = 2 \text{ and } n_\phi = 1 &= \frac{R\alpha^2Z^4}{4^4}\left(\frac{4}{1} - \frac{4}{2}\right)\end{aligned}\right\} \quad (9)$$

The four-fold value of the term gives rise to a *quartet* with the successive relative differences in vibration number :

$$\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 = 1 : 2 : 6. \quad . \quad . \quad . \quad (9a)$$

$\mathbf{n = 5.}$

The successive differences in the vibration numbers in the resulting quintet are in the ratio

$$\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 : \Delta\nu_4 = 3 : 5 : 10 : 30 \quad . \quad . \quad (10)$$

and so forth.

This separation of the *terms* must be distinguished from the *line configuration* which results from combinations of the terms. If the multiplicity lies in the first, that is, the *constant* and *positive*, term of a series (represented in eqn. (5) by ν_1) we have an analogy * to the *doublets*, *triplets* and so forth, which have a *constant difference in wave-number*, in the *subordinate series* of the alkalies, alkaline earths and so forth (cf. Chap. VII, § 1). If the multiplicity lies in the second, that is, the *variable* and *negative* term (represented in eqn. (5) by ν_2) we have an analogy to the *decreasing differences in the vibration numbers*, as have been observed in the *principal series* of the elements which are *not* hydrogen-like (cf. Chap. VII, § 1). On account of the negative sign of the variable term the components here succeed one another in the inverse sense to the structures resulting from the positive first term. If both the constant positive term and the variable negative term are multiple, complicated line-configurations result through superposition, an impression of which is given by the figures in the next section.

§ 3. Comparison with the Results of Experiment

The constant term $1/2^2$ of the Balmer series of hydrogen gives rise to a *doublet of constant difference of wave-number*. The value $\Delta\nu_H$ of this difference will serve as a unit in the sequel. Thus by eqn. (7) of the preceding section and since $Z = 1$,

$$\Delta\nu_H = \frac{R\alpha^2}{2^4} = 0{\cdot}3636 \pm 0{\cdot}0006 \text{ cm.}^{-1}. \quad . \quad . \quad (1)$$

Here we have set $\alpha^2 = (5{\cdot}305 \pm 0{\cdot}008) \,.\, 10^{-5}$ and $R = 1{\cdot}097 \,.\, 10^5$. The calculation of α^2 is based on the numbers

$$e = (4{\cdot}770 \pm 0{\cdot}005) \,.\, 10^{-10}, \; h = (6{\cdot}547 \pm 0{\cdot}008) \,.\, 10^{-27}.$$

Of the numerous experimental determinations we shall refer to only the oldest and the newest. The oldest was that carried out by

* The analogy is incomplete, because the line-structure in the case of such elements is not hydrogen-like.

Michelson * in 1887 by the interferometer method, which gave the values

for H_α	H_β
$\Delta\nu = 0{\cdot}32$	$0{\cdot}33$ cm.$^{-1}$.

The most recent determination is that of G. Hansen,† which was carried out with the support of the Zeiss works, Jena; excellently prepared Lummer-Gehrcke plates were used. The following uncorrected values for the doublet-separation were found among others:

for	H_α	H_β	H_γ	H_δ	H_ϵ
$\Delta\nu =$	$0{\cdot}316$	$0{\cdot}317$	$0{\cdot}328$	$0{\cdot}322$	$0{\cdot}324$ cm.$^{-1}$

Thus $\Delta\nu_H$ is appreciably constant within the series. This corresponds with the origin of $\Delta\nu_H$ from the *first constant* series term, cf. the end of the preceding section. The difference in magnitude between the observed and the calculated value (1) is explained in part by the influence of the second variable term (see below).

Direct observation is rendered difficult on account of the blurred character of the H-lines. This blurred character is due to the heat motion of the emitting H-atoms and their Doppler effect. The higher the temperature the greater the velocity due to heat-motion, the higher the atomic weight the smaller the velocity due to heat-motion. Hence in the case of the hydrogen atom the heat motion is particularly intensive; in this case we must go down to the lowest temperatures to obtain tolerably sharp lines. A further reason for the blurring of the hydrogen lines is the Stark effect (Chap. VI, § 3). This effect produces far stronger separations in the case of hydrogen than other atoms. It occurs not only in artificially applied fields, but also under the electrical action of neighbouring atoms, which distort the electronic orbits of the reference-atom.

But there is an *indirect method of observation*, which was used by Paschen (see below) and which enables the value of $\Delta\nu_H$ to be deduced from the fine-structure of the lines of a more favourable atom (He^+). Paschen ‡ finds

$$\Delta\nu_H = \begin{cases} 0{\cdot}3645 \pm 0{\cdot}0045 \text{ cm}^{-1} \text{ (in 1916)} \\ 0{\cdot}358 \text{ to } 0{\cdot}363 \text{ cm.}^{-1} \text{ (in 1927)} \end{cases} \quad . \quad . \quad (2)$$

This value agrees well with the theoretical value (1). *This accounts qualitatively and quantitatively for the hydrogen doublet which was formerly so perplexing.*

The doublet which arises from the constant term has superposed on itself in the Balmer series the *multiplicity of the second variable* term,

* Phil. Mag., **24**, 466 (1887); **34**, 280 (1892).

† Ann. d. Phys., **78**, 558 (1925); Dissertation, Jena; cf. in particular Table 5.

‡ Ann. d. Phys., **50**, 901 (1916); **82**, 689 (1927).

according to theory (cf. the end of the preceding section). Consequently the two doublet-components consist for their part of a triplet in the case of H_α, a quartet in that of H_β, a quintet in that of H_γ, and so forth.

We illustrate the structure of H_α in Fig. 69. We begin with the *doublet lines* I and II, which correspond with the first term $1/2^2$. II follows on I in the sense of *increasing* wave-numbers. To both lines we add the triplet *abc* which arises from the second term $1/3^2$,

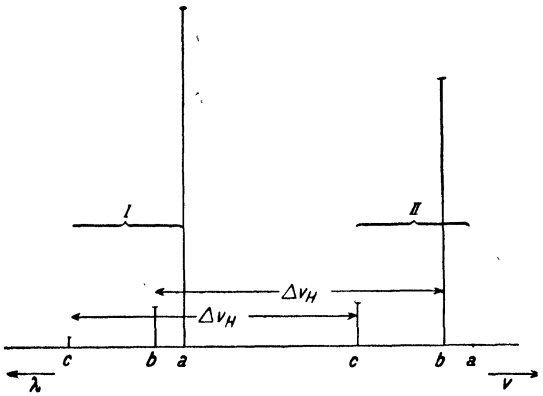


FIG. 69.—Fine-structure of H_α. The structure I, II originates in the relativistic subdivision of the end level $n = 2$, the structure *abc* from that of the initial level $n = 3$. The heights of the lines represent the intensities calculated wave-mechanically. The line II*a* vanishes.

namely, in the sense of decreasing wave-numbers on account of the *negative* sign of the second term. Hence we have not two separate lines I, II, but two *groups* of lines I and II, each consisting of 3 lines *abc*, that is, of 6 lines in all, one of which is of vanishingly small intensity. The intensities have been represented in the figure by the length of the vertical lines. The lines *abc* bear the characteristic separation-ratios to each other, given by eqn. (8*a*) of the preceding section:

$$\Delta\nu_1 : \Delta\nu_2 = ab : bc = 1 : 3.$$

The doublet-separation I II $= \Delta\nu_H$, eqn. (7) of the preceding section, occurs twice, namely between the similarly named components *bb*, *cc*. (The fact that it does not also occur between *aa* is because the short wave *a*-component has vanishingly small intensity.) The triplet separations $\Delta\nu_1$, $\Delta\nu_2$ are expressed as follows in terms of $\Delta\nu_H$ according to eqn. (8) of the preceding section:

$$\left.\begin{aligned}\Delta\nu_1 &= \frac{1}{2}\frac{R\alpha^2}{3^4} = \frac{1}{2}\frac{2^4}{3^4}\Delta\nu_H = \frac{8}{81}\Delta\nu_H \\ \Delta\nu_2 &= \frac{3}{2}\frac{R\alpha^2}{3^4} = \frac{3}{2}\frac{2^4}{3^4}\Delta\nu_H = \frac{8}{27}\Delta\nu_H\end{aligned}\right\} \quad . \quad . \quad (3)$$

Fig. 70 illustrates in the same way the line-structure of H_β. We again start out from the *doublet-lines* I II that correspond to the first term $1/2^2$ and add to it the quartet *abcd* in *decreasing* wave-numbers, which arises from the second negative term $1/4^2$. Of the 8 lines that result in this way only 5 have non-vanishing intensity again. According to eqn. (9*a*) of the preceding section the lines *abcd* bear the characteristic separation-ratios for quartets :

$$\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 = ab : bc : cd = 1 : 2 : 6.$$

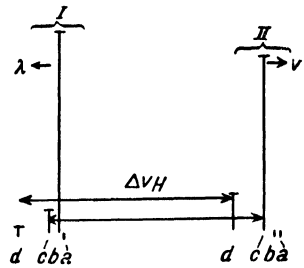


FIG. 70.—Fine structure of H_β. I, II corresponds as in Fig. 69 to the structure of the end level $n = 2$, *abcd* to that of the initial level $n = 4$. Heights of lines = wave-mechanical intensities. The lines I*a*, II*a*, II*b* vanish.

The doublet distance I II $= \Delta\nu_H$ occurs again twice (on account of the intensity of the satellite lines vanishing in part), namely, between *cc*, *dd*.

The differences in the wave-numbers of the quartet are, by eqn. (9) of the preceding section, in terms of $\Delta\nu_H$:

$$\left.\begin{aligned} \Delta\nu_1 &= \frac{1}{3}\frac{R\alpha^2}{4^4} = \frac{1}{3}\frac{2^4}{4^4}\Delta\nu_H = \frac{1}{48}\Delta\nu_H, \\ \Delta\nu_2 &= \frac{2}{3}\frac{R\alpha^2}{4^4} = \frac{2}{3}\frac{2^4}{4^4}\Delta\nu_H = \frac{1}{24}\Delta\nu_H, \\ \Delta\nu_3 &= 2\frac{R\alpha^2}{4^4} = 2\frac{2^4}{4^4}\Delta\nu_H = \frac{1}{8}\Delta\nu_H \end{aligned}\right\} \quad . \quad . \quad (4)$$

Thus the two groups of lines I and II have contracted at H_β as compared with H_α ; the number of lines has remained the same, namely, 5.

From Figs. 69 and 70 we read off the reason why the observed hydrogen doublet of the Balmer series does not quite coincide with the ideal hydrogen doublet. The ideal hydrogen doublet denotes the distance between similarly named lines *aa*, *bb*, and so forth. In actual measurements, however, we adjust to the intensity *maxima* of the groups of lines I and II, whose separations are less than $\Delta\nu_H$. *The ideal hydrogen doublet would be correctly measured only when we arrive at the limit where the high members of Balmer's series occur* (H_δ, H_ϵ, . . .), for which the fine-structure arising from the second term contracts more and more to the pure doublet of the first term. The observations of Hansen communicated above correspondingly show an increase of $\Delta\nu$ with increasing order number in the Balmer series ; but this increase is less than it should be according to theory. We remark, however, that the $\Delta\nu$ observed by Hansen for H_α nearly coincides with the separation that we obtain if we calculate the intensity-centres of gravity in the groups of lines I and II for H_α according to wave-mechanics.

We now come to the true test of our theory, the spectra of ionised helium. They were photographed by Paschen * and were interpreted in close collaboration with the author whose theory of fine-structure was put forward at the same time and was definitely confirmed in Paschen's results.

Why are the spectra of He^+ more favourable for our purpose than those of H ? Both are of the same degree of simplicity and theoretical accessibility, both being produced by one electron and a nucleus. But the He-lines are sharper than the H-lines ; the He-atom is four times as heavy as the H-atom, hence its lines are less widened by the Doppler effect due to heat motion ; moreover, the He-nucleus is twice as strongly charged as the H-nucleus, and hence its lines are also less influenced by the Stark effect (cf. the next chapter). Nevertheless the separation of the components is also not complete in the case of He and makes great demands on the resolving power of the spectroscopes used.

We deal first with the Fowler series, which is erroneously called the " principal series of hydrogen " (cf. Chap. II, § 2, p. 74), the formula for which runs, if we disregard all relativistic influences,

$$\nu = 4R\left(\frac{1}{3^2} - \frac{1}{n^2}\right), \; n = 4, 5, 6 \ldots \quad . \quad . \quad (5)$$

The following lines (or more accurately the groups of lines) belong to it :

$n =$	4	5	6	7	8
$\lambda =$	4686	3203	2733	2511	2385

They form the transposition, effected by the factor 4, of the infra-red series of hydrogen discovered by Paschen into the violet region.

The group of lines $\lambda = 4686$ (initial term quadruple, final term triple) consists virtually of $4 \cdot 3 = 12$ components ; the latter term produces a triplet I, II, III with the characteristic separations $\Delta\nu_1 : \Delta\nu_2 = 1 : 3$, the former a quartet *a*, *b*, *c*, *d* with a reversed sequence of the lines with the separations $\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 = 1 : 2 : 6$.

In the top line of Fig. 71 we see the relative theoretical position of the twelve components. The intensities here assumed (lengths of the vertical lines) have again been calculated by wave-mechanics for the case where the atoms are subjected to no disturbing influences of any sort (direct-current discharge) ; then only 8 of the 12 components are to have non-vanishing intensity, the lines I*d*, II*a*, III*a* and III*b* fall out. The component II*d* of the quartet II overlaps with the quartet I. All the component separations are expressed rationally in terms of the fine-structure component α^2 and hence are rational multiples of the hydrogen doublet $\Delta\nu_H$. For example, by eqn. (8)

* Bohr's Helium Lines, Ann. d. Phys., **50**, 901 (1916).

on page 261 and eqn. (1) on page 262, we obtain in wave-numbers :

$$(\mathrm{II}a - \mathrm{I}a) = (\mathrm{II}b - \mathrm{I}b) = \ldots = 8(\tfrac{2}{3})^4\Delta\nu_{\mathrm{H}}$$
$$(\mathrm{III}a - \mathrm{II}a) = (\mathrm{III}b - \mathrm{II}b) = \ldots = 24(\tfrac{2}{3})^4\Delta\nu_{\mathrm{H}}$$

and by eqn. (9) on page 261 and eqn. (1) on page 262 :

$$(\mathrm{I}c - \mathrm{I}d) = (\mathrm{II}c - \mathrm{II}d) = \ldots = 32(\tfrac{2}{4})^4\Delta\nu_{\mathrm{H}}$$

and so forth.

For comparison we have given in the second row the experimental picture, such as is obtained in an intense spark-discharge (great current-density). If we start from the right-hand side we see that in the group

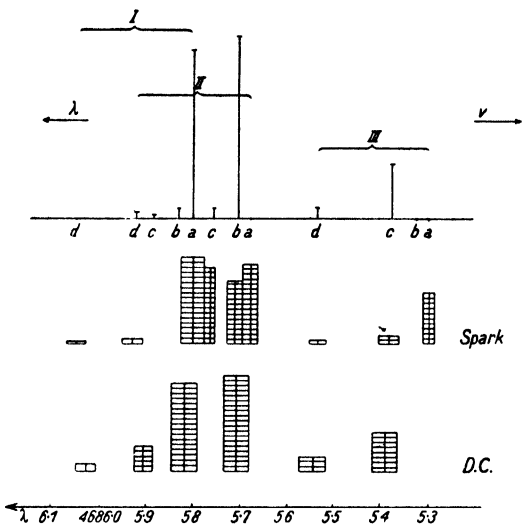


FIG. 71.—Fine-structure of λ4686 (He^+, $n = 4 \rightarrow n = 3$). At the top of the figure is shown the theoretical resolution and wave-mechanical intensity distribution calculated for D.C. discharge (no disturbance due to the electric fields of neighbouring atoms). In the middle is an experimental picture for condensed spark discharge representing the visual impression recorded by Paschen. The same for D.C. discharge is shown at the bottom. Here four of the twelve components vanish theoretically, namely, I*d*, II*a*, III*a*, III*b*.

III the adjacent components *ab* are fused together, but the lines *c* and *d* are separated. The width and height of the rectangles in the picture exhibit the width and strength of the observed lines. The lines *a* and *b* are also fused together in the group II and I, the line I*ab* coming out more strongly than the line II*ab*. The weak line II*c* appears fused in the picture with I*ab*. The line I*c* is not separated from II*d*.

It was precisely this picture which, on account of its wonderful completeness, served Paschen for calculating the ideal hydrogen doublet, cf. page 263.

In order that the experimental difficulties of obtaining the photographs may not be underestimated we call attention to the scale of wave-lengths attached to the figures. It shows that the distance between the extreme lines III*a* and I*d* does not even amount to 0·8Å.

The picture assumed a different aspect when, instead of the intense spark-discharge an *ordinary direct current* was used to excite the helium tube ; the difference lay in *the intensities but not in the position of the lines* (cf. the lower row of Fig. 71). Here the intensities also approach the theoretical values represented in the top row, for example, in the fact that the lines III*ab* are absent in the picture given by the direct current.

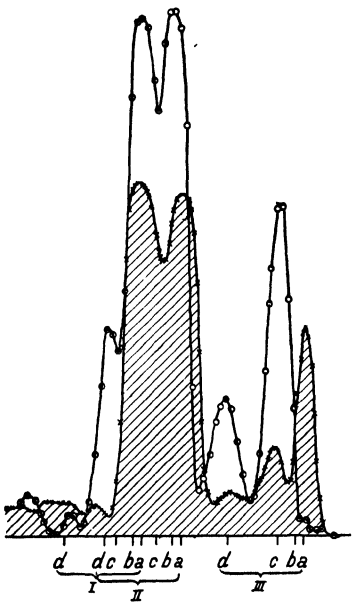


FIG. 72.—Photometer curve of the fine-structure of λ4686 (He^+) according to Paschen : ○ with D.C. discharge, **X** with condensed spark discharge. The area below the curve corresponding to the latter is shaded. The theoretical positions of the lines are indicated by small vertical dashes placed below the curves.

In Fig. 72 we are able to give photometric measurements kindly communicated by Professor Paschen. They are derived from two original photographs taken in the third order, which have also been taken into account in Fig. 71 in representing the visual impression, and which are here represented objectively by means of the galvanometer deflections of a thermo-electric photometer. We see instead of the rectangles drawn earlier continuous curves of photographic density with well-defined maxima. These lie exactly over each other in both photographs ; the differencse are only differences in intensity.

We pass over in the series (5) to the group of lines :

$$\lambda = 3203, \quad \nu = R\left(\frac{1}{3^2} - \frac{1}{5^2}\right).$$

It consists theoretically of the combination of a triplet with a quintet, —as a whole then, of 15 components, of which again only 8 are to have non-vanishing intensity. The quintet is (on account of the denominator 5^4) contracted more strongly than the preceding quartet, and that is why the quintets I and II hardly overlap any more here. In the experimental picture (direct-current photograph) II*cd* appears

as the strongest, I*bcd* and II*e* as the second strongest components. III*d* is weaker, and the components III*e* and I*e* are quite weak.

The experimental direct-current photograph of the next group of lines

$$\lambda = 2733, \quad \nu = \mathrm{R}\left(\frac{1}{3^2} - \frac{1}{6^2}\right)$$

becomes particularly simple. The sextet of the second term is here already contracted so far that it appears unseparated everywhere in

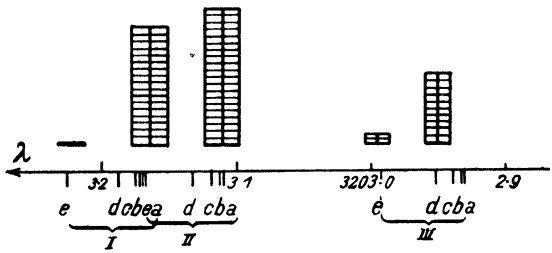


FIG. 73.—Fine-structure of λ3203 with D.C. discharge (H^+, $n = 5 \rightarrow n = 3$) according to the visual impression recorded by Paschen. The theoretical positions of the lines are shown beneath. Of the fifteen components the following vanish theoretically in the D.C. picture—I*a*, I*e*, II*a*, II*b*, III*b*, III*c*.

observation. It is in accordance with this that Fig. 74 exhibits the *pure triplet of the first term with the characteristic separation-ratio* 1 : 3.

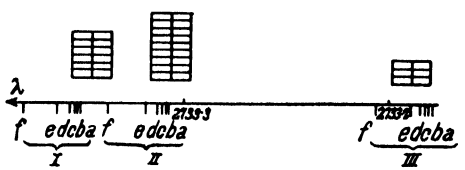


FIG. 74.—Fine-structure of λ2733 with D.C. discharge (He^+, $n = 6 \rightarrow n = 3$) according to the visual impression recorded by Paschen. The theoretical positions of the lines are shown beneath. Of the eighteen components the following vanish theoretically in the D.C. picture—I*a*, I*b*, I*f*, II*a*, II*b*, II*c*, III*a*, III*b*, III*c*, III*d*.

Paschen has also investigated the second of the He^+-series mentioned on page 75, the so-called **Pickering series,** formerly called erroneously the " second subordinate series of hydrogen " :

$$\nu = 4\mathrm{R}\left(\frac{1}{4^2} - \frac{1}{n^2}\right), \quad n = 5, 6, 7 \ldots .$$

It is the counterpart to the Brackett infra-red series of hydrogen (cf. p. 73), but is displaced towards the violet owing to the presence of the factor 4.

Owing to the first term the fine-structure is a quartet with the separation ratios 1 : 2 : 6 ; the far narrower multiplicity arising from

the second term could not be resolved. The three first lines of the quartet also overlapped to form a diffuse component; in addition to this, however, the fourth line of the quartet, which was further separated, could in most cases be measured as a weak component on the violet side. The wave-lengths of the principal lines of this series have already been given in accordance with Paschen's measurements in Table 3 on page 95 and have been tabulated with the neighbouring Balmer lines.

We have now to explain the data given above about the intensity distribution in the fine-structure pictures, that is, we must discuss the *selection-* and *intensity-rules* that hold for H and He^+. Historically we must remark that these rules are more complicated than was originally assumed. The change in the state of affairs occurred in 1926

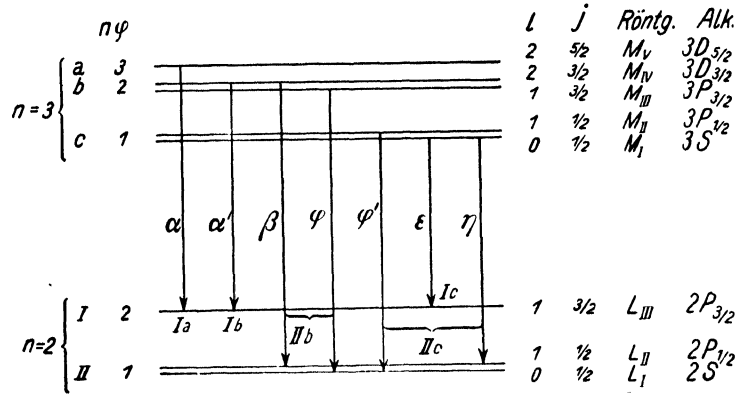


FIG. 75.—Old (on the left) and new (on the right) quantum notation of the hydrogen levels. On the extreme right is given the schematic representation of the corresponding Röntgen- and alkali-terms. The scheme of H_α levels is shown. Against the arrows are placed the symbols denoting the corresponding Röntgen lines.

when Goudsmit and Uhlenbeck discovered the spin of the electron. Whereas previously we characterised the individual hydrogen-like energy-level by means of *two* quantum numbers n and n_ϕ, we must now denote it by *three* quantum numbers:

$$n,\ l,\ j, \text{ where } j = l \pm \tfrac{1}{2}.$$

The introduction of j with the characteristic addition $\pm \frac{1}{2}$ points to *electron spin*, that is, to wave-mechanics refined relativistically.

How the allocation of n, l, j to the earlier n, n_ϕ-levels is to be performed is illustrated in the case of H_α (Fig. 75). Thus we are concerned with the fine-structure of the terms $n = 2$ and 3. On the left-hand side of the figure we have given the earlier notation with n and n_ϕ; each pair of levels shown close together in the figure but coincident in reality has the same n_ϕ; n_ϕ runs through the values

1, 2, . . . n. On the right-hand side we have written down the new notation. l runs through the values 0, 1, . . . $n-1$. In each pair of coincident levels *the l-values differ by unity*, whereas the j-values are *equal*. The j-values differ by unity in the case of each pair of neighbouring levels separated by relativity. The fact that for every n the uppermost level bears only *one cipher* is due to the circumstance that l may at most equal $n-1$ and j at most $l+\frac{1}{2}=n-\frac{1}{2}$. Thus we assign to the hydrogen levels the same quantum numbers as to the X-ray terms in the preceding chapter, cf. Fig. 66, page 243 ; that is, we interpret the H-spectrum like that of the X-ray terms as a doublet spectrum. But in the case of H the above-mentioned peculiarity occurs, that two levels having the same n, j always coincide. Besides the new quantum numbers we have also given on the right-hand side of Fig. 75 the corresponding X-ray levels in the system of notation of Chapter IV, and also the alkali terms, for later use, by specialising which we can derive our hydrogen levels. We shall not delay here by explaining the alkali terms.

For the l's and j's *selection rules* hold, which we already know from X-ray spectra :

$$\Delta l = \pm 1, \Delta j = \pm 1 \text{ or } 0 \quad . \quad . \quad . \quad . \quad (6)$$

These rules were introduced empirically into X-ray spectra and were confirmed by the scheme of terms. We shall regard them here, too, as facts of experience ; in the succeeding chapter (cf. also note 7) we shall find a provisional foundation for them, and in the second volume (on wave-mechanics) we shall establish them on a permanent and definitely circumscribed basis :

The application of our selection rules to Fig. 75 shows directly that on the whole we have 7 possible transitions, of which, however, in the case of hydrogen 2 in two separate cases are identical : they have been bracketed together at the bottom of the figure. Hence only 5 components of the fine-structure are left. If we call those arrows that lead to the upper final level as group I and those to the lower as group II and if we number the initial levels, in so far as they do not coincide, from above downwards as a, b, c, then the pairs of transitions that are identical in themselves are called IIb and IIc ; on account of the selection rules the transition IIa ($\Delta l = 2$, $\Delta j = 2$) is forbidden, and that is why we gave it the intensity zero in the earlier Fig. 69. At the middle of the arrows we have appended the names of the X-ray lines, for which of course no coincidence in pairs occurs.

The same Fig. 75 may, however, serve to display the structure of the Balmer lines H_β, H_γ, ... In the case of H_β the final term has the same multiplicity as in the case of H_α ; the initial term $n=4$ differs from the initial term at H_α in that we have to draw the level

that was uppermost before double (we have to add $l = 3$, $j = \frac{5}{2}$) and we have also to add a simple level ($l = 3$, $j = \frac{7}{2}$) which now becomes the uppermost level. These two additional levels may not be combined either with I or with II (on account of $\Delta l = 2$ or 3). For this reason the number of components in H_β and all the following Balmer lines remains the same, namely 5, and several components have the intensity zero (in the case of H_β they are I*a*, II*a* and II*b*).

We come next to the He^+-line $\lambda = 4686$ (Fig. 76) : three-fold final term, four-fold initial term, or, if we also include the coincident levels, five-fold final term (M-levels), seven-fold initial term (N-levels). The number of transitions is seen from Fig. 76 to be 13, of which,

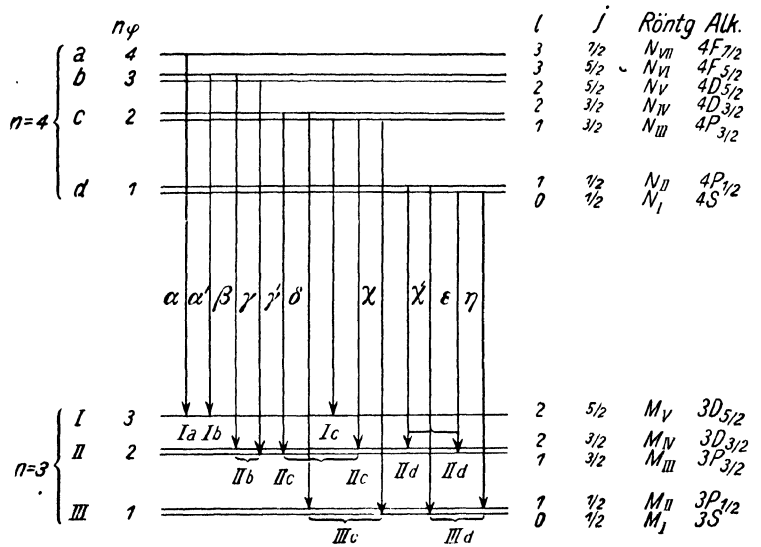


FIG. 76.—New quantum notation (on the right) of the scheme of levels of λ4686 (He^+). Arranged as in Fig. 75.

however, 5 pairs (those that are bracketed) become identical. Eight therefore remain. The old method of counting (3 quartets I*a* . . . III*d*) gave 12 components. Four of them, namely I*d*, II*a*, III*a*, and III*b*, are forbidden by our selection rules, and have therefore not been drawn in Fig. 76. In the earlier Fig. 71 they are of zero intensity. The corresponding X-ray lines belong to the M-series ; their symbols have not been given in Fig. 66.

The number of components 8 also remains preserved in the case of the higher lines of the He^+-lines.

Our selection rules are put out of action by strong electric fields, cf. Chapter VI, § 1, and Chapter VII, § 2. That is why in Fig. 71 the " spark discharge " exhibits more components than the " direct-

current discharge" picture; for example, in the former the components III*ab* are represented,* whereas they are absent in the latter. In other respects, too, the intensity conditions differ somewhat in the two pictures.

We now arrive at the **intensity rules.** We adopt an essentially empirical standpoint, precisely as in the case of X-ray spectra, because a full theoretical treatment is possible only on a wave-mechanical basis. We therefore make the following statements:

Those transitions are strong in which j and l change in the same sense. Moreover, the transitions with increasing l's are weak compared with those of decreasing l's. Since the combination of $\Delta l = \mp 1$ with $\Delta j = \pm 1$ does not come into question here any more than in the case of the X-ray spectra (cf. p. 245), we must distinguish between four cases:

$\Delta l = -1,\ \Delta j = -1$	strongest.
$\Delta l = -1,\ \Delta j = 0$	less strong.
$\Delta l = +1,\ \Delta j = +1$	weaker
$\Delta l = +1,\ \Delta j = 0$	weakest.

Compare with this our scheme of transitions in Fig. 76 and our data about intensities for H_α in Fig. 69. The strongest components are I*a* and II*b* (of the type $\Delta l = -1$, $\Delta j = -1$, in the case of II*b* in each of the two transitions here fused together). The components I*b* and II*c* (of the type $\Delta l = -1$, $\Delta j = 0$) are less strong; I*c* (of the type $\Delta l = +1$, $\Delta j = +1$) is still weaker. The type $\Delta l = +1$, $\Delta j = 0$, which we must regard as the weakest, does not show itself separately but only fused with II*c*.

In the case of $\lambda = 4686$, too (we are dealing with the direct-current picture in Fig. 71), the strongest components are of the type $\Delta l = -1$, $\Delta j = -1$, namely III*c*, II*b*, I*a*. The fact that II*b* comes out more strongly than I*a* may be related to the fact that in II*b* two transitions of this type are fused together. The weaker components belong to the type $\Delta l = -1$, $\Delta j = 0$, and so forth. The component I*d* should, theoretically, be absent in the direct-current picture.

The quantitative values for the intensities drawn in Figs. 69, 70 and 71 have been calculated by wave-mechanics; they are in agreement with our qualitative rule of intensity but cannot be accounted for here.

§ 4. Relativistic Doublets in the X-ray Region

There is a direct road from the minute hydrogen doublet over the fine-structures of ionised helium to the doublets of the X-ray spectra.

* Paschen remarks, however, *loc. cit.*, Ann. d. Phys., **82**, 689, in agreement with Leo, Ann. d. Phys., **81**, 757, that this component is probably to be ascribed in a large measure to a He-band. The intensity originally estimated by Paschen and represented in Fig. 71 would be too great for a line that is "forbidden," and that has only been called up by the field.

The hydrogen doublet is produced in the field of a singly charged nucleus, the line-structure of He^+ in the vicinity of a doubly charged nucleus; the X-ray spectra come from the interior of the atom and hence originate in the field of a highly charged atomic nucleus. The magnification factor of the fine-structure as compared with the hydrogen doublet amounts to 2^4 in wave-numbers in the case of He^+; but in the case of the X-ray spectra of an element of atomic number Z it is multiplied * by a number of the order of magnitude Z^4, which in the case of uranium is

$$92^4 = 7{\cdot}2 \,.\, 10^7.$$

The salient facts of experiment are known to us from Chapter IV, §§ 5 and 6. We shall discuss chiefly the L-series. The "L-doublet" arises between the lines $(\alpha'\beta)$, $(\gamma'\delta)$, $(\epsilon\eta)$, $(\zeta\theta)$, ... The interpretation of these constant doublet-differences was contained in Table 14, page 214; all lines of the L-series start from different initial states and end in the L-shell, and the difference in the levels L_{III} and L_{II} determines the L-doublet.

We can now give the reason for the difference in the L_{III}- and L_{II}-levels. The K-shell belongs to the quantum-number 1 and is therefore *simple*. The L-shell has the quantum sum 2 and is therefore *threefold*, by the arguments of Chapter IV; we shall, however, at present deal only with L_{III} and L_{II}. L_{III} has the quantum-numbers $l = 1$, $j = \frac{3}{2}$, $n_\phi = 2$, $n = 2$ and L_{II} has, analogously, $l = 1$, $j = \frac{1}{2}$, $n_\phi = 1$, $n = 2$ (see Fig. 75). According to the term-formula (6*a*), p. 260, L_{II} therefore has the lesser energy (due regard having been paid to the sign), that is, lies lower than L_{III}.

The "L-term" is the positive first term of the L-series. Our data about the constancy of the L-doublets and the intensity ratio of its components are therefore particular applications of the general assertions of §§ 2 and 3, page 262 *et seq.*, about doublets, triplets of constant difference of vibration-number and about the intensity of such "doublet-combinations."

Eqn. (6*a*) on page 260 also gives a completely satisfactory quantitative expression for the L_{III}- and the L_{II}-terms. With $Z = \frac{E}{e}$ we obtain:

* This statement refers to the difference $\Delta\nu$ in wave-number. The difference $\Delta\lambda$ in wave-length, however, is essentially independent of Z (cf. p. 236). Since in the spectrometer the wave-length λ is measured in relation to the crystal lattice-constant d [cf. eqn. (3) on p. 188] the accuracy of the fine-structure measurements comes out practically the same for all atomic numbers Z. The fact that the fine-structures in the X-ray region can be measured with so much more ease and accuracy than those on the visible region is not due to the greater value of $\Delta\nu$, but to the much smaller value of d, the much finer lattice, which may be used, thanks to the smallness of the wave-lengths.

$$\left.\begin{aligned}\nu_{III} &= R\left(\frac{E}{e}\right)^2\left[\frac{1}{2^2}+\frac{1}{4}\frac{\alpha^2}{2^4}\left(\frac{E}{e}\right)^2+\frac{1}{8}\frac{\alpha^4}{2^6}\left(\frac{E}{e}\right)^4+\frac{5}{64}\frac{\alpha^6}{2^8}\left(\frac{E}{e}\right)^6+\ldots\right]\\ \nu_{II} &= R\left(\frac{E}{e}\right)^2\left[\frac{1}{2^2}+\frac{5}{4}\frac{\alpha^2}{2^4}\left(\frac{E}{e}\right)^2+\frac{21}{4}\frac{\alpha^4}{2^6}\left(\frac{E}{e}\right)^4+\frac{429}{64}\frac{\alpha^6}{2^8}\left(\frac{E}{e}\right)^6+\ldots\right]\end{aligned}\right\} \quad (1)$$

The difference between the two terms gives the magnitude of the L-doublet in wave-numbers, namely :

$$\Delta\nu_L = \nu_{II} - \nu_{III} = R\left(\frac{E}{e}\right)^4\frac{\alpha^2}{2^4}\left[1+\frac{5}{2}\frac{\alpha^2}{2^2}\left(\frac{E}{e}\right)^2+\frac{53}{8}\frac{\alpha^4}{2^4}\left(\frac{E}{e}\right)^4+\ldots\right] \quad (2)$$

Our method of representing the L-doublet is expressed quite completely and rationally by the fine-structure constant $\alpha^2 = 5{\cdot}3 \cdot 10^{-5}$, the Rydberg frequency $R = R_\infty$ and the nuclear number $\frac{E}{e}$. We must first get clear about the latter number.

We know that the K-shell is situated within the L-orbit, and that the electrons of the K-shell screen the nuclear charge. But the L-shell is also occupied by several electrons and they also exert a screening action on the true nuclear charge. In place of the " true nuclear charge " we therefore have an " effective nuclear charge " which is smaller than Z. We set

$$\frac{E}{e} = Z - s \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Since we cannot calculate the " screening-number " s beforehand by theory we derive it from observation, that is, we treat it as a disposable parameter. To obtain a first idea of its value we, moreover, discard the higher relativistic terms in (2) and write

$$\Delta\nu_L = \frac{R\alpha^2}{2^4}(Z-s)^4 \quad . \quad . \quad . \quad . \quad (4)$$

This is the theoretical (or perhaps, owing to the presence of the parameter s, the half-empirical) formula to a first approximation, which is transposed from hydrogen. We compare it with the empirical formula which we developed at the end of § 5 of Chapter IV, eqn. (2), page 225 :

$$\frac{\Delta\nu}{R} = \frac{5{\cdot}3 \cdot 10^{-5}}{2^4}(Z-3{\cdot}5)^4 \quad . \quad . \quad . \quad (5)$$

These two formulæ agree not only in their general structure but also in their numerical value. We see here a preliminary confirmation of our relativistic view of the L-doublet by the results of observation and further derive as the empirical value of our screening-number $s = 3{\cdot}5$.

By introducing the value of the hydrogen doublet from eqn. (1) on page 262,

$$\Delta\nu_H = \frac{R\alpha^2}{2^4},$$

we may write eqn. (4) in the following form :

$$\Delta\nu_L = \Delta\nu_H\,(Z - s)^4 \quad . \quad . \quad . \quad . \quad (6)$$

We illustrate this in Fig. 77. Here we have plotted Z as abscissæ and have taken as our ordinates the values of $\Delta\nu_H$ calculated according to eqn. (6) from the $\Delta\nu$'s of Table 18 on page 223 and divided by $(Z - s)^4$. We see how the interpolated curve drawn through these points approaches a constant limit for small Z's—a limit which agrees excellently with our ideal hydrogen doublet.

The fact of fine-structure may therefore be followed throughout the whole system of the elements, from hydrogen to uranium. The L*-doublet appears as a direct copy of the hydrogen doublet.*

We shall not, however, stop at the first approximation in our quantitative account of the L-doublet, but shall also take into account

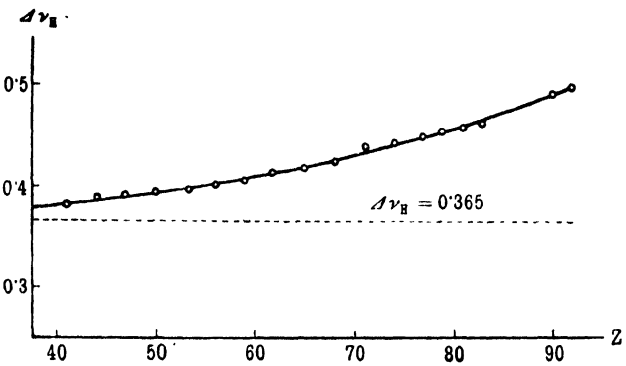


FIG. 77.—The $\Delta\nu_H$ values, calculated with the help of equation (6) from the observed values of $\Delta\nu_L$, approach with decreasing Z the constant limit of the hydrogen doublet $\Delta\nu_H = 0{\cdot}36$ cm.$^{-1}$ (dotted line).

the higher relativity corrections. This will at the same time give us a means of judging the accuracy of our value $s = 3{\cdot}5$ for the screening-number and will convince us that the L-doublet is represented within the limits of experimental error accurately by our relativistic formula for the whole series of elements.

We may proceed by calculating the value of $E/e = Z - s$ separately for each element from formula (2). That is, we start from

$$\frac{\Delta\nu}{R} = \frac{\alpha^2}{2^4}(Z - s)^4\left(1 + \frac{5}{2}\frac{\alpha^2}{2^2}(Z - s)^2 + \frac{53}{8}\frac{\alpha^4}{2^4}(Z - s)^4 + \ldots\right) \quad (7)$$

and derive the square root by applying the Binomial Theorem after multiplying by $2^4/\alpha^2$. In this way we obtain

$$\frac{2^2}{\alpha}\sqrt{\frac{\Delta\nu}{R}} = (Z - s)^2\left(1 + \frac{5}{4}\frac{\alpha^2}{2^2}(Z - s)^2 + \frac{81}{32}\frac{\alpha^4}{2^4}(Z - s)^4 + \ldots\right) \quad (8)$$

We eliminate the term in $(Z - s)^4$ from (7) and (8) by forming

$$\frac{2^2}{\alpha}\sqrt{\frac{\Delta\nu}{R}} - \frac{5\Delta\nu}{R} = (Z - s)^2\left(1 - \frac{19}{32}\frac{\alpha^4}{2^4}(Z - s)^4 + \ldots\right) \quad . \quad (9)$$

TABLE 21

Z	$\Delta\nu/R$	$Z - s$	s	Z	$\Delta\nu/R$	$Z - s$	s
41 Nb .	6·90	37·53	3·47	63 Eu .	47·17	59·51	3·49
42 Mo .	7·7	38·5	3·5	64 Gd .	50·64	60·50	3·50
44 Ru .	9·49	40·54	3·46	65 Tb .	54·36	61·51	3·49
45 Rh .	10·48	41·53	3·47	66 Dy .	58·24	62·51	3·49
46 Pd .	11·57	42·55	3·45	67 Ho .	62·43	63·52	3·48
47 Ag .	12·69	43·52	3·48	68 Er .	66·81	64·52	3·48
48 Cd .	13·97	44·52	3·48	70 Yb .	76·08	66·49	3·51
49 In .	15·29	45·50	3·50	71 Lu .	81·11	67·47	3·53
50 Sn .	16·72	46·51	3·49	73 Ta .	92·46	69·52	3·48
51 Sb .	18·30	47·53	3·47	74 W .	98·49	70·52	3·48
52 Te .	20·00	48·55	3·45	76 Os .	111·08	72·51	3·49
53 I . .	21·70	49·51	3·49	77 Ir . .	118·53	73·53	3·47
55 Cs .	25·59	51·50	3·50	78 Pt .	125·85	74·52	3·48
56 Ba .	27·74	52·50	3·50	79 Au .	133·62	75·52	3·48
57 La .	30·01	53·46	3·54	81 Tl .	150·20	77·51	3·49
58 Ce .	32·05	54·33	3·67	82 Pb .	159·12	78·50	3·50
59 Pr .	35·02	55·48	3·52	83 Bi .	169·02	79·55	3·45
60 Nd .	37·86	56·51	3·49	90 Th .	249·37	86·51	3·49
62 Sm .	43·95	58·50	3·50	92 U . .	277·91	88·51	3·49

Mean : $s = 3{\cdot}487$.

Here we may also use the first approximation from eqn. (4) in the correction term on the right-hand side without introducing an appreciable error. We then obtain

$$(Z - s)^2 = \left(\frac{2^2}{\alpha}\sqrt{\frac{\Delta\nu}{R}} - 5\frac{\Delta\nu}{R}\right)\left(1 + \frac{19}{32}\alpha^2\frac{\Delta\nu}{R}\right) \quad . \quad . \quad (10)$$

The numerical implications of this formula are shown in Table 21. The first column repeats the values of $\Delta\nu/R = L\beta - L\alpha'$ from Table 18. The second gives the values of $Z - s$ calculated by eqn. (10), where we have set $\alpha^2 = 5{\cdot}305 \cdot 10^{-5}$ (cf. § 6). In the third column we have the values of the screening-constant s that follow from the values of $Z - s$. The mean of all the values of s amounts to

$$s = 3{\cdot}50.$$

As we see, the individual values of s fluctuate about the mean value in a quite unsystematic way.

More important than the constancy of s is the accuracy with which the quantum-number 2 is confirmed by our calculation and the relativistic law for the progressive increase in the doublet-interval

is confirmed. The latter also explains the increasing curvature of the graphs for $\sqrt{\nu/R}$ in Figs. 57 and 59 of the K- and L-series. If the X-ray spectra could be represented rigorously by a formula of the Balmer-Moseley type, $\sqrt{\nu/R}$ could be represented, as a function of the atomic number, by means of a straight line. The effect of taking into account the relativity corrections of the first and higher orders is to give an increasing upward bend to the straight line as Z increases.

Not only the L-doublet but also the M- and N-doublets confirm our relativistic fine-structure formula.

From observations of the L-series the doublets $(\alpha'\alpha)$ and $(\phi'\phi)$ are known to us; we called them M-doublets (cf. Table 14, p. 214) because their origin is due to the differences in the M-levels. $(\alpha'\alpha)$ represents the difference $(M_V M_{IV})$, $(\phi'\phi)$ the difference $(M_{III} M_{II})$, corresponding to the following scheme derived from Table 14:

$$\begin{matrix} \alpha' \ldots M_{IV} \to L_{III} & \phi' \ldots M_{II} \to L_I \\ \alpha \ldots M_V \to L_{III} & \phi \ldots M_{III} \to L_I. \end{matrix}$$

The M-shell belongs to the quantum-number $n = 3$. From the general expression of the terms, (6*a*), on page 260, we calculate for $n = 3$ the term-differences for $n_\phi = 2$ and 3, and also for $n_\phi = 1$ and 2. These are the differences in the values of the levels $M_{IV} - M_V$ and $M_{II} - M_{III}$, respectively. We denote them by $\Delta\nu_1$ and $\Delta\nu_2$ and have, by the equation mentioned, if we set $Z = E/e$,

$$\frac{\Delta\nu_1}{R} = \left(\frac{E}{e}\right)^4 \frac{\alpha^2}{3^4}\left[\frac{1}{2} + \frac{25}{32}\frac{\alpha^2}{3^2}\left(\frac{E}{e}\right)^2 + \frac{317}{256}\frac{\alpha^4}{3^4}\left(\frac{E}{e}\right)^4\right] \quad . \quad (11)$$

$$\frac{\Delta\nu_2}{R} = \left(\frac{E}{e}\right)^4 \frac{\alpha^2}{3^4}\left[\frac{3}{2} + \frac{279}{32}\frac{\alpha^2}{3^2}\left(\frac{E}{e}\right)^2 + \frac{13059}{256}\frac{\alpha^4}{3^4}\left(\frac{E}{e}\right)^4\right] \quad . \quad (12)$$

The ratio of the two would be—if we neglect the higher powers of α^2 and take E/e as having an equal value in both formulæ—equal to 1 : 3, in agreement with eqn. (8*a*) on page 261. In this case we should have the hydrogen triplet with which we are already so familiar. But the assumption that E/e is the same in each case no longer applies. *The hydrogen triplet resolves into two hydrogen-like doublets.* The levels which in a certain sense accidentally coincide in hydrogen (cf. for example, Fig. 75 for the case of H_α) separate in the X-ray spectra and give rise, for $n = 3$, to the five M-levels M_I to M_V, of which the two pairs $(M_{II}M_{III})$ and $(M_{IV}M_V)$ are the relativistic or regular doublets in question.

The calculation for $(\alpha'\alpha)$ has been carried out by E. Hjalmar * on the basis of his precision methods. The object is to show that eqn. (11) represents the observations on $(\alpha'\alpha)$ for all values of Z if

* Zeits. f. Physik, **3**, 262 (1920).

a new "screening-constant" s be suitably chosen, where, as in the case of the L-doublet, we set

$$E/e = Z - s,$$

and calculate s empirically. The calculation is carried out in the manner of eqns. (7) to (10) of the present section, the last of which here runs :

$$(Z - s)^2 = \left(\frac{3^2}{\alpha}\sqrt{\frac{2\Delta\nu}{R}} - \frac{225}{16}\frac{\Delta\nu}{R}\right)\left(1 + \frac{589}{1024}\alpha^2\frac{\Delta\nu}{R}\right). \quad . \quad (13)$$

We find that for all elements between $Z = 41$ and $Z = 74$ a remarkably constant value is obtained for s, namely,

$$s = 13{\cdot}0, \quad . \quad . \quad . \quad . \quad (14)$$

the fluctuations appearing to be quite unsystematic.

In precisely the same way eqn. (12) represents the M-doublet $(\phi'\phi)$ in the L-series. The fact that this doublet is considerably further separated than the doublet $(\alpha'\alpha)$ in the L-series agrees at least qualitatively with the ratio 3 : 1 of the separations between the components in the hydrogen triplet. It is also possible to calculate a screening-constant s from the observations of $(\phi'\phi)$ on the basis of (12). The formula analogous to (13) now runs :

$$(Z - s)^2 = \left(\frac{3}{\alpha}\sqrt{\frac{6\Delta\nu}{R}} - \frac{279}{16}\frac{\Delta\nu}{R}\right)\left(1 + \frac{191}{32}\alpha^2\frac{\Delta\nu}{R}\right) \quad . \quad (15)$$

and gives *

$$s = 8{\cdot}5 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

Just as the M-shell belongs to the quantum-number 3, so the N-shell belongs to the quantum-number 4. By setting $n = 4$, $n_\phi = 4$ and 3, 3 and 2, and 2 and 1, respectively, in the general expression for the terms (6a) on page 260, and forming the differences, we obtain the three doublets :

$$\Delta\nu_1 = N_{VI} - N_{VII}, \quad \Delta\nu_2 = N_{IV} - N_V, \quad \Delta\nu_3 = N_{II} - N_{III},$$

which, in the case of hydrogen, owing to the coincidence of three pairs of levels, combine to form the quartet $\Delta\nu_1 : \Delta\nu_2 : \Delta\nu_3 = 1 : 2 : 6$ (cf. eqn. (9a) on p. 262), namely,

$$\frac{\Delta\nu_1}{R} = \left(\frac{E}{e}\right)^4\frac{\alpha^2}{4^4}\left[\frac{1}{3} + \frac{23}{54}\frac{\alpha^2}{4^2}\left(\frac{E}{e}\right)^2 + \frac{1069}{1944}\frac{\alpha^4}{4^4}\left(\frac{E}{e}\right)^4\right] \quad . \quad (17)$$

$$\frac{\Delta\nu_2}{R} = \left(\frac{E}{e}\right)^4\frac{\alpha^2}{4^4}\left[\frac{2}{3} + \frac{56}{27}\frac{\alpha^2}{4^4}\left(\frac{E}{e}\right)^2 + \frac{5905}{972}\frac{\alpha^4}{4^4}\left(\frac{E}{e}\right)^4\right] \quad . \quad (18)$$

$$\frac{\Delta\nu_3}{R} = \left(\frac{E}{e}\right)^4\frac{\alpha^2}{4^4}\left[2 + 20\frac{\alpha^2}{4^2}\left(\frac{E}{e}\right)^2 + \frac{809}{4}\frac{\alpha^4}{4^4}\left(\frac{E}{e}\right)^4\right] \quad . \quad (19)$$

* For the numerical data required for calculating this screening-constant and that of the N-doublet, see A. Sommerfeld and G. Wentzel, Zeits. f. Physik, **7**, 86 (1921); G. Wentzel, *ibid.*, **16**, 46 (1923), and further, from a more general point of view, L. Pauling, Proc. Roy. Soc., A, **114**, 181 (1927).

Of these three regular doublets only the last may be derived as an " N-doublet ($\chi\chi'$) of the L-series " (cf. p. 214) to a sufficient degree of accuracy from direct measurements of distances between lines. Here again the relativistic doublet fully proves its worth ; we obtain as the screening-number from a formula analogous to (13), (15),

$$s = 17{\cdot}0 \quad . \quad . \quad . \quad . \quad . \quad (19a)$$

To arrive at the other N-doublets we are compelled to derive them indirectly from the combination of several differences of lines. Corresponding to the values so obtained for the separations of the doublets we get, according to the formulæ (17) and (18), the following approximate values for the screening-constants : *

$$s = 34 \quad . \quad . \quad . \quad . \quad . \quad (17a)$$

and

$$s = 24{\cdot}4 \quad . \quad . \quad . \quad . \quad (18a)$$

respectively.

It is remarkable that the screening-constants s of the M- and the N-levels appear to be approximately integral multiples of a unit quantity which lies between 4·2 and 4·3 : †

$(M_{III}\ M_{II})\ 8{\cdot}5 = 2 \,.\, 4{\cdot}25$; $(M_V\ M_{IV})13{\cdot}0 = 3 \,.\, 4{\cdot}3$
$(N_{III}\ N_{II})\ 17{\cdot}0 = 4 \,.\, 4{\cdot}25$; $(N_V\ N_{IV})\ 24 = 6 \,.\, 4{\cdot}0$; $(N_{VII}\ N_{VI})\ 34 = 8 \,.\, 4{\cdot}25$.

The L-shell, for which $s = 3{\cdot}5$, appears, however, to form an exception to the rule.

The increase of the screening-constant s from 3·5 for the L-doublet to 24 and 34 for the N-doublet is quite satisfactory from the point of view of the model since it points to an increase in the number of interposed electrons, likewise the increase of s in the transition from $\Delta\nu_2$ and $\Delta\nu_1$ in the M-series or from $\Delta\nu_3$ to $\Delta\nu_2$ and $\Delta\nu_1$ in the N-series. For $\Delta\nu_3$ refers to elliptic orbits of great eccentricity which closely approach the nucleus, that is, which are only slightly screened whereas $\Delta\nu_2$ and $\Delta\nu_1$ refer to orbits of small eccentricity for which the screening is naturally expected to be strong. Hence although from the point of view of wave-mechanics we must be cautious about taking the orbital ideas too literally, we nevertheless see that in a qualitative way there is much truth in them.

To conclude we shall touch on a matter which was a mystery until Dirac's theory of the relativistic electron appeared and which can therefore be fully dealt with only when we discuss this theory in the second volume of the present work ; namely, the allocation of quantum-numbers to the regular doublets on the one hand and to the irregular doublets on the other. On pages 244 and 270 we assigned quantum-numbers l, j to the levels in such a way that the regular doublets were given by adjacent j's and equal l's, and the

* The screening-constant of $N_{VI}N_{VII}$ appears to show a systematic decrease below Z = 74.

† A. Sommerfeld, Journ. Opt. Soc. Amer., 7, 503 (1923).

irregular doublets by adjacent l's and equal j's. In contrast with this we have now assigned two adjacent values of n_ϕ to the two levels of a regular doublet (cf., for example, Fig. 75), whereas according to our earlier assertion we should have $n_\phi = l + 1$ (p. 115), so that differences in the n_ϕ-values should cause differences in the l-values. The apparent contradiction is removed by Dirac's theory, which shows that the quantum-numbers l, j are actually required for distinguishing between the hydrogen terms and the combinations between them, but that for calculating the relativistic term-differences it is necessary to introduce a quantum-number that corresponds to our n_ϕ. By applying Dirac's theory for hydrogen to the X-ray spectra we can justify our procedure in the present and the preceding chapter although we cannot yet explain it satisfactorily.

§ 5. Irregular or Screening Doublets

The law governing irregular doublets was discovered by G. Hertz,* 1920. We may regard as a typical doublet of this kind the difference

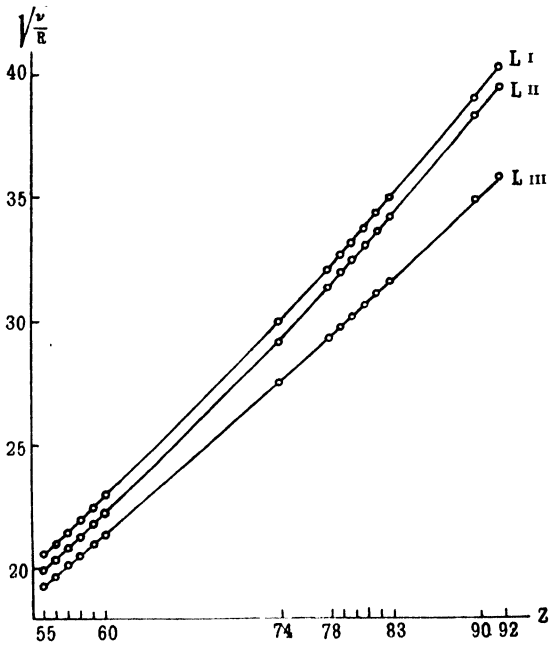


FIG. 78.—Law governing the irregular doublets of the Röntgen spectra illustrated by the L-levels : $\Delta\sqrt{\nu/R}$ for all atomic numbers Z is approximately constant for the irregular doublet $L_I L_{II}$. The regular doublet $L_{II} L_{III}$ shows considerable increase of $\Delta\sqrt{\nu}/R$.

* Zeits. f. Physik, **3**, 19 (1920). Hertz's measurements have been replaced in Table 22 by the more accurate measurements of Coster and Lindsay. These confirm Fig. 78.

in the limits $L_I L_{II}$, which was measured by Hertz. The measurements made by him refer to the elements Cs 55 to Nd 60; they are plotted in Fig. 78, which is taken from his paper and which also includes the differences in the limits $L_I L_{II}$ measured by Duane and Patterson for the elements W 74 to U 92. This figure expresses the following law: *if we plot* $\sqrt{\nu}$ *in the manner of Moseley the graphs for* L_I *and* L_{II} *run appreciably parallel to each other*, in contrast to the lines L_{II} and L_{III}, which move away from each other more and more as Z increases, in accordance with the law for regular doublets.

Thus the law governing screening doublets states in general that the difference in the $\sqrt{\nu}$-values of the two doublet components is approximately constant. Table 22 illustrates this for ($L_I L_{II}$). Here

TABLE 22

	$L_I - L_{II}$	$\sqrt{L_I} - \sqrt{L_{II}}$	$\sqrt{M_I} - \sqrt{M_{II}}$	$\sqrt{M_{III}} - \sqrt{M_{IV}}$	$\sqrt{N_I} - \sqrt{N_{II}}$	$\sqrt{N_{III}} - \sqrt{N_{IV}}$	$\sqrt{N_V} - \sqrt{N_{VI}}$
47 Ag . .	21·9	0·66	0·53	1·33	0·29	1·32	—
51 Sb . .	22·5	0·62	0·64	1·15	0·80	0·87	—
52 Te . .	23·8	0·63	0·61	1·20	0·58	1·09	—
53 I . .	25·0	0·65	0·59	1·21	0·68	1·04	—
55 Cs . .	26·9	0·67	0·57	1·24	0·45	1·12	—
56 Ba . .	27·6	0·67	0·57	1·22	0·48	1·12	—
57 La . .	28·7	0·68	0·55	1·23	0·47	1·13	—
58 Ce . .	29·2	0·67	0·58	1·22	0·49	1·13	—
66 Dy . .	35·5	0·70	0·60	1·23	0·46	1·32	2·5
68 Er . .	37·0	0·70	0·59	1·24	0·42	1·29	2·6
69 Tu . .	38·0	0·70	0·58	1·27	0·39	1·35	2·7
70 Yb . .	39·2	0·71	0·57	1·28	0·45	1·38	2·8
71 Lu . .	39·7	0·71	0·57	1·29	0·37	1·34	2·8
72 Hf . .	40·7	0·71	0·59	1·23	0·49	1·36	2·7
74 W . .	42·4	0·72	0·59	1·27	0·48	1·41	2·6
78 Pt . .	48·1	0·76	0·52	1·33	0·27	1·55	2·5
79 Au . .	45·8	0·71	0·57	1·23	0·61	1·40	2·5
81 Tl . .	48·2	0·72	0·62	1·24	0·66	1·17	2·2
82 Pb . .	47·4	0·70	0·65	1·23	0·68	1·35	2·2
83 Bi . .	48·5	0·70	0·66	1·18	0·76	1·12	2·1
90 Th . .	58·2	0·76	0·71	1·24	—	—	2·0
92 U . .	60·4	0·76	0·67	1·26	0·54	1·28	2·0

we have copied in the first column the ν/R-differences from Table 20, page 238; in the second column we have tabulated under the heading $\sqrt{L_I} - \sqrt{L_{II}}$ the differences in the $\sqrt{\nu/R}$-values for both levels. These differences are exactly constant within the region of Hertz's observations, having the value 0·66; after that they increase slowly and continuously to 0·76.

But the same law holds, as Wentzel * has shown, for all those level-differences of the M- and N-shell which we have not already recognised as relativistic doublets. These are those doublets in the scheme on page 242 which are bracketed together downwards, that is, below the M-limits $M_I M_{II}$ and $M_{III}\, M_{IV}$, the N-limits $N_I N_{II}$, $N_{III}\, N_{IV}$, $N_V\, N_{VI}$. The ν/R-values used for them in Table 22 are likewise derived from the table of terms on page 238. Although only small differences and quantities that are indirectly derived occur in this table there is no doubt about the approximate constancy of the succession of numbers.

Hertz interprets the law by expressing the wave-number ν of each individual limit approximately as a Moseley formula, and he obtains

$$\frac{\nu}{R} = \frac{1}{n^2}(Z - \sigma)^2, \quad \sqrt{\frac{\nu}{R}} = \frac{Z - \sigma}{n} \quad . \quad . \quad . \quad (1)$$

where σ denotes a new screening number. If σ_1 and σ_2 are the values of σ that belong to the two levels of the irregular doublet, it follows from the second of eqn. (1), since these levels always belong to the same shell, that is, have the same n, that

$$\Delta\sqrt{\frac{\nu}{R}} = \frac{\sigma_1 - \sigma_2}{n} = \frac{\Delta\sigma}{n} \quad . \quad . \quad . \quad . \quad (2)$$

This is the *law of irregular doublets* established by Hertz. From the first of eqns. (1) it simultaneously follows for $\Delta\nu$ itself that

$$\frac{\Delta\nu}{R} = \frac{2\Delta\sigma}{n^2}\left(Z - \frac{\sigma_1 + \sigma_2}{2}\right) \quad . \quad . \quad . \quad . \quad (3)$$

From eqn. (3) we can draw the following comparison between regular and irregular doublets : *in the case of irregular doublets the wave-number difference $\Delta\nu$ increases essentially linearly with the atomic number, in the case of regular doublets it increases with the fourth power of the atomic number. Again, in the case of irregular doublets the difference $\Delta\lambda$ in wave-lengths decreases as the atomic number increases ; actually it varies as the inverse cube. In the case of the regular doublets it is, as we know, appreciably constant.*

But the expression (1) is still very incomplete and only arranged to fulfil the present purpose. We supplement it by combining it with the general expression (6*a*) on page 260. The essential feature is that we should choose the screening-number in the *first* term (principal term or Moseley term) different from the screening-number in the *higher terms* (*relativistic correction terms* of the first, second, . . . order). We denote the former number σ, as in (1), and the latter s, as in the

* Dissertation, Munich, 1921. Cf. Zeits. f. Physik, **6**, 84 (1921).

preceding section. In this way we obtain the *general term-expression* for X-rays :

$$\frac{\nu}{R} = \frac{1}{n^2}(Z - \sigma)^2 + \frac{\alpha^2}{n^4}(Z - s)^4\left(\frac{n}{n_\phi} - \frac{3}{4}\right) + \frac{\alpha^4}{n^6}(Z - s)^6\left[\frac{1}{4}\left(\frac{n}{n_\phi}\right)^3 + \frac{3}{4}\left(\frac{n}{n_\phi}\right)^2 - \frac{3}{2}\frac{n}{n_\phi} + \frac{5}{8}\right] + \ldots \quad (4)$$

From this formula we obtain our earlier formulæ for the *regular* doublets, if we give the same value to the constants σ and s in the two levels of such a doublet. The principal term then exactly cancels when the differences are formed.

With the help of (4) we can also immediately formulate exactly the law of irregular doublets. For by (4) eqn. (2) is incomplete, because in forming it we left out of account the relativistic correction terms. It is in agreement with this that the $\Delta\sqrt{\nu/R}$-values in Table 22 are not rigorously constant ; in the case of ($L_I L_{II}$) and ($M_I M_{II}$), at anyrate, they exhibited a small systematic variation. But on the basis of formula (4) Hertz's law can now be made more rigorous.

For this purpose we start from (4) and form the expressions,

$$\frac{\nu_{red}}{R} = \frac{(Z - \sigma)^2}{n^2} = \frac{\nu}{R} - \frac{\alpha^2}{n^4}(Z - s)^4\left(\frac{n}{n_\phi} - \frac{3}{4}\right) - \ldots \quad (5)$$

which we call " reduced terms." Since we know * the screening-numbers s in the terms involving α^2, α^4 . . . from the relativistic doublets, we can calculate ν_{red} numerically from ν. Table 23 shows how Table 22 changes in the case of L- and M-levels, if we insert the $\sqrt{\nu_{red}/R}$-values in place of the $\sqrt{\nu/R}$-values. In the case of the N-levels the relativistic reduction becomes inappreciable compared with the mean error. Hence these levels already led to appreciably constant differences in Table 22 and did not require to be taken up in Table 23.

The rigorous form of Hertz's law thus runs : *not the values* $\Delta\sqrt{\nu/R}$ *but* $\Delta\sqrt{\nu_{red}/R}$ *are exactly constant for every irregular doublet.* According to our definition of reduced terms in (5) this of course denotes nothing else than that the screening-differences $\Delta\sigma$ are constant. In the last row of Table 23 we again encounter, as on page 280, a remarkable integral relationship : the means of the $\Delta\sqrt{\nu_{red}/R}$-values are approximately multiples of 0·57. Since by (5) these values differ from the values of $\Delta\sigma$ only by the integer n, *the* $\Delta\sigma$'s *are also whole multiples of* 0·57. The same relationship holds for the $\Delta\sigma$'s in the N-levels, in which,

* This is not the case with L^{-}_1, M^{-}_1, N^{-}_1 levels. But in their case we can determine s by postulating the rule of constant $\Delta\sigma$'s as valid also for the lowest screening-doublets. Cf. G. Wentzel, Zeits. f. Physik, **16**, 46 (1923). The corresponding s-values are 2·0 for L_1, 6·8 for M_1 and 14 for N_1.

as has been mentioned, ν_{red} can be identified with ν, that is, the $\Delta\sigma$ in question can be derived directly from Table 22.

TABLE 23

Elements and their Atomic Numbers	Reduced Values of $\sqrt{L_I} - \sqrt{L_{II}}$	$\sqrt{M_I} - \sqrt{M_{II}}$	$\sqrt{M_{III}} - \sqrt{M_{IV}}$
47 Ag	0·61	0·51	1·31
51 Sb	0·55	0·62	1·12
52 Te	0·57	0·58	1·17
53 I	0·58	0·56	1·18
55 Cs	0·59	0·54	1·21
56 Ba	0·59	0·54	1·19
57 La	0·60	0·51	1·20
58 Ce	0·59	0·54	1·19
59 Pr	0·59	0·56	1·19
60 Nd	0·59	0·51	1·19
62 Sm	0·59	0·51	1·20
63 Eu	0·58	0·52	1·19
64 Gd	0·58	0·53	1·19
66 Dy	0·58	0·54	1·18
68 Er	0·58	0·53	1·19
69 Tu	0·58	0·51	1·22
70 Yb	0·58	0·50	1·23
71 Lu	0·58	0·50	1·24
72 Hf	0·58	0·51	1·18
74 W	0·57	0·51	1·21
78 Pt	0·59	0·43	1·26
79 Au	0·53	0·47	1·15
81 Tl	0·53	0·52	1·16
82 Pb	0·50	0·55	1·15
83 Bi	0·50	0·56	1·09
90 Th	0·50	0·58	1·14
92 U	0·49	0·54	1·15
Mean value :	$0·56_7$	$0·52_9$	$1·18_8$

We now tabulate the $\Delta\sigma$'s so obtained for all our screening doublets :

$$\begin{aligned}
(L_IL_{II}) &\quad 2 \,.\, 0·57 \\
(M_IM_{II}) &\quad 3 \,.\, 0·57 \\
(M_{III}M_{IV}) &\quad 2 \,.\, 3 \,.\, 0·57 \\
(N_IN_{II}) &\quad 4 \,.\, 0·56 \\
(N_{III}N_{IV}) &\quad 2 \,.\, 4 \,.\, 0·56 \\
(N_VN_{VI}) &\quad 4 \,.\, 4 \,.\, 0·6
\end{aligned}$$

From the $\Delta\sigma$'s we turn to the absolute values of the σ's, which are calculated by means of eqn. (5).

Fig. 79 represents these absolute values graphically as a function of Z. The parallelism of the σ-curves within one and the same shell confirms our more rigorous form of Hertz's law. But, moreover, it

shows that the σ's are neither independent of Z nor equal to the s's. Rather the σ's are always greater than the s's and increase with Z, while, as we know, the s's are exactly constant. The increase of the σ's is explained by the circumstance that not only the inner but also the outer electrons, whose number increases with Z contribute to the screening-numbers σ, whereas they have no influence on the s's. Bohr calls this effect "external screening." We shall investigate it more closely in Chapter VII and shall there also refer back to the details of Fig. 79. In particular we shall there discuss all the striking *irregularities* in the course of the curves for the rare earths, since these irregularities are connected with the re-arrangement of the N-shell.

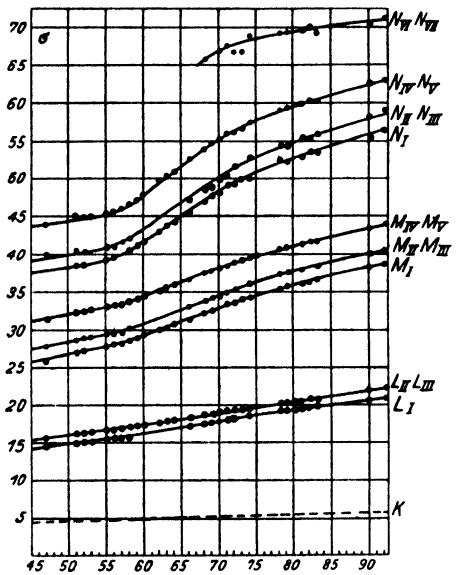


FIG. 79.—The screening-number σ of the irregular doublets as a function of the atomic number.

Not only in the case of the X-ray spectra but also in the case of those of the visible region our laws for the regular and irregular doublets as well as Moseley's law have been shown to be valid. We shall revert to this discussion in Chapter VII.

§ 6. Universal Spectroscopic Units. Spectroscopic Confirmation of the Theory of Relativity

Three main-streams of research in modern theoretical physics are confluent in our theory of fine-structure: the electron theory, the quantum theory, and the theory of relativity. This is shown in a particularly striking way in the structure of our *fine-structure constant:*

$$\alpha = \frac{2\pi e^2}{hc}. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here *e is the representative of the electron theory, h fittingly represents the quantum theory,* and *c comes from the theory of relativity*; c may in fact be regarded as characterising the latter theory as compared with the classical theory.

We derive the value of α spectroscopically by measuring the hydrogen doublet (best indirectly, by measuring the He^+-lines, since

direct measurement is too inaccurate, cf. p. 263). The relationship between α and $\Delta\nu_H$ is, by eqn. (1), § 3,

$$\Delta\nu_H = R\alpha^2/2^4 \quad . \quad . \quad . \quad . \quad (2)$$

which, if we use the value $\Delta\nu_H = (0{\cdot}3636 \pm 0{\cdot}0006)$ cm.$^{-1}$—cf. eqn. (1) in § 3—leads to

$$\alpha^2 = (5{\cdot}305 \pm 0{\cdot}008) \,.\, 10^{-5}, \quad \alpha = (7{\cdot}283 \pm 0{\cdot}006) \,.\, 10^{-3}. \quad (3)$$

It must be recalled that we may also write the definition (1) for α [cf. eqn. (13*b*) on p. 254 for hydrogen, i.e. Z = 1] :

$$\alpha = \frac{p_0}{p_1}, \quad p_0 = \frac{e^2}{c}, \quad p_1 = \frac{h}{2\pi}. \quad . \quad . \quad . \quad (1a)$$

Here p_0 is an elementary moment of momentum which is intimately connected with the relativistic Kepler motion, in particular with the motion of its perihelion (cf. eqn. (13*a*) on p. 253), and p_1 is the moment of momentum of the first quantum state. The factor 2π which is apparently arbitrary in the definition (1) for α is appropriately legitimised by our definition (1*a*).

We must also remark that Eddington * has proposed the thesis that $1/\alpha$ is a *whole number* which can be obtained by counting up Dirac matrices, its value being 136 or (by another method of counting) 137. The last value gives in close agreement with (3),

$$\alpha = \tfrac{1}{137} = 7{\cdot}2993 \,.\, 10^{-3}.$$

It is clear that if Eddington's thesis can be founded on incontrovertible grounds it will have disclosed an intimate relationship between the three theories which we called the main-streams of modern physical thought at the beginning of this section.

We are now in a position to bring to its conclusion the idea of *spectroscopic units*, which was taken up as early as page 90 and was carried a step further on page 95. The three equations

$$R_H = \frac{2\pi^2 m_0 e^4}{h^3 c(1 + m_0/m_H)} \quad . \quad . \quad . \quad . \quad (4)$$

$$R_{He} = \frac{2\pi^2 m_0 e^4}{h^3 c(1 + m_0/m_{He})} \quad . \quad . \quad . \quad . \quad (5)$$

$$\alpha = \frac{2\pi e^2}{hc} \quad . \quad . \quad . \quad . \quad . \quad (6)$$

give us three equations for determining the three unknowns, e, m_0 and h, that is, for determining the three most important universal constants of physical nature. We must also note that the masses m_H and m_{He} which also occur in these equations can be reduced to terms of the electronic charge by means of the very accurately known electrochemical equivalent and the ratios of the atomic weights of He and H,

* A. S. Eddington, Proc. Roy. Soc., **122**, 358 (1928); **126**, 696 (1930).

by means of eqn. (1) on page 5 and footnote 1 on page 93. Our determination of the three unknowns e, m_0 and h involves only spectroscopic measurements and hence is based on the most trustworthy observations. On the other hand, the original determination of h from heat-radiation data entails the measurement of high temperatures, that of e/m_0 from deflection experiments entails the measurement of high potentials, neither of which measurements are as free from error as the spectroscopic measurements. The determination of h from the short-wave limit of the X-ray spectra also requires the measurement of high potentials.

The eqns. (4), (5) and (6) can be expressed in such a form that from (4) and (5) we can obtain e/m_0 (in e.s.u.), as has already been done on page 95 and which led in conjunction with Houston's values for R_H and R_{He} to

$$\frac{e}{m_0} = (1{\cdot}761 \pm 0{\cdot}001) \,.\, 10^7 c \quad . \quad . \quad . \quad (7)$$

With its help we there also arrive from R_H and R_{He} at

$$R_\infty = 109737{\cdot}42 \pm 0{\cdot}06 \text{ cm.}^{-1} \quad . \quad . \quad . \quad (8)$$

The significance of $R\infty$ is

$$R_\infty = \frac{2\pi^2 m_0 e^4}{h^3 c} = \frac{2\pi^2 (e^2/h)^3}{e(e/m_0)c} \quad . \quad . \quad . \quad (9)$$

Our method of writing the last term in eqn. (9) includes the combination e^2/h, which also occurs in (6). We can eliminate it from (6) and (9) and obtain

$$R_\infty = \frac{\alpha^3 c^2}{4\pi e(e/m_0)}, \quad e = \frac{\alpha^3 c^2}{4\pi R_\infty (e/m_0)} \quad . \quad . \quad (10)$$

We need now only to refer back to eqn. (6) to obtain the value of h as well, namely,

$$h = \frac{2\pi e^2}{\alpha c} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

To be consistent we should now calculate the value of α from the empirical value of $\Delta\nu_H$, in accordance with (2). But the values for e and h so calculated would leave too much play in the matter of accuracy. We have therefore already given that value of α in eqn. (3) which we had obtained in § 3 with the help of the theoretical formula from the best values of e and h obtained from observations. We write down once again the values for e and h used in the process,

$$e = (4{\cdot}770 \pm 0{\cdot}005) \,.\, 10^{-10}, \quad h = (6{\cdot}547 \pm 0{\cdot}008) \,.\, 10^{-27} \quad (12)$$

Hence our programme of using only spectroscopic units cannot yet be carried out fully. Although we have stressed the importance of specifying the universal constants as accurately as possible we have

been compelled for the present to borrow from non-spectroscopic measurements.

We have already indicated in Chapter IV, § 2, page 198, a spectroscopic method of determining Loschmidt's number L and hence of calculating the elementary charge *e*. This " X-ray spectroscopic " method, however, assumes that the crystal lattice is flawless and that we have an accurate knowledge of the density of the crystal in the parts of the crystal involved in the reflection. Until these points are fully clear, this method, too, remains an interesting but unfulfilled programme.

Finally we revert once again to the beginning of this chapter, in particular to the part where we deal with the law according to which the mass of the electron (and mass generally) depends on the velocity. According to the theory of relativity this law runs :

$$m = \frac{m_0}{\sqrt{1-\beta^2}} = m_0\,(1 + \tfrac{1}{2}\beta^2 + \ldots) \quad . \quad . \quad (13)$$

The older " absolute " theory which assumed that there was an absolute space or ether and that the electron was spherical in shape, had as its law of the charge of mass,*

$$m = \tfrac{3}{4}m_0\frac{1}{\beta^2}\left(\frac{1+\beta^2}{2\beta}\log\frac{1+\beta}{1-\beta} - 1\right) = m_0(1 + \tfrac{6}{5}\beta^2 + \ldots) \quad (13a)$$

The test as to which of these two formulæ is valid was regarded as the *experimentum crucis* for or against the theory of relativity. The direct proof in the electrical sphere (by means of cathode rays or β-rays) was attempted by Kaufmann (cf. Chap. I, § 4), but was only achieved many years later by his successors by more refined methods.† We shall endeavour to arrive at a decision here by spectroscopic means.‡

Connected with the law of variability of mass is the law according to which the kinetic energy depends on the velocity. We know according to the theory of relativity that

$$\left.\begin{aligned} \mathrm{E}_{kin} = (m - m_0)c^2 &= m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right) \\ &= \frac{m_0c^2\beta^2}{2}(1 + \tfrac{3}{4}\beta^2 + \ldots) \end{aligned}\right\} \quad . \quad . \quad (14)$$

* First derived by M. Abraham. See his *Theorie der Elektrizität*, Vol. II, 3rd edn., pp. 162 and 175.

† Cl. Schäfer and G. Neumann, Ann. d. Phys., **45**, 529 (1914), in which a method suggested by A. Bucherer is developed ; Ch. E. Guye and Ch. Lavanchy, Arch. de Genève, **41**, 286 (1916).

‡ The idea of trying this test was first suggested to the author by W. Lenz. It was worked out by K. Glitscher in his Munich dissertation, 1917 ; cf. also Ann. d. Phys., **52**, 608 (1917).

whereas the absolute theory asserts * that

$$E_{kin} = \tfrac{3}{4}m_0c^2\left(\frac{1}{\beta}\log\frac{1+\beta}{1-\beta} - 2\right) = \frac{m_0c^2\beta^2}{2}(1 + \tfrac{3}{5}\beta^2 + \ldots) \quad (14a)$$

We have now to treat the Kepler problem of elliptic motion in the case of a hydrogen-like atom according to the absolute theory and from it to calculate the fine-structure of the spectral lines. We first find that as our second Kepler law we have the law of areas, which is valid here, quite independently of the law of variability of mass ; the law of areas states that the moment of momentum

$$p = p_\phi = mr^2\dot{\phi}$$

is constant (r and ϕ are the polar co-ordinates reckoned from the nucleus, which is assumed to be immovable). The momentum in the ϕ-direction (projection of the momentum on the tangent to the circle $r = \text{const.}$) is then $mr\dot{\phi} = p/r$, and the total impulse is $mv = m\beta c$. From these two we get the momentum in the r-direction according to Pythagoras's theorem as

$$p_r = m\dot{r} = \sqrt{(mv)^2 - p^2/r^2}.$$

The quantum conditions are :

for the azimuth ϕ :

$$\int_0^{2\pi} p_\phi d\phi = 2\pi p = n_\phi h, \quad p = \frac{n_\phi h}{2\pi} \quad . \quad . \quad . \quad (15)$$

for the radius vector r :

$$\int p_r dr = \oint\sqrt{(mv)^2 - \frac{p^2}{r^2}}\,dr = n_r h \quad . \quad . \quad (16)$$

The integration extends over the whole range of values of r, that is, from r_{min} to r_{max} and back to r_{min}.

To be able to evaluate the integral (16) we must know mv as a function of r. But at present we know m and hence also $mv = m\beta c$ by (13a) only as a function of β. We may, however, use the energy-law and the formula (14a) for the kinetic energy to obtain β as a function of r. The energy law runs, if we set the nuclear charge equal to Ze and hence the potential energy equal to $-Ze^2/r$,

$$E_{kin} = W - E_{pot} = W + \frac{Ze^2}{r}.$$

If we use eqn. (14a) here, we obtain

$$\frac{m_0c^2\beta^2}{2}(1 + \tfrac{3}{5}\beta^2) = W + \frac{Ze^2}{r}.$$

To determine β and $mv = mc\beta$ from this we proceed in steps by substituting the first approximation in the correction term of the second

* Cf. M. Abraham, *loc. cit.*

order. We write the result in a form which embraces the absolute theory and the relativity theory ; namely, in view of (13) and (13*a*),

$$(mv)^2 = 2m_0\left(W + \frac{Ze^2}{r}\right)\left[1 + \frac{\gamma}{m_0c^2}\left(W + \frac{Ze^2}{r}\right)\right] \quad . \quad (17)$$

where γ has the significance :

$\gamma = \frac{2}{5}$ for the absolute theory, $\gamma = \frac{1}{2}$ for the theory of relativity.

We now use eqn. (17) in the quantum condition (16), whose integrand now appears as a simple function of r. The integration may be performed according to the scheme given in Note 4 under (*a*), and gives finally

$$1 + 2\gamma\frac{W}{m_0c^2} = \left\{1 + \frac{2\gamma(\alpha Z)^2}{\left[n_r + \sqrt{n_\phi^2 - 2\gamma(\alpha Z)^2}\right]^2}\right\}^{-\frac{1}{2}} \quad . \quad (18)$$

Our generalised eqn. (18) is distinguished from the relativistic eqn. (26) on page 256 only in having $2\gamma\alpha^2$ in place of α^2 on the right-hand side and $2\gamma W$ in place of W on the left-hand side. Consequently the power expansion at the beginning of § 2 of this chapter may be applied directly in our present eqn. (18). For example, in the expression (6) for the term on page 259 we have only to write $2\gamma\alpha^2$ instead of α^2. From this it follows, however, that all our theorems about fine-structure remain intact so long as we replace α^2 by $2\gamma\alpha^2$. Hence *the relative magnitudes of the fine-structures*, for example, the interval 1 : 3 between the components in the hydrogen-like triplet, and so forth, also *remain preserved in the absolute theory ; only the absolute magnitudes of the fine-structures are reduced by the factor*

$$2\gamma = \tfrac{4}{5}$$

in comparison with the theory of relativity.

This holds in particular for the hydrogen doublet, which would be, according to the absolute theory,

$$\Delta\nu_H = \frac{4}{5}\frac{R\alpha^2}{2^4} = \frac{4}{5}0{\cdot}36 = 0{\cdot}29 \text{ cm.}^{-1} \quad . \quad . \quad (19)$$

This value for the hydrogen doublet is incompatible with Paschen's or Houston's measurements of the He^+*-lines.* The same may be said of the hydrogen doublets in the X-ray region, the L-doublets, and so forth. *Taking the results all together we may draw the conclusion that the absolute theory comes to grief on the spectroscopic facts.*

CHAPTER VI

POLARISATION AND INTENSITY OF SPECTRAL LINES

§ 1. Bohr's Correspondence Principle in the Case of the Hydrogen Atom

WHEREAS the quantum theory of light deals primarily only with vibration *numbers*, classical optics gives us a deep insight into the *forms* of the vibrations in that it distinguishes whether polarisation occurs or not, and, if so, whether it is linear or circular, and it determines the relative intensities of the vibration components from the type of motion of the exciting particle. How may these results be made use of for the quantum theory of light? The decisive word in this connexion belongs to wave-mechanics. By describing the quantum states as wave states it is able to make quantitative mathematical statements about the intensity of the light. In contrast with this we must here at this stage of our account remain satisfied with the qualitative and approximate assertions made by the correspondence principle in matters relating to intensity. Nevertheless we must note at once that the statements about *polarisation* and *selection rules*, which we shall derive presently from the correspondence principle, also remain preserved in wave-mechanics.

The first hint as to how to formulate the correspondence between *classical theory and quantum theory* is given by the hydrogen spectrum. The frequency that is emitted in the transition from the m^{th} to the n^{th} orbit is, according to the quantum theory,

$$\nu_{qu} = \mathrm{R}\left(\frac{1}{n^2} - \frac{1}{m^2}\right) \quad . \quad . \quad . \quad . \quad (1)$$

It differs from the frequency ν_{cl} which is emitted according to the classical theory. In the latter theory the vibration occurs in rhythm with the frequency at which the orbit is traversed (identity of the optical and mechanical frequencies); the emitted fundamental vibration is equal to $1/\tau$, where τ is the time of revolution. In addition, overtone vibrations occur, at least in the case of elliptic orbits. According to eqn. (4*a*) on page 85 or, more generally, to eqn. (17) on page 113, we therefore have for the fundamental vibration

$$\nu_{cl} = \frac{1}{\tau} = \frac{2\mathrm{R}}{n^3} \quad \text{or} \quad \frac{2\mathrm{R}}{m^3}, \quad . \quad . \quad . \quad (2)$$

respectively, according as the initial orbit m or the final orbit n is considered. Eqn. (1) may be written

$$\nu_{qu} = \mathrm{R}\frac{(m-n)(m+n)}{n^2m^2} \quad . \quad . \quad . \quad (3)$$

If $\Delta n = m - n = 1$ and $n \gg 1$, ν_{qu} asymptotically approaches the value

$$\nu_{qu} = \frac{2\mathrm{R}}{n^3} = \frac{2\mathrm{R}}{m^3} = \nu_{cl} \quad . \quad . \quad . \quad . \quad (3a)$$

Thus *the frequency given by the quantum theory for two neighbouring orbits of very large quantum numbers becomes identical with the classical fundamental frequency of the motion.*

If, on the other hand, $\Delta n > 1$ but n is still $\gg \Delta n$, it follows from (3) that

$$\nu_{qu} = \frac{2\mathrm{R}}{n^3}\Delta n = \frac{2\mathrm{R}}{m^3}\Delta n = \nu_{cl}\Delta n \quad . \quad . \quad . \quad (3b)$$

This means that *the higher quantum transitions merge into the overtone vibrations of the classical frequency.*

We shall express this relationship in a still more striking way. If $\mathrm{J} = nh$ denotes the phase-integral for the principal quantum number n it follows that $h = \dfrac{\Delta \mathrm{J}}{\Delta n}$. The quantum frequency-condition $h\nu = \Delta \mathrm{W}$ may therefore be re-written in the form

$$\nu_{qu} = \frac{\Delta \mathrm{W}}{\Delta \mathrm{J}}\Delta n \quad . \quad . \quad . \quad . \quad . \quad (4)$$

On the other hand, $\mathrm{W} = -\mathrm{R}h/n^2$. Hence by (2) the fundamental vibration corresponding to the orbital motions is given by

$$\nu_{cl} = \frac{1}{h}\frac{d\mathrm{W}}{dn} = \frac{d\mathrm{W}}{d\mathrm{J}}.$$

Combining with this the overtone vibrations we obtain as the spectrum of the revolving electron, on classical theory,

$$\nu_{cl} = \frac{d\mathrm{W}}{d\mathrm{J}}\Delta n \quad . \quad . \quad . \quad . \quad . \quad (5)$$

The difference between the quantum and the classical frequency is simply that between the *quotient of the differences and the differential quotient.* The same difference occurs quite generally when we pass from atomic theories to continuum theories.

We now also understand why the classical and the quantum frequencies approach each other asymptotically when n has great values or, rather, when $n \gg \Delta n$. For, if we consider W as represented graphically as a function of n we find that for great values of n the

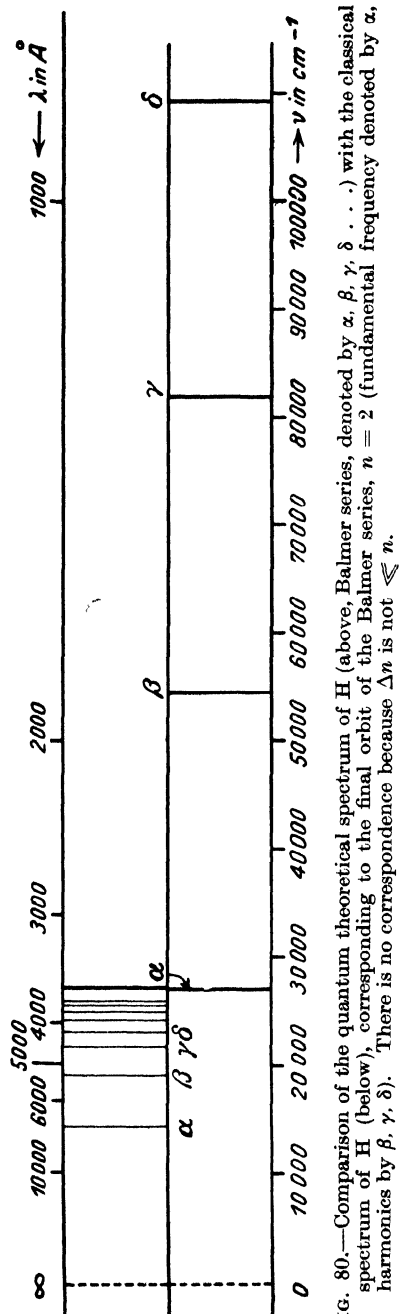


FIG. 80.—Comparison of the quantum theoretical spectrum of H (above, Balmer series, denoted by $\alpha, \beta, \gamma, \delta \ldots$) with the classical spectrum of H (below), corresponding to the final orbit of the Balmer series, $n = 2$ (fundamental frequency denoted by α, harmonics by β, γ, δ). There is no correspondence because Δn is not $\ll n$.

chords and the tangents, and the quotient of the differences and the differential quotient become more and more nearly coincident.

When n has sufficiently great values there is *coincidence* and when n has moderately great values there is a *correspondence* between the results of the classical and the quantum theory. Corresponding to the fundamental vibration of the classical theory we have the quantum transition $\Delta n = 1$, and corresponding to every overtone vibration we have, according to the equations (4) and (5) the quantum transition whose Δn is equal to the order of the overtone vibration.

This is illustrated in Fig. 80. Between the two top lines we have the Balmer series in the scale of the ν's, exactly as in Fig. 19 on page 69. The frequency $\nu = 0$ is shown as a dotted line on the left-hand side, and the series limit $\nu = R/2^2$ is given on the right. Between the two bottom lines we show the classical spectrum for the final orbit $n = 2$. As a result of eqn. (2) its fundamental vibration coincides with the series limit and has been denoted by α since it corresponds to the line H_α. The first overtone vibration which corresponds to H_β, lies at twice the distance from the zero-line, the second overtone vibration lies at three times the distance, and so forth. Hence in order to visualise the correspondence kinematically we must displace the classical spectrum towards the left-hand side so that the infinitely distant overtone vibration coincides with

the series limit and the fundamental vibration coincides with H_α. The fact that there is nothing to be seen of a coincidence of the higher series lines is, of course, due to the fact that the condition $n \gg \Delta n$ is by no means fulfilled, but that rather $n = 2$ here and $\Delta n \gg 2$ for the higher lines of the series.

In spite of the formal correspondence or coincidence (in some cases) there is actually a considerable difference in the point of view. On the classical theory all the vibrations are emitted *simultaneously* while the orbit is being traversed. The whole vibration spectrum owes its origin to one uniform process. From the quantum point of view, however, every line of the spectrum corresponds to another individual process and another kind of quantum transition. The individual processes do not occur simultaneously but *independently of one another*. The experimental results obtained in the excitation of spectral lines (cf. in particular, the section on electron collisions in Chap. VII) confirm without exception the point of view of the quantum theory.

The correspondence in the frequencies according to the two different theories is by no means accidental; rather it has its root in the part played by the classical theory of radiation as an approximation, obtained by using the idea of a continuum, to discontinuous reality. Does it apply only to frequencies and not to vibration forms and intensities, that is to polarisations and amplitudes? This can hardly be denied for the large quantum numbers. But Bohr demands further that the amplitudes and so forth given by classical calculation shall also apply approximately in the case of moderate and small quantum numbers.* It is precisely this extension that renders his Correspondence Principle so fruitful. Following on Fig. 80 we formulate this principle as follows: *in displacing the spectrum from its classical into its quantum position we must leave each line the intensity and polarisation (if it occurs) which it has according to the classical theory. The Correspondence Principle asserts that in this way we obtain the intensity and polarisation of the actual spectral lines perfectly correctly in the case of quantum numbers that are sufficiently great, and approximately correctly in the case of moderately great quantum numbers.*

We must bear in mind that the question of intensity is in reality a *statistical problem*. The quantum theory considers individual events in the atom and offers no measure for the frequency with which they occur. But it is this frequency of occurrence that is involved in all questions of intensity. The classical theory of radiation, however, uses mechanics to derive from a given orbital curve the complex of vibrations contained in it together with their amplitudes. In contrast with this the Correspondence Principle asserts that:

* Cf. the dissertation by H. A. Kramers, *Intensities of Spectral Lines*, Copenhagen Academy, 1919.

the unknown statistics of individual quantum processes is actually given by the classical calculation; by calculating the amplitudes of the classical spectrum we obtain the correct numbers for the frequency of occurrence of the corresponding quantum processes.

This procedure is not, however, unique, and this in itself characterises it as an approximative process. In calculating the classical amplitudes, are we to use as our basis the initial orbit or the final orbit or an intermediate orbit defined by taking an average of these two? The Correspondence Principle offers no answer. It is easy to see that with the asymptotic condition $\Delta n \ll n$ the amplitudes that are obtained from the initial or the final orbit or from an intermediate orbit must come out appreciably the same. But when Δn and n have values that are not very different from each other a certain arbitrariness remains. Wave-mechanics disposes of this arbitrariness by taking into account both the initial and the final orbit in determining the intensity; and it uses them symmetrically.

Another difficulty is connected with the particular circumstances of the hydrogen spectrum. The Kepler problem without relativity is a degenerate problem. It is quantised by the principal quantum number n, which determines the energy of the orbit (its major axis) but leaves the form of the orbit (eccentricity) undetermined. Let us consider, for example, the final orbit of the Balmer series, $n = 2$. If we disregard the fine-structure we cannot distinguish whether the circular or the elliptic orbit of Fig. 27 occurs. But then the amplitude ratios of the emitted spectrum would remain undetermined. Actually, the circular orbit is given by

$$x = a \cos 2\pi\nu t, \quad y = a \sin 2\pi\nu t \quad . \quad . \quad . \quad (6)$$

where $\nu = 1/\tau$ stands for the classical frequency of revolution. The classical vibration here consists of only the fundamental vibration ν; the amplitudes of all the overtone vibrations 2ν, 3ν, . . . are zero. The polarisation is circular for an observer in the z-direction. The position is different with the elliptic orbits. If we imagine its principal axis to be the co-ordinate axes and likewise to be functions of the time, then they assume the form of infinite Fourier series:

$$\left.\begin{aligned} x &= a \cos 2\pi\nu t + a' \cos 4\pi\nu t + a'' \cos 6\pi\nu t + \ldots \\ y &= b \sin 2\pi\nu t + b' \sin 4\pi\nu t + b'' \sin 6\pi\nu t + \ldots \end{aligned}\right\} \quad . \quad (7)$$

The particular form of this expansion * results on the one hand from the periodicity of the orbit and on the other from the fact that even

* The coefficients of this expansion are Bessel functions with multiples of the eccentricity as argument. The absence of overtone vibrations in eqn. (6) is due analytically to the circumstance that Bessel functions of vanishingly small argument and non-vanishing index vanish. The name Bessel indicates that the theory of these functions was elaborated precisely in connection with the Kepler problem.

and odd numbers are involved in the dependence of the time on the x- and the y-co-ordinate respectively. That we must add the higher terms in both the equations (7) is seen directly from the fact that the motion in the ellipse is not uniform. All the overtone vibrations are now present. Their amplitudes relative to the fundamental vibration are given by

$$\sqrt{a^2 + b^2} : 4\sqrt{a'^2 + b'^2} : 9\sqrt{a''^2 + b''^2} : \ldots .$$

The factors 4, 9, . . . associated with the overtone vibrations result from the fact that the emission is not given by the co-ordinates themselves but by their second differential quotients, the accelerations. Hence in elliptic motion we have a different distribution of intensity in the spectrum, as calculated on classical theory, than in the circular motion. In the present case we may, however, say that the observed intensity which is due to the emission of radiation from very many atoms, arises from both kinds of transition (into a circular or an elliptic orbit) and is obtained by superposing the partial intensities due to these transitions. The statistical weights (probability factors) that must be associated with these transitions can be determined only again when we deal with wave-mechanics.

The ambiguities in the manipulation of the Correspondence Principle vanish in the particular case where the Fourier coefficients have the value zero for the initial and the final orbit. In that case we can without fear of error assign the value zero to the emission. The Correspondence Principle then becomes specialised into a rigorous **Selection Principle**: it forbids the occurrence of those spectral lines which have no corresponding partial vibrations in the Fourier series in question.

A very simple illustration of this is again given by the hydrogen spectrum. Can a transition be effected from one circular orbit to another ? In the case of the circular orbit all the overtone vibrations in eqn. (6) are absent. Since these vibrations correspond to the quantum transitions $\Delta n > 1$ we must infer that such transitions can never lead from one circle to another. If we assume the final orbit of the Balmer series to be a circle the initial orbit of $H_\beta(4 \to 2)$, of $H_\gamma(5 \to 2)$, and so forth, must necessarily be elliptical ; it is only in the case $H_\alpha(3 \to 2, \Delta n = 1)$ that we can pass from circle to circle. From this we see that the different ways of generating lines, which we enumerated for the Balmer series on page 114, become restricted by the selection principle and that Fig. 22 on page 90 which used only circles is too diagrammatic.

To formulate the selection principle still more rigorously we shall use as our basis the non-degenerate hydrogen atoms (Chap. V) or a diagrammatic atom *not* hydrogen-like (Chap. VII). In both cases the azimuth ϕ of the revolving electron or of the external " series electron,"

plays the part of a cyclic variable, as it does not occur in the energy-expression and hence has a constant moment of momentum $p_\phi = p$. The obvious difference as compared with the degenerate Kepler ellipse is that ϕ does not change purely periodically but exhibits a " secular " motion, rotating its perihelion. To visualise this let us fix our attention on the first figure of Chapter V. We write

$$\phi = \omega t + \Phi(n, t)$$

and take ω to stand for the angular velocity of the secular motion. The remainder Φ which is left when ωt has been deducted from ϕ is purely periodic and depends, as in the case of the degenerate problem, only on the principal quantum number n. No secular term occurs in the case of the r-co-ordinate. Hence we write

$$r = \mathrm{R}(n, t)$$

and form *

$$x + iy = re^{i\phi} = e^{i\omega t}\mathrm{F}(n, t) \quad . \quad . \quad . \quad (8)$$

The function F, which is composed of R and Φ, has the same properties and periodicity as Φ and likewise depends only on n. F may be expanded in a Fourier series in multiples of $2\pi\nu t$, such as we have already written down explicitly in eqn. (7). If we make $\omega = 2\pi\nu_0$, so that ν_0 denotes the frequency of revolution of the secular motion, we obtain from (8)

$$x + iy = e^{2\pi i\nu_0 t}\sum_{-\infty}^{+\infty}(s)\ \mathrm{C}_s\, e^{2\pi i s\nu t} \quad . \quad . \quad . \quad (9)$$

where we have used negative values for the summation letter s for the sake of simplicity. A striking feature here is the difference in the two exponents of e : in the case of ν_0 the integral factor is absent, which is denoted by s in the case of ν. That is, the integer assigned to ν_0—say s_0—has the value 1, or, since we may reverse the sign of i in (9) the values ± 1. Now, s denotes the order of the overtone vibrations and, by the Correspondence Principle, the magnitude of the quantum transitions $\Delta n = s$. If all the s's occur all the Δn's are allowed by the Correspondence Principle. On the other hand, the azimuthal quantum number n_ϕ belongs to the azimuth ϕ and the integer s_0 corresponds to the quantum transition Δn_ϕ. From $s_0 = \pm 1$ we deduce by the Correspondence Principle that

$$\Delta n_\phi = \pm 1 \quad . \quad . \quad . \quad . \quad (10)$$

In place of n_ϕ we shall use the wave-mechanical symbol $l = n_\phi - 1$ (cf. p. 115; the relativistic difference between l and n_ϕ or $n_\phi - 1$,

* Cf. Note 7, in particular (e).

which expressed itself in Fig. 75, p. 270, may here be left out of account). Instead of (10) we may also write

$$\Delta l = \pm 1 \quad . \quad . \quad . \quad . \quad (10a)$$

The azimuthal quantum number l can change only by unity. Besides $|\Delta l| < 1$ also $\Delta l = 0$ is forbidden ; *the intensity of the corresponding quantum transitions is zero.*

Hitherto we have assumed the orbit to be *plane*, which is certainly true in the case of the Kepler ellipse and the rather simple atoms that are not hydrogen-like ; so long as we schematically regard the forces exerted by the atomic core on the series electron as *central forces* and disregard *electron spin*. But if the atom is situated in an external field of force the orbit will be *spatial*, so that a z-component will have to be added to the x- y-motion. Let the external field be parallel to and symmetrical about the z-axis. In contrast with the azimuth ϕ measured in the orbital plane, the equatorial azimuth ψ measured in the xy-plane (equatorial plane) has now a cyclic character. Its secular motion does not influence the z-component. This may be put in the form

$$z = \sum_{-\infty}^{+\infty} (s)\, D_s\, e^{2\pi i s \nu t} \quad . \quad . \quad . \quad . \quad (11)$$

whereas we have retained the assumption (9) for the x- y-co-ordinates. (For further details see Note 7 (f))

The absence of the exponent in $\nu_0 t$ in (11) may be interpreted as meaning that here $s_0 = 0$. We denote the equatorial quantum number corresponding to the cyclic co-ordinate ψ by m and, applying the Correspondence Principle, assume that the *quantum transition*

$$\Delta m = 0 \quad . \quad . \quad . \quad . \quad . \quad (12)$$

is allowed, whereas equation (9) states that the *quantum transitions*

$$\Delta m = \pm 1 \quad . \quad . \quad . \quad . \quad (12a)$$

may also occur with finite intensity.

The superposition of an external force thus transposes the selection principle from the azimuthal quantum number l in a somewhat changed form to the equatorial quantum number m. This renders the azimuthal quantum freely variable : in proportion as the plane orbit is deformed into a spatial (twisted) orbit by external fields the originally forbidden transitions for which

$$\Delta l = 0 \text{ and } |\Delta l| > 1 \quad . \quad . \quad . \quad . \quad (13)$$

occur with appreciable intensity.

The appearance of new spectral lines in discharge tubes of high current density (cf. Chap. VII, § 2) bears witness to this and agrees entirely with the conclusions here drawn.

But the expressions (9) and (11) for the orbits not only contain statements about intensity but also about the polarisation of the light, which is emitted, according to the classical theory, when the series electron traverses the orbit in question. According to the Correspondence Principle the statements about polarisation also apply to the quantum emission.

It is true that the polarisation has been observed only in the case where an external field is present. In the force-free case the orbits are arbitrarily distributed in space and hence the polarisations corresponding to them escape observation. But in the presence of an external field the polarisation phenomenon can be measured most easily.

From eqn. (9) we read that for a field of force directed along the z-axis: *corresponding to the quantum transition*, $\Delta m = \pm 1$, *we have circular polarisation in the plane perpendicular to the lines of force; corresponding to the quantum transition*, $\Delta m = 0$, *we have linear polarisation parallel to the lines of force.*

We shall have more to say about the polarisation conditions when we deal with the Stark and the Zeeman effects in the present chapter. Compare also the ideas due to Rubinowicz given in Note 8, which link together quantum theory and electrodynamics and signify the first step towards quantum-electrodynamics, which is still wrapt in obscurity at the present time.

§ 2. The Orbits of the Hydrogen Electron in the Stark Effect

The influence of the electric field on the emission of the Balmer lines was discovered by J. Stark * in 1913, and was examined by him in the succeeding years experimentally in an exemplary fashion as far as all the details of the fine-structure † and polarisation, not only for hydrogen, but for a series of other elements, He, Li, etc. It was a happy coincidence that in the same year, 1913, Bohr's spectral theory was proposed and was elaborated far enough to be able to grapple with the problem of the electrical resolution of hydrogen lines. The solution of the problem was obtained simultaneously and along essentially similar lines by K. Schwarzschild ‡ and P. Epstein || in 1916. Whereas the classical theory failed completely, the quantum theory yielded all the many details of Stark's observations of the fine-structure in such complete coincidence with experiment that it was no longer possible to doubt the correctness and unambiguity of the solution found.

* Berliner Sitzungsber., Nov., 1913; Ann. d. Phys., **43**, 965 and 983 (1914). A summary has been given by J. Stark, *Elektrische Spektralanalyse*. Leipzig (Hirzel), 1914.

† Göttinger Nachr., Nov., 1914.

‡ K. Schwarzschild, *Zur Quantentheorie*, Berliner Sitzungsber., April, 1916, published on 11th May, the day of Schwarzschild's death.

|| P. S. Epstein, Zur Theorie des Starkeffektes, Ann. d. Phys., **50**, 498 (1916).

We shall just shortly remark on the experimental difficulties of the problem. The object was to subject hydrogen atoms during their emission to a powerful electric field of, say, 100,000 volts per cm. This was not possible with the ordinary arrangement of the Geissler tube, in which the hydrogen lines are usually produced. Geissler tubes are comparatively good conductors ; an electric field in it simply collapses. Stark, therefore, used in place of the Geissler tube the luminescence of a canal-ray tube in a layer directly behind the perforated cathode. By using an oppositely charged electrode placed parallel and close to the cathode, he was able to generate a uniform and measurable electric field in a space of a few millimetres. The shortness of the space between the electrodes of this additional field not only favours the production of the resulting great potential drop but also prevents (in accordance with the peculiar laws of the production of the dark space in discharge tubes) the occurrence of a spontaneous discharge between the electrodes. The potential difference is great enough to influence effectively the canal-ray ions that fly through the perforated cathode in the usual way and to distort perceptibly the electronic orbits which are being traversed in them.

In contradistinction to Stark, Lo Surdo * uses as a means of influencing the phenomenon of luminescence no additional field but the field of the discharge tube itself, and, indeed, the part within the dark space of the cathode. Thus his method sacrifices quantitative definiteness and homogeneity of field but offers special advantages for the purpose of qualitative observations. For this reason many experimenters, particularly in Japan, use Lo Surdo's method. The successful and accurate investigations of Rausch von Traubenberg † on hydrogen lines, however, were done with Stark's original arrangement.

The general experimental results of Stark and Lo Surdo, respectively, were :

1. Every Balmer line becomes *split up* into a number of components.

2. The number of components increases with the *series number* of the line.

3. The components *are linearly polarised when viewed transversally* (transverse effect), being polarised partly parallel to the field (π-components) and partly perpendicularly to it (σ-components).

We must then first define clearly what these terms usually signify. In the case of the π-components *the direction of the electric vibration* in the light ray at the point of observation is *parallel* to the lines of force of the external field ; in that of the σ-components, the direction of the electric vibration is *perpendicular* to these lines of force. Thus it is not the position of the optical plane of polarisation, as shown by a

* Cf. his general report in Phys. Zeits., **30**, 750 (1929). For atoms other than hydrogen see the report by R. Ladenburg, *ibid.*, p. 369.

† Accad. dei Lincei, **23**, 83, 117, 143, 252, 326 (1914).

Nicol's prism, that is to serve to distinguish "π" and "σ." Since, as we know, the plane of polarisation in the light ray is perpendicular to the direction of electrical vibration (or, what is the same, it passes through the plane of magnetic vibration), we should have to transpose the terms π and σ if we judged them according to the plane of polarisation. The use of the words "parallel" and "perpendicular," as here applied, arose historically out of the ideas of the classical wave-theory. If we imagine a vibrating electron to be added to the place at which the emitting atom is situated, then the wave emitted by this electron would have, according to the classical view, a direction of electric vibration that would have the same direction as the component of acceleration of the electron ($\dot{v}_n$ in Fig. 7, p. 24) that is effective in the direction of emission in question. The π- and the σ-components thus arise, in classical language, from vibrations of an exciting electron, which take place parallel or perpendicularly to the lines of force of the external field.

4. When viewed *longitudinally* (longitudinal effect) the π-components are *invisible* and the σ-components are *unpolarised.*

5. The intense π-components in general lie on the *outside*, and the intense σ-components on the *inside.*

6. In the case of hydrogen the resolution and the polarisation are distributed *symmetrically* on both sides of the original line, but in the case of other atoms, the distribution is largely *unsymmetrical.*

7. The distances of the components from the centre are, in the case of hydrogen, whole *multiples of a certain smallest distance between the lines*, and actually, measured in the scale of vibration numbers, there is the same line-interval for the various hydrogen lines.

8. The resolution (in particular, this smallest line-interval) increases *proportionally with the field.* In the case of more intense fields there is observed in addition to the linear Stark effect one of the second order, and if the intensity is still further increased a Stark effect of the third order manifests itself.

We have already formed in Chapter II, page 114, a general theoretical idea of the cause of the Stark effect. We spoke there of the various possible ways in which one and the same Balmer line may be produced by circular or elliptic orbits with the same quantum sum. These various modes of origin certainly coincide in one line if no external field of force is present (and if we leave out of consideration the relativistic fine-structure). But they become separated if a powerful electric field is imposed.

Thus *the Stark effect denotes the artificial separation of the various possible modes of production, which originally coincided in a Balmer line, of the initial and the final orbit, this separation being effected by the application of an external electric field.* And, owing to the spatial position of the orbits, the composition of the same quantum sum out of *three* quantum numbers is involved. This is easily understood from

the fact that the effect of the electric field on the orbits of the hydrogen electron will be found to depend not only on the shape and size (two quantum numbers) but also on the spatial position of the orbit with respect to the electric lines of force (third quantum number). These orbits are in the electric field, no longer, of course, circular and elliptic orbits; or, expressed more generally, the states disturbed by the electric field differ from the undisturbed states of the hydrogen atom. Our object is to select from all the mechanically possible orbits those that are distinguished by having quantum values; this is accomplished by choosing three appropriate quantum numbers and expressing the orbital energy as a function of them. Corresponding to each such quantum triplet in the initial and the final orbit we have in general a different component in the Stark fine-structures. This explains immediately the increasing number of components in the sequence of lines H_α, H_β, H_γ . . . . : as the quantum sum of the initial orbit gradually increases the number of quantum triplets into which this sum may be resolved also increases and with it, the number of components of the corresponding resolution due to the Stark effect, as shown photographically, also increases.

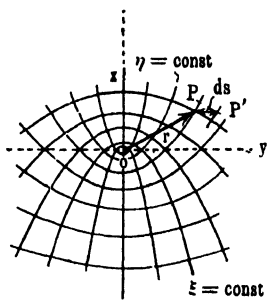


FIG. 81.—Replacement of the plane cartesian co-ordinates x, y by the parabolic co-ordinates ξ, η. The new co-ordinate lines are given by equations (1) when ξ = constant and η = constant.

We now consider the mechanical problem: how does an electron move when under the influence of a fixed nuclear charge Ze (in the case of the hydrogen atom this $Z = 1$) and under the simultaneous action of an external homogeneous electric field of force of the intensity F? This problem is contained in the more general one: how does a point-mass move when under the influence of two arbitrary and arbitrarily placed fixed (Newton-Coulomb) centres of attraction? The appropriate co-ordinates for the treatment of this general problem are (according to Jacobi) the parameters of the families of confocal ellipses and hyperbolæ that are described about the two centres as foci, together with the angle reckoned from the line connecting the centres. If one of the centres is taken off to infinity whilst its attractive power correspondingly increases, the general problem reduces to our special one; at the same time the systems of confocal ellipses and hyperbolæ resolve into two families of confocal parabolas of which the second fixed centre, the nucleus, is the focus, and the field direction through it is the common axis. We call the parameters of these two parabolic systems ξ and η. They, together with the angle ψ counted from the direction of the axis, are the co-ordinates which we shall have to use in our special problem.

In Fig. 81, O represents the nucleus, x the direction of the lines of force. The parabolas $\xi = \text{const.}$, $\eta = \text{const.}$, respectively have the equations

$$\frac{y^2}{\xi} + 2x = \xi, \qquad \frac{y^2}{\eta} - 2x = \eta \quad . \quad . \quad . \quad (1)$$

For each point P (x, y) of the plane we calculate by means of these equations the parameters ξ, η of the two parabolas which intersect at P. These two parameters may serve in place of x, y to define the point P, and hence also to determine the position of the electron within the plane of the diagram ("meridian plane") The parabolas $\xi =$ const. have as their axis the negative direction of x, the parabolas $\eta =$ const. the positive direction of x.

The simplest way of introducing parabolic co-ordinates is as follows. In the meridian plane we define an $X + iY$ related to the complex variable $x + iy$ by

$$x + iy = \tfrac{1}{2}(X + iY)^2 \quad . \quad . \quad . \quad . \quad (2)$$

By equating the real and the imaginary parts we get

$$x = \tfrac{1}{2}(X^2 - Y^2), \quad y = XY \quad . \quad . \quad . \quad (3)$$

If we eliminate Y and X, respectively from these two equations we have

$$\frac{y^2}{X^2} + 2x = X^2 \quad \text{and} \quad \frac{y^2}{Y^2} - 2x = Y^2 \quad . \quad . \quad (4)$$

The equations become identical with (1) if we write

$$\xi = X^2, \ \eta = Y^2 \quad . \quad . \quad . \quad . \quad (5)$$

From (2) we form the line-element in the plane, that is, the distance between two neighbouring points PP′; this is again done most simply by using imaginaries. By differentiating (2) we obtain

$$dx + idy = (X + iY)(dX + idY)$$

and by taking the absolute value

$$ds^2 = dx^2 + dy^2 = (X^2 + Y^2)(dX^2 + dY^2) \quad . \quad . \quad (6)$$

From (5), however, it follows that

$$dX^2 = \frac{d\xi^2}{4\xi}, \quad dY^2 = \frac{d\eta^2}{4\eta},$$

and hence

$$ds^2 = \frac{1}{4}(\xi + \eta)\left(\frac{d\xi^2}{\xi} + \frac{d\eta^2}{\eta}\right) \quad . \quad . \quad . \quad (7)$$

If, however, we take the absolute value in eqn. (2) we obtain the distance r of any point P of the plane from the origin O:

$$r^2 = x^2 + y^2 = \tfrac{1}{4}(X^2 + Y^2)^2 = \tfrac{1}{4}(\xi + \eta)^2 \quad . \quad . \quad (8)$$

In Fig. 81 the lengths $OP = r$ and $PP' = ds$ are shown.

We now suppose the plane of the figure to be rotated about the x-axis and we call the angle of rotation ψ. The y-co-ordinate hitherto used then denotes the distance ρ from the axis of rotation. The rectangular space-co-ordinates, xyz, which are now to be introduced are expressed as follows in terms of the plane co-ordinates hitherto used, which we shall now call x' and y', and the angle ψ :

$$x = x', \quad y = y' \cos\psi, \quad z = y' \sin\psi.$$

The line-element in space then becomes

$$ds^2 = dx^2 + dy^2 + dz^2 = dx'^2 + dy'^2 + y'^2 d\psi^2 \quad . \quad (9)$$

If we take the value of $dx'^2 + dy'^2$ from (7) and express y' by (3) and (5), in terms of ξ and η, (9) becomes

$$ds^2 = \frac{1}{4}(\xi + \eta)\left(\frac{d\xi^2}{\xi} + \frac{d\eta^2}{\eta}\right) + \xi\eta d\psi^2 \quad . \quad . \quad (10)$$

From (10) we obtain for *the expression of the kinetic energy in parabolic co-ordinates* (μ = mass of the electron) :

$$\mathrm{E}_{kin} = \frac{\mu}{2}\left(\frac{ds}{dt}\right)^2 = \frac{\mu}{2}\left\{\frac{1}{4}(\xi + \eta)\left(\frac{\dot{\xi}^2}{\xi} + \frac{\dot{\eta}^2}{\eta}\right) + \xi\eta\dot{\psi}^2\right\} \quad . \quad (11)$$

The potential energy is

$$\mathrm{E}_{pot} = -\frac{\mathrm{Z}e^2}{r} + e\mathrm{F}x,$$

where $\mathrm{Z}e$ = nuclear charge, F = field-strength, $-e\mathrm{F}$ = force of the field on the electron ; r and x are given in parabolic co-ordinates by (8), (3) and (5). Hence

$$\begin{aligned}\mathrm{E}_{pot} &= -\frac{2\mathrm{Z}e^2}{\xi + \eta} + \frac{e\mathrm{F}}{2}(\xi - \eta) \\ &= \frac{1}{2(\xi + \eta)}\{-4\mathrm{Z}e^2 + e\mathrm{F}(\xi^2 - \eta^2)\} \quad . \quad . \quad (12)\end{aligned}$$

Parabolic co-ordinates offer a considerable advantage over rectilinear co-ordinates in enabling the potential energy to be expressed in this manner without root signs in terms of ξ and η.

From (11) we obtain for the *momenta* p_ξ, p_η, p_ψ by differentiating with respect to the parabolic velocity co-ordinates $\dot{\xi}$, $\dot{\eta}$, $\dot{\phi}$ in the manner of eqn. (5) on page 78 :

$$p_\xi = \frac{\mu}{4}(\xi + \eta)\frac{\dot{\xi}}{\xi}, \quad p_\eta = \frac{\mu}{4}(\xi + \eta)\frac{\dot{\eta}}{\eta}, \quad p_\psi = \mu\xi\eta\dot{\psi} \quad . \quad (13)$$

Hence, expressed as a function of the momenta, (11) may be written as follows :

$$\mathrm{E}_{kin} = \frac{1}{2\mu(\xi + \eta)}\left\{4\xi p_\xi^2 + 4\eta p_\eta^2 + \left(\frac{1}{\xi} + \frac{1}{\eta}\right)p_\psi^2\right\} \quad . \quad (14)$$

The sum of (12) and (14) is the expression for the total energy in parabolic position and momentum co-ordinates or, by page 101, the *Hamiltonian function* H. It is invariable during the motion and is equal to the energy-constant W. Hence we have

$$2\mu(\xi+\eta)W = 4\xi p_\xi^2 + 4\eta p_\eta^2 + \left(\frac{1}{\xi}+\frac{1}{\eta}\right)p_\psi^2 - 4\mu Ze^2 + \mu eF(\xi^2-\eta^2) \quad (15)$$

In accordance with the rule in Chapter II, page 101, we here set

$$p_\xi = \frac{\partial S}{\partial \xi}, \quad p_\eta = \frac{\partial S}{\partial \eta}, \quad p_\psi = \frac{\partial S}{\partial \psi}$$

and obtain the partial differential equation for the action function S in the following form :

$$4\xi\left(\frac{\partial S}{\partial \xi}\right)^2 + 4\eta\left(\frac{\partial S}{\partial \eta}\right)^2 + \left(\frac{1}{\xi}+\frac{1}{\eta}\right)\left(\frac{\partial S}{\partial \psi}\right)^2 = 2\mu(\xi+\eta)W + 4\mu Ze^2 - \mu eF(\xi^2-\eta^2) \quad (16)$$

and ψ is a cyclic co-ordinate. Hence

$$\frac{\partial S}{\partial \psi} = p_\psi = \text{const.} \quad . \quad . \quad . \quad . \quad (17)$$

and eqn. (16) becomes

$$4\xi\left(\frac{\partial S}{\partial \xi}\right)^2 + 4\eta\left(\frac{\partial S}{\partial \eta}\right)^2 = 2\mu(\xi+\eta)W + 4\mu Ze^2 - \mu eF(\xi^2-\eta^2) - \left(\frac{1}{\xi}+\frac{1}{\eta}\right)p_\psi^2 \quad (18)$$

We write the terms depending on ξ on the left-hand side, those dependent on η on the right-hand side, and in this way we have sucessfully separated the variables. The separated parts must be equal to the same constant, which we may conveniently denote by $-2\mu\beta$:

$$4\xi\left(\frac{\partial S}{\partial \xi}\right)^2 - 2\mu\xi W - 2\mu Ze^2 + \mu eF\xi^2 + \frac{1}{\xi}p_\psi^2 = -4\eta\left(\frac{\partial S}{\partial \eta}\right)^2 + 2\mu\eta W + 2\mu Ze^2 + \mu eF\eta^2 - \frac{1}{\eta}p_\psi^2 = -2\mu\beta.$$

Hence we obtain

$$\frac{\partial S}{\partial \xi} = p_\xi = \sqrt{f_1(\xi)}, \quad \frac{\partial S}{\partial \eta} = p_\eta = \sqrt{f_2(\eta)} \quad . \quad . \quad (19)$$

where f_1 and f_2 have the following significance :

$$\left.\begin{aligned} f_1(\xi) &= \frac{1}{4\xi}\left\{2\mu\xi W + 2\mu(Ze^2-\beta) - \mu eF\xi^2 - \frac{1}{\xi}p_\psi^2\right\} \\ f_2(\eta) &= \frac{1}{4\eta}\left\{2\mu\eta W + 2\mu(Ze^2+\beta) + \mu eF\eta^2 - \frac{1}{\eta}p_\psi^2\right\} \end{aligned}\right\} \quad . \quad (20)$$

From this expression we may without further calculation draw a general inference about the form of the orbital curves. We see from (19) and (20) that during the motion ξ remains restricted to values for which $f_1 > 0$, since $\partial S/\partial\xi$, i.e. p_ξ must be real. The extreme values that ξ can assume are thus the roots of $f_1(\xi) = 0$. We denote them by ξ_{min} and ξ_{max}. In the case $F = 0$ where $f_1 = 0$ becomes a quadratic equation in ξ there are only two positive roots. In the case $F \neq 0$ a third root comes up from infinity but is of no interest to us. We take ξ_{max} and ξ_{min} to denote those two roots that proceed by continuous development from those that occur in the case $F = 0$. What holds for ξ holds equally well for η. Here, too, there are two real positive values η_{min} and η_{max} between which η is enclosed.

By repeating the argument of page 103 we next show that in the course of the motion ξ increases continuously from ξ_{min} to ξ_{max}. For if ξ were to change its direction of progress we should necessarily have $\dot{\xi} = 0$. But by (13) we should then have $p_\xi = 0$. Now ϕ_ξ can vanish only if $f_1 = 0$, that is if $\xi = \xi_{max}$ or ξ_{min}. Thus ξ as it comes from ξ_{min}, reverses for the first time at the point $\xi = \xi_{max}$. Whereas $p_\xi > 0$ hitherto, the negative sign of the square root now applies; by (13) when $p_\xi < 0, \dot{\xi} < 0$. The decrease of ξ now continues until $\xi = \xi_{min}$, where it reverses, its values again increasing gradually, and so forth. *We see that during the motion ξ remains restricted to the region between ξ_{min} and ξ_{max} and runs through the intervening values in opposite directions alternately.* The same applies to η, in which case also the roots η_{min} and η_{max} of $f_2(\eta) = 0$ form the reversing points or " libration limits " (see p. 105) for the successive values of the η-co-ordinate.

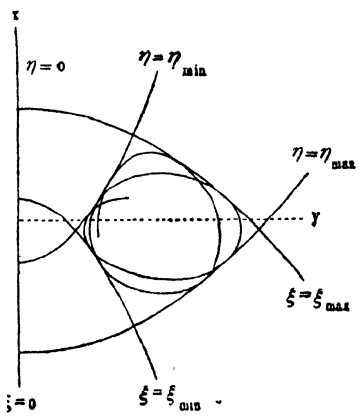


FIG. 82.—Orbital curve of the hydrogen electron in the Stark effect (without relativity) showing the librational motion inside the curved quadrilateral η_{min}, η_{max}, ξ_{min}, ξ_{max} of the figure. The figure must be regarded as rotating about the x-axis (direction of the field).

The main features of the form of the orbits in the Stark effect are now exposed. In Fig. 82 we exhibit the curved quadrangle which is formed by the parabolas $\xi = \xi_{min}$, $\xi = \xi_{max}$, $\eta = \eta_{min}$, and $\eta = \eta_{max}$. *The orbital curve is enclosed within these limits; it alternately touches a ξ- and an η-limit, and in the course of time closely covers the whole of the curved quadrangle.* Our figure exhibits the conditions only in the meridian plane, that is, in a plane ψ = const. Besides the motion in this plane a rotation of the plane in space about the direction of the

lines of force takes place in which the moment of momentum p_ψ is constant. By eqn. (13) there corresponds to it a quantity, the rotational velocity, $\dot{\psi}$, which is variable within certain limits. The plane orbital curve shown in the figure becomes *a spatial orbital curve which continually coils round the direction of the lines of force.*

Having dealt with the mechanical aspect of the problem we turn to the quantum aspect. We apply the quantum conditions to our co-ordinates ξ, η, ψ, that is, we postulate

$$\oint p_\xi d\xi = n_\xi h, \quad \oint p_\eta d\eta = n_\eta h, \quad \int_0^{2\pi} p_\psi d\psi = n_\psi h \quad . \quad (21)$$

where n_ξ, n_η, n_ψ denote whole numbers. We call n_ψ the *equatorial quantum number.* The integration with respect to ψ stretches over all positions ψ of the meridian plane from 0 to 2π. Since p_ψ is constant by eqn. (17), we have

$$2\pi p_\psi = n_\psi h, \quad p_\psi = n_\psi \frac{h}{2\pi} \quad . \quad . \quad . \quad (22)$$

Let us call n_ξ and n_η *parabolic quantum numbers.* The integration over ξ and η extends over the whole range of values of these variables, that is from ξ_{min} to ξ_{max} and back again for ξ, and similarly for η. In the first two of the equations (21) this closed path of integration is denoted by the sign $\bigcirc$. If we substitute (19) in these two equations we obtain

$$\oint \sqrt{f_1(\xi)d\xi} = n_\xi h, \quad \oint \sqrt{f_2(\eta)d\eta} = n_\eta h \quad . \quad . \quad (23)$$

By (20) both integrals have the same form. We combine them in

$$\oint \sqrt{\mathrm{A} + 2\frac{\mathrm{B}}{r} + \frac{\mathrm{C}}{r^2} + \mathrm{D}r}\, dr = 2nh \quad . \quad . \quad (24)$$

On the right-hand side of this equation n stands for n_ξ in the one case and n_η in the other. The factor 2 in front of n has been taken over from the left-hand side [denominator 4 in $f(\xi)$]. In the one case the coefficients A, B, C, D, denote

$$\mathrm{A}_1 = 2\mu\mathrm{W}, \quad \mathrm{B}_1 = \mu(\mathrm{Z}e^2 - \beta), \quad \mathrm{C}_1 = -\left(\frac{n_\psi h}{2\pi}\right)^2, \quad \mathrm{D}_1 = -\mu e\mathrm{F} \quad (24a)$$

in the other case they denote

$$\mathrm{A}_2 = 2\mu\mathrm{W}, \quad \mathrm{B}_2 = \mu(\mathrm{Z}e^2 + \beta), \quad \mathrm{C}_2 = -\left(\frac{n_\psi h}{2\pi}\right)^2, \quad \mathrm{D}_2 = +\mu e\mathrm{F} \quad (24b)$$

The left-hand side of (24) has been worked out in Note 4 under (*b*). By eqn. (8) it becomes to a first approximation :

$$-2\pi i\left\{\sqrt{\mathrm{C}} - \frac{\mathrm{B}}{\sqrt{\mathrm{A}}} - \frac{\mathrm{D}}{4\mathrm{A}^{\frac{3}{2}}}\left(\frac{3\mathrm{B}^2}{\mathrm{A}} - \mathrm{C}\right)\right\} \quad . \quad . \quad (25)$$

Consequently, if we arrange (24) in terms of B, we obtain from (24)

$$B = \sqrt{A}\left(\sqrt{C} - \frac{nhi}{\pi}\right) + \frac{D}{4A}\left(C - \frac{3B^2}{A}\right) \quad . \quad . \quad (26)$$

We regard the term in D as a correction term (external field small compared with the nuclear field) and hence replace B^2/A in it by the following approximation (to the first degree) derived from (26) :

$$\frac{B^2}{A} = \left(\sqrt{C} - \frac{nhi}{\pi}\right)^2, \quad C - \frac{3B^2}{A} = -2C + \frac{6nhi}{\pi}\sqrt{C} + 3\left(\frac{nh}{\pi}\right)^2 \quad (26a)$$

Hence we obtain from (26)

$$B = \sqrt{A}\left(\sqrt{C} - \frac{nhi}{\pi}\right) + \frac{D}{4A}\left(\frac{3n^2h^2}{\pi^2} + \frac{6nhi}{\pi}\sqrt{C} - 2C\right) . \quad (27)$$

This single equation really stands for two equations. We use it in the one case with

$$B = B_1 = \mu(Ze^2 - \beta), \quad D = D_1 = -\mu eF, \quad n = n_\xi$$

and in the other with

$$B = B_2 = \mu(Ze^2 + \beta), \quad D = D_2 = \mu eF, \quad n = n_\eta$$

whereas

$$A = 2\mu W \quad \text{and} \quad C = -(n_\psi h/2\pi)^2$$

in each case. We then form half the sum of the two equations which result in this way. This causes the separation constant β to vanish, and we obtain

$$\mu Ze^2 = \sqrt{A}\left(\sqrt{C} - \frac{(n_\xi + n_\eta)hi}{2\pi}\right) + \frac{\mu eF}{4A}\left(\frac{3}{2}\frac{(n_\xi^2 - n_\eta^2)h^2}{\pi^2} + \frac{3(n_\xi - n_\eta)hi\sqrt{C}}{\pi}\right). \quad (28)$$

We then substitute

$$\sqrt{C} = -\frac{n_\psi hi}{2\pi}$$

(the reason for the choice of sign is given in Note 4) and calculate A to a first degree of approximation, that is, for $F = 0$,

$$A = -\frac{4\pi^2(\mu Ze^2)^2}{(n_\xi + n_\eta + n_\psi)^2h^2} = -\frac{4\pi^2(\mu Ze^2)^2}{n^2h^2} . \quad . \quad (29)$$

where we have set $n = n_\xi + n_\eta + n_\psi$. We substitute this value in the correction term of eqn. (28) which involves F and now calculate A to a second approximation :

$$A = -\frac{4\pi^2(\mu Ze^2)^2}{h^2n^2} - \frac{3h^2F}{4\pi^2Ze}n(n_\eta - n_\xi) \quad . \quad . \quad (29a)$$

Dividing by $-2\mu h$ we obtain

$$-\frac{W}{h} = \frac{2\pi^2\mu Z^2e^4}{h^3n^2} + \frac{3hF}{8\pi^2\mu Ze}n(n_\eta - n_\xi) \quad . \quad . \quad (30)$$

The first term on the right-hand side is the *unperturbed Balmer term;* it emerges from our calculation in parabolic co-ordinates precisely, as it must, as in the earlier calculation with polar co-ordinates. The second term gives the *perturbation of the first order* arising from the electric field and contains, as we shall see in the next section, the whole manifold of phenomena, which Stark has observed in the case of the different Balmer lines.

We have yet to make a few remarks about the character of degeneracy of the problem and its quantum numbers. In the limit $F \to 0$, for which the right-hand side of (30) reduces to its first term, the system is *doubly degenerate.* Instead of depending on the three numbers n_ξ, n_η, n_ψ it depends only on the principal quantum number n. Here n is defined in parabolic co-ordinates as the quantum sum :

$$n = n_\xi + n_\eta + n_\psi.$$

Instead of using n_ψ we shall in future, however, use the number

$$m = n_\psi - 1, \quad m = 0, 1, 2, \ldots \quad . \quad . \quad (31)$$

as the true equatorial quantum number, in a manner analogous to the true azimuthal quantum number l in the Kepler problem (cf. p. 115). As in the case of l so here this definition is wave-mechanical in origin. In wave-mechanics the quantities m and l occur from the outset as *non-negative integers.* Our principal quantum number n is then, in the case of the Stark effect,

$$n = n_\xi + n_\eta + m + 1 \quad . \quad . \quad . \quad . \quad (32)$$

which is fully analogous to the principal quantum number

$$n = n_r + l + 1 \quad . \quad . \quad . \quad . \quad (32a)$$

in the case of the Kepler problem. From $m \geqq 0$ it follows that

$$n_\psi \geqq 1$$

which implies that $n_\psi = 0$ *is forbidden.* This decree, forbidding $n_\psi = 0$, was supposed to arise on the older theory from the necessity of avoiding a collision of the electron with the nucleus, exactly as the decree $n_\phi = 0$ in the case of the Kepler problem (see p. 115). Nowadays we prefer the wave-mechanical explanation to this pseudo-graphical reason, as already mentioned on page 115. The decree $n_\psi = 0$ will be found to be of fundamental importance in the next section.

Our present three parabolic quantum numbers n_ξ, n_η, m have the common characteristic of being able to assume all non-negative integral values *including zero.* Hence it follows for the principal

quantum number that it can assume all positive integral values except zero.

In contrast with the limiting case $F = 0$ we find that for a non-vanishing F the problem is *simply degenerate* to a first approximation. The complete expression (30) depends on the two quantum numbers or combination of quantum numbers :

$$n \text{ and } n_\eta - n_\xi.$$

All three quantum numbers including m, however, present themselves only when we pass on to the quadratic Stark effect, that is, when we retain the terms involving F^2 in the energy-expression (cf. Note 9), as it is only then that the degeneracy is *completely eliminated.*

As above remarked, while the energy in passing to the limit $F \to 0$ assumes the *same* value in calculating with parabolic and polar co-ordinates, the *orbital curves* in the two cases come out differently. They are, of course, in accordance with general mechanical laws, ellipsis with the nucleus as a focus also in the case of the parabolic co-ordinates. But they are not represented by the Fig. 27, page 117, which arose from quantising in polar co-ordinates. Quantising in parabolic co-ordinates leads to a selection from the totality of mechanically possible orbits which is different from that given by quantising in polar co-ordinates. We shall describe the difference between the two sets of ellipses in greater detail in the last section of this chapter.

Even if this difference is intelligible from the point of view of degenerate systems it remains unsatisfactory from the physical point of view. It remains equally unsatisfactory from the wave-mechanical point of view, where we no longer speak of orbits but of states and allow the mechanical orbits only to be regarded as carriers of quantum numbers. But we may bridge over the contrast between the two sets of orbits or states by means of the following considerations.

The force-free Kepler motion is a degenerate problem only if we treat it according to classical mechanics ; from the relativistic point of view the degeneracy is eliminated, at least in the problem for the plane. But our treatment of the Stark effect has been carried out here in parabolic co-ordinates on the basis of classical mechanics ; our quantising of the Stark effect thus holds only so long as classical mechanics applies. This is the case with strong * electric fields but not when the fields are arbitrarily weak. The simplest way of distinguishing whether a field is strong or weak is as follows : Let $\Delta\nu_F$ be the resolution produced in a Balmer line by an electric field F.

* The external field must *not* of course be so strong that our perturbation calculation fails. This calculation assumes that the external field is very small compared with the attraction due to the nucleus. In the case of the higher quantum numbers n (great distance from the nucleus) the internal field may become of the order of magnitude of the nuclear field. Our perturbation method then becomes invalidated and the orbit may become impossible in given cases ; cf. Fig. 84 of the next section.

On the other hand, let $\Delta\nu_H$ be the natural doublet interval of the Balmer lines which has its origin in relativistic mechanics. If $\Delta\nu_F < \Delta\nu_H$, the field is to be called weak ; if $\Delta\nu_F \gg \Delta\nu_H$, as is always the case in observations of the Stark effect, we call the field strong. In the latter case the quantising described in the present section is correct, in the former it fails.

The difficult question—interesting from the point of view of method —as to how the quantising is to be performed in the case of very weak fields has been answered by H. A. Kramers.* But since, after what we have said, it is of no account † for interpreting the Stark effect in hydrogen we shall not discuss it here. But we wish to emphasise that this form of motion investigated by Kramers interposes itself between the parabolic quantising for intense fields and the relativistic quantising for vanishingly small fields. Hence it is really not permissible to effect the passage to the limit $F \to 0$ from the side of the parabolic quantising as we did above. In forbidding this we at the same time dispose of the lack of continuity in the orbits and states in passing from parabolic to polar co-ordinates, which was a necessary consequence of the conditions of degeneracy.

§ 3. The Resolution of the Balmer Lines in the Stark Effect

If ΔW_1 and ΔW_2 denote the changes of energy produced by the electric field in the initial and the final states, the change of frequency or the *resolution* is calculated from the formula

$$h\Delta\nu = \Delta W_1 - \Delta W_2.$$

The second term on the right-hand side of eqn. (30) in the preceding section therefore gives

$$\Delta\nu = \frac{3hF}{8\pi^2\mu Ze}\{n_2(n_\eta + n_\xi)_2 - n_1(n_\eta - n_\xi)_1\} \quad . \quad . \quad (1)$$

The indices 1 and 2 here used refer to the initial and the final states. For hydrogen, of course, $Z = 1$. Eqn. (1) must be supplemented by a *selection principle* and a *polarisation rule*, as developed in § 1, pages 298 to 300.

The selection and the polarisation rules are clearly independent of the absolute normalisation of the equatorial quantum number. It is therefore immaterial whether we express them in terms of the earlier n_ψ or in $m = n_\psi - 1$. We agree to prefer the latter.

* Zeits. f. Phys., **3**, 199 (1920).

† But Kramers' investigation is essential for the Stark effect of non-hydrogen atoms. This effect is quadratic in F, just as for hydrogen when the fields are very weak. The linear Stark effect which predominates in the case of strong fields in hydrogen, is a consequence of the degeneracy of the hydrogen atoms (cf. the end of the present section). In the case of non-hydrogen atoms the degeneracy is cancelled by the internal atomic field and hence no linear Stark effect is possible.

In the first place we read off from (1) the experimental results tabulated under 7 and 8 on page 302: all the line-resolutions $\Delta\nu$ in the Balmer series are *whole multiples* of a *minimum line-interval*,

$$a = \frac{3hF}{8\pi^2\mu e} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

As the field-strength increases so does a, and hence the whole resolution picture of each Balmer line increases *proportionally to* F.

Equally directly we read off from (1) the empirical result 6 on page 302: in every Balmer line the resolution is symmetrical on both sides of the original line. For if the transition

$$(n_\xi n_\eta m)_1 \rightarrow (n_\xi n_\eta m)_2 \quad . \quad . \quad . \quad . \quad (3)$$

is possible according to the selection principle, so also is the transition

$$(n_\xi n_\eta m)_2 \rightarrow (n_\xi n_\eta m)_1 \quad . \quad . \quad . \quad . \quad (3a)$$

If the former leads to a component at the distance $+\Delta\nu$ from the original line, then by (1) the latter leads to a component at a distance $-\Delta\nu$. Also the *polarisation* is the same for both components, since (cf. pp. 299, 300) it depends only on m and since m is left unchanged in the two transitions that are being compared. The fact that also the intensities of the two transitions are equal cannot be proved here, as we have no final intensity rule available, but in view of experimental results and the more rigorous wave-mechanical theory we may here assert it.

Concerning the polarisation our polarisation rule states the following: if

$$\Delta m = m_1 - m_2 = \pm 1 \quad . \quad . \quad . \quad (4)$$

then a wave is emitted (see p. 300) which is circularly polarised about the direction of the lines of force. Such a wave appears in the transverse effect in all circumstances as polarised *perpendicularly to the lines of force* (in the sense more closely defined on p. 301). In the longitudinal effect it would be observed as a circular wave if only one process of emission were observed. In reality, however, every observation represents an average of many elementary processes. Of their total number the transitions $\Delta m = -1$ occur just as often as the transitions $\Delta m = +1$. If the former lead to right-handed circular polarisation, the latter lead just as often to left-handed polarisation. The superposition of these two therefore brings it about that *no polarisation* is observed in the direction of the lines of forces.

If, however,

$$\Delta m = 0 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

the polarisation is linear in the direction of the lines of force (cf. p. 300) Consequently in the transverse effect *linear polarisation parallel to*

the lines of force is observed. In the longitudinal effect the same components of the resolution are *invisible* according to the general rules of kinematics which do not allow emission to occur in the direction of the vibration. These deductions agree literally with the experimental results detailed under 3 and 4 on pages 301, 302.

We next consider successively the resolutions of H_α, H_β, H_γ, H_δ and introduce the abbreviation

$$\Delta = \frac{\Delta\nu}{a} = n_2(n_\eta - n_\xi)_2 - n_1(n_\eta - n_\xi)_1 \quad . \quad . \quad (6)$$

By (2) and (3) Δ denotes the displacement, measured in terms of the unit a, of the component in question as compared with the original line. We tabulate all the possible transitions and enumerate them according to the magnitude of the equatorial quantum number m, by making m pass through all its values from the maximum in each case to its smallest value, zero.

In the case of H_α we have $n_1 = 3$, $n_2 = 2$, and hence

$$\Delta = 2(n_\eta - n_\xi)_2 - 3(n_\eta - n_\xi)_1 \quad . \quad . \quad . \quad (7)$$

By eqn. (32) in the preceding section we have simultaneously that

$$m_1 \leqq 2, \; m_2 \leqq 1.$$

in that the sum of the three non-negative numbers n_ξ, n_η and m becomes equal to 2 or 1, respectively. For the *parallel components* $\Delta m = 0$ we find that $m_1 = 0$ drops out, since m_2 can at most equal 1. We therefore begin our enumeration with $m_1 = 1$. Whereas the corresponding final orbit is fully determined, being (001), there are two initial orbits belonging to $m_1 = 1$, namely (101) and (011). The two transitions that are accordingly possible are

$$101 \rightarrow 001 \quad \text{and} \quad 011 \rightarrow 001$$

and differ only, like the transitions (3) and (3*a*), in having the first two quantum numbers interchanged ; they thus give rise to symmetrically placed components. In our table we record only the first of the two transitions, that leading to a positive Δ, and imagine the symmetrical components produced by interchanging the first two quantum numbers to be added. We then consider $m_1 = 0$. Here there are three transitions that lead to a positive Δ ; they are given in the first column of Table 24. The last column is calculated by eqn. (7) as the difference of the two preceding columns. As a whole the electrically resolved line H_α consists, on both sides, of four π-components at intervals Δ to be taken from Table 24.

Passing on to the *perpendicular* components we begin with $m_1 = 2$, $m_2 = 1$, corresponding to the first transition $002 \rightarrow 001$ given in Table 25. Starting from $m_1 = 1$, $m_1 = 0$ there are two transitions that are clearly shown in the table. The component $\Delta = 0$ arises in two

TABLE 24

H_α, π-components, $m_1 = m_2$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$3(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
101 → 001	− 3	0	3
110 → 010	0	+ 2	2
200 → 100	− 6	− 2	4
200 → 010	− 6	+ 2	8

TABLE 25

H_α, σ-components, $m_1 = m_2 \pm 1$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$3(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
002 → 001	0	0	0
101 → 100	− 3	− 2	1
101 → 010	− 3	+ 2	5
200 → 001	− 6	0	6
110 → 001	0	0	0

ways ; besides it there are three transitions having a positive Δ and, of course, just as many having a negative Δ.

For comparison we examine the result of observations by Stark. Fig. 83 is a slightly modified reproduction of Stark's original figure redrawn from the scale of $\Delta\lambda$'s in the scale of $\Delta\nu$'s. The lengths of the vertical strokes denote the intensities of the resolved components as estimated by Stark. The attached numbers represent the resolution (in wave-numbers), expressed as multiples of the fundamental unit a, that is, our Δ.

We see that *as far as* $\Delta = 4$ *the theoretical expectation agrees fully with the observations made for* H_α. For example the positions 0 and 1 are free of π-components and occupied by σ-components, whereas the reverse is the case at the positions 2, 3, 4, both according to theory and experiment. Theory indicates a few other components of greater resolution, 8 as π-components, 5 and 6 as σ-components, which are not indicated by experiment. This is due to the small intensity of these lines. For Schrödinger * has shown by a wave-mechanical calculation that the π-component in question must be a thousand times weaker and the σ-components in question a hundred times weaker than the average of the observed components. Hence their absence in Stark's photographs is quite in order.

* Ann. d. Phys., **80**, 437 (1926), or in his Collected Papers (Blackie).

In the same way the resolutions of H_β, H_γ, H_δ give a convincing impression of the accuracy of the theory.

The following tables do not require much elucidation. In the

TABLE 26.

H_β, *π-components*, $m_1 = m_2$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$4(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
201 → 001	− 8	0	8
111 → 001	0	0	0
300 → 010	− 12	+ 2	14
300 → 100	− 12	− 2	10
210 → 010	− 4	+ 2	6
210 → 100	− 4	− 2	2

TABLE 27

H_β, *σ-components*, $m_1 = m_2 \pm 1$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$4(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
102 → 001	− 4	0	4
201 → 010	− 8	+ 2	10
201 → 100	− 8	− 2	6
111 → 010	0	+ 2	2
210 → 001	− 4	0	4
300 → 001	− 12	0	12

case of the π-components of H_β we have to begin our enumeration with $m_1 = 1$ again on account of $m_1 = m_2$ and $m_2 \leqq 1$. There are two transitions from $m_1 = 1$ and four transitions from $m_1 = 0$ which, according to the selection principle, lead to π-components on the positive side ($\Delta > 0$). The symmetrical components on the negative side also arise here by interchanging the first two quantum numbers in the transition scheme of the initial and the final orbits and these are to be supposed added. There is an exactly equal number, namely six, of transitions that lead to positive (or negative) σ-components.

The agreement with the experimental picture of the resolution in Fig. 83 is again very striking. All the theoretical components have been observed. In addition there are shown in Fig. 83 a very weak $\Delta = 4$ among the π-components and a doubtful $\Delta = 12$; among the σ-components a weak $\Delta = 0$ and a doubtful $\Delta = 8$. The σ-component $\Delta = 4$, which is strongest according to observation arises, according to Table 27, in two ways, which partly accounts for its

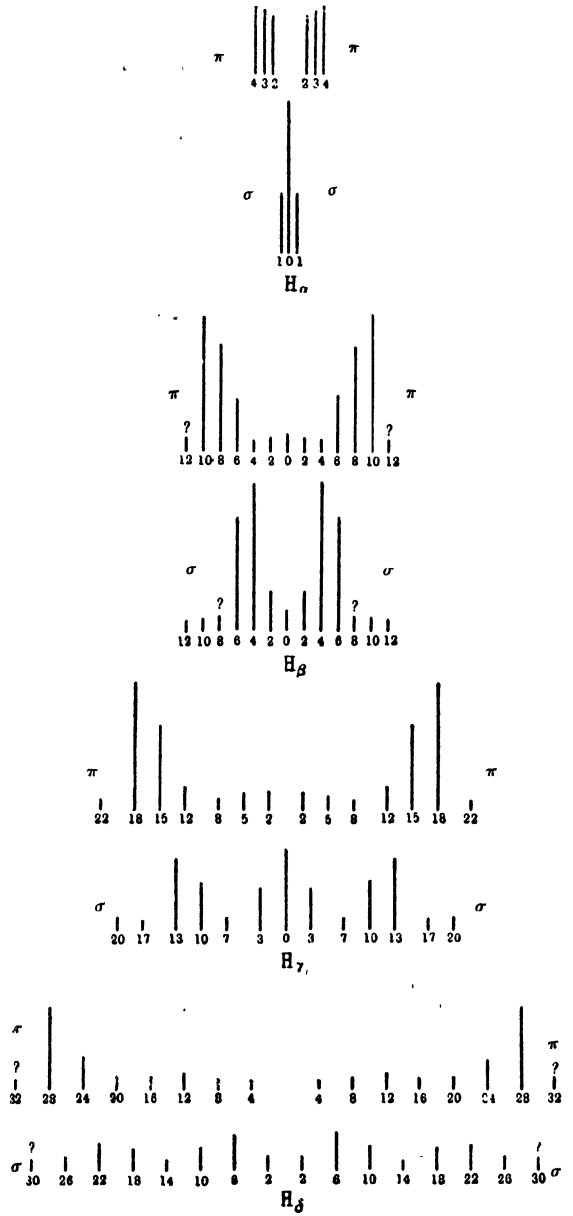


FIG. 83.—Resolution of the Balmer lines in an electric field according to observations by J. Stark. A scale of wave numbers (cm.$^{-1}$) is used, and the π- and σ-components are shown separately. The length of the lines represents the visually estimated intensity. Doubtful components have a question mark placed against them. The numbers give directly the value of Δ (cf. equations (6) and (2)).

predominating intensity. For a more detailed discussion of the intensity questions we must in this case, too, refer to Schrödinger's paper.

In the case of H_γ there is exceptionally perfect agreement between theory and observation. The theoretical tabulation gives the following :

TABLE 28

H_γ, *π-components*, $m_1 = m_2$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$5(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
301 → 001	− 15	0	15
211 → 001	− 5	0	5
400 → 010	− 20	+ 2	22
400 → 100	− 20	− 2	18
310 → 010	− 10	+ 2	12
310 → 100	− 10	− 2	8
220 → 010	0	+ 2	2

TABLE 29

H_γ, *σ-components*, $m_1 = m_2 \pm 1$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$5(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
202 → 001	− 10	0	10
112 → 001	0	0	0
301 → 010	− 15	+ 2	17
301 → 100	− 15	− 2	13
211 → 010	− 5	+ 2	7
211 → 100	− 5	− 2	3
400 → 001	− 20	0	20
310 → 001	− 10	0	10
220 → 001	0	0	0

The photograph of the observed results is, according to Fig. 83, completely identical with these theoretical results. The same applies to H_δ

TABLE 30

H_δ, *π-components*, $m_1 = m_2$

$(n_\xi n_\eta m)_1 \to (n_\xi n_\eta m)_2$	$6(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
401 → 001	− 24	0	24
311 → 001	− 12	0	12
221 → 001	0	0	0
500 → 010	− 30	+ 2	32
500 → 100	− 30	− 2	28
410 → 010	− 18	+ 2	20
410 → 100	− 18	− 2	16
320 → 010	− 6	+ 2	8
320 → 100	− 6	− 2	4

TABLE 31

H_δ, *σ-components*, $m_1 - m_2 \pm 1$

$(n_\xi n_\eta m)_1 \to n_\xi n_\eta m)_2$	$6(n_\eta - n_\xi)_1$	$2(n_\eta - n_\xi)_2$	Δ
302 → 001	− 18	0	18
212 → 001	− 6	0	6
401 → 010	− 24	+ 2	26
401 → 100	− 24	− 2	22
311 → 010	− 12	+ 2	14
311 → 100	− 12	− 2	10
221 → 010	0	+ 2	2
500 → 001	− 30	0	30
410 → 001	− 18	0	18
320 → 001	− 6	0	6

The inner regularity of the resolution pictures is illuminated by the following remarks.

In the case of H_β and H_δ *only even multiples of the interval* Δ *occur*, both in theory and experiment (the theoretical reason is that the common divisor 2 of the principal quantum number n in the first and second terms of the series expression for H_β and H_δ also occurs as a factor in the quantity Δ).

In the case of H_β *the components are partially polarised; in* H_γ and H_δ *they are completely polarised*, both in theory and in experiment again: This is expressed in the theory by the fact that in the scheme of H_β the Δ-values of the π- and the σ-series partly coincide, whereas in H_γ and H_δ they do not.

The sequence of components in the series of lines H_α, H_β, H_γ, H_δ *become less and less dense.* The interval between neighbouring components amounts to 1 for H_α, 2 for H_β, alternately 3 or 4 for H_γ, 4 fundamental units without exception for H_δ.

For more exact experimental data about intensity we refer to a paper by Mark and Wierl *; they have become of particular interest since it has become possible to compare them with the results of wave-mechanical calculations.

It now appears almost self-evident that besides the interval relationships of the components also *the absolute values of the intervals* should be correctly given by the theory. The absolute magnitude of the resolution is given by the constant a in eqn. (2) and depends on the field F. This cannot be determined very accurately by experiment (hardly to within 1 per cent.). Hence we may calculate the field intensity as Epstein and, more recently, Rausch von Traubenberg have done, from a measured resolution, that is, use the resolution in the Stark effect as a means for accurately measuring an electric field,

* Zeits. f. Phys., **53**, 526 (1928); **55**, 156 (1929).

precisely as has occasionally been done with the resolution in the Zeeman effect for measuring a magnetic field. The field-strength measured in this way deviates only slightly from the experimental measurement.

Whereas in Stark's case the field-strength amounted to about 100,000 volt/cm., Rausch von Traubenberg succeeded in producing field-strengths of over a million volt/cm. In the latter case terms in F^2 and F^3, which we neglected in our formula (30) on page 310, become appreciable. The quadratic Stark effect (proportional to F^2) is particularly constructive because in it the wave-mechanical calculation gives a somewhat different result from that of the older theory (cf. Note 9), whereas in the linear Stark effect which has alone been treated hitherto there is full agreement between both theories. The measurements made by Rausch von Traubenberg and Gebauer * completely

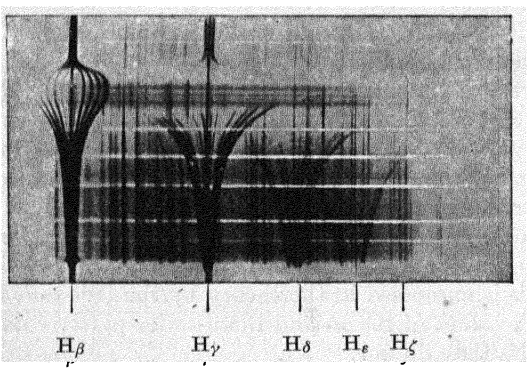


FIG. 84.†—Lo Surdo photograph of the Balmer lines taken by H. Rausch v. Traubenberg, R. Gebauer and G. Lewin. The electric field increases from below upwards (from about 100,000 to 1·14 million volts/cm.) and at the very top suddenly become zero again. The lines H_γ to H_ζ cease to exist at certain points in the ever-diminishing field in the order H_γ to H_ζ. The violet Stark components are more persistent than the red.

confirm the wave-mechanical formula for the quadratic Stark effect and hence restrict the validity of the account here given to the *linear* Stark effect. The measurements just mentioned have been obtained essentially by the quantitative arrangement devised and used by Stark. In Fig. 84 we exhibit a more qualitative photograph obtained by the same author with Lo Surdo's arrangement, partly in order to give one illustration of results obtained by this arrangement for non-hydrogen atoms, for which it is particularly important and partly to show the various " existence limits " of the Stark components, which occur in the figure. The field increases in the figure from below upwards and then again becomes zero at the upper edge. The horizontal

* Zeits. f. Phys., **54**, 307 (1929); **62**, 289 (1930).

† Taken from the *Naturwissenschaften*, **18**, 329 (1930), by kind permission of the publisher, Julius Springer, Berlin.

bright lines correspond to stretched wires that served as marks in measuring the field. The increase of resolution with the field shows the effects of higher order together with the linear effect. The figure acquires a particular significance, however, in that it exhibits the fading out of the different lines for different field-strengths. The line H_ϵ ceases to exist at lower intensities of field than the line H_δ, the latter sooner than H_γ, whereas in the case of H_β the existence limit has not been reached even at a million volt/cm. Moreover, it is shown throughout that the long-wave components fade out sooner than the short-wave components. Both these phenomena were first explained by wave-mechanical methods by Lanczos * but may also be understood directly on the basis of orbital ideas, as we shall see in the last section of the present chapter.

§ 4. The Normal Zeeman Effect

In 1896 Zeeman discovered that the lines of the series spectra may be influenced by magnetic means. In the simplest case there appear instead of one line, when viewed *longitudinally*, that is when the ray is in the direction of the magnetic lines of force, two lines (**Zeeman doublet; longitudinal effect**), but when viewed *transversely*, that is when the ray is perpendicular to the magnetic lines of force, instead of one line, three lines are observed (**Zeeman triplet; transverse effect**). Of the latter three lines one occupies the position of the original unresolved line, and the other two are displaced by equal amounts to greater or smaller wave-lengths, and occupy the same position in the spectrum as the two lines of the doublet in the longitudinal effect (cf. Figs. 85, *a* and *b*). The displacement amounts to

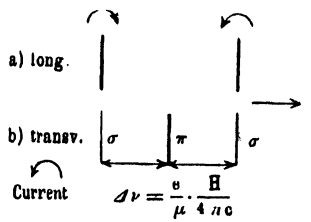


FIG. 85.—Normal Zeeman effect. *a* represents the longitudinal effect (observation parallel to the lines of force), *b* the transverse effect (observation at right angles to the lines of force).

$$\Delta\nu = \frac{e}{\mu}\frac{H}{4\pi c} = 4{\cdot}67 \,.\, 10^{-5} \,.\, H \quad . \quad . \quad . \quad (1)$$

where H = the intensity of the magnetic field in absolute units (Gauss). If we wish to measure ν in sec.$^{-1}$, we have to take e on the right side of the equation as the *electrostatic* charge of the electron; but if we measure ν in cm.$^{-1}$ as a "wave-number," then e is the charge on the electron measured in electromagnetic units, and $e/\mu = 1{\cdot}761 \,.\, 10^7$ is the specific charge on the electron measured in the same way. The numerical value $4{\cdot}67 \,.\, 10^{-5}$ in eqn. (1) refers to the latter method of

* Naturwiss., **18**, 329 (1930); Zeits. f. Phys., **62**, 518 (1930).

measuring ν, and thus gives the displacement $\Delta\nu$ in the scale of wave-numbers.

In the first observations of Zeeman the lines were not completely separated, because the resolution was too feeble and the lines were too wide. But he succeeded in establishing beyond doubt the presence of polarised light at the extreme edges of the line configuration. The type of the polarisation is indicated in our figure. The symbols π and σ (parallel and perpendicular—German *senkrecht*—to the lines of force) mean the same as on page 301. They refer not to the position of the optical plane of polarisation but to the direction of the electrical vibrations in the ray at the place of observation. In the longitudinal scheme the *circular arrows* denote that *circular polarisation* was observed, and, as is shown, the sense in the two lines of the doublet is opposite. In general, in the short-wave component the sense of the circular polarisation is the same as that of the positive current in the coils of the electromagnet, which produces the magnetic field.

We first wish to emphasise that our two figures *a* and *b* express the same facts under different circumstances of observation. The π-component of the transverse effect must be ineffective in the longitudinal effect and that is why in Fig. 85*a* no line occurs at the position of the transverse π-component. Actually, this π-component arises from a vibration phenomenon for which the direction of the lines of force is a line of symmetry of the intensity or (expressed in the language of the older theory), it is due to the vibration of an electron, which moves in the direction of the lines of force). But such a vibration, as we know and have already used in the Stark effect on page 314, emits no light. On the other hand, the circular components that occur in the longitudinal effect are due to a vibration phenomenon, in which the plane of vibration is perpendicular to the lines of force (in words of the old theory), due to the vibration of an electron, which describes a circle in this plane. Such a vibration phenomenon, however, sends out in the transverse direction linearly polarised light, whose electric force vibrates in the plane of vibration perpendicular to the magnetic lines of force, likewise analogous to the circumstances in the Stark effect, cf. page 313. Hence the σ-components of the transversal scheme correspond to the circular components of the longitudinal scheme. Accordingly, it is sufficient to study the Zeeman effect in only one direction, for example, in the transverse direction which is more convenient for purposes of observation : transverse observation is also preferable because it allows all components to manifest themselves and this may be of decisive importance for the analysis of a spectrum, particularly in studying the anomalous Zeeman effect (see below).

The facts so far described are fully explained by *Lorentz's Theory of the Zeeman Effect.* This is based on the assumption of quasi-elastically bound electrons, which excite vibrations in the ether that

*effect.** This rule was discovered experimentally by Preston long before there was a theory of the anomalous Zeeman effect.

In conformity with Note 7 (*f*) we take over the *selection and polarisation rules*, which were there obtained, for our magnetic quantum number m. We may have $\Delta m = 0$ or ± 1; $\Delta m = 0$ gives π-components, $\Delta m = \pm 1$ gives σ-components.

We can now easily state the Zeeman effect for any arbitrary combination of terms. For the initial level we have: energy W_1 is equal to the sum of the energy W_1^0 when no field is present plus the additional magnetic energy ΔW_1 which we must obtain from eqn. (10). The same applies to the second term. The observed line-frequencies follow from these values if we form the differences:

$$h\nu = W_1^0 - W_2^0 + \Delta W_1 - \Delta W_2 = h\nu_0 + h\Delta\nu$$

where ν_0 denotes the frequency when no field is present. If we make our measurements from this frequency we obtain in

$$\Delta W_1 - \Delta W_2 = h(\nu - \nu_0) = h\Delta\nu = m_1 g_1 - m_2 g_2 \quad . \quad (11)$$

all the frequencies of the resolution pattern.

Let us consider, say, the combinations $l = 0,\ j = \frac{1}{2} \to l = 1,\ j = \frac{3}{2}$ and $l = 0,\ j = \frac{1}{2} \to l = 1,\ j = \frac{1}{2}$. We find it expedient to

TABLE 33

	m	$-\frac{3}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{3}{2}$
$l = 0, j = \frac{1}{2}$	mg		-1	1	
$l = 1, j = \frac{3}{2}$	mg	$-\frac{6}{3}$	$-\frac{2}{3}$	$\frac{2}{3}$	$\frac{6}{3}$
		$\frac{-5, -3, (-1), (1), 3, 5}{3}$			

TABLE 34

	m	$-\frac{1}{2}$	$\frac{1}{2}$
$l = 0, j = \frac{1}{2}$	mg	-1	1
$l = 1, j = \frac{1}{2}$	mg	$-\frac{1}{3}$	$\frac{1}{3}$
		$\frac{-4, (-2), (2), 4}{3}$	

* In Chapter VIII we shall make this rule more restrictive by formulating it more rigorously.

write down in tabular form first the possible m-values and underneath them the values of mg for the first term $l = 0$, $j = \frac{1}{2}$ and then those for the second term $l = 1$, $j = \frac{3}{2}$ or $\frac{1}{2}$. We put the mg-values over a common denominator and bracket the transitions $\Delta m = 0$ (π-components) in order to distinguish them from the combinations $\Delta m = \pm 1$ (σ-components).

In Figs. 87 and 88 the two Zeeman-types are shown as observed transversely. They are particularly interesting because they represent resolution-patterns of the two D-lines; Fig. 87 corresponds to the line D_2, Fig. 88 to the line D_1. These " D line types " have been known and measured since the very beginning of the researches into the Zeeman effect.

It is readily seen that the Zeeman effect in general contains the more components the greater the number of inner quantum numbers

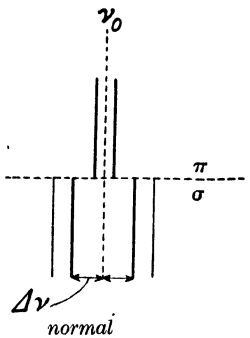


FIG. 87.—Anomalous Zeeman effect of the combination $l = 0, j = \frac{1}{2} \to l = 1, j = \frac{3}{2}$ (doublet-system of the D_2-line type). ν_0 = position of the line without a field, π- and σ-components are shown separately.

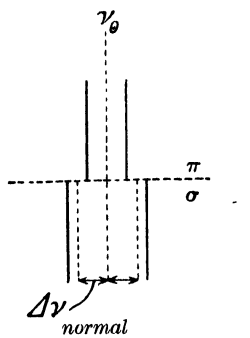


FIG. 88.—Anomalous Zeeman effect of the combination $l = 0, j = \frac{1}{2} \to l = 1, j = \frac{1}{2}$ (doublet-system of the D_1-line type). Otherwise as in Fig. 87.

that combine, because as j increases the number of magnetic term-levels increases in accordance with the factor $2j + 1$ (see above). The fine-structures of the hydrogen lines H_α, H_β, for example, should show a quite complicated Zeeman-type. Before discussing it we must limit more accurately the range of validity of eqns. (10) and (9). We had assumed that the precession of M about j occurs so rapidly that the component $M_\perp$ perpendicular to j cancels out when averaged over the time. This signifies that the precession of M about j (or of l about j) must occur much more rapidly than that of j about the direction of the field, as otherwise $M_\perp$ would not vanish when the time-mean is taken.

Now it is shown in Note 7 (a) that corresponding to the *classical frequency of precession about* j we have that *quantum transition of energy*, in which j alone changes while all the other quantum numbers

remain unchanged, that is a change of energy of the magnitude of the term resolutions when no field is acting (cf. for example, Fig. 75, p. 270). On the other hand, corresponding with the precessional frequency of j about H we have the quantum transition in which only m_j namely, the projection of j on H changes—that is, an energy-change of the order of magnitude of the Zeeman-resolutions. By the Correspondence Principle we may assume that the energy-changes are small if the precession is slow, and vice versa. *Hence our assumption about the velocities of precession denotes that in the case of a term with a definite* l *the field-free resolution which is given by* j *should be much greater than the resolution of those individual* j*-levels caused by the magnetic field.*

But what happens if the magnetic field is much more intense ? (In the ordinary investigations of the Zeeman effect it is of the order of $3 \cdot 10^4$ to $4 \cdot 10^4$ gauss.) If the magnetic field is *gradually made more intense* the outer precession will gradually attain the order of magnitude of the inner precession. This denotes mechanically that we are no longer able to calculate as above, as if j remains fixed for a first approximation and as if the (uniform) inner precession of l and s took place about this axis. Rather, the external field will appreciably disturb the internal field and will loosen the (magnetic) coupling between l and s, thus converting the previously uniform precession about j into an irregular precession. In the Fourier expression for the motion the harmonics of the precessional frequencies then present themselves ; this signifies, according to the Correspondence Principle, that in addition to the transitions $\Delta j = 0, \pm 1$, also those of greater amount occur, namely $\Delta j = \pm 2$. Theoretically and experimentally * this transgression of the selection rule is an effect which occurs in passing from weak to strong fields. We can deal with it more fully only when we come to Chapter VIII.

If, finally, *the external field becomes so strong that it predominates considerably over the internal field*, that is, if the term-resolutions produced by the external field have become much greater than the " natural " field-free resolutions, we may disregard the mutual action of the two magnetic moments entirely. For l and s individually we have directional quantising relative to the magnetic field H ; l and s perform their precession about the H-direction independently of each other. Strictly speaking, there is no sense in this case in talking of the total moment of momentum j of the atom, for this can be defined only so long as we may regard the atom as almost closed and the external field as only a small perturbation.

We call the projections of l and s in the direction of H m_l and m_s ; according to the rules of directional quantising (Chap. II, § 8 ; cf. also the note on p. 333), we obtain analogously to eqn. (7),

$$m_l = l, l-1, \ldots -(l-1), -l \quad . \quad . \quad (12a)$$

* F. Paschen and E. Back, Physica, **1**, 261 (1921).

and $$m_s = s, \ldots - s.$$

The last equation reduces in our case, on account of $s = \frac{1}{2}$, to

$$m_s = \tfrac{1}{2}, -\tfrac{1}{2} \quad . \quad . \quad . \quad . \quad (12b)$$

These are the only values permissible for m_s.

The additional magnetic energy ΔW is composed of the contributions of the two magnetic moments. By eqns. (6) and (2) we obtain for the contribution of l

$$\Delta W_l = m_l M_B H,$$

and for the contribution of s, by eqns. (6) and (3),

$$\Delta W_s = 2m_s M_B H.$$

In all we obtain

$$\Delta W = (m_l + 2m_s) M_B H \quad . \quad . \quad . \quad (13)$$

or if we use as our unit the resolution of the normal Zeeman effect (see eqns. (8*a*) and (10)),

$$\Delta W = m_l + 2m_s \quad . \quad . \quad . \quad . \quad (13a)$$

The *selection and polarisation rules* here run somewhat differently from those in the case of the weak field. The magnetic moment of s now no longer has an appreciable effect on the orbital revolution l. Consequently the spin-frequencies in the Fourier expansion of the orbital motion now no longer occur. This signifies that the corresponding quantum transition in m_s is zero : $\Delta m_s = 0$. On the other hand, the precession of l about H gives us the selection principle $\Delta m_l = \pm 1$ and circular polarisation about H (σ-components) for the Fourier expression of the components of the electric moment perpendicular to H. In the same way the expression for the components parallel to H give the selection principle $\Delta m_l = 0$ and linear polarisation parallel to H (π-components). (Compare the analogous remarks about m and j in Note 7 and in § 1 of the present chapter.)

According to formula (13*a*) a term with a given n, l resolves in *a strong magnetic field in such a way that the level intervals become integral multiples of the intervals in the normal Zeeman effect.* Actually m_l and $2m_s$ are integers ($m_s = \pm \frac{1}{2}$, see above). For the Zeeman effect of a combination of two terms (n, l) we obtain from (13*a*), precisely as in eqn. (11),

$$\Delta W_1 - \Delta W_2 = h(\nu - \nu_0) = (m_l + 2m_s)_1 - (m_l + 2m_s)_2. \quad (14)$$

From (14) we conclude that the selection rules that here hold for m_l and m_s are

$$\Delta W_1 - \Delta W_2 = h(\nu - \nu_0) = 0, \pm 1 \quad . \quad . \quad (15)$$

This means that *all combinations of terms (n, l) exhibit the normal Lorentz triplet in transverse observation if the field is sufficiently intense,* that is,

a π-component appears in the position of the field-free line and two σ-components at the "normal" distance on both sides.

What does "field-free" line stand for here? Clearly, our result (13*a*) was derived as if we were dealing with an atomic model in which there was no mutual action between l and s and on which a magnetic field H acts. In that case we should need to take into consideration the mutual action between l and s only in a higher degree of approximation. The order of magnitude of the perturbations is here just the reverse of that in the case of weak fields, where the inter-action (ls) had to be set down as the most important contribution and then the action of the magnetic field became added as giving a higher degree of approximation. In a corresponding manner earlier the field-free term-level was simply the term n, l, j without a field. But here s has no influence in the approximation of zero order on the orbital motion (on account of the absence of the interaction (ls)); in the approximation we have a model without a spin, from which we should have to calculate the field-free level (n, l). In Chapter VIII we shall find on the basis of a "semi-classical" formula for the Zeeman-resolutions, which is confirmed by wave-mechanics, that the π-component of our Lorentz triplet coincides with the "centre of gravity" of the field-free doublet-resolution. This centre of gravity divides the original doublet-resolution of the term (n, l) in the ratio $l : l + 1$ and lies nearer to the level which has the greater j.

If, as above suggested, we proceed one step further in the calculation of the perturbation, we find that ΔW in (13*a*) becomes supplemented on account of the interaction between l and s by an amount of the order of magnitude of this interaction, that is, of the magnitude of the doublet-resolution of the (n, l)-term. The individual lines of our normal Zeeman effect (15) become subdivided through this into several components that are distant from one another by the amount of the doublet-intervals. According to our assumptions (doublet structure $\ll$ magnetic resolution) the latter intervals are small compared with the intervals between the three lines of the normal Zeeman effect (15). For the combination $l = 0 \rightarrow l = 1$ the pattern has the following appearance (see Fig. 89).

We shall be able to give the quantitative basis for Fig. 89 only when we arrive at Chapter VIII.

It is clear then that the magnetic field produces a transformation of the resolution-pattern which is in general very complicated. So long as the doublet-resolutions are great compared with the resolutions due to the magnetic field we have the *anomalous Zeeman effect*, which is described by eqns. (9) and (10). The magnetic transformation which appears in strong fields is called the *Paschen-Back Effect* after its discoverers.* The final state, which is given by eqn. (13*a*), is

* F. Paschen and E. Back, Ann. d. Phys., **39**, 897 (1912); **40**, 960 (1913).

reached when the magnetic resolutions have become great compared with the doublet-resolutions. *There is sense in talking of weak or strong magnetic fields only in relation to the original term-resolutions.* If these are themselves small, as in the case of hydrogen, the Paschen-Back effect appears even at comparatively low field-strengths.

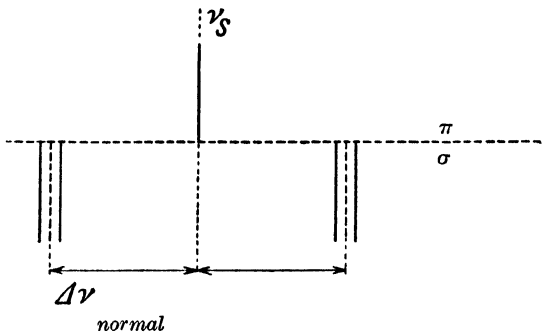


FIG. 89.—Paschen-Back effect of the combination $l = 0 \rightarrow l = 1$. The two Zeeman effects of Figs. 87 and 88 are combined together in this figure. ν_s = position of the C. of G. of the two " field-free " lines ν_0 of Figs. 87 and 88. Fine-structure resolution of the σ-components of the Lorentz triplet in the lines taken two at a time, whose mutual interval is equal to 2/3 of the original field-free j-resolution of the P-terms ($l = 1$) (*cf.* Chap. VIII).

Let us calculate in particular the intensity of field for which in the case of hydrogen the magnetic resolutions are of the same order as its fine-structure. We obtain

$$h\Delta\nu_{\mathrm{H}}c \cong \mathrm{M_B H}.$$

The factor c is necessary because we reckon $\Delta\nu_{\mathrm{H}}$ in cm.$^{-1}$ and not in sec.$^{-1}$. Using the value (p. 321)

$$\Delta\nu_{normal} = \frac{\mathrm{M_B H}}{hc} = 4{\cdot}67 \,.\, 10^{-5}\ \mathrm{H\ (cm.^{-1})}$$

and (p. 262) $\Delta\nu_{\mathrm{H}} = 0{\cdot}36$ (cm.$^{-1}$) :

$$\mathrm{H} \cong 7700 \text{ gauss}.$$

In the case of hydrogen the question of the magnetic transformation appears to be still more complicated than in that of the model hitherto considered. For in the fine-structure the distances between the levels having a fixed n and different l's are of the same order of magnitude as those between levels having a fixed n, l and different j (cf. Fig. 75, p. 270). Hitherto we have spoken only of this last sub-division of the (n, l)-terms into j-levels as being small compared with the magnetic resolutions and we have tacitly assumed that the l-terms are still far removed from one another, as is actually so in the case of the alkalies. It is easy to see, however, that a strong magnetic field also in the case of hydrogen produces essentially the same effect theoretically as that described in Fig. 89, namely, a normal Zeeman triplet

whose components appear sub-divided into individual lines, whose distances from one another are again of the order of magnitude of the fine-structure. This is confirmed by the measurements so far as they can be carried out in face of the difficulties involved.

§ 6. The Adiabatic Hypothesis

At the first Solvay Congress,* in the year 1911, H. A. Lorentz proposed the question as to how a simple pendulum behaves when its length is shortened by holding the thread between two fingers and drawing it up between them. If it has initially exactly the correct energy that corresponds as an energy element to its frequency, then at the end of the process when the frequency has become increased this energy would no longer suffice to make up a full energy element.

Einstein at once furnished the correct reply in saying that the suspending thread must be shortened *infinitely slowly* and then the energy would increase proportionally to the frequency and would continue to be equal to an energy element.

This answer is covered by Ehrenfest's **Adiabatic Hypothesis.**† We formulate it as follows: Let us consider any arbitrary mechanical system and an arbitrary initial state of motion which is correctly quantised. We now alter the state infinitely slowly by gradually imposing an arbitrary external field of force or by gradually altering the inner constitution of the system (length, mass, charge, connections). This causes the original state of motion to be transformed by mechanical means to a new state of motion. **For the new conditions of the system this new state of motion is a quantum-favoured state if the original state was so under the original conditions; it corresponds to the same quantum numbers $n_1, n_2, \ldots$ as the latter.**

The expression "*Adiabatic Hypothesis*" is taken from thermodynamics. Just as in an adiabatic change of state in thermodynamics the co-ordinates that determine the heat motion are not directly affected, but only indirectly while no heat is added from without and the conditions of the system are altered (for example, the volume, the position in the gravitational field, and so forth), so in the applications of the adiabatic hypothesis to the quantum theory the motion of the system is not controlled directly by external agency; for such agency acts, not on the co-ordinates of the motion, but on a parameter of the system. Just as in thermodynamics an adiabatic change of state is to be regarded as a chain of states of thermal equilibrium,

* Rapports du Congrès, Paris, 1912, p. 450.

† First set up by P. Ehrenfest in connexion with the problems of "cavity radiation" in Ann. d. Phys., **36,** 91 (1911), §§ 2 and 5, and then applied by him to other problems; see Verh. d. Deutsch. Physikal. Ges., **15,** 451 (1913); Amsterd. Academy, **22,** 586 (1913); Phys. Zeitschr., **15,** 657 (1914). A detailed survey for systems of several degrees of freedom is contained in Ann. d. Phys., **51,** 327 (1916). Cf. also J. M. Burgers, *ibid.*, **52,** 195 (1917).

so in the quantum theory the adiabatic transformation from the original to the final quantum state has to occur infinitely slowly, that is by passing through intermediate states of equilibrium of motion. Quantities that remain unaltered during this transformation are called **adiabatic invariants.** The quantum numbers that fix the original state are by the adiabatic hypothesis themselves such invariants. All other adiabatic invariants must be expressible in terms of these simplest invariants.

There are three characteristics that are both necessary and at the same time sufficient for adiabatic processes. 1. *The infinitely slow or reversible* element of the process. In thermodynamics phenomena are also known that occur without the addition of heat but are irreversible (for example, the diffusion of a gas when no cotton-wool aperture is used). Such processes are not adiabatic in the present sense. 2. The *effect* not on the *co-ordinates of the motion* but on one or more *parameters* of the system that remain constant in the original motion. 3. The *unsystematic* or *irregular nature of the influence* (effecting the alteration) in relation to the phases of motion. Even in the case of the simple pendulum we could intentionally carry out the shortening of the thread in such a way that the energy of motion there remains constant, if we draw up the thread only at the points at which the motion is periodically reversed. In that case, as Warburg remarked at this Solvay Congress, a contradiction to Einstein's assertion and to the quantum theory would arise. Such intentional or methodical alterations are then in no case to be included in the category of adiabatic processes.

We next consider the mechanical aspect of the question. The fact that in ordinary mechanics we set aside the adiabatic processes is not because they are less interesting, but because they are more difficult in comparison with the ordinary problems of mechanics. In the case of the simple pendulum, we easily attain our object by direct calculation without having to seek support from the general laws of adiabatic invariance, which we shall develop from this example.

Let l be the length of the pendulum, m its mass (concentrated at a point), ϕ the angle of the instantaneous deflection, c the amplitude, and ν the frequency, so that

$$2\pi\nu = \sqrt{g/l} \quad . \quad . \quad . \quad . \quad (1)$$

The tension S acting on the thread is, as we know,

$$S = mg\cos\phi + ml\dot{\phi}^2$$

in which the first part is due to gravity, the second to the centrifugal force. If we shorten the thread infinitely slowly by $|\,dl\,|$, we have to perform work against the tension ; its amount is

$$dA = \overline{S}\,|\,dl\,| = -\,mg\,\overline{\cos\phi}dl - ml\overline{\dot{\phi}^2}dl \quad . \quad . \quad (2)$$

The horizontal bar denotes that the time average is to be taken and indicates that during the shortening by the amount dl many swings of the pendulum are to occur. The negative sign occurs because $|dl|$ is to denote a shortening, so that dl itself is negative. From

$$\phi = c \sin (2\pi\nu t + \gamma)$$

it follows that

$$\overline{\cos\phi} = 1 - \tfrac{1}{2}\overline{\phi^2} = 1 - \frac{c^2}{4}, \quad \overline{\phi^2} = (2\pi\nu)^2\frac{c^2}{2} = \frac{g}{l}\frac{c^2}{2} \qquad . \quad (3)$$

thus

$$dA = -mg\left(1 - \frac{c^2}{4}\right)dl - mg\frac{c^2}{2}dl = -mg\left(1 + \frac{c^2}{4}\right)dl.$$

The one part, $-mgdl$, of this work dA is used to raise the mean position of the weight mg. The remainder

$$dA' = -mg\frac{c^2}{4}dl \qquad . \quad . \quad . \quad . \quad (4)$$

increases the energy E of the motion of the pendulum. From (3) we see that the mean kinetic energy

$$\overline{E}_{kin} = \frac{m}{2}l^2\overline{\phi^2} = mgl\frac{c^2}{4} \qquad . \quad . \quad . \quad . \quad (5)$$

In the case of the pendulum the total energy E is, as we know, twice as great, and hence its differential is

$$dE = mg\frac{c^2}{2}dl + mglcdc \qquad . \quad . \quad . \quad . \quad (6)$$

By equating (4) and (6) we obtain

$$-\tfrac{3}{4}\,cdl = ldc.$$

Integrating,

$$\tfrac{3}{4}\log l = -\log c + \text{const.}$$

$$l^{\frac{3}{4}} = \text{const.} \qquad . \quad . \quad . \quad . \quad (7)$$

From this it follows that when the pendulum is shortened adiabatically the angular amplitude c increases, as may easily be seen by performing the experiment, whilst at the same time the linear amplitude lc decreases. Concerning the energy we conclude by comparing (5) and (7) that it increases when the pendulum is shortened adiabatically, as is evident from the work dA' performed ; it is inversely proportional to $\sqrt{l}$.

By squaring (7), and inserting the values of lc^2 from (5) and $\sqrt{l}$ from (1), we may write (7) in the form

$$\frac{\overline{E}_{kin}}{\nu} = \text{const.} \qquad . \quad . \quad . \quad . \quad (8)$$

Eqn. (8) is an illustration of the general law: the **action integral** (cf. p. 100, eqn. (14)),

$$2\int_0^\tau \mathrm{E}_{kin}dt = 2\tau\overline{\mathrm{E}}_{kin} = \frac{2}{\nu}\overline{\mathrm{E}}_{kin} \quad . \quad . \quad . \quad (9)$$

taken over a period is an adiabatic constant.

The adiabatic invariance of the quantity (9) already played a part in the general investigation made by Boltzmann to base the second law of thermodynamics on statistical considerations. Its relation to the quantum theory is clear from the eqn. (24) of Chapter II, § 7, where the quantum of action written down in our present eqn. (9) led to the introduction of the *principal quantum number* n *in the case of purely periodic motions.* From here we have a bridge to the more general class of *conditionally periodic systems, in which each individual phase-integral or each of the corresponding quantum numbers* n_l *is an adiabatic invariant.* (In adiabatic processes it is forbidden to pass through a degenerate system, as we shall show in Note 10.) In the particular case of the harmonic oscillator, and hence also of the pendulum, (9) becomes identical with $\overline{\mathrm{E}}/\nu$. Hence by setting (9) equal to nh we get back to Planck's quantum law: $\overline{\mathrm{E}} = nh\nu$.

We next use the adiabatic hypothesis to fill in a gap that was left in § 4 in the Zeeman effect.

To deal at the outset with the simplest case we consider a hydrogen atom in which the electronic orbits are circular in a plane which is perpendicular to the magnetic lines of force. Let a and ω be the radius and angular velocity in the circular orbit when the field is zero, and let $a + \Delta a$, $\omega + \Delta\omega$ be the same quantities when the field H has been imposed adiabatically. The flux of lines of force through the orbit is $\mathrm{H}\pi a^2$. Since we regard it as a small quantity (of the order of the increments Δa, $\Delta\omega$, whose squares and products may be neglected) it suffices to use in it the original a instead of $a + \Delta a$. By Faraday's law of induction, the flux of the lines of force gives the whole electromotive force that is excited by the increasing field in the "circular current" of radius a, that is the work performed on the current element. Our rotating electron, the charge of which is e in E.S.U., represents a current which, measured in E.M.U., is of intensity $e\nu/c = e\omega/2\pi c$ (cf. p. 127). Thus, by setting the work performed equal to the change of energy $\Delta\mathrm{W}$ of the electron, we get

$$\mathrm{H}\pi a^2 \cdot \frac{e\omega}{2\pi c} = \Delta\mathrm{W} \text{ or } \frac{1}{2c}e\mathrm{H}a^2\omega = \Delta\mathrm{E}_{kin} + \Delta\mathrm{E}_{pot} \quad . \quad (10)$$

Now

$$\mathrm{E}_{kin} = \frac{\mu}{2}a^2\omega^2, \qquad \Delta\mathrm{E}_{kin} = \mu(a^2\omega\Delta\omega + a\omega^2\Delta a) \quad . \quad (11)$$

$$\mathrm{E}_{pot} = -\frac{e^2}{a}, \qquad \Delta\mathrm{E}_{pot} = \frac{e^2}{a^2}\Delta a = \mu a\omega^2\Delta a \quad . \quad . \quad (12)$$

where μ = mass of the electron. In the last transformation we use the equation for the centrifugal force

$$\mu a\omega^2 = \frac{e^2}{a^2} \quad . \quad . \quad . \quad . \quad (13)$$

By substituting (12) and (11) in (10) and dividing by $\mu a^2\omega^2$, we get

$$\frac{\Delta\omega}{\omega} + 2\frac{\Delta a}{a} = \frac{e}{2\mu}\frac{\mathrm{H}}{\omega c} \quad . \quad . \quad . \quad . \quad (14)$$

A second equation is obtained from the circumstance that during the adiabatic change of state the dynamical laws, here the equation of centrifugal force, are to remain valid throughout. In eqn. (13) we wrote down this equation only to a first approximation for the field zero. In general it is

$$\mu(a + \Delta a)(\omega + \Delta\omega)^2 = \frac{e^2}{(a + \Delta a)^2} + \frac{e}{c}\mathrm{H}a\omega$$

or, when multiplied by $(a + \Delta a)^2$,

$$\mu(a + \Delta a)^3(\omega + \Delta\omega)^2 = e^2 + \frac{e}{c}\mathrm{H}a^3\omega \quad . \quad . \quad (15)$$

From this, by using (13) and dividing by $2ma^3\omega^2$, we get

$$\frac{\Delta\omega}{\omega} + \frac{3}{2}\frac{\Delta a}{a} = \frac{e}{2\mu}\frac{\mathrm{H}}{\omega c} \quad . \quad . \quad . \quad . \quad (16)$$

By comparing (16) and (14) we see at once that

$$\Delta a = 0, \quad \Delta\omega = \frac{e}{2\mu}\frac{\mathrm{H}}{c} = \mathfrak{o} \quad . \quad . \quad . \quad (17)$$

Hence, *when the magnetic field is introduced adiabatically the radius* a *remains unchanged, the rate of rotation is changed by the amount* $\mathfrak{o}$ *of the Larmor precession* (cf. eqn. (2) of p. 324), *being increased or diminished according to the direction of the field.*

The same calculation may be carried out for a circular or elliptic path inclined to the lines of force, and the result is : as the magnetic field increases gradually, the size and the shape of the orbit remains preserved (corresponding to $\Delta a = 0$) ; but the rate of rotation becomes changed in that the angular velocity $\mathfrak{o}$ about the axis of the lines of force becomes added. But this means : *the orbit as a whole performs a precessional motion.*

The limitation to a *gradually, that is infinitely slowly, increasing field* is absolutely necessary. The precessional orbit arises from the original one with the fixed orbital plane only if we pay due attention to the necessary initial velocity of the electron in the direction of precession (perpendicular to the lines of force). If the field is introduced suddenly, the momentary velocity of the electron is not affected ; for a change of velocity to come about it is necessary that the electron

traverse its orbit one or more times during the time that an appreciable change of the magnetic intensity of field takes place.

So far we have been dealing with *adiabatic mechanics*. The *quantum* aspect of the adiabatic change comes into question only if we wish to allocate quantum numbers to the changed motion. In the case of the circular orbit that is simply placed perpendicular to the lines of force, this has to occur, by the adiabatic hypothesis, thus : let the initial circular orbit (a, ω) be quantised, that is, let it be such that

$$\mu a^2 \omega = \frac{n_\varphi h}{2\pi} . \quad . \quad . \quad . \quad . \quad (18)$$

Then the altered motion $(a, \omega \pm \mathbf{0})$ is also quantised, and corresponds also to the quantum number n_ψ. But this correspondence does not mean that now the formula

$$\mu a^2(\omega \pm \mathbf{0}) = \frac{n_\varphi h}{2\pi} \quad . \quad . \quad . \quad . \quad (19)$$

holds, which would contradict the preceding eqn. (18) ; but rather, (18) *still remains valid*. Whereas, however, the left side of (19) denotes the moment of momentum in the stationary system of reference, the left side of (18) represents the moment of momentum in the system of reference of which the precession is $\pm \mathbf{0}$. Thus the latter, not the former, is quantised. This is extended still further then to the general case of elliptic motion. *The precessional orbits in the magnetic field correspond to the same quantum numbers as the Kepler ellipses in the case when no magnetic field is present ; but the phase integrals are not to be calculated with reference to the stationary, but with reference to the precessional co-ordinate system.*

This was, as a matter of fact, the method that we followed in § 4 (p. 327), and which is accordingly justified by the adiabatic hypothesis. The particular simplicity of the Zeeman effect now consists in the circumstance that in it the adiabatically altered orbits are identical in shape with the original orbits, and differ from them only in their precessional motion.

The conclusions here drawn from the adiabatic hypothesis agree in general with the results obtained in Note 5 under (*c*). In eqn. (18) we are dealing with the canonically conjugate momentum co-ordinate denoted by $\bar{p}$; the left-hand side of eqn. (19) corresponds to the now elementary moment of momentum, denoted by p, which is not quantised.

Another application of the adiabatic hypothesis concerns the shape and position of the orbits * in the Stark effect in the limit when the electric field becomes vanishingly small, Lim $F \to 0$. We know (p. 311) that these orbits are Kepler ellipses, but that they differ from

* Communicated personally by W. Pauli, in the course of a conversation during the preparation of an earlier edition of the present volume.

the Kepler ellipses in the force-free case, or, better expressed, from those in the magnetic field of vanishing field intensity Lim $H \to 0$. Our object is to prove the relationship between the two groups of Kepler ellipses ; we abbreviate them thus $K_{f=0}$, $K_{H=0}$.

The field F is to be in the direction of the x-axis as before. The potential energy of the electron in the field is eFx. The total energy is W, and is composed partly of kinetic energy, partly of potential energy in the field of the nucleus and in the external field F ; it remains constant during the motion so long as the external field is kept constant. If it is altered by an amount δF, the total energy alters by the amount $\delta W = ex\delta F$. Since the change δF of the field is to take place infinitely slowly, we may replace x by the time-mean $\bar{x}$ for one or more revolutions and write

$$\delta W = e\bar{x}\delta F.$$

We follow Bohr * in calling $\bar{x}$ the x-co-ordinate of the " electric centre of gravity." The idea is as follows. We replace the succession of positions of the motion of the electron in its orbit *in time* by the distribution of a charge *in space* in such a way that for every element of the orbit there is a charge proportional to the time taken to traverse it. This method was first developed by Gauss for the perturbation problem of planetary orbits and signifies *au fond* the approximation of the process in time by using the first term of its Fourier expansion. In our case, where the field F is homogeneous, we may, moreover, replace the charge distribution by its *centre of gravity*, and allow the force of the field $-eF$ to act at this point. For reasons of symmetry the centre of gravity S lies on the major axis of the ellipse, namely at the distance

$$s = \tfrac{3}{2}\epsilon a \quad . \quad . \quad . \quad . \quad . \quad (20)$$

from the nucleus in the direction of the aphelion ; here ϵ is the numerical eccentricity, which is equal to the distance of the focus from the centre of the ellipse divided by the semi-major axis. Eqn. (20) is easily proved as follows :

The charge density on the elliptic arc is $(-e)dt/\tau$; the position of the centre of gravity on the major axis, along which we measure the co-ordinate ξ, is given by

$$\bar{\xi} = \int \xi \frac{dt}{\tau} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

By the law of sectional areas

$$p = \mu r^2 \frac{d\phi}{dt}$$

where μ denotes the mass of the electron.

* In Part II of the paper mentioned on p. 118 Bohr linked up the treatment of the Stark effect with the position of this electric centre of gravity.

Hence it follows that

$$dt = \frac{\mu}{p} r^2 d\phi \quad . \quad . \quad . \quad . \quad (22)$$

and also that

$$p\tau = \mu \int_0^{2\pi} r^2 d\phi = 2\pi\mu ab = 2\pi\mu a^2 \sqrt{1-\epsilon^2} \quad . \quad . \quad (23)$$

If we substitute (22) in (21) and take into account that $\xi = r \cos \phi$, we obtain

$$\bar{\xi} = \frac{\mu}{p\tau} \int_0^{2\pi} r^3 \cos \phi d\phi \quad . \quad . \quad . \quad . \quad (24)$$

But by the equation to the ellipse

$$\frac{1}{r} = \frac{1 + \epsilon \cos \phi}{a(1-\epsilon^2)} \quad . \quad . \quad . \quad . \quad (25)$$

and hence by (24) and (23)

$$\bar{\xi} = \frac{\mu a^3 (1-\epsilon^2)^3}{p\tau} \int_0^{2\pi} \frac{\cos \phi d\phi}{(1 + \epsilon \cos \phi)^3} = \frac{a(1-\epsilon^2)^{\frac{3}{2}}}{2\pi} \int_0^{2\pi} \frac{\cos \phi d\phi}{(1 + \epsilon \cos \phi)^3} \quad (26)$$

At the same time we deduce from (25) and (23) that

$$\int_0^{2\pi} \frac{d\phi}{(1 + \epsilon \cos \phi)^2} = \frac{2\pi}{(1-\epsilon^2)^{\frac{3}{2}}} \quad . \quad . \quad . \quad (27)$$

and by differentiating (27) with respect to ϵ

$$\int_0^{2\pi} \frac{\cos \phi d\phi}{(1 + \epsilon \cos \phi)^3} = -\frac{3\pi\epsilon}{(1-\epsilon^2)^{\frac{5}{2}}} \quad . \quad . \quad . \quad (28)$$

If we substitute this in (26) we obtain

$$\bar{\xi} = -\tfrac{3}{2}\epsilon a \quad . \quad . \quad . \quad . \quad (29)$$

This proves eqn. (20) since, except for the sign, s coincides with $\bar{\xi}$. The negative sign of $\bar{\xi}$ clearly asserts that the centre of gravity S lies on the negative ξ-axis, that is, between the nucleus and the aphelion, whereas the positive ξ-axis was directed from the nucleus to the perihelion. Since ϵa denotes the distance of the nucleus from the centre of the ellipse, the centre of gravity S bisects the distance from the centre to the other focus of the ellipse.

Hence if Θ denotes the angle between the x-axis, that is, the direction of the field and the ξ-axis, namely, the major axis of the ellipse, we have, by (20) or (29),

$$\bar{x} = \tfrac{3}{2} a\epsilon \cos \Theta \quad . \quad . \quad . \quad . \quad (30)$$

If the field increases from 0 to F the change in energy is

$$\Delta W = \int \delta W = \int_0^F e\bar{x}\delta F = e\bar{x}F \quad . \quad . \quad . \quad (31)$$

In the last term of this equation we have assumed $\bar{x}$ independent of F. In other words, we have neglected the change of $\bar{x}$ resulting from the increasing field as this involves only a term in F^2 in the expression for ΔW and this is of no account. We may therefore use the value (30) for $\bar{x}$.

On the other hand, we take the value of ΔW from eqn. (30) of § 2. We then obtain, by equating the two expressions for ΔW,

$$e\bar{x}F = -\frac{3h^2F}{8\pi^2\mu Ze}n(n_\eta - n_\xi),$$

$$\bar{x} = -\frac{3h^2}{8\pi^2\mu Ze^2}n(n_\eta - n_\xi) = \tfrac{3}{2}a\frac{n_\xi - n_\eta}{n} \quad . \quad . \quad (32)$$

In the last equation we have substituted the well-known value $a = n^2h^2/4\pi^2\mu Ze^2$ for the major axis of the Kepler ellipse. Comparing (32) with (30) we see that

$$\epsilon \cos \Theta = \frac{n_\eta - n_\xi}{n} \quad . \quad . \quad . \quad . \quad (33)$$

Whereas in the case of the Kepler ellipse $K_{H=0}$ *the semi-axis* (cf. eqn. 16c on p. 113) *and the eccentricity* ϵ *were fixed by the quantum numbers alone* (there they were n_ϕ and n), *there enters into the expression* ϵ *for the Kepler ellipse* $K_{F=0}$ *the non-quantised angle* Θ. *The limiting cases* $K_{H=0}$ *and* $K_{F=0}$ *thus actually differ from one another.*

Our eqn. (32), deduced from adiabatic considerations, allows us to draw a conclusion not only about the shape but also about the position of the orbits. For we read out of (32) that : if $n_\xi > n_\eta$, then $\bar{x}$ must > 0, that is, *the electron in traversing its orbit remains longer on the front side of the nucleus than on the rear side ;* if $n_\xi < n_\eta$ then $\bar{x} < 0$, *and the orbit conversely is longer on the rear side than on the front side of the nucleus.* Here the front side denotes that which faces in the direction of the lines of force ($x > 0$).

As we see from formula (1) on page 312, in the Stark effect the line-displacement due to the *initial orbit* always predominates considerably over that due to the final orbit. Thus if $n_\xi > n_\eta$ in the initial orbit, $\Delta\nu$ becomes positive, that is, the corresponding component of the line-resolution lies on the short-wave side of the original line. If $n_\xi < n_\eta$ in the initial orbit, $\Delta\nu$ becomes negative and we have a long-wave component. Combining this with the preceding result, we may say : *the short-wave (long-wave) components in the Stark effect are due to transitions in which the initial orbits lie more on the front side (rear side, respectively) of the nucleus.*

This remark is useful for interpreting * certain differences of intensity between the long- and short-wave components,† which have been observed in rapid canal rays of hydrogen.

We are now also in a position to explain the fading away (*Aussterben*) of the lines qualitatively (cf. Fig. 84, p. 320). We first consider the red components: for them we have $n_\xi < n_\eta$ for the initial state, $\bar{x} < 0$. The *aphelion* of the initial orbit lies in the negative direction of the field if we reckon from the nucleus, in the direction of the *positive* (positively charged) plate of the condenser by which we may picture the electric field to be produced. On this side the initial orbit of the field is perturbed to an extraordinary degree because the attractive force of the field acts in opposition to the nuclear attraction. In this case the orbit may clearly be perturbed if the field is sufficiently intense. On the other side of the nucleus the initial orbit will be forced back by the field against the nucleus. Now for the violet components; here we have in the initial state $n_\xi > n_\eta$, $\bar{x} > 0$. The *aphelion* of the initial orbits lies towards the *negative* plate and the orbit is forced back towards the nucleus by the field. On the *perihelion* side the orbit may again be perturbed, but only when the field-strengths are greater than before, because the orbit now passes by more closely to the nucleus than in the case of the red components. Hence we see: the violet and the red components may be perturbed if the fields are sufficiently intense, the red being perturbed sooner than the violet. This agrees perfectly with the findings of Fig. 84. Furthermore, we see that the orbits with greater values for the principal quantum number n are more easily perturbed because they have greater orbital dimensions than those with smaller values for n. This is also shown in the measurements: H_β persists longest, then, in turn, H_γ, H_δ, H_ϵ, H_ζ. If we calculate quite roughly with circular orbits (radius $a = a_0 \cdot n^2$, where a_0 = radius of the first hydrogen orbit), we obtain as the condition for the perturbation of the orbit

$$\frac{e^2}{{a_0}^2 n^4} \cong e\mathrm{F},$$

that is, a decrease of the critical field-strengths in the ratio $1/n^4$. If we set $\mathrm{F} = 10^6$ volt/cm., we obtain ‡

$$n = \sqrt[4]{\frac{e}{{a_0}^2 \cdot \frac{10^6}{300}}} \sim 8{\cdot}4,$$

that is, a value which is obviously too great, as is shown by Fig. 84, but nevertheless it is of the correct order of magnitude.

* Cf. N. Bohr, Phil. Mag., **30**, 405 (1915); A. Sommerfeld, Jahrbuch f. Rad. und Elektr., **17**, 417 (1921); A. Rubinowicz, Zeits. f. Phys., **5**, 331 (1921). Translated into the language of wave-mechanics by Fr. Slack, Ann. d. Phys., **82**, 576 (1927).

† J. Stark, Elektr. Spektralanalyse, § 14 and § 33; H. Lunelund, Ann. d. Phys., **45**, 517 (1914); Wierl, Dissertation, Munich, 1927; Ann. d. Phys., **82**, 563 (1927).

‡ The factor $\frac{1}{300}$ is necessary in order to bring the volts to electrostatic units.

CHAPTER VII

SERIES LAWS IN GENERAL

§ 1. Experimental Results Connected with the Series Scheme

ON the basis of extensive experimental results spectroscopists have developed a number of physical points of view bearing on the arrangement of the lines into separate series, such as the structure and the multiplicity of the lines, the readiness with which they appear, their dependence on temperature, their diffuseness or sharpness, their behaviour in the Stark effect or under pressure and so forth. From this there emerged as the final criterion that a line belonged to a definite series the possibility of its fitting into a formula representing the regular sequence of lines. For the sake of brevity we shall begin here with the expression of the series in formulæ ; the individual data of experiment may then be derived conveniently in the reverse direction from this description.

We must preface our remarks by stating that at present it has by no means been possible to prove the existence of series in the case of all elements. The series character dominates only the first three vertical columns of the periodic system. Towards the end of the periodic system, from the sixth to the eighth vertical column, the number of lines increases enormously (as in the case of the Fe-lines and in the triads altogether) ; here the multiplet structure (cf. Chap. VIII) comes into prominence and the series scheme recedes. Corresponding elements, which lie in a vertical column in the periodic system, behave in an analogous manner as regards their spectral manifestations, for example, they all show a clear series character or all show a confused accumulation of lines that apparently belong to no series. This is in agreement with the view already expressed in Chapter III, § 3, that the visible spectra originate at the surface of the atom and hence exhibit similar behaviour if the surface structure is similar.

Every series is constructed, like Balmer's series, from the difference of two terms, a *constant first term* and a *variable second term.* We also call the latter the *current term.* As in the Balmer series so, generally, the current term depends on a whole number n, the current number, and approaches the limiting value zero as n goes to infinity. From our earlier remarks (see p. 72) we already know that the true

goal of spectroscopy is the terms themselves and not the lines which are formed by *combining* the terms. We shall now give the usual definition of the current term for the Principal Series, the I and II Subordinate Series and so forth.

The Principal Series * (*Hauptserie*) is characterised by the letter P ; its current term is written thus :

$$\text{H.S.} \ldots\ldots\ldots n\text{P}.$$

The integer n distinguishes the successive lines or members of the series. The letter P serves to indicate the atomic constants that play the decisive part for this term. nP does not denote the product of the current number n with an atomic constant P but symbolises a certain function of n whose form we shall develop in the next section. The same applies to the following symbols nD, nS, nF, ...

The First Subordinate Series (*Nebenserie*), also called the **Diffuse Subordinate Series,** is characterised by the letter D. The current term of the I Subordinate Series is written thus :

$$\text{I. N.S.} \ldots\ldots\ldots n\text{D}.$$

The Second Subordinate Series is also called the **Sharp Subordinate Series.** Hence we use the letter S and denote its current term by

$$\text{II. N.S.} \ldots\ldots\ldots n\text{S}.$$

When a method was found of analysing the infra-red part of the spectrum the so-called **Bergmann Series** became added to the three series types above given which had already been known longer. We shall denote it by the letter † F and shall write its current term thus :

$$\text{B.S.} \ldots\ldots\ldots n\text{F}.$$

A survey of the complete set of series terms is given by the scheme :

1S	2S	3S	4S	5S	6S . . .
	2P	3P	4P	5P	6P . . .
		3D	4D	5D	6D . . .
			4F	5F	6F . . .
				5G	6G . . .
					6H . . .

* Formerly it was customary to use small letters instead of capitals, e.g. p in the case of the Principal Series. We here follow the American practice (Russell and Saunders, Astrophys. Journ., **61,** 64 (1925)), which has become general and which is capable of being extended in many directions ; cf. Chap. VIII.

† The name " Fundamental Series " which is often used instead of the expression Bergmann Series in English and American literature where it is characterised by nB, is founded on the " hydrogen-like " character of the Bergmann series. But this is not a decisive characteristic of the Bergmann series since it occurs still more markedly in the ultra-Bergmann series (see below). If we wish to call a series-term " fundamental " it should be the S-term which, although it is least " hydrogen-like " is in many cases allocated to the " ground-orbit " of the atom. Our excuse for using the symbol nF is that the symbols nD and nS also refer to characteristics, diffuseness and sharpness, which do not always actually occur.

It expresses the fact that the current-number n in the S-term runs through all initial values from 1 to ∞, in the P-term through all values from 2 to ∞, and so forth. Moreover, its last rows indicate that the F-term is followed by higher terms, so-called " ultra-Bergmann terms," in which the values of n start from 5 or 6.

Concerning the *constant term* of our different series we find that in the Principal Series it coincides with the term 1S of the II Subordinate Series ; the constant term in both Subordinate Series is the first term 2P of the terms of the Principal Series ; that of the Bergmann Series is the first term of the I Subordinate Series, namely 3D. Hence the constant terms may be tabulated thus :

H.S.	1S
I N.S.	2P
II N.S.	2P
B.S.	3D

Hence in our four cases the ultimate expressions for the series are

$$\left.\begin{array}{lll} \text{H.S.} & \nu = 1\text{S} - n\text{P} & n = 2, 3, 4, \ldots \\ \text{I N.S.} & \nu = 2\text{P} - n\text{D} & n = 3, 4, 5, \ldots \\ \text{II N.S.} & \nu = 2\text{P} - n\text{S} & n = 2, 3, 4, \ldots \\ \text{B.S.} & \nu = 3\text{D} - n\text{F} & n = 4, 5, 6, \ldots \end{array}\right\} \quad (1)$$

It must not be imagined that the combination of the lines into series and their resolution into two terms are possible without considerable practice and ingenuity. First of all the lines of the various series are all mixed together and must be sorted out according to the criteria mentioned at the beginning of this section. In most cases only a moderate number of lines of any one series is available. To obtain by extrapolation the series limit and hence the constant first term of the series we must first have found an analytical expression for the current-term (cf. § 2). The series limit is then obtained together with the undetermined parameters that occur in the series law by using a graphical or numerical method of approximation.* It is almost always found that the first terms of the series are not given sufficiently accurately. The task of calculating the series is considerably simplified if other series or series limits of the same element are already known. On account of the combination-relationships (see below) between the different series it is always necessary to adjust the results of calculating several series to bring them into harmony. It is obvious that the measured wave-lengths must be corrected for a vacuum † before the series can be calculated.

* Cf. the works mentioned on p. 71, Paschen-Götze, Third Introduction ; Fowler, Part I, §§ IV and V. The method that has been specially developed by Paschen and his followers is described by E. Fues in his Munich Dissertation, Ann. d. Phys., **63**, 1 (1920).

† Cf. the tables of Meggers and Peters, Bureau of Standards, No. 327 (1918), or the table of frequencies given by H. Kayser (Hirzel, Leipzig, 1925), in which the wave-lengths measured in air are directly expressed with the correct values for a vacuum.

The expressions (1) contain the following laws which preceded the series representation historically and led to their enunciation:

1. *The series limits of the* I *and* II *Subordinate Series coincide.* For according to (1) they both lie at the wave-number $\nu = 2P$. The limit of the Bergmann series lies at the wave-length $\nu = 3D$. These limits cannot be observed or observed accurately in most cases but must be calculated by extrapolation.

2. The series limit of the principal series has the wave-number $\nu = 1S$. *The difference between the wave-numbers of this series limit and the common limit of the first and second subordinate series is equal to the wave-number of the first member of the principal series* (**Rydberg-Schuster rule**); the second subordinate series, too, if we extrapolate its expression in series to $n = 1$ leads to the same wave-number with the sign reversed.

So far we have tacitly spoken of *series of simple lines.* But frequently the series lines consist of several components; they are *doublets* or *triplets.* The systematic analysis of this "complex structure" of the terms and its wonderful regularity in the periodic system occupies the whole of the next chapter. The multiplicity that occurs in the II Subordinate Series of the line-configurations is always due to the constant term 2P, because the S-term is always simple. In the I Subordinate Series, too, the multiplicity of the lines is usually caused by this constant term 2P alone, because the multiplicity of the D-terms does not need to be taken into account. The multiplicity of the terms of the principal series is indicated by writing instead of nP in (1):

$$nP_j \begin{cases} j = \frac{1}{2}, \frac{3}{2}, \ldots & \text{Doublet series.} \\ j = 0, 1, 2 \ldots & \text{Triplet series.} \end{cases}$$

Concerning the general significance of the index j and its half-integral values in the case of doublet series, see Chapter VIII.

If we bracket together the lines having the same values for j we speak of a **partial series** (*Teilserie*). The following laws then hold for the partial series that occur in a doublet or a triplet series; these laws have been particularly useful in finding principal and subordinate series.

3. *In the first and the second subordinate series the law of constant differences of frequency (difference of wave-number) hold.* That is: the doublet or triplet differences in the I and II N.S. have a difference $\Delta\nu$ (measured in wave-numbers), which is independent of the member number n of the lines and is identical in the I and II Subordinate Series. Moreover, it coincides with the wave-number difference in the first member of the principal series. This follows immediately from the fact that the multiplicity of the subsidiary series is due to the *constant term* $2P_j$. In Chapter VIII, § 1, we shall illustrate in the case of Li that

this law is, on account of the additional multiplicity of the D-term, only a law of approximation in the I N.S.

4. *The wave-number differences of the principal series decrease to zero as the member number increases.* The reason for this is that in this case the multiplicity is conditioned by the *variable* term, whereas the constant term is, strictly speaking, simple.

From (3) and (4) it follows, in particular, for series limits that :

5. *The partial series of a principal series approach one and the same series limit, as the number of the member increases. The partial series of one and the same subordinate series have series limits that differ from each other by the constant wave-number difference of the partial series in question ; but corresponding partial series of the first and second subordinate series approach the same series limit as* n *increases.*

A further difference between principal series and subordinate series follows from the intensity of the lines in the doublet and the triplet series.

We next consider the example of the D-lines, the first member of the principal series of the Na-spectrum ; as is well known, they form

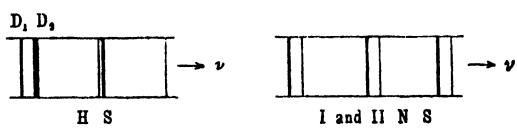


FIG. 90.—States of resolution (represented diagrammatically) in the course of a series—on the left for the H.S., on the right for the II N.S. (The right-hand figure only represents the I N.S. when the resolutions of the current terms are small in comparison with that of the constant P-terms.)

a doublet. The wave-length difference of the lines D_1 and D_2 amounts fairly accurately to 6Å. D_2 is of shorter wave-length and more intense (twice as intense) as D_1. This is to be interpreted in the sense that the number of Na-atoms that emit D_2 is greater than (twice as great as) the number of Na-atoms that emit D_1. In Fig. 90 we show schematically, besides the lines D_1D_2, also the next member of the principal series, in which the doublet interval is already markedly smaller, as also one of the succeeding members, in which the doublet no longer appears resolved. On the other hand, the type of the two subordinate series is indicated in Fig. 90. By Law 3 their constant wave-number difference is equal to that in the first member of the principal series. The distances of the series members from one another, with which we are not at present concerned, have here (just as in the case of the principal series) been chosen arbitrarily in the scale of the ν's. What are of essential interest to us at present are the conditions of intensity. In the subordinate series the more intense component of the doublet is on the opposite side to that in the principal series. The reason for this we see without difficulty by looking at the formulæ (1) is that nP_j occurs in the expression for the principal series with the reverse

sign to that of $2P_j$ in the expressions for the subordinate series. We generalise this for arbitrary doublet and triplet series and enunciate our last proposition as follows :

6. *The order of sequence of the intensities in the doublets and triplets of a principal series is the reverse of that in the corresponding doublets and triplets of a subordinate series.*

For the rest, we have already in Chapter IV, § 5, Fig. 60, established the same fact with reference to the Röntgen spectra for the intensities of Kα, Kα′, as well as for those of Lα, Lα′, Lβ respectively. What was here called, in connexion with series representation, reversal of sign, appeared there, more vividly, as an interchange of initial and final path in the one or the other pair of lines.

As a comprehensive example of the preceding theorems we shall compare in Fig. 91 the line-spectra of potassium with one another; in the first row is the principal series, in the middle is the second

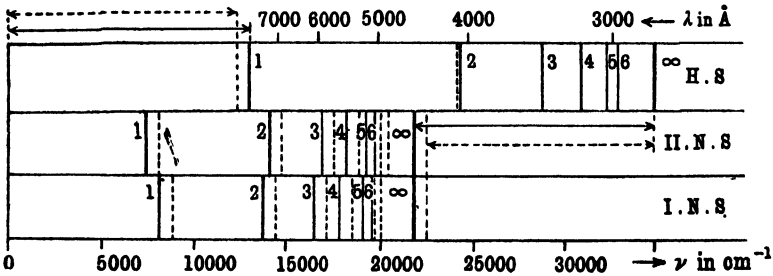


FIG. 91.—The series laws illustrated with potassium as an example. The subordinate series have the same series limit. The difference of the series limits of the H.S. and the N.S. equals the wave-number of the first member of the principal series, and so forth.

subordinate series, and in the bottom is the first subordinate series. The lines have been drawn on the correct scale of their frequencies quantitatively ; but we have magnified the doublet intervals ten times to make them perceptible ; the weaker doublet lines have throughout been drawn as dotted lines.

We see from the figure that the limits of the first and second subordinate series coincide (Theorem 1), both the continuous and the dotted limits (Theorem 5). The limit of the principal series, diminished by the common limit of the first and second subordinate series, gives the frequency of the first member of the principal series (Theorem 2, the Rydberg-Schuster Law ; it is indicated for the continuous and dotted partial series by the continuous and dotted arrow). The doublet intervals are equal and constant in the two subordinate series (Theorem 3) ; in the principal series they decrease rapidly towards the violet (Theorem 4). That is why the limit of the principal series is simple, and that of the subordinate series is double (Theorem 5). The order

of sequence of the intensities of the doublet lines in the principal series is the reverse of that in the subordinate series (Theorem 6).

The spectra of the alkalies being easy to grasp first led to the arrangement of spectral lines into series and to the discovery of the relationships embodied in them. In the elements of the second and third column the character is much more manifold; here there are series types of simple lines, series types of doublets and triplets which in their turn again resolve into principal series, subordinate series and Bergmann series. For a time it was therefore conjectured that in all elements the complete series scheme must consist of doublet, triplet and simple lines. But this conjecture only helped to obscure the true state of affairs. For, as we shall see in Chapter VIII, § 2, the doublet series correspond to a state of ionisation of the atom other than that to which the simple series and the triplet series correspond, which belong together. Doublet series never occur in the same atom (in the same atomic state) in conjunction with triplet and simple series. In the last columns of the periodic system the number of lines and their character becomes more and more complicated, as has already been stated above.

Besides the four series hitherto mentioned there are in the case of all elements numerous other combination lines and combination series. For example, we may combine the term 2S instead of 1S with the P-terms, or 3P instead of 2P with the D-terms. In this way we arrive at a second representative of the H.S. or I N.S. type, which may be represented by the following formulæ analogous to (1):

$$\left.\begin{array}{lll} \text{H.S.} \ldots\ldots & \nu = 2\text{S} - n\text{P} \ldots\ldots & n = 2, 3, 4.5, \ldots \\ \text{I N.S.} \ldots\ldots & \nu = 3\text{P} - n\text{D} \ldots\ldots & n = 3, 4, 5, 6, \ldots \end{array}\right\} \quad (2)$$

The following series are often also represented:

$$\left.\begin{array}{ll} \nu = 3\text{D} - n\text{P} \ldots\ldots & n = 4, 5, 6 \ldots\ldots \\ \nu = 4\text{F} - n\text{D} \ldots\ldots & n = 5, 6, 7 \ldots\ldots \end{array}\right\} \quad (3)$$

Ritz's Combination Principle (p. 72) would even lead us to expect that we may combine every term nS, nP, nD, . . . with every other. We shall see, however, in the next section that under normal conditions this principle is subject to certain limitations.

Helium (neutral helium, not He^+), the element which immediately succeeds hydrogen, already shows a very complicated series scheme that is in many ways very remarkable. It possesses two different series terms that do not combine with one another. We follow Bohr in calling the one **orthohelium**; to it belongs, for example, the intense yellow He-line, the Fraunhofer line D_3 for which $\lambda = 5876$, $\nu = 2p - 3d$.* We call the other series system **parhelium**; it was originally ascribed to an element believed to be different from helium. The series of

* We use small letters here for convenience (see below, in the text).

orthohelium have a fine-structure (triplets), the lines of parhelium are strictly simple.

We make use of the following "**scheme of levels**" ("*Niveauschema*"). Starting from the "energy-level zero" denoted by ∞ (an electron at an infinite distance from the atom) we plot the numerical value of each series term *downwards* and draw a step that is to visualise the term. Since the terms are proportional to the energy of the atom in the corresponding states of motion, each step denotes a possible energy-level of the atom—quite analogously to the earlier figures for the Röntgen region. It is found convenient to denote only the levels of parhelium by capitals (S, P, D), those of orthohelium by

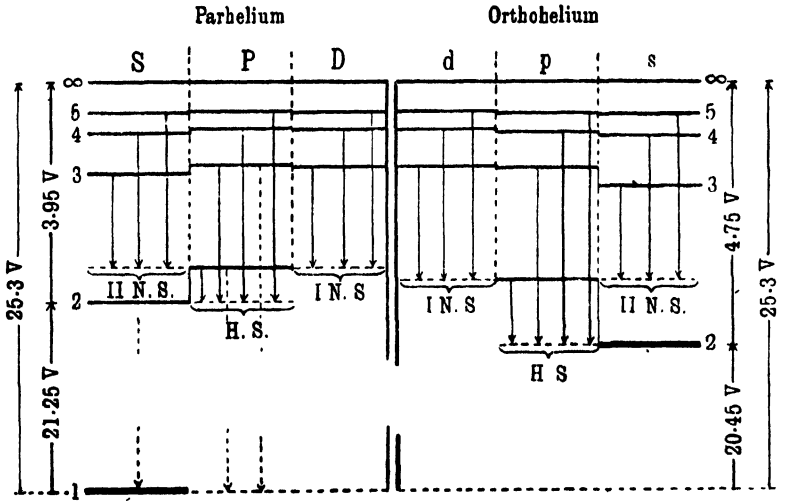


FIG. 92.—Scheme of levels of the helium arc spectrum. The characteristic energy differences in volts are given at the sides (transformation potential, etc., cf. § 3).

small letters (*s*, *p*, *d*), such as were used generally earlier. In our modern systematic notation we should designate them by ^{3}S, ^{3}P, ^{3}D.

Direct transitions between the ortho- and the para-levels are very improbable as is shown by the spectrum.* This is indicated by the two heavy vertical lines separating the levels in the figure. We have omitted the succession of F-terms and higher terms, and also the multiplicity of the levels of orthohelium which on account of their very small separation could not in any case be shown clearly in the figure. The S-levels are numbered from 1 to ∞, the P-levels from

* Th. Lyman (Astrophys. Journ., **60**, 1 (1924)) found the line $\lambda = 591{\cdot}56$ Å. in the ultra-violet and interpreted it as the combination $1S - 2p$; but (according to H. B. Dorgelo, Physica, **6**, 150 (1926)) this line belongs to the neon spectrum. So it appears that there are no "inter-combinations" between the ortho- and the para-system.

2 to ∞, the D-levels from 3 to ∞. On account of Pauli's Principle there is no term in orthohelium analogous to the level 1S in parahelium (cf. Chap. VIII, § 3); all the other levels are represented in parhelium as well as in orthohelium. The level 1S in parhelium and $2s$ in orthohelium have been drawn more thickly to indicate their stability or meta-stability, respectively (cf. § 3). The meaning of the upward arrows shown in the scheme of levels cannot be explained until we get to § 3.

The arrows drawn downwards, being the difference of two terms, represent the emission lines of ortho- and parhelium. Let us consider first the I and II N.S. Their arrows end at the level $2p$ or 2P, respectively, and begin at the level nd, ns or nD, nS respectively. To be able to draw these arrows, the level $2p$ (2P) has been extended by a dotted line in both directions. But the extension does not extend beyond the central partition lines between ortho- and parhelium, since, as we said, the levels of the two heliums do not combine with one another. The length of the arrows increases as the member number increases in the series and finally approaches the limit, which is common to the I and II N.S., but different for ortho- and parhelium.

Passing on to the H.S. (Principal Series) we distinguish between the H.S. with the symbol 1S — nP (cf. eqn. (1)) and those with the symbol 2S — nP and $2s$ — np (cf. eqn. (2)). The H.S. with the symbol 1S — nP lies in the extreme ultra-violet and is denoted in the left side of the figure by dotted arrows. The lines

$$\lambda = 584{\cdot}40\text{Å.}, \quad \nu = 1\text{S} - 2\text{P}$$
$$\lambda = 537{\cdot}08\text{Å.}, \quad \nu = 1\text{S} - 3\text{P}$$

correspond to these arrows.

There is a wide chasm between the levels 2S and 1S which is indicated in the figure by a gap in the arrows. The distance (1S, 2S) is almost five times as great as the distance (2S, ∞), so that it could not be represented accurately to scale in the figure. Since the level $1s$ is missing in orthohelium, there is in its case no H.S. with the symbol $1s$ — np. The main series with the symbols $2s$ — np, 2S — nP are represented in both ortho- and parhelium. The majority of their lines lie in the visible region; only the first line of both series is in the infra-red, as is indicated by the shortness of the corresponding arrow. Their wave-lengths are:

$$\lambda = 10830\text{Å.} \cong 1\mu, \quad \nu = 2s - 2p \text{ (orthohelium)},$$
$$\lambda = 20582\text{Å.} \cong 2\mu, \quad \nu = 2\text{S} - 2\text{P} \text{ (parhelium)}.$$

The first, being the " resonance line " of helium (cf. § 3), is particularly interesting.

The levels with the same numerical coefficients, for example $2s$, $2p$, or $3s$, $3p$, $3d$, have been joined together in the two halves of the figure to a continuous step-like line. As there is no level $2d$ or 2D,

the first of these step-lines breaks off at $2p$ (2P), the second at $3d$ (3D); to the step-line $4s$, $4p$, $4d$ there would become added, if we had included the Bergmann series, the level $4f$. The levels that have in this way been grouped together by means of the common current number n are actually uniform and correspond to one and the same Balmer term R/n^2 as we shall see in the next section.

Hitherto we have spoken only of *emission lines*. They result after previous excitation of the atom, that is, after the atom has been "raised" out of its naturally most stable state or **ground-state** to one that is less stable and from which it strives to escape into a state that is again more stable. Accordingly, corresponding to the ground-state (1S in the case of helium) we have (algebraically) the *smallest amount of energy* or, what comes to the same thing, the *greatest term*.

In the case of *absorption lines*, on the other hand, in so far as they arise in cold vapours, the initial level is always the ground-state of the atom. In our diagram the absorption lines would have to be represented by arrows that start out from the natural or ground level and are directed *upwards*. Hence the lines of the H.S. type $1S - nP$, dotted in the figure, if inverted, therefore represent the absorption lines of cold He-gas. The fact that they all lie in the extreme ultraviolet explains why He-gas is quite transparent in the visible region. Clearly the position of the absorption spectrum is of fundamental importance for the knowledge of the series scheme. It tells us, in particular, that in the case of He the lowest level accessible to spectroscopy (here $2s$) cannot be the true natural or ground orbit.

§ 2. Expressing Series by Formulæ. The Selection Principle for the Azimuthal Quantum

The distinctive property of the hydrogen atom is, spectroscopically, that it exhibits only *one* series spectrum, that of Balmer. The division into principal and subordinate series serves no purpose here, if we disregard fine-structure. We saw the reason of this in Chapter II, § 7; the individual series term depends only on the sum of the azimuthal and the radial quantum numbers, $n = n_\phi + n_r$, and not on these numbers separately. The same applies to the hydrogen-like atoms He^+ and Li^{++}.

The case is different for atoms that are not of the hydrogen type, and hence even for neutral He and Li. Here the pure Coulombian field with the nuclear charge Ze no longer reigns. We distinguish between an external "initial electron" (*Aufelektron*), which is thrown by some agency of thermal or electric origin out of its stable position into an orbit further removed from the nucleus, and the $Z - 1$ inner electrons which essentially describe their normal orbits (we restrict our attention for the present to the *neutral* atom and to the *arc* spectrum

which it emits). This external initial electron moves in the field of the nucleus, which is screened off by the inner electrons. This field is still, indeed, asymptotically a Coulombian field : for sufficiently great distances the nuclear charge $+ Ze$ and the $Z - 1$ electrons near the nucleus act conjointly like a simple point charge $+ e$; but for moderate distances the individual distribution of the electrons near the nucleus enters as a factor. It produces a supplementary field that differs from the Coulombian field. The orbits of the external electron are therefore no longer Kepler ellipses. Nevertheless they are more or less related to the latter, being the more related the further the orbit is removed from the nucleus.

We imagine the supplementary field idealised into a *pure* central field, that is, we write its potential energy as a pure function of the distance r between the nucleus and the external electron. The orbit of the latter then becomes *plane*. In the plane of this orbital curve we measure an azimuth ϕ. We then allocate two quantum numbers n_ϕ and n_r, as once before, to the co-ordinates ϕ and r.

The energy W of the orbit depends on n_ϕ and n_r but no longer merely on their sum, $n_\phi + n_r$, but on some more general function of n_ϕ and n_r :

$$f(n_\phi, n_r) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This means that in the case of elements that are not hydrogen-like the *Balmer series* resolves into a *system of series*. For if we form the difference of two expressions of the type (1) for the initial and the final state with the respective quantum numbers n_{ϕ_1}, n_{r_1} and n_{ϕ_2}, n_{r_2} and then keep *one* quantum number of the initial state, namely n_{ϕ_1}, fixed besides the quantum numbers n_{ϕ_2} and n_{r_2} of the final state, and if we then vary the other n_r, we obtain for every definite value of n_{ϕ_1} a definite series. In this way we obtain a system of series for different n_{ϕ_1}'s.

An important property may be predicted from this function (1). For great values of n_ϕ—great values of n_ϕ denote great sectional areas and hence great average distances from the nucleus—this function transforms into the corresponding Balmer function. We can see that for a sufficiently great n_ϕ,

$$\operatorname{Lim} f(n_\phi, n_r) = \frac{R}{(n_\phi + n_r)^2} \quad . \quad . \quad . \quad (2)$$

A more detailed investigation by the author which will be described in § 4 has given rise to the following expressions for the function $f(n_\phi, n_r)$ * which represent different degrees of approximation.

* Münch. Akad., 1916, p. 131 : Zur Quantentheorie der Spektrallinien, Ergänzungen und Erweiterungen.

(*a*) To a first approximation the atomic field is to be regarded as Coulombian (see above). Its potential energy with respect to the external electron is

$$\mathrm{E}_{pot} = -\frac{e^2}{r}.$$

Corresponding to it we have, as in the case of hydrogen,

$$f(n_\phi, n_r) = \frac{\mathrm{R}}{(n_\phi + n_r)^2} \quad . \quad . \quad . \quad . \quad (3a)$$

(*b*) To a second approximation let the potential energy be represented by

$$\mathrm{E}_{pot} = -\frac{e^2}{r}\left(1 + \frac{c_1}{r}\right).$$

The corresponding value of f becomes

$$f(n_\phi, n_r) = \frac{\mathrm{R}}{(n_\phi + n_r + q)^2} \quad . \quad . \quad . \quad (3b)$$

The quantity q here introduced depends on the constant c_1 of the atomic field, and also on the azimuthal quantum number n_ϕ, but is independent of the radial quantum number n_r. As n_ϕ increases q vanishes in accordance with eqn. (2). R has the same significance as in eqn. (3*a*).

(*c*) To a third approximation the potential energy of the atomic field is represented by means of two constants c_1 and c_2 by

$$\mathrm{E}_{pot} = -\frac{e^2}{r}\left(1 + \frac{c_1}{r} + \frac{c_2}{r^2}\right).$$

This leads to the same form as the expression (3*b*) given as a second approximation. We immediately pass on to

$$\mathrm{E}_{pot} = -\frac{e^2}{r}\left(1 + \frac{c_1}{r} + \frac{c_2}{r^2} + \frac{c_3}{r^3}\right).$$

Then we obtain as the value of f

$$f(n_\phi, n_r) = \frac{\mathrm{R}}{[(n_\phi + n_r + q + \kappa f(n_\phi, n_r)]^2} \quad . \quad . \quad (3c)$$

The same applies to κ as was said just above of q: κ, besides depending on the constants of the atomic field, depends only on n_ϕ and not on n_r and it vanishes for $n_\phi = \infty$.

Hence we obtain as the series term, if we now denote the principal

quantum number $n_\phi + n_r$ by n, to a first, second and third degree of approximation :

$$(n, o) = \frac{R}{n^2} \quad . \quad . \quad . \quad . \quad \text{Balmer.} \quad (4a)$$

$$(n, q) = \frac{R}{(n+q)^2} \quad . \quad . \quad . \quad \text{Rydberg.} \quad (4b)$$

$$(n, q, \kappa) = \frac{R}{[n + q + \kappa(n, q, \kappa)]^2} \quad . \quad \text{Ritz.*} \quad (4c)$$

These three forms of the series term are the same as those which the experimental investigation of series brought to light as the first, second and third stage of development corresponding to the increasing refinement of the methods used. The first form is Balmer's. The second was used by Rydberg in his first attempt to unravel line spectra. The third form was proposed by Ritz and was tested on a whole group of series. The method (n, q, κ) of denoting terms is also due to Ritz. In this last form the term is not expressed explicitly but implicitly since the term also occurs in the denominator of the expression, although only as a correction term attached to the small factor κ.

There can now be no doubt as to how we are to arrange the Principal Series, Subordinate Series and so forth, alongside one another in our general scheme. This is done in the following fundamental Table 35 :

TABLE 35

Current Term of the Symbol	II N.S. *S*	H.S. *P*	I N.S. *D*	B.S. *F*	U.B.S. *G*	. . . *H* . . .
n_ϕ . .	1	2	3	4	5	6
l . . .	0	1	2	3	4	5
q . . .	s	p	d	f	g	h
κ . . .	σ	π	δ	ϕ	—	—

Thus we *ascribe successively increasing values to the azimuthal quantum number n_ϕ in the current or variable term (Laufterm) of the* II N.S., H.S., I N.S., B.S. *and so forth.* Below the value of n_ϕ we have written the values, which are all less by 1, of the wave-mechanical azimuthal quantum number l (cf. p. 115). The symbols for q, namely,

$$q = s, p, d, f \ . \ . \ .,$$

* W. M. Hicks prefers, in his extensive spectral researches, the following formula, which also involves two constants, in place of (4c) :

$$(n, q, \kappa) = \frac{R}{(n + q + \kappa/n)^2}.$$

Cf. *A Treatise on the Analysis of Spectra*, by W. M. Hicks, Cambridge, 1922.

call attention to and correspond with the symbols nS, nP, nD, nF . . . of the preceding section. In the sequel we shall agree to take these symbols as standing directly for the expressions (4*b*) or—in more accurate calculations—(4*c*). The symbols

$$\kappa = \sigma, \pi, \delta \ldots$$

agree with the notation which Ritz used in applying his formula.

We see a first confirmation if our allocation of n_ϕ to the various series terms in the manner in which, as we proceed from left to right, *the resemblance to hydrogen* (or hydrogen-like character) becomes more and more pronounced. In the term of the I N.S. the deviation from the hydrogen type is less than in the term of the principal series ; in the Bergmann term this deviation is already so small that it was possible originally to express this term immediately in the Balmer form. In the subsequent terms nG, nH, which we allow to correspond to the azimuthal quantum numbers $n_\phi = 5$, $n_\phi = 6$, this still occurs nowadays (cf. p. 366 below), that is these terms are usually written as

$$\mathrm{R}/n^2,\ n = 5, 6 \ldots$$

Thus here the limiting case considered in eqn. (2) has already been reached practically.

Particular comment is demanded by the S-term, $n_\phi = 1$, in which the resemblance to hydrogen is least. Even in the alkalies, where the conditions are simplest, the denominator of the term exceeds the integer n by about $\frac{1}{2}$, for example, 0·59 in Li, 0·65 in Na. It was therefore thought necessary formerly to combine the value $\frac{1}{2}$ with the current number n and to write the S-term in the following half-integral form :

$$(n + \tfrac{1}{2}, \mathrm{S}) = 1{\cdot}5\mathrm{S}\ ;\ 2{\cdot}5\mathrm{S}\ ;\ 3{\cdot}5\mathrm{S}$$

and so forth.

Nowadays we explain the particularly marked deviation of the S-term from the hydrogen type as being due to the penetration of the S-orbit into the atomic core (cf. § 4).

Whereas, according to our Table 35, the *azimuthal quantum* n_ϕ has a definite value for each series of terms, the *radial quantum* n_r is able to assume all values from 0 to ∞. Since $n = n_\phi + n_r$ the minimum value of n in every term is n_ϕ, that is, equal to 1 for the S-term, 2 for the P-term and so forth. We have expressed precisely this in our scheme of series terms on page 352. Hence the triangular shape of this scheme signifies a second confirmation of the interpretation of the series terms given in Table 35. We must also note here that the true *current number* is, properly speaking, not the quantum sum (principal quantum number) but the *radial quantum number* n_r, which is in reality the quantum number that can vary to an unlimited extent : $0 \leqq n_r \leqq \infty$. We add here, as will be shown in § 4, that the series

formula, whether in Rydberg's or Ritz's form, is really nothing else than the *radial quantum condition.*

The triangular scheme on page 352 suggests to us to inquire how the principal quantum number is to be rationally normalised, a question which can be solved only in relationship with the periodic system (cf. § 6). In § 6 we shall distinguish the rationally normalised principal quantum number n from the *conventionally normalised* current number n. Whereas we make the latter begin with 1 in the S-terms, 2 in the P-terms and so forth, the former will be normalised by numbers that are greater by some units. It may happen that of the orbital types formerly denoted by n_l (see p. 116) those with smaller values for n will already have been built into the interior of the atom as structural orbits and hence are no longer available on the outside of the atom for virtual spectroscopic orbits. We shall meet with numerous examples in § 6.

Hitherto our orbits have been restricted to the *neutral atom* and the arc spectrum emitted by it. Theory indicates a unique way of generalising the spectral formula so that it applies to the singly and multiply ionised atom and the *spark spectra* emitted by it. In place of R we have simply

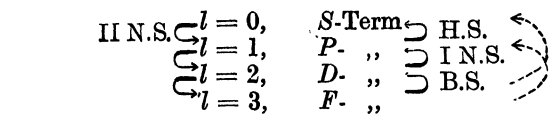
$$4\mathrm{R},\ 9\mathrm{R},\ 16\mathrm{R}\ \ldots \qquad (5)$$

in the spark spectra of the first, second, third . . . order, the values of the atomic constants q and κ being simultaneously altered. We know the simplest example of a spark spectrum of the first order, namely He^+ (p. 95); the simplest example of a spark spectrum of the second order is given by Li^{++} (p. 96).

In the next section we shall consider the conditions of excitation under which the individual series are produced. We shall there find *further confirmatory evidence* justifying our allocation of the azimuthal quantum number n_ϕ to the various series terms.

But we gain absolute certainty that this allocation is correct only if we adduce the selection principle (Chap. VI, § 1). According to this principle we must expect only those combinations of the S-, P-, D-, F-terms in which *the azimuthal quantum number differs by one unit,* $\Delta n_\phi = \pm 1$, or, what comes to the same thing, $\Delta l = \pm 1$.

Let us write down the rows of series terms in the order of increasing azimuthal quantum number l:



The arrows on the right-hand side of the terms denote those transitions from an initial to a final state in which the azimuthal quantum number decreases by 1 ($\Delta l = l_1 - l_2 = +1$), those on the left-hand

side denote transitions in which the quantum number increases by 1 ($\Delta l = l_1 - l_2 = -1$).

For example, the principal series arises from the transition shown at the top on the right-hand side, corresponding with its symbolic representation :

$$\nu = 1S - nP, \quad n = 2, 3, 4 \ldots .$$

The characteristic feature is the combination of the P-term ($l = 1$) with the S-term ($l = 0$). Our selection principle clearly allows the following series equally well :

$$\nu = 2S - nP, \quad \nu = 3S - nP \ldots$$

which correspond to the transition $1 \rightarrow 0$ for l. Their occurrence was discussed in eqn. (2) of the preceding section and again, particularly, in Fig. 92 in connection with helium.

The I Subordinate Series is characterised by the middle transition on the right-hand side, corresponding with the series formula,

$$\nu = 2P - nD, \quad n = 3, 4, 5. \ldots$$

The essential feature here is the combination of the P-term with the D-term ($l = 1$ with $l = 2$) ; instead of 2P we might also have 3P, 4P, according to our selection principle. Such transitions have actually been observed, although less often than the lines of the I Subordinate Series in the narrower sense.

The lowest arrow on the right-hand side leads to the following symbolic representation of the Bergmann series :

$$\nu = 3D - nF, \quad n = 4, 5, 6 \ldots$$

or of the Bergmann series of higher order :

$$\nu = 4D - nF, \quad n = 4, 5, 6, 7 \ldots .$$

The ultra-Bergmann term with their combinations

$$4F - nG, \quad 5G - nH$$

would follow below on the right-hand side of our scheme. According to Paschen and Götze they occur in all alkalies, in He and so forth, and are written, on account of their hydrogen-like character,

$$4F - R/5^2, \quad R/5^2 - R/6^2.$$

Whereas the series $4F - nG$ lie ordinarily in the infra-red region and hence mostly escape observation, they are displaced in the case of spark spectra, owing to the increase in the value of the Rydberg constant, cf. (5), into the visible region. Fowler * discovered a series rich in lines, of this type in the spark spectrum of Mg but described it

* Phil. Trans. R. Soc., **214A**, 225 (1914). On p. 121 of Fowler's report the interpretation $4f - mf$ is retained but is marked with a sign of interrogation.

contrary to the selection principle, as $4F - nF$. This interpretation is possible as an approximation only because the terms nG differ only very slightly from nF (and both are of the Balmer type). Nevertheless Fowler finds himself compelled to speak of " inaccurate combinations " between nF and $4F$. The correct interpretation $4F - nG$ was found by Roschdestwensky ; * this disposes of the contradiction to the selection principle and the combination principle.

Further examples of ultra-Bergmann series are given by the spark spectra of higher order (Al^{++}, Si^{+++}), which were first investigated by Paschen and Fowler, and later, also by other experimenters (cf. § 8).

We next consider the left-hand side of our scheme. The uppermost arrow belongs to the II Subordinate Series. Its symbolic representation is

$$\nu = 2P - nS, \quad n = 2, 3, 4. \ . \ . \ .$$

When n is differently normalised (cf. p. 365 and § 6) we may again write 3P, 4P . . . in place of 2P.

The two lower arrows on the left-hand side lead to series which have been observed, for example, in the calcium singlet series as particularly intense lines ; they are of the form of eqn. (3) in § 1.

Summarising we may say : *those combinations which the selection principle allows lead to the commonest and strongest series* (Principal Series, I and II Subordinate Series, Bergmann Series). We may regard this discovery as a further confirmation of the *allocation of the various series terms to the azimuthal quantum number.*

But there are also exceptions to the selection principle, both some in which the azimuthal quantum number remains unchanged ($\Delta l = 0$), and others in which it changes by more than one unit, for example, $\Delta l = 2$. J. Stark † and his co-workers have shown in the case of neutral helium that series of this kind are invisible under ordinary discharge conditions and are produced only by applying intense electric fields.

The series in question are :

$$\begin{cases} \nu = 2P - nP \ . \ . \ . \ n = 3, 4, 5 \\ \nu = 2S - nD \ . \ . \ . \ n = 3, 4, 5 \\ \nu = 2S - nS \ . \ . \ . \ n = 3, 4, 5. \end{cases}$$

They have been shown to occur in parhelium and orthohelium. The first of these series was called the III Subordinate Series by Lenard,

* Verhandl. des optischen Instituts in Petersburg, No. 8, Berlin, 1921.

† J. Stark, Neue im elektrischen Felde erscheinende Hauptserien des Heliums. G. Liebert, Der Effekt des elektrischen Feldes auf ultraviolette Linien des Heliums. G. Liebert, Eine neue Heliumserie unter der Wirkung des elektrischen Feldes. O. Hardtke, Über die Bedingungen für die Emission der Spektren des Stickstoffs, Ann. d. Phys., **56**, 577, 589, 610, 633 (1918). Further, J. Stark, Ann. d. Phys., **48**, 210 (1915); J. Koch, *ibid.*, **48**, 98 (1915).

who first observed them in the alkalies. The first and the third of the above series are examples of the transition $\Delta l = 0$, the second of the transition $\Delta l = 2$. In our scheme on page 365 the series belonging to the transition $D \rightarrow S$ has been represented by the dotted arrow shown above on the right. Isolated lines of this series have also been observed occasionally in other elements, for example, in all the alkalies. Foote, Meggers and Mohler * have even found that when the current density is very great the line 1S — 3D surpasses all the other lines in intensity in the spectrum of Na and K. It is very remarkable that S. Datta † obtained the same line in absorption in the case of K (cold vapour). These and other ‡ experimental results appear to show that the combinations 1S — 3D and so forth occur in the alkalies without its being necessary to make an electrical perturbation caused by an external field or neighbouring atoms responsible for the transgression of the selection rule. Moreover, there are combinations between the F- and the P-term which have been variously measured and which also contradict the selection rule; in our scheme on page 365 they are indicated by the lower dotted arrow. In Cs combinations between 3D and the terms nG have been found,|| but they have certainly been caused only under abnormal conditions of emission (electric fields). Finally we must mention that transgressions of the selection principle (transitions with $\Delta l = 2, 3, 4$, and so forth) occur in external electric fields at smaller field-strengths the greater the current number of the combinations in the series.¶ This is, in fact, to be expected from the qualitative considerations in Chapter VI, § 1 (at the end): the greater the current number, the more intense is the action of the electric field and hence the selection rules are transgressed at correspondingly weaker field-strengths.

In Chapter VI, § 1, we deduced the selection principle specially for field-free emission, but we showed at the same time that it is put out of action by strong electric fields. This case has been shown to occur in the experiments of Stark, Foote-Meggers-Mohler, Meissner, Hansen-Takamine-Werner and Schüler as well as in the researches on the Stark effect. In the combinations 1S — 3D and so forth in the alkalies we are probably dealing with *quadrupole radiations*.** Our discussion of the correspondence principle in Chapter VI and Note 7 depends on the assumption of a *dipole moment* for the atom; we

* Astrophys. Journ., **55**, 145 (1922); cf. also Foote and Mohler (reference on p. 129).

† Proc. Roy. Soc., **99**, 69 (1921); **101**, 539 (1922).

‡ Cf. G. M. Shrum, N. M. Carter and H. W. Fowler, Phil. Mag., **3**, 27 (1927).

|| K. W. Meissner, Ann. d. Phys., **65**, 378 (1921).

¶ H. M. Hansen, T. Takamine and S. Werner, Danske Vidensk. Selsk. V. 3, (Observations in Hg); H. Schüler, Zeits. f. Physik, **35**, 336 (1925) (Observations in Zn).

** This has been made very probable in the meantime by the results of investigations on the transverse Zeeman effect (E. Segrè, Zeits. f. Physik, **66**, 827 (1930)). Cf. also Ittmann and Brinkman, Naturwiss., **19**, 292 (1931).

disregarded higher moments in the charge distribution of the atom. If we take them into consideration we obtain for the polarisation and selection rules of those lines that correspond to these higher moments other results than those for dipole radiation ; in particular, we obtain for the first quadrupole radiation to be expected the selection rule $\Delta l = 0, \pm 1, \pm 2$. The possible transition $\Delta l = +2$ corresponds exactly to the case of our lines 1S — 3D. These selection rules have been proved to hold in wave-mechanics by A. Rubinowicz.*

The selection principle gives precision to the combination principle, restricting its unlimited range and increasing its practical value. Ritz's formulation of the combination principle : *every series term may be combined with every other term to form a spectral line* is now expressed in the improved form : *every series term may normally be combined with every other series term whose azimuthal quantum number differs from the first by unity ; combinations which contradict this restriction are not excluded in principle but require special conditions of excitation or have the character of quadrupole radiation.*

We closed the preceding chapter with a representation of the series scheme of helium ; we shall close the present section with the series scheme of the alkalies, which is particularly clear and typical. The terms are again represented as energy-levels, corresponding to their proper physical definition ; the ratios of the magnitudes correspond to sodium. The steps on the extreme left belong to the S-terms, those adjacent to them on the right belong to the P-terms, the next to the D-terms and so forth. The numbers (1, 2, 3, . . .) on the left attached to each succession of steps denote the current numbers ; for example, the sequence 3 comprises the terms 3S, 3P, 3D. (This conventional current number is different in the S-term and the P-term from the rational principal quantum number n, normalised according to the periodic system, cf. § 6.) In agreement with the actual behaviour of the terms the lengths of the steps (between one level and the next) decreases as we proceed upwards and vanishes entirely at ∞, which corresponds to the zero level of the energy, namely, when the reference electron (*Aufelektron*) is at an infinite distance from the atom. The transitions from one level to a lower level are characterised by arrows and represent the lines of the H.S., I N.S., and so forth. We have denoted not only 1S — nP but also 2S — nP as H.S. The D-line is represented by the arrow 1S — 2P on the left-hand side below. It was not possible to represent the double character of the P-level in the figure, so that the two components D_1 and D_2 are shown by the same arrow. In contrast with Fig. 92 we find that in the alkalies the ground-state 1S is easily accessible optically (cf. the end of the preceding section). The lines of the H.S., namely 1S — nP, among them the D-lines above all, appear in cold Na-vapour as strong

* A. Rubinowicz, Zeits. f. Physik, **65**, 662 (1930).

absorption lines ; the same applies generally to the alkalies and the noble metals. The selection principle manifests itself in Fig. 93 in that all the arrows connect only two such levels as are adjacent in the sequence S, P, D, F.

Finally we remark that the discussion in this section is based on a perfectly definite model of the atom, namely, that of an atomic core around which an outer " radiating electron " (*Leuchtelektron*) is revolving. The quantum numbers n, n_r, l of this electron are at the same time to characterise the whole atomic state. We make this assumption when we write down the series formulæ on pages 362 *et seq.* This

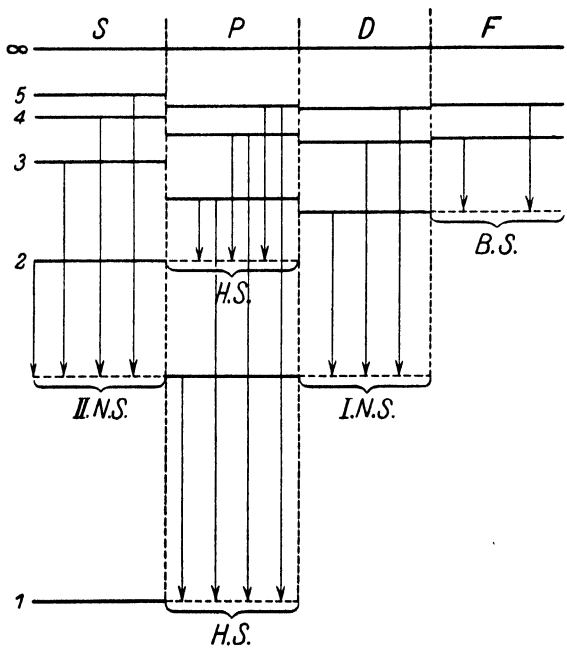


FIG. 93.—Scheme of levels of an alkali spectrum (Na). The numbers on the left denote current numbers.

signifies that the quantum numbers which must be ascribed to the individual electrons of the atomic core do not enter into the formula for the series. According to Pauli's Principle this is always the case when the atomic core forms a closed shell (alkalies, Cu, Ag, Au, Tl, and so forth) ; cf. Chapter VIII, § 3. Furthermore, we shall see in Chapter VIII that even when the atomic core consists of a closed shell and an s-electron, the quantum numbers n, l of the radiating electron at the same time determine those of the whole atom. The alkaline earths and also Zn, Cd, Hg have an electronic configuration of this type. All these spectra are constructed relatively simply ;

they have doublet, singlet or triplet characters and exhibit well-developed series. But if the quantum numbers of the core also play a part, the more complicated types of spectra arise, which we shall discuss later in Chapter VIII.

§ 3. Testing the Series Scheme by the Method of Electronic Impact

The most direct test of Bohr's ideas, the one that is most free of theoretical elements, is the method of electronic impact.* It was initiated by Franck and Hertz † in 1913 and has since been elaborated by many other investigators.

The decisive discovery by Franck and Hertz consisted in the following observations. If electrons that escape from a glowing wire are accelerated by means of a finely regulated accelerating potential and are sent through mercury vapour at a low pressure, then at a potential difference of 4·9 volts the Hg-line $\lambda = 2537$ is found to be radiated. Franck and Hertz were able to show that the associated $h\nu$ corresponds exactly to the energy of 4·9 volts, in the sense of eqn. (1*a*) given below.

Lenard ‡ must be mentioned as the predecessor of Franck and Hertz in the production and measurement of slow electronic velocities. The rather qualitative observations of Gehrcke and Seeliger || (alteration of the average colouring of the luminescence of gases as the velocity of the exciting cathode rays is varied) also preceded the decisive experiments of Franck and Hertz.

Franck and Hertz had as their immediate successors McLennan ¶ and his collaborators who used similar methods in studying the atoms analogous to Hg, namely, Cd, Zn, Mg, Ca, Sr, Ba, and so forth, and the luminescence caused in them by electronic collisions. In all cases one definite line first appeared, the so-called "resonance line" (see below), which plays a similar part to $\lambda = 2537$Å. in the case of mercury; these resonance lines appeared at a well-defined voltage, the "resonance voltage." When the accelerating voltage on the colliding electrons was gradually increased up to a certain limiting value the complete spectrum of the atom was finally observed. This second limit of the accelerating potential corresponds to the ionisation of the atom and is called the "ionisation potential" (see below). Hence the (rough) optical observation of the process of excitation thus distinguishes three different stages: no emission below

* Comprehensive reports are given in: J. Franck and P. Jordan, Anregung von Quantensprüngen durch Stösse, Handbuch der Physik (Geiger-Scheel), Vol. 23, 641, Springer, 1926. This report has also been reprinted separately in Vol. 3 of the collection "Struktur der Materie," Springer. There is a somewhat older but good account by Foote and Mohler, *The Origin of Spectra*, New York, 1922.

† Verh. d. Deutsch. Physik. Gesells., **15**, 34, 373, 613, 929; **16**, 12, 457, 512 (1914); **18**, 213 (1916).

‡ Heidelberger Akad. Abh., Nr. 34 (1911); Nr. 17 (1914).

|| Verh. d. D. Phys. Ges., **14**, 335 (1912).

¶ For example, McLennan and Henderson, Proc. Roy. Soc., **91**, 485 (1915).

the resonance potential, a "single-line spectrum" when the first stage has been passed, and a multi-line spectrum when the ionisation potential has been exceeded.

This division into three stages is not essential; between the single-line spectrum and the complete series of lines there are transition stages. It is possible to choose the conditions so that at intermediate potentials more than one line but not the whole series spectrum is excited. G. Hertz * succeeded, for example, in exciting besides the resonance line any desired additional portion of the series spectrum; in Hg he successfully excited all the lines of lower excitation voltages than 8 volts but none of higher.

Another direct follower in the field opened up by the original experiments of Franck and Hertz on mercury vapour was Rau.† He found, particularly in the case of the lines of neutral He, that to excite successive members the excitation voltage had to be increased from line to line. This furnishes a quite general and decisive confirmation of Bohr's series scheme: *the higher members of a series require higher energy-levels, and hence higher excitation voltages become necessary.* At the same time, this is a general refutation of all the older theories of series that regarded the higher members as, in some sense, overtones of the lower members, and that sought to find a mechanical connexion between their emission and that of the lower ones. While this fact holds within one and the same series, another circumstance is of no less importance for us; it is concerned with a comparison of the excitation voltages of lines of different series: *the requisite excitation voltages increase in the sequence* H.S., I N.S., and, as we may with reason add, B.S. The H.S. appears first, that is at the smallest excitation; the first subordinate series, second subordinate series, and so forth then follow. This agrees fully with the views put forward in the preceding section. Actually, the most important factor for the excitation of a series is the realisation of the initial orbits that correspond to the *second* series term. This is the P-term in the case of principal series, the D-term in the first subordinate series, and the B-term in the Bergmann series. According as the realisation of these initial orbits require smaller or greater amounts of energy, the series may be excited with less or with greater ease.

From the *optical* methods in which the result of the excitation is observed in a spectroscope or spectrograph we now come to the *purely electrical* methods in which not only the excitation but also the observation of the excitation effect is made by electrical methods.

The first decisive researches by Franck and Hertz were concerned with the question of the elastic collisions between electrons on the one hand and gaseous atoms or molecules on the other hand. The electrons that escape from the hot wire are accelerated by a potential

* Zeits. f. Physik, **22**, 18 (1924).
† Würzburger phys. med. Gesellschaft., 1914, p. 20.

and traverse the gas under examination, being finally received on an electrode ; the current represented by them is measured by means of a galvanometer or electrometer. In the case of the inert gases and the electro-positive metallic vapours the galvanometer at first indicates, when the potential is gradually raised in the gas chamber, a gradual increase of the current passing to earth, but then a sharp limit occurs, which marks the first occurrence of inelastic collisions, that is, of collisions that are accompanied by loss of energy and that entail a change of constitution in the structure of the atom or molecule struck. This first maximum in the potential-current curve is followed by other maxima or kinks, which occur at regular intervals, showing that the electrons, after having lost their velocities in a first inelastic encounter have for a second or third time, owing to their further passage through the potential drop, attained a velocity that once again permits them to lose their energy in inelastic collisions. The distance between such successive bends of the curve measures in volts the energy that was transferred to the atom during the inelastic collision, that is, determines a characteristic constant of the atom struck. The efficiency of the collisions is very small ; even in the most favourable circumstances, in the immediate vicinity of a maximum of the current-potential curve, it amounts to only 1 per cent. ; that is, of all the electrons that collide only one in every hundred transfers its energy to the atom with which it collides.*

Besides equating the energies in a collision we must also equate the momenta before and after. Joos and Kulenkampff † show that the latter equation lowers the value of the excitation limit as compared with that obtained by taking the energy only into account in the ratio m/μ, where m denotes the mass of the impinging particle and μ the " resultant mass " [cf. p. 91, eqn. (3)] of the impinging particle and that with which it collides. In the case of electronic collisions for which μ is nearly equal to m the correction becomes inappreciable ; in the case of ionic collisions it leads to an increase of the excitation limit of the order of magnitude 2.

The occurrence of inelastic collisions in which particular events occur is no more remarkable than elastic collisions in which nothing particular occurs. Whereas the inelastic collisions denote a discontinuous transition from one quantum state to another, the elastic collisions show that the atom persists in its quantum state and is not capable, as in mechanics, of a continuous change of energy ‡ so far as

* Herthor Sponer, Zeits. f. Physik, **7**, 185 (1921).

† Phys. Zeits., **25**, 257 (1924).

‡ Of course the atom *as a whole* takes up a very small amount of translation energy in collisions ; the atom with its electrons here behave like the " elastic spheres " of the gas theory. See in this connexion J. S. Townsend, Proc. Roy. Soc., **120**, 519-522, 1928, Phil. Mag., **61**, 1150, 1930, and V. A. Bailey, Zeits. f. Physik, **68**, 834, 1931. For other results (Ramsauer-Townsend effect) which arise from the study of elastic collisions of electrons with gas atoms or molecules, see H. L. Brose and E. H. Saayman, Ann. d. Phys., **5**, pp. 797-852, 1930, where numerous references are given.

its inner configuration is concerned. Hence we have either *no* change of energy or a discontinuous change of finite amount, corresponding to the general character of the quantum processes.

The original method was later elaborated in manifold ways. Instead of allowing the electrons to acquire their velocities whilst incurring many elastic encounters with gas molecules, it is preferable for many purposes to accelerate them along a distance that is less than their mean free path (that is, to use a low pressure and a short distance between the cathode and the grid which acts as the positive potential). The electrons that have been endowed with the desired velocity in this way are then allowed to enter into the actual collision chamber, which is essentially free of fields, and the size of which is made large and offers opportunity for a sufficient number of collisions with the gas particles under examination. Finally, the electrons are completely debarred from making all further progress, owing to the agency of a stronger opposing field. Thus they do not reach the measuring electrode connected with the galvanometer at all. Rather, what are measured by the galvanometer are the positive ions that are formed, whether directly or indirectly, by the primary electrons during the inelastic collisions. Positive ions are produced *directly* if the velocity of the electrons is sufficient to *ionise* the atoms struck. They are produced *indirectly* if the transferred energy, although not able to eject an electron right out of the atomic configuration, yet suffices to raise one of the electrons belonging to the atom out of its natural orbit into one that is richer in energy. When the electron belonging to the atom returns from this new orbit to one that is poorer in energy (nearer the nucleus), it emits light ; in atoms that are more easily ionisable, which belong to the collecting electrode or which, under certain circumstances, are mixed as impurities with the gas under examination, this light acts photo-electrically and thus also produces positive charges that make themselves observed in the current which flows through the galvanometer.

To discriminate between these two effects, namely, the direct ionisation effect and the indirect photo-electric effect, was a matter of great experimental importance. Bohr * was the first to call attention to the possibility of this indirect effect and showed numerically that it probably occurred in Franck and Hertz's deduction of the values 4·9 volts for Hg and 20·5 volts for He. Davis and Goucher † succeeded in carrying out experimentally the unambiguous differentiation between the original ionisation and the photo-electric effect by means of an ingenious arrangement and connexion of fields for the case of Hg, and fully confirmed Bohr's point of view. We cannot here enter into the details of the method and of the manifold improvements which

* Phil. Mag., **30,** 394 (1915), § 3 ; Gesammelte Abhandlungen, p. 117 (also in English in his collected papers).

† Phys. Rev., **10,** 101 (1917) ; **13,** 1 (1919).

have been made to it in the sequel, but must refer the reader to the reports quoted at the beginning of the chapter. There, too, will be found the interesting and much-varied forms of the current-voltage curves and their discontinuities.

Before passing on to the proper quantitative results of the method of electronic collisions, we wish to give the transformation formula which, by means of the $h\nu$-relation, leads us from the wave-length λ of a spectral line to the voltage necessary to excite it. It is clearly

$$h \cdot c/\lambda = e \cdot V.$$

If we here express V in volts, that is, set $V \cdot 10^8$ in place of the potential difference V initially considered measured in electromagnetic C.G.S. units, and if, further, we use for e the value $1{\cdot}59 \cdot 10^{-20}$ (that is, electromagnetic C.G.S. units), and measure λ, instead of in cms., in terms of $\mu\mu = 10^{-7}$ cms., we get

$$V \text{ (volts)} \times \lambda(\mu\mu) = \frac{h \cdot c}{e} \cdot 10^{-1} = 1234 \quad . \quad . \quad (1)$$

Ladenburg * has called attention to the particular convenience of using this formula.

For example, if we calculate the excitation potential corresponding to the Hg-line $\lambda = 2537$ Å. $= 253{\cdot}7\mu\mu$, and to the D-line of Na, $\lambda = 5890$ Å. $= 589{\cdot}0\mu\mu$, we get by (1), respectively,

$$V = \frac{1234}{253{\cdot}7} = 4{\cdot}9 \text{ volts, and } V = \frac{1234}{589{\cdot}0} = 2{\cdot}1 \text{ volts} \quad . \quad (1a)$$

We may also use in place of (1) the equivalent relation (as is often done in English books)

$$V \text{ (volts)} \times \lambda \text{ (Ångstrom)} = 12345 \quad . \quad . \quad (1b)$$

Let us now calculate the excitation potentials that correspond to the series limits to which these two series belong. The series limits are given as limits of term values in cm.$^{-1}$. Since

$$\nu = \frac{1}{\lambda(\text{cm.})} = \frac{10^7}{\lambda(\mu\mu)} = \frac{10^8}{\lambda(\text{Å.})}$$

it follows from (1) that

$$V \text{ (volts)} = 12345 \cdot 10^{-8} \nu \quad . \quad . \quad . \quad . \quad (2)$$

From the spectroscopic tables we see that the limit of series to which (see below) the Hg-line 2537 Å. belongs, $\nu = 84181$ cm.$^{-1}$, and that of the principal series (H.S.) of sodium, $\nu = 41449$. Hence we get from (2)

$$\left.\begin{aligned} V &= 12345 \cdot 10^{-8} \cdot 84181 = 10{\cdot}39 \text{ volts} \\ \text{and} \quad V &= 12345 \cdot 10^{-8} \cdot 41449 = 5{\cdot}11 \text{ volts} \end{aligned}\right\} \quad . \quad . \quad (2a)$$

for the mercury and the sodium line respectively.

* Zeits. f. Electrochemie, 1920, p. 265.

We call the last two potentials the **ionisation potentials** of the initially neutral Hg- or Na-atom. For, just as the series limit is a measure of the energy that is liberated when the electron makes a transition from infinity, so the corresponding potential in volts is a measure of the energy that must be used up to remove the electron to infinity. We assume that the final orbit of the spectral process (the initial orbit of the ionisation process) is actually the ground orbit of the neutral atom. For example, in the case of neutral He, we should certainly not, from the conditions represented in Fig. 92, calculate its ionisation voltage from the limit of the visible principal series, as in this case the final orbit of the principal series (called 2*s* and 2S, respectively, by us) lies far above the ground orbit. in the energy scale.

But we use for the two numbers in volts calculated in (1*a*) the term **resonance potential,** which we interpret as meaning the following: If the work done in the electronic collision does not, indeed, suffice to bring about ionisation, it may yet suffice to lift an electron out of its ground orbit into the ("energetically") next highest orbit. Let the ground-state be 1S and the next higher level be 2P, as in the case of the Na-atom (Fig. 93). The atom that has been excited in this way will, if left to itself, tend to return to the stable configuration of the ground orbit, thus causing the emission of monochromatic light. For, according to the principle of selection, the transition $2P \rightarrow 1S$ will be possible for it, and it is the *only* way in which the excited atom can revert to its unexcited state. In this process the *whole* energy V that is given to the atom by the colliding electron will be emitted as monochromatic radiation of wave-length λ equivalent, by eqn. (1), to V. This re-emission of the whole transferred energy is called resonance (linking up with the old views of the theory of vibrations); hence we get the expressions **resonance line** and **resonance potential.** The conception of resonance line thus implies two things: first, that its final orbit is the ground orbit of the atom, and second, that its initial orbit is the (energetically) next highest orbit from which the return to the ground orbit, and only to this, is possible, being accompanied by the emission of monochromatic light.

In the case of the hydrogen atom our theoretical knowledge of the ionisation potential or the resonance potential harmonises perfectly with the views developed in the present volume; in this case it is possible to obtain values from eqn. (2) without having recourse to experimental data.

In the case of hydrogen the ionisation potential is determined by the limit of the Lyman series, that is, by Rydberg's number R. By eqn. (2*a*) we therefore get in volts

$$V = 12345 \cdot 10^{-8} \cdot 10968 = 13{\cdot}53 \text{ volts} \quad . \quad . \quad (3)$$

In ergs it is given by the equivalent formula:

$$hc\nu = h \cdot cR = 2{\cdot}15 \cdot 10^{-11} \text{ erg} \quad . \quad . \quad . \quad (3a)$$

where ν denotes as in (2) the wave-number and hence $c\nu$ is the corresponding frequency.

We pass on from (3) to the excitation potentials (*Anregungsspannungen*) of the Lyman and the Balmer lines. For the first line of the Lyman series (cf. p. 74)

$$\nu = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right), \quad \lambda = 1215{\cdot}7\text{Å}.$$

we get, since its wave-number amounts to $\frac{3}{4}$ of that of the series limit, $\frac{3}{4}$ of the ionisation potential, thus

$$V = \tfrac{3}{4} \,.\, 13{\cdot}53 = 10{\cdot}15 \text{ volts} \quad . \quad . \quad . \quad (3b)$$

But for the first line of the Balmer series we do not get, as its ν-value might lead us to think, 5/36 of the ionisation potential, but rather, it must be noted, that when the atom is in its natural state, that is in its ground orbit, the electron must first be raised from its ground orbit into the 2-quantum orbit and *then* into the 3-quantum initial orbit of the line H_α. In this way the excitation potential for H_α comes out equal to that of the second line of the Lyman series, that of H_β equal to the third Lyman line, and so forth. Thus we get

$$\text{for } H_\alpha \ldots \nu = \tfrac{8}{9} \,.\, 13{\cdot}53 = 12{\cdot}03$$
$$\text{for } H_\beta \ldots \nu = \tfrac{15}{16} \,.\, 13{\cdot}53 = 12{\cdot}68, \text{ etc.}$$

Our calculations have so far been made with the H-atom. If we start with the H_2-molecule instead, we have first to split the molecule into H-atoms by supplying the energy necessary for dissociation. The most exact value for this quantity follows—somewhat indirectly from the analysis of the band-spectrum of the H_2-molecule. According to Dieke and Hopfield * it amounts to

$$D = 4{\cdot}4 \pm 0{\cdot}1 \text{ volts} \quad . \quad . \quad . \quad . \quad (4)$$

This dissociation potential cannot be checked by experiments involving electron collisions. For no kink is observed in the current-potential curves for H_2-gas at the point $V = 4{\cdot}4$ volts. Rather, dissociation occurs in electron collisions always in conjunction with the excitation of at least one of the two atoms released in the process of dissociation. We shall show in connexion with the theory of band spectra (Chap. IX, § 5) why no precise and unambiguous results are obtained in electron collision experiments with H_2 and, indeed, molecules generally, in contrast with those performed with atoms. We shall add here the principal data for the H_2-molecule :

Ionisation potential $H_2 \rightarrow H_2^+ +$ electron . . 15·34 volts.
Excitation potential as far as the initial state of the emission bands ($\lambda \sim 1050$Å.) . . . . at 11 volts.

* Zeits. f. Physik, **40**, 299 (1927). Almost the same result was obtained by E. E. Witmer, Phys. Rev., **28**, 1223 (1926), and—by thermal means—Isnardi, Zeits. f. Electrochemie, **21**, 405 (1915).

From the H-atom and H-molecule we now pass on to the hydrogen-like He^+-atom. Here we must first get to know the energy of formation of He^+ from the He-atom experimentally if we wish to draw conclusions based on the hydrogen-like character of He^+. This energy of formation (*Bildungswärme*) or the ionisation potential of the neutral He-atom which is proportional to it will be denoted by I. As we have indicated in Fig. 92 (arrow furthest to the left), I = 24·5 volts. We may now write down, for example, the second order ionisation potential of He. It is

$$I + 4 \cdot 13{\cdot}5 = 78{\cdot}5 \text{ volts} \quad . \quad . \quad . \quad (5)$$

Actually, to deprive the hydrogen-like atom He^+ of its electron, we require work four times as great as in the case of the H-atom. As shown by the formula, this follows at once from the factor Z^2 in the He-series ; in more pictorial language, we may say that one factor 2 arises out of the doubled nuclear charge of He^+ as compared with H, and the other factor 2 from the halved distance of the electron from the nucleus as compared with that in the case of H. In the curves given by the observations of Franck and Knipping,* as well as in those of F. Horton,† an ionisation step occurs of the value given above, which clearly corresponds to the tearing off of *both* electrons of the He-atom in *one* elementary act. Formula (5) gives, at the same time, the total energy − W of the neutral helium atom.

We pass on to calculate the excitation potential of the line

$$\nu = 4R\left(\frac{1}{3^2} - \frac{1}{4^2}\right), \quad \lambda = 4686\text{Å}.$$

For this the electrons of the He^+-ion must be removed not to infinity but only as far as the 4-quantum orbit, the initial orbit of 4686. The work necessary for this is

$$4Rch\left(1 - \frac{1}{4^2}\right) = \frac{15}{16} \cdot 4 \cdot 13{\cdot}5 = 50{\cdot}1 \text{ volts}.$$

Thus if we start from the neutral state of the He-atom the excitation voltage of 4686 comes out as

$$I + 50{\cdot}1 = 74{\cdot}6 \text{ volts} \quad . \quad . \quad . \quad (5a)$$

Actually, this line occurred in the experiments of Rau mentioned above at potentials lying between 75 and 80 volts, in that at 75 volts no trace of the line appeared but at 80 volts it was present with full intensity.

We now consider neutral helium. In this case it was necessary first to establish the ground-level 1S in Fig. 92 by the method of electronic collisions. (As on p. 358 we use the capital letters in referring to " parhelium " and the small letters for " orthohelium.") A positive

* Phys. Zeitschr., **20**, 481 (1919). † Proc. Roy. Soc., **95**, 408 (1920).

result was obtained by Franck and Knipping * who detected the first inelastic collision at 19·75 volts. If we subtract this from I = 24·5, we have 4·75. If, on the other hand, we transform the limit of the H.S. of orthohelium, $\nu = 38453$, into volts by eqn. (2), we obtain 4·75 volts again. Hence, using Fig. 92, *we conclude that the ground level* 1S *lies* 19·75 volts *below the final level* 2*s of the* H.S. *of orthohelium*, $\nu = 2s - np$.

The first inelastic collision at 19·75 volts is therefore to be interpreted as

$$19{\cdot}75 \text{ volts} = 1S - 2s.$$

Following Franck we call this the **transformation potential** (*Umwandlungsspannung*). The slightly higher step which is clearly distinguishable from 19·75 in the current-potential curves of Franck and Knipping is

$$20{\cdot}55 \text{ volts} = 1S - 2S.$$

The difference

$$20{\cdot}55 - 19{\cdot}75 = 0{\cdot}80 = 2s - 2S$$

corresponds exactly to the difference between the limits of the optical H.S. of orthohelium and parhelium.

To visualise these conditions we refer again to Fig. 92; on the right-hand side of the figure we see how the ionisation potential is formed from the transformation potential 19·75 and the H.S. limit of orthohelium, whereas on the left-hand side it is formed from the energy-level 20·55 and the H.S. limit of parhelium.

TABLE 36

Observed	Calculated †	Series Name	Wave-length
19·75	..	1S — 2*s*	..
10·55	20·55	1S — 2S	..
21·2	21·12	1S — 2P	584·4 Å
22·9	22·97	1S — 3P	537·1 ,,
..	23·62	1S — 4P	522·2 ,,
..	23·92	1S — 5P	515·7 ,,
24·6	24·5	1S	(502) ,,

The next steps may be read from Table 36, and have also been drawn in Fig. 92 on the left as dotted arrows. They correspond to the ultra-violet H.S. of parhelium that must at the same time be the

* Phys. Zeits., **20,** 481 (1919); Zeits. f. Physik, **1,** 320 (1920). The numerical values given in these papers have all been reduced by 0·75 volt to bring them into agreement with the wave-lengths of Lyman. Cf. J. Franck, Zeits. f. Physik, **11,** 155 (1922), where the reason for this correction is shown to be due to an error in calibration.

† Obtained by adding to 19·75 volts the amounts of energy that follow from the series scheme.

absorption series of unexcited He. The wave-lengths given in Table 36 have all been observed in a high vacuum spectrograph by Lyman,* except the extrapolated series-limit $\lambda = 502$.

The absence of the level $1s$ from the orthohelium levels (cf. p. 359) explains the distinctive position taken up in the series system of He by $2s$ (it is indicated in Fig. 92 by indicating the level $2s$ in heavier type). For, once this state has been excited, it cannot again be destroyed by monochromatic emission. It is therefore called the **metastable** state by Franck and Reiche.† The term " transformation potential " applied to the 19·75 volts points to the transformation from the stable state 1S to the metastable state $2s$. In this connexion the observation by Franck is interesting that the transformation $1S - 2s$ occurs only in impure He ; in perfectly pure samples of the gas the transformation potential $1S \rightarrow 2s$ vanishes entirely from the current-potential curve.

The level 2S is also metastable inasmuch as the transition $2S \rightarrow 1S$ which, from the energy view, is alone possible here is excluded by the principle of selection. Nevertheless the stability of 2S is much less than that of $2s$, because in the case of $2s$ there becomes added to the restrictions imposed by the *principle of selection* the evidently much more effective " partition " restriction (imposed by the fact that levels of ortho- and parahelium may not be combined).

Hence we interpret the difference in the stability of the $2s$- and the 2S-levels in the following way : From the initial state $2s$ the electron must first be raised to the limit of the orthohelium system in order to fall thence down the succession of steps of the parhelium system to the normal state 1S. If, however, the electron starts from the initial state 2S, it need only be raised to the state 2P in order to be able to pass spontaneously to 1S with the emission of energy. Consequently in our Fig. 92 the level $2s$ but not 2S has been printed in darker type and so made comparable with the ground-level 1S.

At the same time the particular position of $2s$ explains the character of the line $\lambda = 10830$Å. $\cong 1\mu$ as a " resonance line." From the initial state $2p$ the He-atom can pass over only to $2s$, whilst the transition to 2S or 1S is excluded owing to our central partition in Fig. 92. In this way the line $2s - 2p$ is different from the line $2S - 2P$, $\lambda = 20582 \cong 2\mu$. From the initial state 2P there is possible the transition to 2S as well as to 1S. Actually, according to an investigation by Paschen,‡ $\lambda = 2\mu$ exhibits incomplete resonance, but $\lambda = 1\mu$ complete resonance. This means that if helium gas receives radiation $\lambda = 1\mu$, it remits all the absorbed light as light of the same wave-length, whereas, if it receives radiation $\lambda = 2\mu$, it radiates out only a fraction of the absorbed light as light of the same wave-length. The fact that in each case a certain excitation of the He-gas was

* Astrophys. Journ., **60**, 1 (1924). † Zeitschr. f. Phys., **21**, 635 (1920).
‡ Ann. d. Physik, **45**, 625 (1914).

necessary to provoke absorption, is in accordance with the circumstance that neither 2*s* nor 2S is the ground orbit of the unexcited He.

The heavier inert gases neon and argon had already been investigated in the earliest papers by Franck and Hertz. Final values were only obtained after G. Hertz * had refined the method. The excitation potentials are then manifested not as kinks in the current-potential curve but as sharp maxima, since by using a differential method only those electrons are counted that have lost their velocity almost entirely as a result of the inelastic collision. The results are :

TABLE 37

	Excitation Potential	Ionisation Potential	
Ne	16·6 18·5	21·5	Referred to the helium transformation potential, 19·75 volts
Ar	11·55 13·0 13·9	15·3	

We now come to the metallic vapours, firstly to the alkalies which are distinguished by the simplicity of the scheme giving their series. The final orbit of the H.S. is here at the same time the ground orbit (cf. § 2, p. 369) ; the principal series therefore appears as an absorption series in the cold vapour. The first line of the H.S. (in the case of Na, this is the D-line) is at the same time a resonance line, and its excitation potential may straightway be calculated, by eqn. (1*a*), from its wave-length known from optical observations. The potential so determined leads to the first inelastic collision. In the same way the limit of the H.S. gives the ionisation potential by eqn. (2*a*).

How perfectly observation and calculation agree even quantitatively is shown in the following Table 38. In the column under " obs." (observed) the values of the resonance and ionisation potentials measured by the method of electronic collisions, and under " calc." (calculated) the values obtained for the same quantities from the optical data by eqns. (1) or (2), respectively, are given. The optical data themselves are tabulated under headings " resonance line " and " series limit." Whereas the limit 1S of the principal series is simple, the resonance line $1S - 2P_j$, $j = \frac{1}{2}, \frac{3}{2}$ (cf. p. 354), is double, but separated by so small an interval that it must appear simple in electronic collision. In passing we must note that the position of the series limit is given by numbers regularly decreasing as the atomic number increases. (In the resonance *line* that is compounded from the

* Zeits. f. Physik, **18**, 307 (1923) ; G. Hertz and R. K. Kloppers, *ibid.*, **31**, 463 (1925) ; G. Hertz, Naturwiss., **12**, 1211 (1924).

TABLE 38

	Resonance Potential in Volts		Resonance Line in Å.U. $1S - 2P_j$	Ionisation Potential in Volts		Series Limit in cm.$^{-1}$ $1S$	Observer
	Obs.	Calc.		Obs.	Calc.		
Li .	—	1·840	6708·2	—	5·368	43 484·45	—
Na .	2·12	2·093	5895·9	5·13	5·116	41 448·59	Tate and Foote, Phil. Mag., **36**, 75 (1918)
		2·094	5889·9				
K .	1·55	1·603	7699·1	4·1	4·321	35 005·88	Same as for Na
		1·610	7664·9				
Rb .	1·6	1·553	7947·6	4·1	4·159	33 684·80	Foote, Rognley and Mohler, Phys. Rev., **13**, 59 (1911)
		1·582	7800·2				
Cs .	1·48	1·380	8943·6	3·9	3·877	31 406·70	Same as for Rb
		1·448	8521·2				

difference of two terms this regularity (cf. Li) is a little obscured.) This and the correspondingly proportional decrease of the ionisation potential denotes at the same time a weakening of the electro-positive character of the alkalies as the atomic number increases.

The conditions are much more involved in the case of divalent metallic vapours. Here, as already mentioned (p. 357), there occur a series system of triplet lines and one of lines of a simple structure, which combine among themselves. We shall denote the former in the case of He by the symbols s, p_j, d_j, . . ., $j = 0, 1, 2$ and $1, 2, 3$, respectively. (The general systematic notation is ^3S, ^3P_j, ^3D_j for the triplet levels, and ^1S, ^1P, ^1D for the singlet levels.) The whole matter of the allocation of the results obtained by optical and electrical observations became finally cleared up through the work of Davis and Goucher (cf. p. 374) on the excitation of Hg-vapour. The interest was here centred in the resonance line of mercury $\lambda = 2537$, which we have already mentioned several times ; the fact that it is at the same time the ground line of the absorption spectrum shows that its final orbit also represents the ground orbit in the Hg-atom. As Paschen has shown,* $\lambda = 2537$ is a combination line of the system of simple and triplet lines. It has the formula

$$\nu = \frac{1}{\lambda} = 1S - 2p_1 ;$$

both terms are defined with perfect accuracy from our knowledge of the triplet and the simple lines series. For we have

$$1S = 84181{\cdot}5, \quad 2p_1 = 44768{\cdot}9$$

* Ann. d. Phys., **35**, 876 (1911).

and so we get the resolution

$$\nu = 39412{\cdot}6 = 84181{\cdot}5 - 44768{\cdot}9.$$

Since, in the process of emission, the first term (we discard the sign) determines the energy of the final orbit, and the second term determines that of the initial orbit, we write at the lowest energy-level of Fig. 94 the number — 84181·5, and at the next lowest the number, — 44768·9. It is between these two levels that both the process of emission (arrow downwards) as well as that of absorption (arrow upwards) takes place.

In addition, we consider the line $\lambda = 1849$ Å. situated still further in the ultra-violet. As it likewise occurs not only as an emission line but also as an absorption line in cold mercury vapour, it must start out from or, respectively, tend towards the same ground level, the natural orbit of the electron at the periphery of the atom. This is confirmed by its expression in terms. For, according to Paschen (*loc. cit.*), $\lambda = 1849$ is the line of the principal series of simple lines and is therefore expressed by the formula

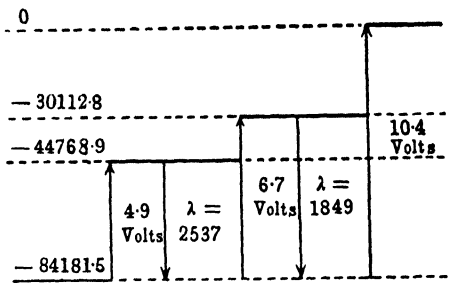


FIG. 94.—The characteristic potentials of the Hg arc spectrum according to the method of electron impact. On the left are the corresponding spectroscopic term values.

$$\nu = \frac{1}{\lambda} = 1S - 2P$$

in which 2P = 30112·8 and we have the resolution

$$\nu = 54068{\cdot}7 = 84181{\cdot}5 - 30112{\cdot}8.$$

In accordance with this we have therefore to add in Fig. 94, above the two energy-levels hitherto considered, one that is higher and to which we assign the number — 30112·8. The emission and the absorption of $\lambda = 1849$ then takes place between this upper level and the lowest level, and they are indicated by oppositely directed arrows. Above this upper level there has been drawn in the figure a still higher top level, which denotes the removal of the electron to infinity and represents the energy 0. According to eqn. (2) the following numbers of volts correspond to the above-mentioned wave-numbers :

$$\begin{aligned} \nu &= 84181{\cdot}5, \quad V = 10{\cdot}39 \text{ volts.} \\ &= 54068{\cdot}7, \quad V = 6{\cdot}67 \quad \text{,,} \\ &= 39412{\cdot}6, \quad V = 4{\cdot}68 \quad \text{,,} \end{aligned}$$

Actually, Davis and Goucher have confirmed that at the value 4·9 volts given by Franck and Hertz (cf. p. 371) the line $\lambda = 2537$ flashes forth. At the same time, however, they succeeded in proving that an ionisation of Hg-vapour did not yet occur at this potential. Furthermore, they detected signs of the emission of the line $\lambda = 1849$, likewise without ionisation, when the potential was 6·7 volts. *Ionisation was shown beyond doubt to occur at a potential of* 10·4 *volts.*

But these circumstances are exactly repeated in the case of all elements of the second column of the periodic table. In all cases, $1S - 2p$ is the first excitation limit, $1S - 2P$ the second, and $1S$ itself the ionisation potential. How completely the measurements obtained from electronic collisions agree with spectroscopic data is shown in Table 39. The values tabulated under "calc." have here, too, been determined from eqns. (1) and (2).

TABLE 39

	Excitation Potential in Volts		$1S - 2p_1$ $1S - 2P$	Ionisation Potential in Volts		Series Limit in cm.$^{-1}$ $1S$	Observer
	Obs.	Calc.		Obs.	Calc.		
Mg	2·65	2·70	4571·33	7·75	7·61	61 663·0	Foote and Mohler, Phil. Mag., **37**, 33 (1919). Mohler, Foote and Meggers, Journ. Opt. Soc. Amer., **4**, 364 (1920). Bur. of Stand. No. 403, 1920
	4·42	4·32	2852·2	—	—	—	
Ca	1·90	1·88	6572·8	6·01	6·08	49 304·8	Mohler, Foote and Stimson, Bur. of Stand. No. 368, 1920; Phys. Rev. **14**, 534 (1920)
	2·85	2·92	4226·7	—	—	—	
Sr	—	1·79	6892·8	—	5·67	45 924·31	—
		2·68	4607·5				
Ba	—	1·56	7911	—	5·19	42 029·4	—
		2·23	5535·5				
Zn	4·18	4·02	3076·0	9·3	9·35	75 758·6	Tate and Foote, Phil. Mag., **36**, 64 (1918). Mohler, Foote and Meggers, *loc. cit.*
	5·65	5·77	2139·3				
Cd	3·95	3·78	3261·2	8·92	8·95	72 532·8	Same as for Zn
	5·35	5·39	2288·8				
Hg	4·9	4·86	2536·5	10·2	10·39	84 181·5	Same as for Mg (Foote-Meggers-Mohler)
	6·7	6·67	1849·5				

In addition to these results very detailed measurements carried out in the case of mercury in particular by Franck and Einsporn * have brought into evidence a whole series of higher energy-levels,

* Zeitschr. f. Phys., **2**, 18 (1920).

for example, $1S - 3P$, $1S - 4P$, $1S - 3p_1$, $1S - 4p_1$, in the current-potential curves. It is of particular interest that the transitions

$$1S - 2p_2 \quad \text{and} \quad 1S - 2p_0$$

that are not observed optically and that are excluded by a selective principle governing the inner quantum numbers (cf. Ch. VIII, § 1) make themselves observed in the current-potential curves as bends.*

The ionisation potential of the second order, that is the formation of a double positive ion, has also been determined by Foote, Meggers, and Mohler † for the alkaline earths, the first being Mg. This ionisation potential of the second order corresponds to the H.S. limit of the doublet spark lines, just as the ordinary ionisation potential corresponds to the limit of the H.S. of simple lines. It naturally lies somewhat higher than the latter (15 volts instead of 7·6 volts for Mg).

We have described here, of course, only those results of the method of electronic impact that are particularly instructive and immediately intelligible. We must emphasise, however, that even in complicated cases where the energy-levels have not been investigated spectroscopically this method enables us to derive direct information, for example, about series limits (by means of the ionisation potential). ‡

Finally we add for the sake of contrast with the excitation by means of electronic impact *a method of purely optical excitations*. It has been developed by Füchtbauer || for Hg-vapour.

Concerning the experimental arrangement we say only this: a quartz tube filled with mercury vapour was illuminated by radiation from a quartz mercury vapour lamp. The latter emits into the former tube practically only such lines of its spectrum as have wave-lengths greater than or equal to $\lambda = 2537$ Å. (as all light for which $\lambda < 2537$ is held back by the thick quartz walls of the lamp). In the first (the outer) tube only $\lambda = 2537$ is absorbed initially, since the Hg-vapour is in the state given by the ground orbit 1S; but, owing to the absorption, a fraction of its atoms pass into the state $2p_1$. Hence this fraction is enabled to re-emit not only the line $1S - 2p_1$ but also, for example, the blue line

$$2p_1 - 1s, \quad \lambda = 4358$$

(as, indeed, all lines of the type $2p_1 - X$, for which $2p_1$ is the initial level of the absorption). In this way the new atomic state

* They also occur as starting-points for band spectra. Cf. Lord Rayleigh, Proc. Roy. Soc., **114**, 620 (1927).

† Phil. Mag., **42**, 102 (1921); **43**, 659 (1922); Astrophys. Journ., **55**, 145 (1922).

‡ A tabulation of characteristic potentials of arc and spark spectra, in which, however, almost only purely optical data are used, is also contained in Chemical Reviews, **5**, 85 (1928), by A. A. Noyes and A. O. Beckmann, which is quoted in the book by Goudsmit and Pauling, *Structure of Line Spectra*, p. 168, McGraw-Hill, New York (1930).

|| Phys. Zeits., **21**, 635 (1920). Our own explanation, which is a little simpler than that given in this paper, follows on the report by G. Joos, cf. p. 509.

$2s$, $\nu = 21834$ arises. If the energy-quantum of $\lambda = 2537$, $\nu = 39413 > 21834$ is again absorbed in the latter, the series-electron is driven out and the atom is ionised. When the atom is again neutralised the whole arc spectrum of mercury results from the cascade-like transitions of the electrons into a series of individual processes. This spectrum was photographed in almost its complete form by Füchtbauer as a second consequence of the primary irradiation with 2537. The fact that 2537 was actually the only primary exciting radiation was proved by Füchtbauer by causing the line 2537 to be absorbed by a thin plate of glass; the radiation of long-wave light was then found to cease at once.

Füchtbauer's experiments are also instructive in that they bring into evidence the finite "time of relaxation" (*Verweilzeit*) of atoms in their excited states. Actually there is, for example in the state $2p_1$, a finite probability that a further energy-quantum will link up with $2p_1$ only if the atom persists in the state $2p_1$ for a finite time.

In the general questions concerning the statistical equilibrium of excited atoms and molecules an important part is played by a process involving a certain reversal of the phenomenon that occurs in electronic collisions with atoms; it was introduced by Klein and Rosseland.* We represent the process of electron collision by the following scheme (upper arrow):

$$\text{greater amount of electronic energy} \underset{\leftarrow}{\rightarrow} \begin{cases} \text{energy of excitation} + \text{smaller} \\ \text{amount of electronic energy.} \end{cases}$$

On the left-hand side we have the energy of the colliding electron; it is partly converted in exciting the atom and the remainder is taken up by the escaping electron in the form of kinetic energy. But, as Klein and Rosseland showed, the converse process (indicated by the lower atoms) is also possible to a considerable degree of probability. A relatively slow electron approaches an excited atom (cf. right-hand side of the scheme). The atom passes into a state of lower energy without emitting radiation. The energy that is liberated becomes added to the kinetic energy of the colliding electron so that it moves away from the atom with greater energy. Atoms may collide with other atoms or with molecules according to the same scheme. This converse process (denoted by the lower arrow) is called *collision of the second kind* to distinguish it from the collision of the first kind which formed the subject of this paragraph.

By means of collisions of the second kind the energy which is communicated to one type of atom by inward radiation, that is, from outside (*Einstrahlung*) is transferred to another kind of atom which is thus enabled to emit definite energy-steps of its spectrum. This process is called "sensitised fluorescence" by Cario and Franck.† Good

* Zeits. f. Physik, **4**, 46 (1921).

† G. Cario and J. Franck, Zeits. f. Physik, **17**, 202 (1923); H. Kopfermann, *ibid.*, **21**, 316 (1924).

examples of this are given by mixtures of Hg-vapour with vapours of Tl, Cd, Bi and so forth.

§ 4. Quantum Theory of the Series Formula. Penetrating and Non-penetrating Orbits

The simplified assumptions under which we can treat spectral orbits have been characterised in § 2: the atomic field due to the electrons enveloping the nucleus is regarded as an invariable central field, that is, its potential energy V is assumed to be a pure function of r. This becomes added to the potential energy of the screened nucleus, which we may write down in the form $-\frac{Ze^2}{r}$. Here e denotes the charge of the "reference electron" or "series electron," Ze the nuclear charge so far as it is not screened by the electronic envelope, $Z = 1$ corresponds to the neutral atom and gives the arc spectrum $Z = 2$, $Z = 3$ . . . correspond to the singly, doubly, . . . ionised atom and give the arc spectra of the first, second, . . . order. These assumptions do not hold actually but lead us further than we might ordinarily expect.

One consequence of these assumptions is that the orbit lies in a plane passing through the nucleus and may be described by means of the polar co-ordinates r, ϕ. Here the azimuth ϕ is cyclic, that is, its moment of momentum is constant: $p_\phi = p$. The *azimuthal quantum condition* gives

$$2\pi p = n_\phi h.$$

The expression for the energy runs as for the Kepler ellipse (p. 110) with the addition of the potential energy V of the atomic field:

$$\frac{1}{2m}\left(p_r^2 + \frac{p^2}{r^2}\right) - \frac{Ze^2}{r} + V = W \quad . \quad . \quad . \quad (1)$$

Hence it follows that

$$p_r = \sqrt{2m\left(W + \frac{Ze^2}{r} - V\right) - \frac{p^2}{r^2}} \quad . \quad . \quad . \quad (1a)$$

Hence we have the *radial quantum condition*:

$$\oint p_r dr = \oint \sqrt{2m\left(W + \frac{Ze^2}{r} - V\right) - \frac{p^2}{r^2}}\, dr = n_r h \quad . \quad (2)$$

The integration with respect to r is here again to be taken over the full range of r, from r_{min} to r_{max} and back again to r_{min}. We must regard this equation, if n_r is given, as an *equation for determining* W.

Below it we write the same integral, but for $V = 0$. This corresponds in a certain sense to the hydrogen case, but *only* in a certain sense; for we do not wish to regard the W in it as the hydrogen energy but the same quantity as in equation (2). Accordingly

we have on the right-hand side of the following equation not the perfect integer n_r, as in the case of hydrogen, but an imperfect number which we shall call n_r':

$$\oint \sqrt{2m\left(W + \frac{Ze^2}{r}\right) - \frac{p^2}{r^2}}\, dr = n_r' h \quad . \quad . \quad . \quad (3)$$

This **effective radial quantum number** n_r' differs from the former integral number n_r by a certain **quantum defect** Δ. We write

$$n_r = n_r - \Delta \quad . \quad . \quad . \quad . \quad (4)$$

and also introduce an **effective principal quantum number,**

$$n_{eff} = n_r' + n_\phi,$$

as a counterpart to the proper integral principal quantum number $n = n_r + n_\phi$. We then have also

$$n_{eff} = n - \Delta \quad . \quad . \quad . \quad . \quad (4a)$$

From the equations (2) and (3) it now follows that

$$h\Delta = \oint dr \left\{ \sqrt{2m\left(W + \frac{Ze^2}{r} - V\right) - \frac{p^2}{r^2}} - \sqrt{2m\left(W + \frac{Ze^2}{r}\right) - \frac{p^2}{r^2}} \right\} \quad (5)$$

From equation (5) we infer generally that

$$\Delta > 0.$$

This is equivalent to the statement that V is always < 0, that is, that in (5) the first positive roots predominate over the second. To see this, let us imagine the electronic envelope to be replaced by a single rigid negatively charged spherical surface. Under the influence of the reference (outer) electron this sphere is repelled but the nucleus is attracted by the electron. Towards the outside the sphere acts as if its charge were concentrated at its centre. This centre lies beyond the nucleus on the line connecting the reference-electron with the nucleus. Hence on this connecting line we have a *dipole* whose positive pole the nucleus tends towards the reference-electron. Such a dipole exerts an *attraction* on the reference-electron. Its potential is negative. Hence we have

$$V < 0, \quad \Delta > 0 \quad . \quad . \quad . \quad . \quad . \quad (6)$$

as was asserted. Thus the influence of the inner atomic field always tends to *magnify the term*, as compared with that of the corresponding hydrogen term or, as we may also say, tends to *strengthen the binding* on the series-electron.

We revert to equation (3). This has the same form as the radial quantum condition in the case of hydrogen, equation (11) on page 111 (with the value for $\partial S/\partial r$ given in (10) on p. 111). For this reason the result with respect to the calculation of W is the same as for

hydrogen, equation (14) on page 112, with the one difference that now n_r is to be replaced by n_r' and hence n by $n - \Delta$ or n_{eff}. Hence the term value to be taken from (3) is

$$-\frac{W}{h} = \frac{RZ^2}{(n_\phi + n_r')^2} = \frac{RZ^2}{(n-\Delta)^2} = \frac{RZ^2}{n_{eff}^2} \quad . \quad . \quad . \quad (7)$$

The expression "quantum defect" for Δ is obviously justified by this notation; it means the defect as compared with the hydrogen term of the same principal quantum number n.

So much for the general aspect. We must now consider in detail the distinction: non-penetrating and penetrating orbits.

(*a*) **Non-penetrating Orbits.**—If the orbit has its course permanently in the outside of the atomic core, we may expand V over its whole range in a uniform series with increasing negative powers of r, such as we represented in § 2, to different degrees of approximation by means of the terms $-e^2c_1/r^2$, $-e^2c_2/r^3$, . . . The integrals (5) are calculated in this case according to notes (4) and (11) and give us to a second or third degree of approximation Rydberg's or Ritz's form for the term (p. 363), and hence for Δ we have the values

$$-\Delta = q \quad \text{and} \quad -\Delta = q + \kappa(n, q, \kappa) \quad . \quad . \quad (8)$$

To determine Δ we shall proceed graphically. For this purpose we rewrite equation (1*a*) in the following form, for V = 0 in the first place:

$$p_r = \frac{p}{r}\sqrt{\left(1 - \frac{r}{r_{max}}\right)\left(\frac{r}{r_{min}} - 1\right)} \quad . \quad . \quad . \quad (9)$$

Actually this equation expresses the real character of p_r for $r_{min} < r < r_{max}$ and also gives correctly the term $-p^2/r^2$ in (1*a*). Moreover, it has the correct zeros; for $p_r = 0$ for $r = r_{min}$ and $r = r_{max}$. Fig. 95 depicts equation (9) graphically; r is drawn as the abscissa, p_r as the ordinate. The curve for p_r is closed, the upper half ($p_r > 0$) corresponds to the forward motion from r_{min} to r_{max}, the lower half to the backward motion from r_{max} to r_{min}. The axis of X is intersected perpendicularly at r_{min} and r_{max}. The steepness of the curve at r_{min} and the small slope at r_{max} arise from the numerator $1/r$ in (9).

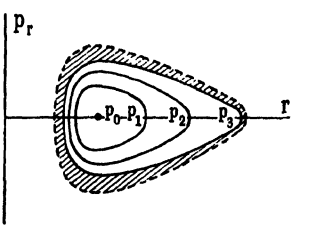


FIG. 95.—Dependence of the function p_r (radial momentum) of equation (9) on r (distance from the nucleus) for different values of the radial quantum number, p_0, p_1, p_2 . . . correspond to $n_r = 0, 1, 2$ . . . for hydrogen. For non-hydrogen like terms of equal energy p_3 is modified to the dotted curve (diagrammatic).

The figure exhibits a group of curves p_r, which are denoted by p_0, p_1, p_2 . . . and which we shall suppose correspond to the quantum numbers

$n_r = 0, 1, 2. \ldots$ The radial quantum condition demands that the surface between each two successive curves of the group must equal h.

To pass from hydrogen ($V = 0$) to a term ($V < 0$) unlike that of the hydrogen type, we have only to increase the term under the radical in (9), corresponding to the addition of $-V$ in (1a). The character of the curves remains preserved in this process. The dotted line shows the change in the most extreme curve of the group. We must emphasise again that the two curves have the same W but not the same n_r. Hence if one curve was quantised (n_r an integer) the other curve *cannot* be. The small shaded region between the dotted and the continuous curve represents in accordance with eqn. (5) the quantum defect Δ.

The course of the orbital curve in the (r, ϕ)-plane will be similar to that in the case of hydrogen. The chief difference as compared with the Kepler ellipse consists in a rotation of the perihelion similar to that which we encountered in the relativistic Kepler ellipse (cf. Fig. 67, p. 254). The magnitude of the perihelion motion is obtained as on pages 252 *et seq.* from the energy equation. We take p^2 outside the bracket in (1) and set

$$s = \frac{1}{r}, \quad \frac{p_r}{p} = \frac{1}{r^2}\frac{dr}{d\phi} = -\frac{ds}{d\phi}$$

and break off V as on page 362 (under (b)) after the first term ; that is, we set

$$-V = Ze^2\frac{c_1}{r^2} = Ze^2c_1s^2.$$

Here we have added the factor Z in order to include spark spectra. In this way we obtain from (1)

$$p^2\left[\left(\frac{\partial s}{\partial \phi}\right)^2 + s^2\right] = 2m(W + Ze^2s + Ze^2c_1s^2).$$

By differentiating with respect to ϕ we obtain a linear differential equation of the second order which we may at once write in the form of eqn. (10) on page 253 :

$$\frac{d^2s}{d\phi^2} + \gamma^2(s - C) = 0,$$

$$\gamma^2 = 1 - \frac{2mZe^2c_1}{p^2}, \quad \gamma^2 C = \frac{mZe^2}{p^2}.$$

The integration of this differential equation was performed on page 253 and led to the perihelion rotation of eqn. (14) there :

$$\Delta\phi = \frac{2\pi}{\gamma}(1 - \gamma).$$

Inserting the given value of γ we obtain (treating c_1 as a small perturbation):

$$\Delta\phi = \frac{2\pi mZe^2}{p^2}c_1 = \frac{(2\pi)^3 mZe^2}{h^2}\frac{c_1}{n_\phi^2}.$$

Thus the perihelion rotation increases, as should be, when c_1 increases (growing intensity of the supplementary atomic field) and decreases as n_ϕ increases (in the order of sequence of the terms S, P, D . . .). In general it is much more marked than in the relativistic case of hydrogen (cf. the factor c^2 in the denominator of eqn. (10*a*), p. 253) but still represents only a slow perturbation in comparison with the motion in the orbit.

(*b*) **Penetrating Orbits** (*Tauchbahnen*).—Schrödinger * was the first to show by using Na as an example that the *s*-orbits penetrate into the atomic core (into the L-shell in Na). To prove this he assumes

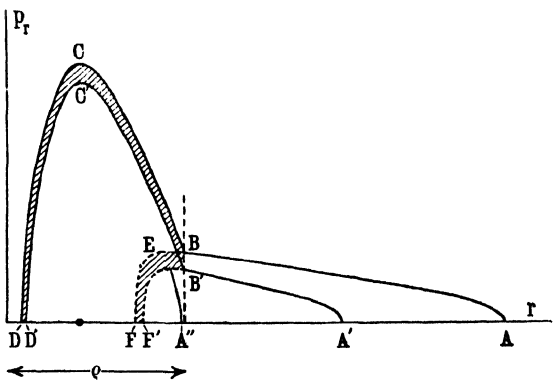


FIG. 96.—p_r (radial momentum) as a function of r for penetrating orbits. On the left of $r = \rho$ lies the region of the interior of the atom.

for simplicity that the K-shell is contracted on to the nucleus and the L-shell may be replaced by a spherical shell having a uniformly distributed total charge $-8e$ and an appropriately chosen radius ρ. The result of the orbital calculation is a quantum defect $\Delta = 0{\cdot}74$, which is nearly constant for all *s*-terms.

In the sequel we shall follow a method given by Wentzel.† In Fig. 96 we draw the two extreme curves similarly to those in Fig. 95 and cut off by means of a parallel to the axis of ordinates at the distance $r = \rho$ (ρ is an approximate measure of the radius of the atomic core) those parts of the curves that would lie in the interior of the atomic core. For these parts the effective charge Z in eqn. (1*a*) is to be assumed appreciably greater than for the external parts of the curves, to the right of $r = \rho$. If Z was equal to 1 in the region outside the atomic

* Zeits. f. Physik, **4**, 347 (1921). † *Ibid.*, **19**, 53 (1923).

core, and if we are dealing with the penetration into the L-shell, then $Z = 9$ in the interior, because the nuclear charge is now screened off by 8 units less. We treat this change by 8 units in Z as occurring suddenly although in reality it will be balanced out more uniformly (construction of the L-shell from the sub-groups L_I, L_{II}, L_{III}), particularly in view of the wave-mechanical relationships. Thus in our figure we draw the p_r-curve at the point $r = \rho$ with the same constant co-ordinate but with a tangent which is directed upwards but is not constant. The slope increases as r decreases ; finally there is a rapid decrease to the value $r = r_{min}$. The latter is of course appreciably smaller than in the case of the non-penetrating orbits, other conditions being equal.

Let us investigate the external p_r-curve of the figure a little more closely. The double area between the axis of abscissæ and the train of curves ABCD is our radial phase-integral in eqn. (2) and is hence equal to $n_r h$. On the other hand, the double area ABEF represents the phase-integral for the corresponding non-penetrating orbit and differs only slightly from the phase-integral for the case of hydrogen calculated with the same W, since the quantum defect Δ of the non-penetrating orbits is always small, according to (*a*). Hence the double area ABEF is appreciably equal to $n'_r h$ by (3) and the double excess area BCDFEB represents, sufficiently accurately, by (5), the quantity $h\Delta$.

We compare this surface with the corresponding surface B′C′D′F′E′B′ for our internal train of curves. The two surfaces are almost equal since the two strips BCDD′C′B and BEFF′B′ shaded in the diagram nearly coincide.* Hence it follows that the quantum defect Δ is independent of n_r not only in non-penetrating but also in penetrating orbits. Thus Δ besides depending on the atomic field depends appreciably only on the azimuthal quantum number n_ϕ and is a characteristic constant of the series. We may now also set $-\Delta = q$, say, and may therefore also apply the series formula (7) in Rydberg's form to the penetrating terms.

If we compare our present Fig. 96 with the preceding Fig. 95 we see immediately that the quantum defect Δ is now much greater than before. Whereas in the case of the shaded area in Fig. 95 we were dealing with a relatively small correction, the present area BCDFEB which represents the quantum defect is comparable with the total surface ABCD which represents the quantum number n_r and may amount to several units.

This gives rise to an uncertainty in the definition of the quantum numbers. From spectroscopic experiments only the term denominator n_{eff} is known, and hence by (4*a*) only the difference between n and Δ. If it should happen that $\Delta > 1$ we cannot immediately decide how great

* For further details see Van Urk, Zeits. f. Physik, **13**, 268 (1923).

n is to be chosen. This uncertainty cannot be overcome in the individual case but only in relationship to the periodic system, cf. § 6.

In Fig. 97 we depict a penetrating orbital curve diagrammatically. Both the external and the internal parts of the orbit run essentially in Kepler ellipses, but the loop inside is much more strongly curved, on account of the higher effective nuclear charge, and hence is attracted much nearer to the nucleus than the outer loop. This corresponds to the greatly raised position of the p_r-curve for $r < \rho$ and the diminished value for r_{min} in Fig. 96.

If the orbital curve, after traversing the inner loop, again leaves the atomic core, it is turned through a finite angle, as shown in Fig. 97. Hence we now have a rotation of the perihelion but many times greater than in (*a*), being magnified to the same extent as the quantum defect Δ is magnified.

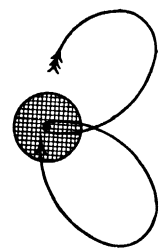


FIG. 97.—Diagrammatic representation of a penetrating orbit. Rotation of the perihelion on account of the stronger attraction in the neighbourhood of the nucleus.

The magnitude of Δ in the penetrating orbits causes a considerable increase of the term, compared with the hydrogen term having the same n, and hence also strengthens the binding of the series electron. A glance at Fig. 97 explains this: the penetrating electron approaches nearer to the nucleus and is more closely related to the atomic configuration than the non-penetrating electron.

(*c*) **Partially Penetrating Orbits.**—There is an intermediate case between penetrating and non-penetrating orbits, to which E. Fues * first called attention.

If we make a very rough calculation for the hydrogen model we see from the formulæ (16*c*) for the semi-axes of the orbital ellipses that for a fixed n_ϕ, that is, in the case of the orbits of a term-series the perihelion approaches the nearer to the nucleus the greater n becomes. It may therefore happen that the first orbits of a series do not penetrate into the atomic core but that a critical value of n, that is, of n_r, is attained after which penetration *does* occur.

Then the quantum defect Δ suddenly becomes larger and in this way we obtain a series whose constant $q = -\Delta$ has a discontinuity between two series terms. The first (non-penetrating) orbits of the series have a small Δ, the higher (penetrating) orbits have a large Δ. It is evident that such anomalies are to be expected only in the case of special dimensions for the orbits and the shells.

In Fig. 98 we depict the course of the quantum defect Δ for each of the cases (*a*), (*b*), (*c*) for a typical case. Δ is plotted as the ordinate

* Zeits. f. Physik, **11**, 376 (1922).

and the value of the term as the abscissa. Since we have by definition

$$\text{term} = \frac{R}{(n - \Delta)^2},$$

the curves $n = \text{const.}$ (which are shown as dotted lines in the figure) are known *a priori*.

(*a*) We have chosen for the non-penetrating orbit the D-term of cæsium. The fact that the graph is perfectly rectilinear denotes that Ritz's formula, eqn. (4*c*) on page 363, is exactly valid, namely that the quantum defect depends accurately in a linear fashion on the term-value in accordance with the formula

$$-\Delta = q + \kappa\,(n, q, x).$$

(*b*) For our penetrating term we have selected the S-term of sodium.

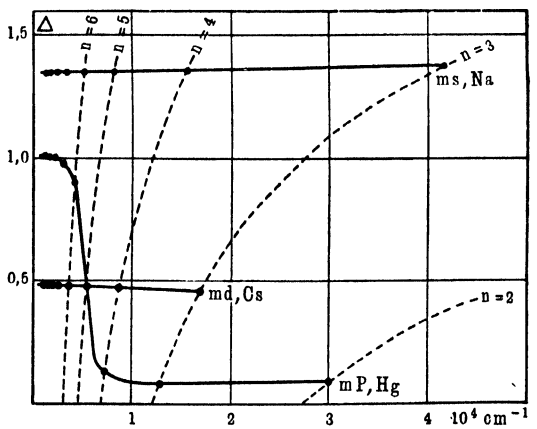


FIG. 98.—The quantum defect Δ as a function of the term-values. The linear dependence denotes validity of the Ritz formula. The ^1P term of Hg becomes penetrating below $n = 4$.

Observe the increase of Δ (here $\Delta = 1{\cdot}4$) which is characteristic for the penetration, and also note the linearity which manifests itself here.

(*c*) As our example of a partially penetrating orbit we have taken the peculiarly anomalous singlet-P-term of mercury. Here we see that the first two or three terms (on the right-hand side of the figure) have about the same Δ, and hence correspond to a Rydberg formula of their own. The same holds of the higher terms $n > 7$ (on the left-hand side of the figure). Between them is a disturbed region which runs in the manner to be expected for a penetrating orbit from the preceding remarks, say for $n = 5$. In our * diagram Δ increases almost by one

* The term $n = 4$ has been supplemented by Wentzel (*loc. cit.* Zeits. f. Physik, **19**) in accordance with observations by G. Wiedmann, Ann. d. Phys., **38**, 1045 (1912). It is possible that the left upper limit of the branch may have to be raised by several units, in which case the numbering of this branch would have to begin not with $n = 6$, but with a correspondingly greater value of n.

unit between $n = 4$ and $n = 7$. Wentzel discusses in the same paper other examples of such anomalies but at the same time emphasises a certain ambiguity in the interpretation for the following reason. The idea of the penetration first presumes *one* outer series electron and a *closed* atomic shell, which is essentially the case of the alkalies. But in our example of Hg we have two valency electrons. It is possible that the anomaly in question may not be due to the penetration of the series electron into the shell of the atomic core but to an inter-action (*Wechselwirkung*) with the other valency electron.

In this section we have taken the orbital idea more literally than appears justified from the wave-mechanical standpoint. Our reason may be stated as follows: the wave-mechanical treatment of complicated atoms is rather laborious and can be carried out only approximatively. But the difference between penetrating orbits and outer, non-penetrating orbits occurs in wave-mechanics too although in a different mode of expression.* The results obtained above remain valid at least qualitatively in the new theory.

§ 5. Application to the Representation of Röntgen Spectra in Terms

We shall now apply the considerations of the preceding section to *inner electronic orbits* and add a few remarks to the theory of X-ray terms. In the term formula for X-ray spectra, Chapter V, § 5, eqn. (4), we empirically introduce two different effective nuclear charge numbers $(Z - s)$ and $(Z - \sigma)$. The screening number s that enters into the relativistic terms (with α^2, α^4, . . .) was independent of Z, whereas the screening number σ that occurs in the main terms increased with Z and was always greater than s. We assert that the difference $\sigma - s$ arises from the influence of the outer shells, within which the motion of the K-, L-, M-shell under consideration occurs. Bohr actually calls $\sigma - s$ the external screening number. The fact that $\sigma - s$ increases with Z is simply explained by the increasing number of the shells added on the outside.

The assumptions of the preceding section may be extended so that we may account roughly for this external screening. For this purpose we must set the potential V in the energy-equation (1), page 387, equal to the action of the external shells (the screening action of the inner shells is taken into account in the value of Z). Let us first restrict ourselves to a single shell which we shall suppose to contain z electrons. Its field may be approximated to by the field of a spherical surface on which the charge $-z \cdot e$ is homogeneously distributed. The potential of this surface charge on an electron $(-e)$ is constant in the interior of the shell, in which the orbit lies, and is equal to ze^2/ρ, where ρ is

* Cf. for example, A. Unsöld, Ann. d. Phys., **82**, 355 (1927).

the radius of the shell. Hence instead of eqn. (1), page 387, we must now write

$$\frac{1}{2m}\left(p_r^2 + \frac{p^2}{r^2}\right) - \frac{Ze^2}{r} = W - \frac{ze^2}{\rho} = W'.$$

The only difference as compared with the preceding section is that the energy constant W appears replaced by a reduced constant :

$$W' = W - \frac{ze^2}{\rho}. \quad . \quad . \quad . \quad . \quad (1)$$

Hence quantising must give the same result for W′ as for W in the preceding section, namely,

$$-\frac{W'}{h} = -\frac{1}{h}\left(W - \frac{ze^2}{\rho}\right) = \frac{R(Z-s)^2}{n^2} \quad . \quad . \quad (2)$$

Here Z has already been reduced by the amount of the "inner screening" and we have disregarded the difference between n and n_{eff} (hydrogen-like character of X-ray spectra). If we also use the expression for the semi-major axis a, eqn. (16a) on page 112, with $Z - s$ instead of Z,

$$a = \frac{h^2}{4\pi^2 me^2} \cdot \frac{n^2}{Z-s} = \frac{e^2}{2Rh} \cdot \frac{n^2}{Z-s},$$

we obtain from (2)

$$-\frac{W}{h} = \frac{R}{n^2}\left((Z-s)^2 - 2(Z-s)z\frac{a}{\rho}\right) \quad . \quad . \quad . \quad (3)$$

If $Z \gg z$ we may write as a sufficient approximation

$$-\frac{W}{h} = R\frac{\left(Z - s - z\frac{a}{\rho}\right)^2}{n^2} \quad . \quad . \quad . \quad (4)$$

Thus the inner screening s is augmented by the "outer screening" $z \cdot a/\rho$, which is always smaller than the number of electrons z, since $a < \rho$.

If several outer shells are present the outer screening consists of the sum of the contributions of the individual shells. In place of (4) we obtain

$$-\frac{W}{h} = R\frac{(Z-\sigma)^2}{n^2}, \quad \sigma = s + a \cdot \sum\frac{z}{\rho} \quad . \quad . \quad (5)$$

Hitherto we have made our calculations without taking into account relativity. But even in the relativistic term formula (eqn. (6a) on p. 260, in which, on account of internal screening, we must replace Z by $Z - s$), if one or more outer shells become added we have merely to constitute the term $-W'/h$ from (1) for $-W/h$, so that we get

$$-\frac{W}{h} = R\left\{\frac{(Z-s)^2}{n^2} + \alpha^2\left(\frac{n}{n_\phi} - \frac{3}{4}\right)\frac{(Z-s)^4}{n^4} + \ldots\right\} - \frac{1}{h}\sum\frac{ze^2}{\rho} \quad (6)$$

As above in (3) and (4) we may now take the shell-potential ze^2/ρ over into the principal term of the expansion, so that the screening number in the principal term becomes increased to the value

$$\sigma = s + a\sum_{\rho}^{z} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

whereas in the higher terms the screening number s, which is independent of Z, remains.

If we pass from one element to the next highest σ becomes increased by the amount a/ρ owing to the addition of an electron. The increase is the greater, the less the radius ρ of the added electronic orbit. Hence if the electron is added not at the surface of the atom but, exceptionally, in an inner shell, as in the case of the triads and the rare earths we expect a more marked increase in the screening number σ with Z. This explains the anomalies in the course of the curves in Fig. 79, page 286, to which we have already referred there.

We have thus explained in their essential features the screening laws derived empirically in Chapter V. In particular our discussion led us to correct only the screening number of the principal member by the amount of the external screening but to leave those of the relativity terms uncorrected and equal among themselves,—which seemed arbitrary when we originally wrote down the term formula on page 284.

The screening numbers were the only empirical factors that occurred in the term formula of the X-rays given on page 284. It is remarkable that they may be approximately * analysed theoretically.

§ 6. Magnitudes of the Terms. Relationship with the Periodic System

We first enumerate some theorems on which the following discussion will be based.

1. The term-value measures the tightness (*Bindungsfestigkeit*) with which the electron is kept in the orbit in question; multiplied by h, it is equal to the corresponding work necessary to detach the electron (*Abtrennungsarbeit*).

2. The inner atomic field increases the tightness of the binding; every term of an element which is not hydrogen-like is greater than the hydrogen term corresponding to the same principal quantum number.

3. The increase in the tightness of the binding is always small in the case of the non-penetrating orbits as compared with the case of penetrating orbits (see § 4*b* of the present chapter).

4. In the case of similar atoms, namely such as stand in the same vertical column of the periodic system, the increase in the corresponding

* A more exact numerical discussion of the outer screening numbers is given by Bohr and Coster, Zeits. f. Phys., **12**, 342 (1923), in particular p. 358.

terms increases with the magnitude of the inner atomic field, that is, with the atomic weight.

5. The series of penetrating orbits is continued in the direction of decreasing principal quantum numbers in the existence of regular electronic orbits that lie entirely inside the atom ; their energy corresponds to certain X-ray terms.

We shall begin our discussion with typical alkali terms. Following Bohr's example, we shall plot the term-values horizontally from the

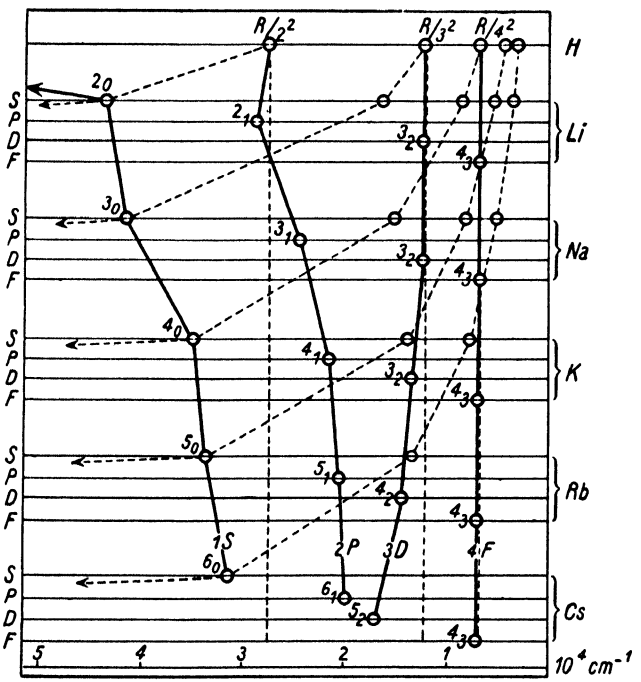


FIG. 99.—Agreement with each other of the corresponding series terms of the alkalies with the hydrogen terms. The symbols 1S, etc., refer to the conventional notation introduced on p. 365, and the symbols 2_0, etc., to the n_l-classification.

boundary on the right-hand side of Fig. 99, and we shall plot the terms S, P, D, F each on a separate horizontal line. The points farthest to the left on these lines represent the first terms of these term-series and are hence (normalised conventionally) successively : 1S, 2P, 3D, 4F. Further to the right we have 2S, 3S, . . . 3P . . . Our figure brings out the binding of the separate term, as represented by the distance of the point in question from the right-hand boundary of the figure (cf. Theorem 1). For the sake of comparison we have drawn the hydrogen terms above those of the alkalies and have

extended them by dotted vertical lines that run the length of the diagram.

In the case of the F-terms we observe the behaviour that is to be expected from Theorems 2 and 4. The connecting line, drawn continuously in the figure, lies throughout a little to the left of the corresponding dotted hydrogen line and deviates increasingly from it as the atomic weight increases.

This does not apply, however, to the P-terms, starting from Na nor to the S-terms, starting from Li. The magnitude of these terms decreases as the atomic weight increases ; here the atomic weight appears to *weaken* the tightness of the bond, in contradiction to Theorem 4. This contradiction is disposed if we call to mind the Tables 7, 8, 9 of Chapter III on pages 159 *et seq.* The ground-state of the alkali-atoms which coincide, as is shown by absorption phenomena (cf. p. 370) with the first S-term, is of the type 2_0, 3_0, 4_0, 5_0, 6_0 in the case of Li, Na, K, Rb, Cs. Hence the reason for the decrease of the S-series terms is due to the fact that the principal quantum number n and hence also the denominator of the term increases by steps in this sequence. All the orbital types n_0 with a smaller n have already been used up as inner X-ray orbits in building up the atom, for example, in the case of cæsium the orbital types 1_0, 2_0, 3_0, 4_0, 5_0 have been used up in forming the K-, L-, M-, N-, O-shell. Corresponding results hold for the P-terms. According to the Tables 7, 8, 9 we find that none of the n_1 orbits are used up in the Li-atom, the orbit 2_1 of this type is used up in the Na-orbit, all the n_1 orbits, up to and including 3_1, 4_1, 5_1 are used up in the case of the K-, R*b*-, C*s*-atoms, respectively. Hence we obtain for the excited P-orbit of the valency electron the orbits 2_1, 3_1, . . . 6_1 for Li, Na . . . Cs, respectively, as shown in our figure.

All these 1S-orbits and all 2P-orbits from Na onwards are *penetrating orbits*. This manifests itself clearly in the *magnitude* of the terms : if they were not penetrating orbits the terms 3_0 and 3_1 of Na, for example, would have to be very nearly equal to the hydrogen term $R/3^2$; it is only in the case of penetrating orbits where the quantum defect Δ may amount to as much as several units (cf. p. 392) are we able to understand, by Theorem 3, the great deviation from the corresponding Balmer term $R/3^2$. On the other hand, the 2P-term of Li, being a non-penetrating orbit, is nearly equal to the Balmer term $R/2^2$, and is in fact a little greater than we should expect from Theorem 2. In the same way we infer from the value of the term that F-terms do not penetrate into the atomic core.

The term 3D is of the type 3_2 in the case of Li, Na, K. In Rb, however, the 3_2-shell is already fully occupied and lies in the interior of the atom (cf. the discussion in Chapter III, § 5). Hence we must ascribe the (rational) orbital type 4_2 to the (conventional) term 3D of Rb. Similarly, for Cs we deduce the type 5_2 for 3D from Table 9 on page 163.

We have yet to add a remark about the oblique dotted lines in the figure. They combine the S-terms of the same orbital type n_0. For example, the dotted line belonging to the type 5_0 connects the term 1S of Rb with the terms 2S of K, 3S of Na, 4S of Li and runs upwards towards the hydrogen term $R/5^2$; in the downward direction it points towards the Cs-term 5_0, which is an X-ray O-term. In contrast with the continuous line connecting the 1S-terms we are here dealing with a line which connects really corresponding S-terms, that is, those belonging to the same orbital type. Consequently this line—again in contradistinction to the line connecting the 1S-terms—confirms our Theorem 4: the value of the term increases regularly as the atomic weight increases and is always greater than the corresponding hydrogen term,—which is here $R/5^2$. The line just mentioned exhibits the same behaviour in this respect as the connecting lines of the 4F-terms, that actually, of course, belong to really corresponding terms of the same orbital type. The deviation towards the left which is relatively much greater than the former deviation is clearly in agreement with the penetration of the S-orbits, as a consequence of which the atomic field exerts a much stronger effect than in the case of the non-penetrating F-orbits.

The contrary behaviour of the continuous and the dotted connecting lines of the S-terms exhibits in a striking manner the antithesis between the conventional and the rational method of denoting terms. The continuous line belongs to the same conventional current number, the dotted line to the same rational quantum number. In the sequel we shall find it convenient to use both notations.

We now consider atoms with two outer electrons. These include besides He the elements of the second column of the periodic system. They all have two kinds of terms, singlet and triplet in their arc spectrum. As in the case of He (p. 358) they may be briefly distinguished as S, P . . . and s, p, . . . terms. The connecting lines of the singlet terms are drawn continuously in Fig. 100, those of the triplet terms as broken lines, and it is just as impossible to indicate the three-fold character of the latter in the scale of the figure as the two-fold character of the alkali-terms in Fig. 99. The terms 1S, 2P and $2p$ (conventionally normalized) of Be, Mg, Ca, Sr, Ba exhibit the same trend as the S- and P-terms of the preceding elements Li, Na, K, Rb, Cs. They are penetrating terms, as is the s-term, which is, however, far smaller than the term 1S and is therefore denoted conventionally by $2s$. On account of Pauli's Principle (cf. Chapter VIII, § 3) there is no term $1s$ which would be comparable in value with 1S; we already know this to be so for the helium spectrum from our discussion on page 359.

A new phenomenon presents itself, however, in the terms 3D and $3d$, as well as in 4F. The former are non-penetrating in the case of

Mg and are little greater than the hydrogen term $R/3^2$. But in the case of Ca they increase strikingly. We must interpret this as meaning that they come within critical reach of the atomic core and run the risk of being bent round into the latter. We shall actually see in § 8 that even in the case of the next heaviest element Sc the 3_2-orbit belongs to the orbital system of the inner part of the atom. At present we infer from this that the corresponding orbits of the following alkaline earths Sr

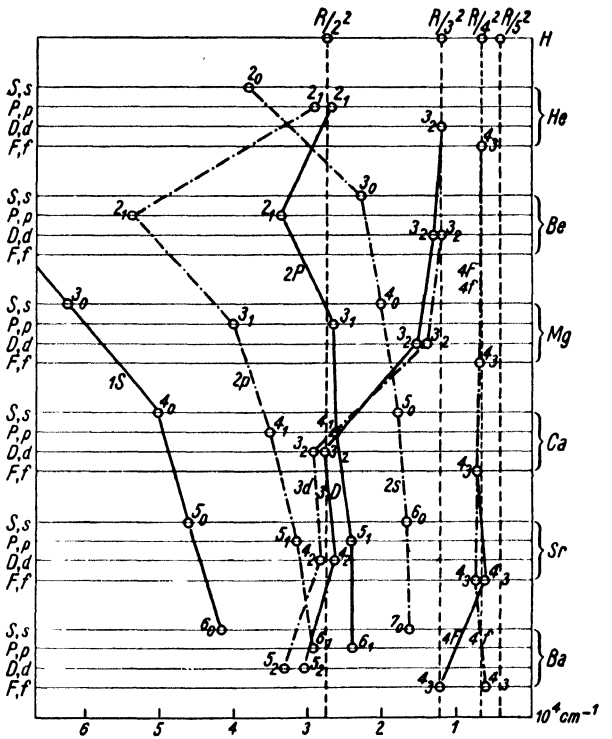


FIG. 100.—The corresponding terms of the arc spectra of the alkaline earth type. Triplet terms corresponding to one another are connected by chain lines, and singlet terms by continuous lines. Small letters denote triplet terms, capitals singlet terms. Notation as in Fig. 99.

and Ba are penetrating orbits of the type 4_2 and 5_2 and that here the orbits 3_2, and in the case of Ba also 4_2, already belong to the interior of the atom (cf. Theorem 5 and Table 9, p. 163).

The behaviour of the term 4F in Fig. 100 is still more interesting. Whereas as in Mg, Ca and Sr it points to a non-penetrating hydrogen-like orbit, it exhibits a critical increase in Ba. It proclaims that the orbital type 4_3 is also about to penetrate and to be drawn into the interior of

the atom.* According to Table 9 this actually occurs at the rare earths, a few steps later than Ba.

So in this case, too, we find excellent accord between the term-values and the periodic system.

Concerning the other sub-group of the second column, the elements Zn, Cd, Hg, we need say only a few words. The terms 1S, 2*s* and 2P, 2*p* are penetrating terms numbered in the same way as the neighbouring elements Ca, Sr, Ba. For the terms 3D, 3*d*, Pauli's Principle leads to the designations 4_2, 5_2, 6_2 for Zn, Cd, Hg, but 4_3, 5_3 for the 4F- and 4*f*-terms.

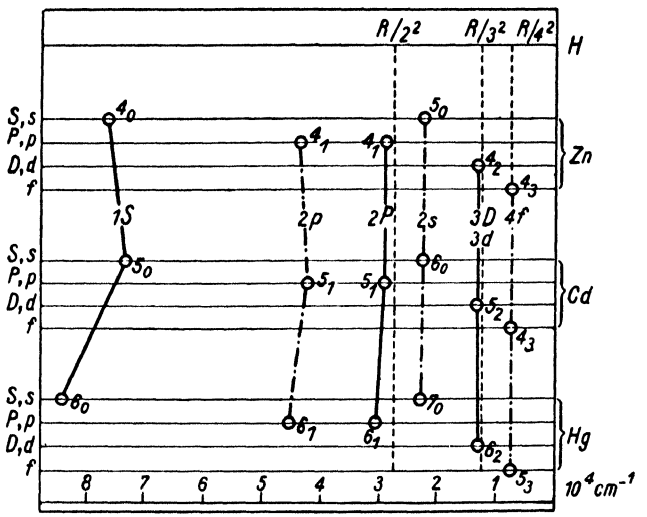


FIG. 101.—The corresponding terms of Zn, Cd, Hg. Notation as in Fig. 99.

In the third column of the periodic system, that is, B, Al, Ga, In, Tl, we have the interesting state of affairs that the greatest term is not an S-term but a doublet P-term. This has led us, in Tables 7, 8 and 10, to place the last bound valency electron not like its two predecessors in an n_0-orbit but in an n_1-orbit, namely in a 2_1-orbit in the case of B, and in a 3_1-, 4_1-, 5_1-, 6_1-orbit, respectively, in the case of Al, Ga, In, Tl; hence the designations for the 2P-terms of these elements given in Fig. 102.

The S-terms are much smaller and are therefore denoted by 2S.

The fact that the ground-term of these elements is a P-term is proved beyond doubt by absorption phenomena. All absorption lines

* This does not, however, agree with the behaviour of the 4*f*-term which we have also included in the figure. Perhaps the first term of the triplet *f*-term series in Ba, such as it is given in the literature of the subject and as it is shown here, does *not* represent the *first* term of this series.

begin, without exception, from the P-level, namely from the *deeper* * level $P_{\frac{1}{2}}$ of the two doublet levels.

We shall discuss further points concerning the structure of the periodic system, such as may be deduced from spectra, in § 8 of the present chapter and in §§ 3, 4, 5 of the next chapter.

§ 7. Series Types with Different Limits. Varying Constitution of the Atomic Core

We have become acquainted with two series systems in the case of helium, the orthohelium terms and the parhelium terms (cf. p. 358).

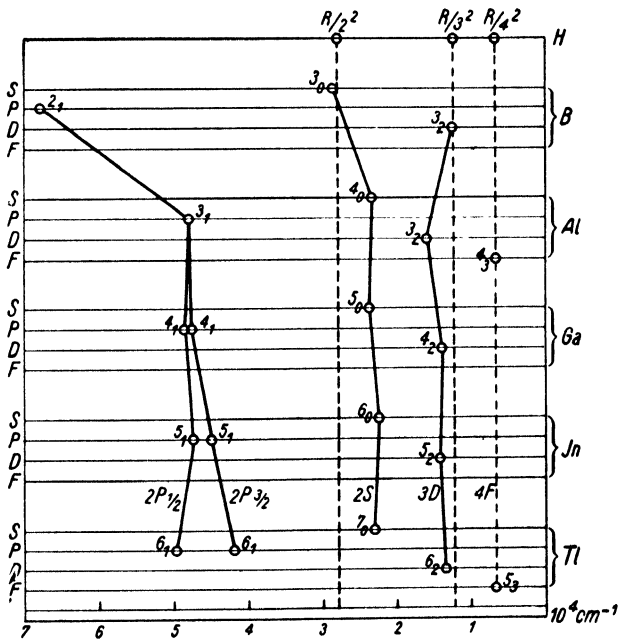


FIG. 102.—The corresponding terms of the spectra of the " earth " type. Notation as in Fig. 99.

In the arc spectra of the second vertical column of the periodic system we encountered two series systems, the singlet and the triplet terms (cf. p. 400). In the next chapter we shall find an increasing number of examples of different series systems that occur simultaneously.

The fitting together of such series terms was comparatively easy for the spectroscopist who worked empirically, because the two types of series in these cases have the same limit. This signifies : the atomic core which remains after the radiating electron (*Leuchtelektron*) has

* W. Grotrian, Zeits. f. Physik, **12**, 218 (1922).

been removed, has the same energy for the singlet and the triplet terms ; this may be made the common zero-level from which we may reckon. We may say with certainty : the atomic core is similarly constituted in both cases ; for example, the atomic core of helium is always the hydrogen-like He^+-ion, no matter whether we start out from para- or ortho-states.

The contrary behaviour first manifested itself in the neon spectrum. Paschen * was the first to succeed, in 1919, in separating out the whole of the neon lines into series. But the series terms resolved into two different groups : the one could be represented without difficulty by formulæ of the Ritz type, the other appeared to require a new kind of series formula. Paschen soon † recognised that this second group could be represented satisfactorily by formulæ of the following type :

$$\frac{R}{(n+q+\ldots)^2} - A, \quad A \sim 782 \text{ cm.}^{-1},$$

that is, by superposing on a Ritz expression a wave-number A which has appreciably the same value for the different terms of this group. This result must be interpreted as meaning that the series limit of the second group differs by the amount A from the series limit of the first group which had been chosen as the conventional zero-level for calculating the terms. (The arbitrariness in the choice of the zero-level is a necessary consequence of the fact that the observations always give only term-differences.)

The explanation of the two series limits in terms of models was given by W. Grotrian.‡ He allocated them to the two L-limits, L_{III} and L_{II}. L_{II} corresponds to the limit " zero " for the one-term series, L_{III} the series limit, which is less by the amount A, for the other term sequence. In both cases the closed neon-shell (the " $L_{II} + L_{III}$-shell " as we expressed it in Chapter III, p. 159) is broken up in such a way that it contains instead of its full number of 6 electrons only 5. A breaking-up of the L_I-shell (2 electrons) signifies a more considerable change in the atomic configuration and does not come into question for the spectroscopy of the visible region.

That this interpretation is correct is proved by the agreement of Paschen's value A with the difference of the terms L_{II} and L_{III}, that is, with the *relativistic* L-*doublet*. This has not, of course, been measured in the case of neon, but may be deduced by extrapolation, which gives a value of the same order of magnitude as A. Eqn. (5) on page 275 gives, for example, $\Delta\nu = 647$ cm.$^{-1}$, which agrees sufficiently well with Paschen's $A = 782$ if we take into consideration the uncertainty in the extrapolation towards such low atomic weights.

* Ann. d. Physik, **60**, 405 (1919). † *Ibid.*, **63**, 201 (1920).
‡ Zeits. f. Physik, **8**, 116 (1921).

Grotrian * shows how certain details in the neon spectrum, discovered by Paschen, may be explained from the mutual position of the term limits or, respectively, of the L-levels that correspond to them. (These details are, for example, the frequent occurrence of a closely adjacent pair of lines, accompanied by a line each at the distance $\pm$ A, the first corresponding to the combination of two " Ritz " terms or two analogous " non-Ritz " terms, the second corresponding to the combination, in each case, of one " Ritz " term with the analogous " non-Ritz " term.)

With regard to nomenclature it must, of course, be emphasized that the distinction between Ritz and non-Ritz terms is arbitrary, since this nomenclature would become reversed if the zero-level were differently chosen.†

This is all that we shall say about the last vertical column of the periodic system. In the first vertical column, that containing the alkalies, there is no multiplicity of the series limits because here the atomic core (inert gas shell) is uniquely defined and the excitation affects only the valency electron. The noble metals Cu, Ag, Au, that are in the same vertical column, will be discussed in Chapter VIII, § 4.

We now come to the second vertical column of the periodic system, in particular, the elements Be, Mg, Ca, Sr, Ba. We here have in the arc-spectrum besides the ordinary triplet terms p, d (which are to be written as ^3P, ^3D if greater detail is desired) also so-called displaced terms, which we shall denote by p', d' in the sequel, which corresponds with the older notation. How they should be denoted according to the modern method of classification will not be discussed till § 3 of the next chapter. Besides the combinations (pd) of the I N.S. we also find (pp') and (dd') occurring, but never (pd') or (dp').

The " dimorphism " (p' in addition to p, d' in addition to d) of the p-term and the d-term, for example in the case of Ca, again denotes the possibility of a double constitution of the atomic core with an energy-difference that corresponds to the difference of the series limits $\infty\, p - \infty\, p'$. What is the nature of the possible re-arrangement in the atomic core of Ca, that is, in the Ca^+-ion ? According to Table 8, page 162, the Ca^+-ion consists normally of the complete K- and L-shell, of the incomplete M-shell of $2 + 6$ electrons (3_0- + 3_1-orbits) and of the beginning of the N-shell with a valency electron of the type 4_0. But according to the same table the completion of the M-shell occurs immediately after Ca by the addition of a 3_2-electron ($n = 3$, $l = 2$). Hence we can understand that besides the *normal Ca^+-ion* also a

* *Loc. cit.* Cf. also G. Wentzel, Phys. Zeits., **24**, 104 (1923), where these relationships are illustrated graphically by means of a levels-scheme.

† According to K. W. Meissner, Zeits. f. Physik, **37**, 238 ; **39**, 172 (1926), the red argon spectrum has the same structure as the neon-spectrum. In argon the interval between the limits is : $\Delta\nu = 1423{\cdot}2$ cm.$^{-1}$ and has been brought into relationship with the interval between the limits M_{II}, M_{III} by Grotrian [Zeits. f. Phys., **40**, 10 (1926)].

"*heteromorphic*" ion can occur which is constituted according to the following scheme:

TABLE 40

Orbital Type	1_0	2_0	2_1	3_0	3_1	3_2	4_0	$n \geq 4$
Normal Ca^+	2	2	6	2	6		1	
Heteromorphic Ca^+ . . .	2	2	6	2	6	1		
Normal terms p, d . . .	2	2	6	2	6		1	1
Heteromorphic terms p', d' .	2	2	6	2	6	1		1
Normal term $3d$ . . .	2	2	6	2	6	1	1	

The table indicates that the occurrence of heteromorphic terms may be accounted for quantitatively as follows.* The 1S term of the spark spectrum corresponds to the normal state of the Ca^+-ion, the 3D term to the heteromorphic state. Both terms are well known spectroscopically:

$$1S = 9{\cdot}57 \,.\, 10^4, \qquad 3D = 8{\cdot}20 \,.\, 10^4.$$

Hence we obtain for the energy-difference in question

$$1S - 3D = 1{\cdot}37 \,.\, 10^4.$$

Now four groups (pp') are known. The strongest lies at $\lambda = 4300$ Å. and forms (together with the lines of other elements) the *Fraunhofer Line* G of the solar spectrum; the second group lies at $\lambda = 3000$ Å. The third group has been analysed by A. del Campo,† and lies at $\lambda = 2560$ Å. A fourth ‡ has been found at 2360 Å. In all four cases a p'-triplet occurs in combination with the same $2p$-triplet. We denote the four p'-triplets by $2p'$, $3p'$, $4p'$, $5p'$; they form the successive terms of a series. We have ||

$$2p' = 10800, \qquad 3p' = 750, \qquad 4p' = -4990, \qquad 5p' = -8330$$

The *negative* sign that occurs at $4p'$ and $5p'$ is exactly what we must expect if the limit $\infty\, p'$ lies higher than the zero point from which we count and which coincides with the limit $\infty\, p$. Cf. the scheme of levels in Fig. 103, where we have included besides the series mp the terms $2p'$, $3p'$, $4p'$, $5p'$ and their extrapolated series limit $\infty\, p'$, as well as the

* G. Wentzel, Phys. Zeits., **24**, 104 (1923); Appendix, *ibid.*, **25**, 182 (1924).

† Trabajos del Laboratorio Fisico, No. 68, Madrid, 1923.

‡ Cf. the beautiful paper by H. N. Russell and F. A. Saunders on the Structure of the Spectra of the Alkaline Earths, Astrophys. Journ., **61**, 38 (1925), which has become so extraordinarily important for the theory of the complicated spectra as expressed in terms of models. The fifth (pp')-group there given for Ca is uncertain.

|| Cf. the tables of Russell and Saunders. Instead of the individual values of the triplet-levels we have formed a sort of position of the centre of gravity for each triplet.

energy-levels of the spark spectrum which have come into question. Whereas the terms $4p'$, $5p'$, calculated relatively to their own series limit naturally have a *positive* value, they must come out *negative* relatively to the series limit ∞p ; as is made clear in the scale attached to our Fig. 103. This scale gives the term values for the arc spectrum, whereas for the spark spectrum it denotes the energies reckoned from the ground level 1S (the sign having been changed and the value having been multiplied by hc).

In the figure we have made the extrapolated limit $\infty p'$ coincide directly with the 3D-term of the spark spectrum of Ca, as is demanded by the above explanation of the accented terms. Calculation shows that this is justified (cf. Wentzel, and Russell and Saunders, *loc. cit.*) if we express the " accented terms " by means of a Ritz formula.

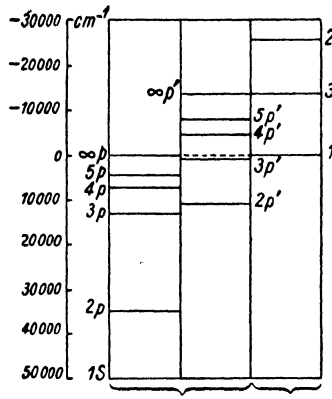


FIG. 103.—The series limits of the Ca spectrum. The " ordinary " p-terms converge on to the 1S-term of the Ca spark spectrum: the displaced or " accented " p-terms on to the 3D-term of the Ca spark spectrum.

Our " accented " Ca-terms are only one example of many. They occur not only in the analogous elements Be, Mg, . . . but in all complicated atoms in which the respective ions are not so uniquely defined as in the alkalies. We shall have to deal exhaustively with this question in the next chapter ; there we shall also discuss the selection rules according to which they combine with each other and with " unaccented " terms.

§ 8. Spark Spectra of Different Orders. "Stripped Atoms" and the Laws Underlying their Structure

We proceed to take up the thread of § 6 and consider the terms of the *spark spectra*, that is, of the ionised atoms, starting with those of the alkaline earths.

The ionised atoms Be^+, Mg^+, Ca^+, Sr^+, Ba^+ are analogous chemically to the preceding alkalies Li, Na, K, Rb, Cs, since they have a valency electron outside a closed inert gas shell, and they are also related to them spectroscopically, since they likewise have a *doublet* spectrum (cf. Chapter VIII, § 2). A comparison of Figs. 99 and 104 then also shows that the S- and the P-terms in both spectra run quite analogously and are therefore to be numbered in the same way. Concerning the values of the terms we have only to remark that, in general, the spark spectra have terms which are four times as great as those of the related arc

spectra of the preceding elements, corresponding to the four times greater value of the Rydberg number (cf. p. 365) ; for our comparison we have therefore given here not the Balmer terms but the four times greater terms of He^+ (cf. the dotted straight lines).

Let us next consider the D-term. In Be^+ and Mg^+ it is normal and hydrogen-like, but in Ca^+ it becomes abnormally great, and even greater than the first term of the P-series. We infer, exactly as in the $3d$-term of Ca (Fig. 100), that it is in danger of being drawn into the atomic core. .This actually occurs in the homologous elements Sr^+ and Ba^+. The 3_2-orbit here runs, according to the tables of atomic structure, in the interior of the atom ; the term 3D is to be numbered rationally as 4_2 and 5_2, respectively, and penetrates into the atomic core.

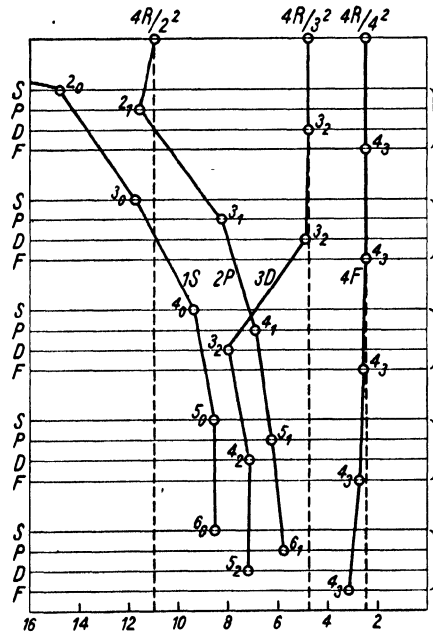


FIG. 104.—Corresponding terms of the alkaline earth spark spectra, compared with the terms of the He^+ spectrum. The symbols 1S, etc., refer to the conventional notation introduced on p. 365, the symbols 2_0, etc., to the n_i-classification.

We further compare the 3D-term of Ca^+ with those of elements that are in the same *horizontal* row instead of, as heretofore, with those of elements in the same *vertical* column. At the same time we introduce a new notation for the spectra of the ionised atoms ; this notation is more convenient, particularly for highly ionised atoms, than that which we have hitherto used (for example, for Ca^+). *We denote the different stages of ionisation with Roman figures, so that the neutral atom is indicated by I, the ionised atoms are denoted in succession by II, III and so forth.*

Instead of K we therefore now write K I ; Ca^+ is now called Ca II, the quadruply ionised vanadium atom, which we shall presently discuss, is denoted by V V. We consider the analogously constructed atoms K I, Ca II, Sc III, Ti IV, V V, all of which consist of an argon shell and *one* outer electron. This is the nineteenth electron in the genesis of the atoms. The accompanying figure 105 will give us an idea of how it is bound.

A little lower we shall discuss how the terms of such highly ionised spectra can be established with certainty.

The terms of Ca II have again been divided by 4 in Fig. 105; in a corresponding manner the terms of Sc III, which may be read off from the figure, represent only $\frac{1}{9}$ of the true term-value, those of V V only $\frac{1}{25}$ of the true value. In K I we have the following order for the terms, $1S = 4_0 > 2P = 4_1 > 3D = 3_2$, which is already known to us. In Ca II 3D has already become > 2P, in Sc III the term 3D has also passed below 1S and thence onwards remains below 1S. That is, the 3_2-orbit becomes the most stable orbit in the case of Sc III and the following spark spectra. In the progressive synthesis of the Sc-atom the nineteenth electron thus attaches itself as a 3_2-orbit. According to our figure the same applies to Ti and V, and certainly also to all the succeeding elements of the iron series. This presages the subsequent filling up of the M-shell and the beginning of the first long period, in agreement with Table 8 on page 162. Whereas the nineteenth electron is bound in a 4_0-orbit in the case of 19 K and 20 Ca, that is, it is bound in the N-shell, we find that in progressively building up 21 Sc it first occurs in the M-shell. It is only when this gap in the M-shell has been filled that the twentieth and the twenty-first electron of Sc again find their stable positions in the N-shell as 4_0-electrons (cf. Table 8). We here have a clear example of the fact that the stability of an electron (here the nineteenth) must be judged differently according to the varying value of the nuclear charge (here for 19 K I; 20 Ca II, 21 Sc III, and so forth).*

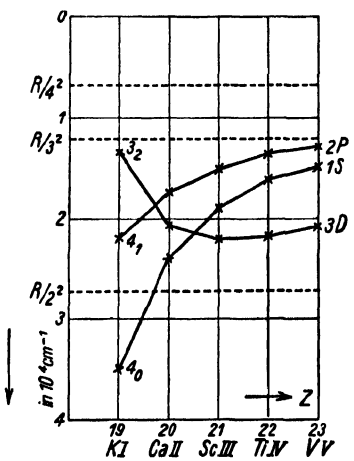


FIG. 105.—The binding of the 19th electron. The term 3D (orbital type 3_2) below Sc III lies lower than 1S and 2P (orbital types 4_0, 4_1).

In Fig. 106 we now contrast the atoms that succeed each other horizontally, Na I, Mg II, Al III, Si IV, P V, S VI, and compare the values of their terms (divided by 4 for Mg II, 9 for Al III, etc., and by

* The same argument and the same figure, qualitatively, as that used for the above series of spark spectra, hold for the series of elements:

Rb I, Sr II, Yt III, Zr IV, and Cs I, Ba II, La III.

The thirty-seventh electron, which is bound in a 5_0-orbit in Rb and Sr, occurs as a 4_2-orbit in 39 Yt; the fifty-fifth electron, which describes a 6_0-orbit in the case of Cs and Ba, is more stable in 57 La as a 5_2-orbit. Hence the filling up of the N-shell starts at Yt; that of the O-shell at La, but the process is interrupted at the rare earths in favour of the final filling up of the N-shell.

36 for S VI). All six atoms are similar either chemically or spectroscopically; chemically they are of the alkaline type, spectroscopically they are of the simple type of the doublet-systems, consisting of an H.S., a I N.S., II N.S., B.S. and so forth. Their terms 1S, 2P, 3D follow each other in beautiful regularity and become more and more hydrogen-like as the charge on the atomic core increases; 1S and 2P asymptotically approach the common value $R/3^2$ (represented in Fig. 106 by a dotted horizontal line), from which 3D never deviates by much. This limiting value bears witness to the fact that Bohr's interpretation of the terms 1S and 2P as 3_0- and 3_1-orbits in the case of Na I and Mg II in Figs. 99 and 104 was correct. Finally, the terms 4F (4_3-orbits) always lie on the straight line $R/4^2$ of hydrogen. The above-mentioned asymptotic approach to the limiting value clearly denotes that at the higher ionisation stage the peculiarities of the atomic field play a less and less important part compared with the increased charge on the atomic core, so that the field becomes more and more Coulombian, that is, the term becomes more and more hydrogen-like. There is no question here of a crossing over of the graph lines as in Fig. 105: we are here dealing with the second small period, in which all the electrons are attached on the outside, whereas the peculiar features of Fig. 105 indicated a long period and the filling of an inner shell.

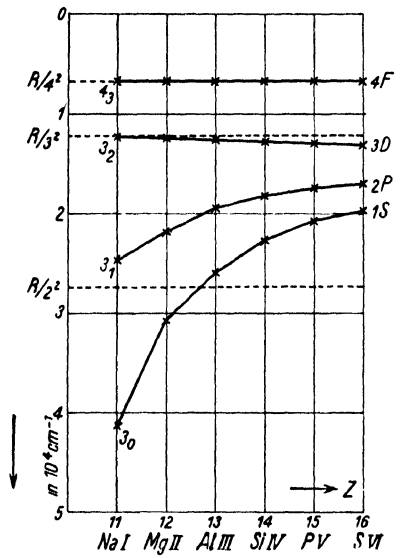


FIG. 106.—The binding of the 11th electron. The symbols 3_0, etc., denote the orbital types n_l of the outer (eleven) electrons.

Figures similar to 105 and 106 can be drawn nowadays for a great number of analogous arc and spark spectra. It will suffice if we here also discuss a figure which is of importance for us, namely that of the spectra from Mg I to S V but we refer the reader who is interested in further details to the special literature on the subject.* We are again dealing with atoms having a closed argon shell, but this time with *two* outer electrons attached. Accordingly we have singlet and triplet terms. The singlets 1S, 2P, 3D have the orbital types 3_0, 3_1, 3_2 and must con

* W. Grotrian, Graphische Darstellung der Spektren von Atomen und Ionen mit 1, 2, 3 Valenzelektronen, Vols. I and II, Springer, 1928. See also Handbuch der Astrophysik, Chap. VI, Springer, 1930.

verge towards $R/3^2$ as the nuclear charge increases. Actually the line connecting the 1S points passes beyond $R/2^2$ although it lies far below it in the case of Mg I. The triplets $2p$, $3d$ also converge towards $R/3^2$; their orbital type is 3_1, 3_2. *On the other hand, there is no term* 1s *of the triplet system;* rather, the triplet S-terms begin with $2s$, to which we had already assigned the type 4_0 in Fig. 100. We here see that this allocation is also confirmed by the spark spectra: the term curve $2s$ crosses the hydrogen straight line $R/3^2$ between Si III and P IV and evidently converges to $R/4^2$; it behaves quite differently from the curve $3d$ which belongs to $R/3^2$. We shall presently meet with a further proof of this fundamental fact. The terms $4f$ (type 4_3) again lie nearly on the straight line $R/4^2$.

In this way the correctness of the allocation of the principal quantum numbers may be proved from the spark spectra for most of the cases discussed in § 6.

Our Figs. 105 to 107 afford an excellent illustration of the way in which the unravelling of the spark spectra has developed. Originally our idea of the spark spectrum was but little clear and was purely empirical. Under the influence of Bohr's theory Fowler, in 1915, represented his photographs of the Mg spark spectrum by series formulæ involving R multiplied by a factor of 4, and immediately afterwards Bohr pointed out the possibility that there might be spark spectra of a higher order, in which 4R would be replaced by 9R, 16R and so forth. Important papers then followed by Paschen on the spark spectra of Al and by Fowler on those of Si. Since the pioneer investigations of Bowen and Millikan, which we shall discuss fully later, many associated sequences of spark spectra have been investigated.

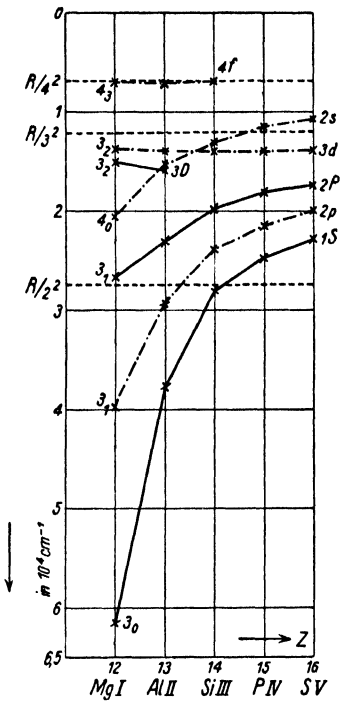


FIG. 107.—The binding of the 12th electron. With the increasing effective nuclear charge the terms continuously approach the straight hydrogen lines ($R/3^2$, etc.) belonging to the same principal quantum number as the terms themselves. Triplet terms (small letters) are connected by chain lines, singlet terms (capitals) by continuous lines.

It is easy to understand from the point of view of atomic structure why we arrive at the second spark spectrum of Al and the third

spark spectrum of Si, and so forth, and only obtain the corresponding higher spark spectra with considerable difficulty. The next step would render it necessary to attack the closed L-shell and to deprive it of an electron. But this would require far higher excitation potentials than those necessary for detaching one of the valency electrons which are much more loosely bound. Nevertheless modern spectroscopists have succeeded in many cases in breaking up the inert gas shells. We gave an example of this in Chapter II, § 1, where we spoke of the hydrogen-like spectra Li III and Be IV. There it was a question of destroying the helium configuration, the K-shell, which is actually considerably more difficult to break into than the inert gas shells of Ne, Ar and so forth.

We follow Millikan and Bowen in calling such highly ionised atoms which result from successive removal of the outer electrons, **stripped atoms.**

In comparing the arc and spark spectra we investigated (for example, in Fig. 107) how the terms divided by the square of the nuclear charge converge to the hydrogen term R/n^2 as the nuclear charge increases. We imagine the terms to be represented by a formula RZ^2/n_{eff}^2 (cf. (7), p. 389, $z = 1$ for arc spectra ; $z = 2, 3, \ldots$ for spark spectra of the type II, III, . . .) ; the points in our figure then give R/n_{eff}^2. Here we thus transfer the deviation from the hydrogen term to the effective principal quantum number n_{eff}. We may instead, of course, transfer the deviation to the nuclear charge and introduce an Z_{eff} in place of Z, so that the term would assume the form RZ_{eff}^2/n^2. Then we should share Moseley's form for the X-ray terms, namely eqn. (4) on page 284, if we neglect the relativity correction there as a rough approximation.

We set $Z_{eff} = Z - \sigma$, where σ stands for the screening action of the atomic core and any outer electrons that may be present on the radiating electron (*Leuchtelektron*). If we now concentrate our attention on a definite term in one of the preceding sequences of the spark spectra, then the screening effect just mentioned certainly remains approximately the same, because the atomic core and the outer electrons retain the same configuration ; σ remains constant and Z increases by one as we pass successively in our sequence from one spectrum to the next highest. From the term formula

$$\nu = \frac{R(Z - \sigma)^2}{n^2}$$

it thus follows that

$$\sqrt{\frac{\nu}{R}} = \frac{Z - \sigma}{n} \quad . \quad . \quad . \quad . \quad (1)$$

$\sqrt{\nu/R}$ is a *linear function of the nuclear charge ;* the angle of inclination

α of this " Moseley straight line " to the Z-axis is given by the (true) principal quantum number :

$$\tan \alpha = 1/n \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) it further follows that : *series of terms with different* σ's, *which belong to the same true principal quantum number, are parallel in the Moseley diagram, all having the direction* $\tan \alpha = 1/n$. In the case of terms that are perfectly hydrogen-like Z_{eff} is of course an integer (being equal to 1 for arc spectra, and equal to 2, 3, . . . for spark spectra of the type II, III, . . .). Then $\sigma = Z - Z_{eff}$ is equal to the total number of electrons which are present in addition to the radiating electron. In the case of terms unlike those of hydrogen σ is, as a rule, smaller. This is immediately evident in the case of penetrating orbits, because there the valency electron comes into internal regions of the atom where the effective nuclear charge is considerably higher than outside.

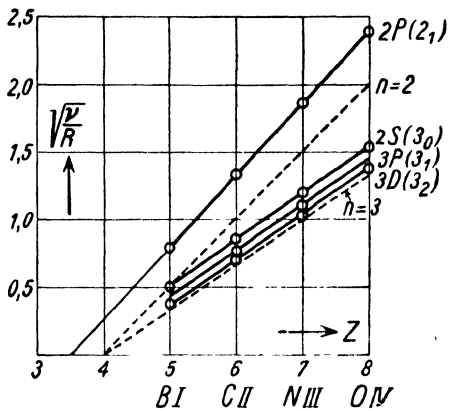


FIG. 108.—The Moseley law in optical spectra. $\sqrt{\text{term value}/R}$ is a linear function of the nuclear charge Z. The term lines run parallel to the corresponding straight lines of hydrogen ($n = 2, 3$). The numbers in brackets are the n_l orbital types. The figure represents the binding of 5th electron. Here the stable terms lie highest in the figure, in contrast to Figs. 105-107.

Abundant examples are given by spark spectra. We shall take as our first the group B I, C II, N III, O IV. In Fig. 108 we have plotted as our ordinates * the $\sqrt{\nu/R}$-values of the terms and as our abscissæ the true nuclear charges. For the sake of clearness the scale of the ordinates has been taken twice as large as the scale of the abscissæ ; thus in the figure $\tan \alpha = 2/n$. The hydrogen lines $n = 2$ and 3 have been drawn in as dotted lines. We see that the terms actually lie rather accurately in straight lines and that further the terms 2P (here the ground terms of the spectra, three outer electrons ! cf. p. 403, Fig. 102, B I) run parallel in our diagram to the straight line $\tan \alpha = 2/2 = 1$, as should be, for they belong to the true quantum number $n = 2$ (cf. Table 7, p. 160). On the other hand, the terms 2S, 3P, 3D run parallel to the straight line $\tan \alpha = 2/3$; its true quantum number is $n = 3$. In the figure the term straight line for 2P is drawn

* The following figures have been taken from the figures given in Grotrian's book, quoted on p. 410.

as far as its intersection with the axis of abscissæ. According to eqn. (1) this point of intersection occurs at the point $Z = \sigma$. The figure gives $\sigma = 3{\cdot}5$, that is, a non-integral value smaller than the value $\sigma = 4$ of the parallel hydrogen straight line $n = 2$. This corresponds to the general assertions made in the preceding section. The hydrogen straight line $n = 3$ also has the same integral value $\sigma = 4$. The term 3D which is almost hydrogen-like arrives at almost the same point of intersection whereas the more penetrating terms 3P and 2S run to the left of it.

As a second example we choose the group Mg I, Al II, Si III, P IV, S V, which we have already considered on page 411 in another con-

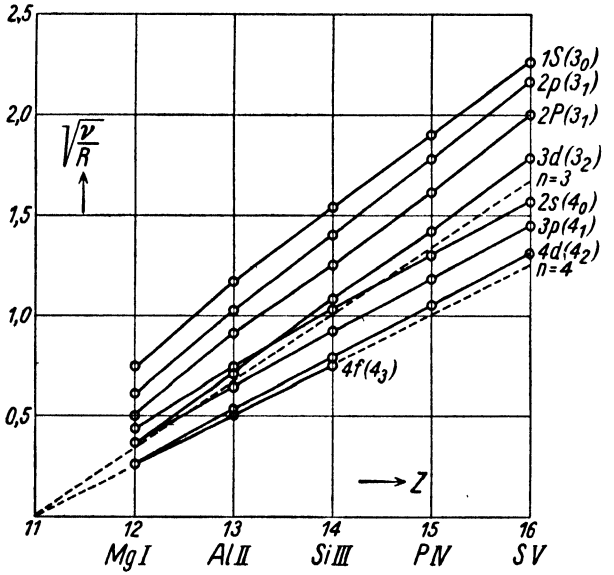


FIG. 109.—The Moseley law in optical spectra. Binding of the 12th electron. Small letters denote triplet terms, capitals singlet terms. Nomenclature as in Fig. 108.

nexion. We there saw that the terms shown in Fig. 107 are almost all *unlike* those of hydrogen ; in our present Fig. 109 this shows itself in that the Moseley straight lines of these terms lie far away from the hydrogen straight lines. *Nevertheless all terms with the principal quantum number* 3 *run appreciably parallel to the straight line* $n = 3$, *and all terms with the principal quantum number* 4 *run appreciably parallel to the straight line* $n = 4$.

As a last example we shall consider the group K I, Ca II, Sc III, Ti IV, V V, which we have also discussed earlier. Here we see that the term 3D (of type 3_2), which runs parallel to the straight line $n = 2$ and lies between Ca II and Sc III, gradually curves away from this

direction at the higher nuclear charges and approaches the direction $n = 3$, to which it belongs according to atomic theory. 1S, 2P and 4D (orbital types, 4_0, 4_1, 4_2) behave similarly: they first run parallel to $n = 3$ and betray that they belong to the quantum number $n = 4$ only if the degree of ionisation is appropriate. 4F (of orbital type 4_3) remains true to its direction $n = 4$ right from the beginning.

In Fig. 110 (as well as in Fig. 109) the term curves intersect; 3D passes beyond 2P and 1S. This, of course, denotes no more than what is stated in Fig. 105 on page 409. 3D is more stable than 2P and 1S in the case of higher nuclear charge; the nineteenth electron, with which we are concerned in our present group, is bound in a 3_2-orbit from Sc III

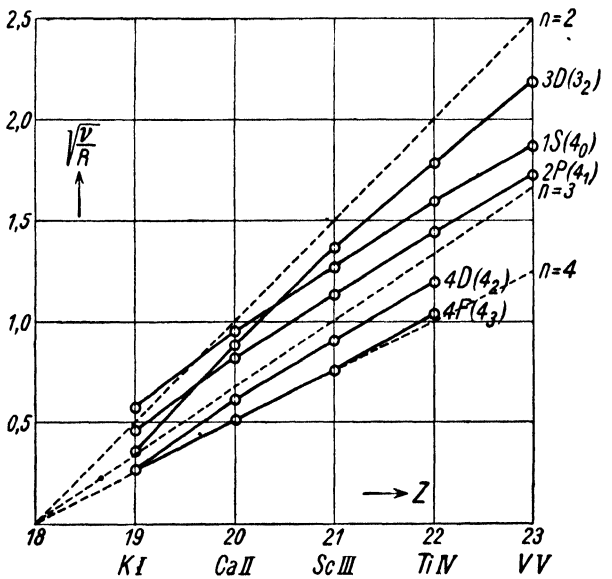


FIG. 110.—The Moseley law in optical spectra. Binding of the 19th electron. Nomenclature as in Fig. 108.

onwards, not in a 4_0-orbit, as in K I and Ca II. Such intersections of the term-curves are possible only when the ionisation has not too high a value, because the straight lines $\tan \alpha = 1/n$ move further and further apart, and so the term-curves also move further and further apart. *In the case of large nuclear charges the terms whose principal quantum number is small are always more stable than those which have a large principal number; in the case of large nuclear charges, then, we have the "ideal" periodic system* (cf. p. 156), *in which the electrons are built in systematically in the order of the principal quantum numbers.* For an intersection it is also necessary that the intersecting term, which has been built in too early as compared with the ideal system, should

not be of the hydrogen type ; for the hydrogen straight lines do not intersect in our diagram.

The validity of Moseley's law having been confirmed so strikingly in this way for optical spectra, we may conjecture that the other laws of X-ray spectra will also hold here. *The law of irregular doublets* is actually already contained in our Figs. 108 to 110. The parallelism of the Moseley straight lines states no more than that such terms form irregular doublets. It also follows from the term formula (1) on page 412 that for two terms having the *same principal quantum number*

$$\Delta\sqrt{\frac{\nu}{R}} = \sqrt{\frac{\nu_1}{R}} - \sqrt{\frac{\nu^2}{R}} = \frac{\sigma_2 - \sigma_1}{n} \quad . \quad . \quad . \quad (3)$$

must be constant, that is, must be *independent of* Z. In X-ray spectra we found that the law of irregular doublets was valid for terms that belong to the same n and j but have l's differing by 1 (cf. pp. 271 and 281). In a corresponding manner any two-term straight lines which have been coupled into an irregular doublet in our present figures also have the same n and different l's. We have been unable to make distinctions hitherto with respect to j simply because the j-fine structure of the terms (multiple structure) would not be appreciable in the small scale of our Figs. 108 to 110.

From the term formula (1) we may now draw a further important inference. We consider the *spectral line* that results from the combination of *two terms of an irregular doublet.* In Fig. 110 an example of such a line is given by the combination $1S_{\frac{1}{2}} - 2P_{\frac{1}{2}}$, which is the weaker line of the strongest doublet of lines in the K 1-spectrum. The frequency of this line comes out as

$$\nu_2 - \nu_1 = \frac{R}{n^2}(2Z(\sigma_1 - \sigma_2) + \sigma_2^2 - \sigma_1^2) \quad . \quad . \quad (4)$$

where σ_1, σ_2 are the screening constants of the two terms ν_1, ν_2 ; n has the same value in both terms because they are to form an irregular doublet. Thus eqn. (4) states : *the frequency resulting from the combination of two terms of an irregular doublet is a linear function of the (true) nuclear charge* Z. This law, which was first discovered by Millikan and Bowen * enables us to calculate beforehand the frequencies and hence the wave-lengths of these lines for the higher spark spectra if we know them, for example, for the arc spectrum and the first spark spectrum. For then we know two points on the straight line which represents the frequency as a function of Z. An important feature is that it is not necessary for this purpose to know precisely the *exact values of the combining* terms. It would also be possible to determine them approximately from Moseley's term law. Bowen and Millikan and their successors were in this way able to identify with certainty a great

* J. S. Bowen and R. A. Millikan, Phys. Rev., **24**, 209 (1924).

number of lines of highly ionised atoms from the material presented by ultra-violet spectra.

Let us take as an illustration the sequence Na I to Cl VII. In Fig. 111 the frequency of the line $1S_{\frac{1}{2}} - 2P_{\frac{1}{2}}$ is plotted as a function of Z; $1S_{\frac{1}{2}}$ here is of the orbital type 3_0, $2P_{\frac{1}{2}}$ is of the type 3_1 (cf. also Fig. 106 on p. 410). Thus the two terms belong to the same principal quantum number 3 and form an irregular doublet, because they also have the same j and l's that differ by unity. We see that the linear law is very well obeyed. In the Cl VII spectrum exact absolute values of the terms are not yet known, but it would be possible to determine the vibration frequency in question with certainty by means of the linear law and confirm it by observation.

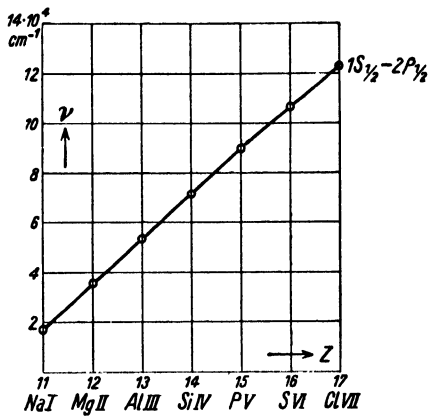


FIG. 111.—A result of the law of irregular doublets. The line frequency ν of the combination of two terms forming an irregular doublet (same n, j different l) is an approximately linear function of the nuclear charge Z.

This identification becomes still more certain in view of the following circumstance: the combination of the 1S-term with the 2P-term gives besides the line $1S_{1/2} - 2P_{1/2}$ just mentioned also the line $1S_{1/2} - 2P_{3/2}$. These two lines together form a pair whose frequency difference is $2P_{1/2} - 2P_{3/2}$. Moreover these two terms $2P_{1/2}$ and $2P_{3/2}$ represent a *relativistic* or a *regular doublet* if we apply the conception of X-ray spectra to optical spectra (cf. p. 270, Fig. 75); for in our example of the Na I to the Cl VII sequence they have the same principal quantum number ($n = 3$, see above), besides having the same l and different j's. It is seen now that *the law of regular doublets also holds quite well for optical spectra.* Thus in our case we know the amount of the difference $2P_{1/2} - 2P_{3/2}$ and hence can specify *where the line* $1S_{1/2} - 2P_{3/2}$ *must lie if the line* $1S_{1/2} - 2P_{1/2}$ *is known.*

To recognise that this law of the regular doublets is valid we must write down the term formula, including the relativity corrections of the first order. From (4) on page 284 we then obtain as our term formula in place of (1)

$$\nu = \frac{R(Z-\sigma)^2}{n^2} + \frac{R\alpha^2(Z-s)^4}{n^4}\left(\frac{n}{n_\phi} - \frac{3}{4}\right),$$

and for the relativistic doublet difference of two terms ν_1, ν_2 with a

constant n (σ and s are the same in both terms, see p. 284),

$$\Delta\nu = \nu_1 - \nu_2 = \frac{R\alpha^2(Z-s)^4}{n^3}\left(\frac{1}{n_{\phi_1}} - \frac{1}{n_{\phi_2}}\right) \quad . \quad . \quad (5)$$

Concerning the allocation of the n_ϕ-values to our l-values, see also the discussion on p. 270 and in particular Fig. 75. We see that for a relativistic doublet the two n_ϕ's that belong to the same value of l are equal to $l + 1$ and l, respectively. So the bracketed expression in (5) becomes

$$\frac{1}{n_{\phi_1}} - \frac{1}{n_{\phi_2}} = \frac{1}{l} - \frac{1}{l+1} = \frac{1}{l(l+1)},$$

and we finally obtain as our *regular doublet formula*,

$$\Delta\nu = \frac{R\alpha^2(Z-s)^4}{n^3 l(l+1)} \quad . \quad . \quad . \quad . \quad (6)$$

This law has been well confirmed in optical spectra. The only empirical quantity is the screening number s, which, moreover, is quite different from σ in the case of X-ray spectra. Formula (6) is of use not only for calculating the doublet resolutions but, surprisingly enough, also for the triplet resolutions (cf. Note 12).

As an example we choose from the sequence Na I to Cl VII the doublet resolution $2P_{\frac{1}{2}} - 2P_{\frac{3}{2}}$ (orbital type 3_1, see Table 41).

The screening numbers s are not constant but exhibit a systematic variation ; but from the values of s for Na I to S VI it would naturally be possible to extrapolate with great certainty the s-value for Cl VII and so determine exactly the above combination 1S — 2P.

TABLE 41

Spectrum	Na I.	Mg II.	Al III.	Si IV.	P V.	S VI.	Cl VII.
$\Delta\nu$ in cm.$^{-1}$	17·18	91·55	234·00	461·84	794·82	1267·10	1889·5
s . . .	7·450	6·606	6·180	5·916	5·741	5·596	5·504

Finally we must mention that all these regularities hold equally well for " heteromorphic " terms (cf. § 7) as for the " unaccented " terms which we have here above considered. For details see the monographs quoted on p. 410.

CHAPTER VIII

THE COMPLEX STRUCTURE OF THE SERIES TERMS

§ 1. Inner Quantum Numbers. Theory of Multiplets

THE regularities in the complex structure of series terms are arithmetically simple and very beautiful. Their power was manifested in unravelling complicated spectra. Their physical foundation is the fact of electron spin and its compounding with the orbital moment of momentum. We shall deal with this in the next section. First we shall develop the empirical data.

We shall proceed inductively by following on the relationships that occur in doublet and triplet systems, which have long been known and have already been touched on in the preceding chapter (for example, on p. 354). The range of these relationships then becomes extended readily into the general scheme of the complex structure of even and odd term-systems.

We begin with the triplet system as the prototype of *odd term systems*. As we know, triplet lines occur in the second column of the periodic system. The P-term is three-fold, the S-term is, as everywhere, simple. Besides the P-term, the D-term, F-term, . . . are also three-fold. The combinations (SP) or (PS) in the principal series or the second subordinate series consist of $1 \cdot 3 = 3$ components, that is, have an ordinary triplet structure.

A new kind of line-configuration with a highly significant structure occurs in the first subordinate series (II N.S.). Here the three-fold P-term combines with the three-fold D-term. We should therefore expect $3 \cdot 3 = 9$ components. But in reality only 6 components occur, the three other possible components being forbidden by selection rules. Adopting a name suggested by Rydberg * we call the whole line-configuration a *composite triplet* (*Zusammengesetztes Triplett*). We prefer to avoid the usual German term *Vollständiges Triplett* (complete triplet) because the characteristic feature of the line-configuration is just its incompleteness, that is, the actual absence of three components. The first unveiling of this structure was one of the

* Ann. d. Physik, **50**, 625 (1893); cf. in particular the section under III. See also the long paper: "Recherches sur la constitution des spectres d'émission des éléments chimiques," Swedish Academy, Vol. XXIII. (A German translation appears in Ostwald's Klassikern, No. 196.)

finest achievements of Rydberg, who accomplished it at a time when the systematic structure of series terms and their multiplicities were still wrapped in deep obscurity.

First we must make a convention about the allocation of indices to the multiple terms. The only rational way of doing this is to attach * to every term an inner quantum number, which we shall denote by J and which will presently be defined. In this way the index, which was formerly only a means of distinguishing terms, acquires a physical meaning. It now distinguishes between the combination possibilities of two terms and enables us to see at once the interval and intensity relationships that are to be expected.

We shall now illustrate the structure of the composite triplet by taking calcium as an example, choosing the I N.S. As in the preceding chapter we shall denote the triplet terms by s, p, d, instead of the more complete ^3S, ^3P, ^3D. . . . In the case of Ca the wave-number

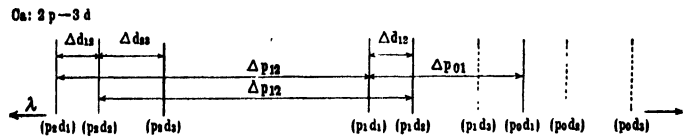


FIG. 112.—The complex triplet $2p - 3d$ of Ca. The dotted lines are missing.

differences arising from the three-fold nature of the P-term and known to us from the H.S. and the II N.S. are

$$\Delta p_{12} = 2p_1 - 2p_2 = 105{\cdot}9 \text{ cm.}^{-1}$$
$$\Delta p_{01} = 2p_0 - 2p_1 = 52{\cdot}3 \text{ cm.}^{-1}.$$

On the other hand, we obtain from the three-fold nature of the D-terms the wave number differences

$$\Delta d_{23} = 3d_2 - 3d_3 = 21{\cdot}6 \text{ cm.}^{-1}$$
$$\Delta d_{12} = 3d_1 - 3d_2 = 13{\cdot}7 \text{ cm.}^{-1}.$$

The whole line-configuration from left to right, that is, in the sense of increasing wave-numbers, consists of 3 + 2 + 1 components ; the lines shown dotted in the figure are not real. The origin of the real components can be read off from the symbols given below the figure ; the dotted lines, from left to right, denote

$$(p_1d_3)\ (p_0d_2)\ (p_0d_3).$$

By varying the thickness of the lines in the figure we have indicated

* This was first done in the preceding (German) edition of the present book and has become generally established, at the suggestion of Russell and Saunders. The earlier conventional allocation of indices followed the order of sequence of the term magnitudes, for example, p_1, p_2, p_3 in the case of the triplet P-term, instead of our notation p_2, p_1, p_0 or the more complete $^3P_2$, $^3P_1$, $^3P_0$ (see below).

that our line-configuration consists of *principal lines* and so-called *satellites*. The principal lines are

$$(p_2 d_3)\ (p_1 d_2)\ (p_0 d_1).$$

Of the satellites the one of longest wave-length, namely $(p_2 d_1)$, is the weakest; it might well be called a satellite of the second order, the others, namely $(p_2 d_2)$ and $(p_1 d_1)$, satellites of the first order.

Formerly it was regarded as strange that the Δp-differences did not occur between the principal lines themselves but between a principal line and a satellite in each case. In our configuration one of the Δp's and one of the Δd's occur *twice* in their respective cases.

It often happens that the d-difference can hardly be separated at all. The line-configuration described then passes over into an ordinary triplet. Its complex structure manifests itself, however, in that the distances between the three lines, as measured from the centre of gravity of one line to that of the other, are not exactly equal to the Δp's of the II N.S. and that between the successive terms of the I N.S. they are not exactly constant. *Hence whereas in the II N.S. the law of constant wave-number differences holds exactly* (p. 354), *it only holds asymptotically for high current numbers* (*Laufzahlen*) in *the I N.S.*

The structure of the composite triplet occurs not only in all combinations $np - md$, independently of the numbers n and m, but also in principle in all combinations of two triplet terms, for example, also in the Bergmann series $3d - mf$.

The suppression of the forbidden components indicates that the term levels differ from one another in a quantum number and that a selection rule holds for this quantum number. Since the *azimuthal quantum, which we shall from now onwards denote by* L *unstead of* l (cf. § 3), is the same, for example, for all *three* p-levels ($L = 1$), it is unable to effect a distinction between these levels. We are compelled to introduce a new quantum number, which we shall call the *inner quantum number and denote it by* J; earlier (Ch. II, § 8, Ch. VI, § 5, Ch. VII, § 1) we denoted it by j. The structure of the composite triplet is accounted for if we fix the following selection rule for J:

$$|\Delta J| \leqq 1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

so that only the following transitions are allowed:

$$\begin{matrix} & \nearrow J-1 \\ J \rightarrow J & \\ & \searrow J+1 \end{matrix} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This selection rule has already been derived in Note 8, equation (11), for the quantum number of the *moment of momentum*. We see that *the actual physical meaning* of J (cf. the analogous discussion in Chapter VI, § 5, equation (1)) *is that it defines the quantum number*

of the total moment of momentum of the atom, that is, it denotes the resultant of the moments of momentum of all the electron orbits with respect to the nucleus and their spin moments of momentum. In Note 7, under (*e*), we have based the selection rule on the correspondence principle.

Whereas the presence or absence of lines fixes only the *relative* values of the J's for the combining term levels it must be regarded as a fortunate accident that when the J's were first introduced,* at least in the case of the triplet system, the correct *absolute* values were given to the J's, as was confirmed by numerous criteria later ; namely, the values J = 1 for the S-term, J = 2, 1, 0 for the three *p*-terms, J = 3, 2, 1 for the *d*-terms, and so forth (cf. Fig. 113).

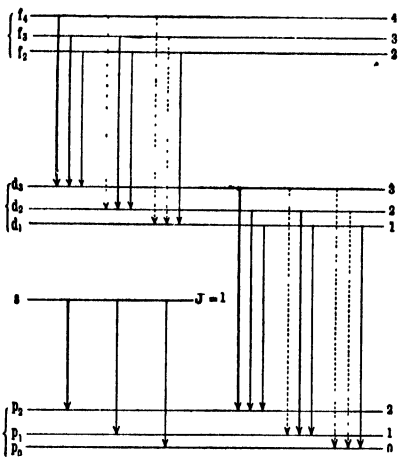


FIG. 113.—Combinations between the triplet terms *s*, *p*, *d*, *f* (diagrammatic). The dotted transitions are forbidden by the J-selection rule.

In virtue of the selection rule (2) we now read off from the figure that in the combinations (*ps*) all three components are possible, but that in the combinations (*pd*) and (*df*) only the six components of the composite triplet are allowed ; in the other three J would have to change by 2 or 3 units.

At the same time the varying thickness of the vertical lines in our figure gives expression to an intensity rule which we have already encountered in a somewhat specialised form in X-ray spectra (p. 245) and in the fine-structures of hydrogen (p. 273), namely : *of the three transitions* (2) *that which moves in the same sense as the transition of the azimuthal quantum number* L *must occur with greatest intensity and the intensity is to decrease the more the more the type of the transition in* J *deviates from that of* L. Accordingly we shall speak of a " strong," or " less strong " and a " weak transition." This " qualitative intensity rule " will be refined in § 9 by means of a quantitative condition. We may now convince ourselves that our earlier remarks about Fig. 112 in referring to principal lines and satellites are summarised in our present qualitative intensity rule. Principal lines arise from the " strong " transitions, in which J decreases by 1, that is, moves in the same sense as the azimuthal quantum number L,

* Ann. d. Phys., **63**, 221 (1920).

which simultaneously decreases from 2 to 1. Satellites of the first order result from the "less strong" transitions $\Delta J = 0$, the satellite of the second order $(p_2 d_1)$ results from the "weak" transition $1 \to 2$ of the inner quantum number, which moves in the sense opposite to that of the transition $2 \to 1$ of the azimuthal quantum number. Our intensity rule is also verified in the combinations (ps). As Fig. 113 indicates the strongest component is $(p_2 s)$, in which J, like L, increases by 1. $(p_1 s)$ is weaker, corresponding to $\Delta J = 0$. The weakest is $(p_0 s)$, because here J decreases by 1, that is, it moves in the contrary sense to L. In § 9 we shall see that the quantitative ratio of these three components is 5 : 3 : 1.

We must consider the combinations (dd') and (pp') between the "heteromorphic" triplet terms of the alkaline earths (cf. Ch. VII, § 7). They do not consist, like the composite triplets, of 3 + 2 + 1 components but of 2 + 3 + 2 components in the case of (dd') and of 2 + 3 + 1 components in the case of (pp'). Their structure may be understood, according to R. Götze,* from the scheme of inner quantum numbers in the following manner.

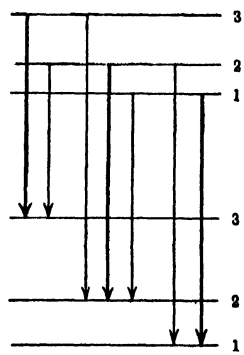


FIG. 114.—Combination (dd') in the triplet system. The lines with $\Delta J = 0$ are the strongest.

In Fig. 114 we depict the group (dd'). The levels d'_3, d'_2, d'_1, being initial levels, lie above and the levels d_3, d_2, d_1, being final levels, lie below. The azimuthal and the inner quantum numbers have been written alongside the levels as earlier. Leading to d_3, J = 3, there are two transitions, namely from d'_3, J = 3, and from d'_2, J = 2. The *transition* $d'_1 \to d_3$ is *forbidden* because it would denote a change of the inner quantum number by *two* units. Leading to d_2 there are three allowable transitions, but to d_1 there are again only two, since the transition $d'_3 \to d_1$ is *forbidden*, because this would make the inner quantum number change by *two* units; all this agrees with the experimental results. As we see, the structure of this line-configuration distinguishes itself in a characteristic way from the composite triplet of the I N.S., but is described by the same *selection rule for inner quantum numbers* as the latter.

But our *intensity rule* is also shown to be valid here. Since the azimuthal quantum number L is the same in the initial and the final state those transitions of the inner quantum number J for which $\Delta J = 0$ are to be regarded as moving in the same sense as L. Actually here, as indicated in Fig. 114, the combinations $d_3 d'_3$, $d_2 d'_2$, $d_1 d'_1$ are

* Ann. d. Phys., **66**, 285 (1921).

the *strongest*. The weaker components lie in the centre group *on either side* of the " principal line " $d_2d'_2$; in the two outer groups we have a satellite either on the *short-wave side* or on the *long-wave side*, that is fundamentally different from the type of the composite triplet in the I N.S. but in complete accord with our intensity rule for the inner quantum numbers.

The same type occurs in the combination (pp') but with the following characteristic difference : whereas in (dd') the line $d_1d'_1$ belonged to the three principal lines the *corresponding line* $p_0p'_0$ *is absent in* (pp').

We take account of this if we supplement the selection rule (2) by the following negative rule (Verbot), which was first enunciated by Landé in another connexion (see below) : *the transition*

$$0 \to 0 \quad . \quad . \quad . \quad . \quad . \quad (3)$$

is forbidden in the case of the inner quantum number. This additional rule, as stated above, makes the group (pp') consist of $2 + 3 + 1$ components, and not, like the group (dd'), of $2 + 3 + 2$ components. There is an apparent exception in the case of Mg which exhibits a group of only five lines, symmetrically disposed with respect to the central line, which is likewise interpreted by Paschen, on account of its Zeeman effect, as a combination (pp'). Here we encounter the peculiarity that the $\Delta p''$s coincide almost exactly with the Δp's, with the result that two components coincide and hence the number of lines is reduced from six to five. We shall show in § 10 that this equality in the resolutions is not fortuitous but can rather be founded quite satisfactorily on the ideas of the model.

The groups (pp') and (dd') are characteristic for all triplet systems and hence also occur in the spectra of ionised atoms such as B II, C III, N IV, Al II, Si III, P IV (cf. the preceding section). Bowen and Millikan call them the " flag " of the corresponding state of ionisation.

Instead of using the Figures 113 and 114 we may also depict the structure of the groups (dd') and (pp') and their relationship with the group (pd) by means of the above number schemes. The uppermost bracketed number denotes in each case the intensity * of the component in question ; below it is the wave-length in international Ångströms and below that the wave-number ν. The differences $\Delta\nu$ between the wave-numbers in the horizontal and in the vertical direction have been printed in italics alongside and below the ν's. The first group (which coincides with Fraunhofer's G) may be described, according to Chapter VII, § 7, as $2p - 2p'$, the central group as $3d - 3d'$, and the last group as $2p - 3d$.

* The intensities in the case of (dd') and (pd) have been taken from the quantitative measurements of the Utrecht Institute (cf. § 9).

		p'				
	J	2		1		0
p	2	(100) 4 302·53 23 235·66	*86·75*	(75) 4 318·65 23 148·91		
		105·87		*105·75*		
	1	(75) 4 283·01 23 341·53	*86·87*	(75) 4 298·99 23 254·66	*47·13*	(75) 4 307·74 23 207·53
				52·30		
	0			(75) 4 289·38 23 306·96		

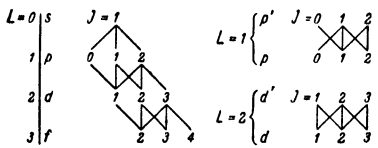
		d'				
	J	3		2		1
d	3	(100) 5 588·74 17 888·15	*40·04*	(13·6) 5 601·28 17 848·11		
		21·70		*21·76*		
	2	(15) 5 581·97 17 909·85	*39·98*	(56) 5 594·46 17 869·87	*26·69*	(13) 5 602·83 17 843·18
				13·92		*13·85*
	1			(13) 5 590·11 17 883·79	*26·79*	(37) 5 598·48 17 857·03

		d				
	J	3		2		1
p	2	(100) 19 771·1 5 055·1	*22·2*	(20) 19 864·3 5 032·9	*13·3*	(1) 19 917·2 5 019·6
				106·6		*105·6*
	1			(56) 19 452·6 5 139·5	*14·3*	(20) 19 506·8 5 125·2
						52·1
	0					(26) 19 310·3 5 177·3

The triangular form of the last as compared with the diagonal form of the two preceding schemes is characteristic of the possibilities of combination given by the inner quantum numbers, just as is the gap in the space $0 \to 0$ in the first scheme. The fact that we have here chosen as an example of the *pd*-group a line-configuration which lies far in the infra-red is because it shows up the equality of the Δp- and the Δd-differences within all three schemes. (Owing to the difficulty involved in making infra-red measurements this equality is, however, rather unsatisfactory.) As regards the intensity the diagonal is emphasised in all three schemes, as is demanded by our intensity rule. The intensities of the (*pd*)-configuration have not, of course, been measured in the infra-red combination $2p - 3d$, but in the visible combination $2p - 4d$. We shall show in § 9 that it is permissible to transfer our measurements in this way.

We summarise our conclusions about the triplet system in an arithmetical scheme which can be generalised very widely :

Scheme A



The connecting lines denote possible combinations ; the unconnected J-values do not admit of combination, in particular, not the values 00 in the scheme for (*pp'*).

Very interesting new material concerning the selection questions are further given by the "*inter-combinations*" *of triplet and singlet terms*, such as occur in the whole group of divalent elements, the alkaline earths and related elements. We need refer only to the resonance line of Hg, $\lambda = 2537$, $\nu = 1S - 2p_1$, and the analogous lines for Zn, Cd, Mg . . . Ba, given in Table 39. As in that table we here denote the singlet terms by S, P, D and the triplet terms by s, p_J, d_J. The following scheme gives a survey of the combinations possible between these two sets of terms :

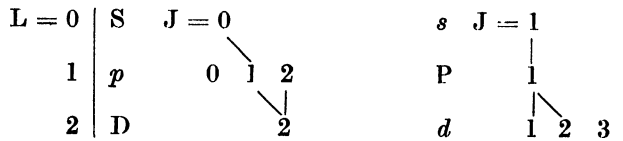
Permissible types : Sp_1, Pd_2, Pd_1, p_2D, p_1D.
Forbidden types : Sp_2, Sp_0, Pd_3, p_0D.

All that we now have to do is to attach to the singlet terms those quantum numbers that enable us to understand from the selection rules why the types specified in the lower line are forbidden. There can be no doubt about the azimuthal quantum numbers : we must set L = 0, 1, 2 for S, P, D. The fact that inner quantum numbers are also active in the singlets is shown directly by the decrees

forbidding certain combinations. We set J = 0, 1, 2 for S, P, D. We then obtain immediately the exclusion (*Verbot*) of Sp_2 from the general selection rule (2) and the exclusion of Sp_0 from the supplementary rule (3). It was the absence of the line Sp_0 that first led to the enunciation of this supplementary rule.*

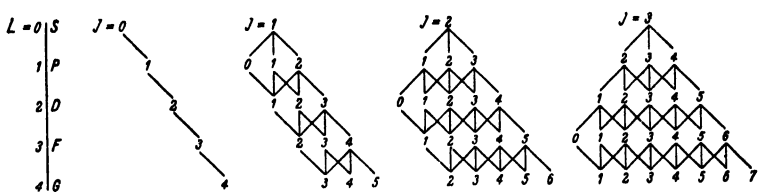
An arithmetical scheme again shows most simply that by assigning the above values to J we have also correctly given the inter-combinations between the P- and the D-terms :

Scheme B



We are now sufficiently prepared to fix the complex structure of the *odd terms* generally ; we leave the *even terms* (doublet, quartet, octet systems) to be dealt with a little later. *To denote the terms generally we now use capital letters and add the multiplicity as an index above and in front of the capital*, for example, in the quintet system ^5S, ^5P, ^5D. The following sections will show that we can now give examples for all the structures that are now to be enumerated :

Scheme C



The above scheme states that the S-term, L = 0, is always simple. The P-term is three-fold (except in the singlet system), the D-term five-fold (except in the singlet and the triplet system). *The number of levels increases in odd steps until J assumes the value 0 for the first time.* After that the number of levels is *permanent.* Hence the singlet system consists of simple terms, because here the quantum number J = 0 already belongs to the S-term. In the triplet system the permanence of the multiplicities is attained in the P-term, in the quintet system it is attained in the D-term, and so forth. If we denote the *J-value of the S-term by S* and the permanent number

* A. Landé, Phys. Zeits., **22**, 417 (1921).

of levels, that is, the multiplicity of the term-system in question by r, then we have generally

$$r = 2S + 1 \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The notation S for the J-value of the S-term at the same time indicates the "spin moment of momentum." *We also call S the spin quantum number.* The maximum value of J increases steadily with L in each row; the minimum value of J first decreases to zero and then likewise increases.

In general we have

$$\begin{cases} J_{max} = S + L \\ J_{min} = |S - L| \end{cases} : \begin{cases} S - L \text{ for } S \geq L \\ L - S \text{ for } S \leqq L \end{cases} \quad . \quad . \quad (5)$$

That is,

$$S + L \geqq J \geqq |S - L| \quad . \quad . \quad . \quad (6)$$

In particular we have from (5) for the S-term ($L = 0$) for any degree of multiplicity

$$J_{max} = J_{min} = S,$$

corresponding to the above remark that the J-value of the S-term is caused by the electron spin alone.

The connecting lines in our scheme tells us what term-levels combine with one another according to the generally valid selection rule $|\Delta J| \leqq 1$. We follow Catalan * in calling the configurations which then result and which are rich in lines *multiplets*. Every wave-number difference $\Delta\nu$ in general occurs *twice* in a multiplet, but at the beginning and at the end of the term sequence only *once* in given cases, namely, when in our scheme only one connecting line runs towards one of the two term-levels whose energy difference is given by the $\Delta\nu$ in question. For example, let us compare the combinations (PD) in the quintet or the septet system with that in the triplet system; they do not consist, like the latter, of $3 + 2 + 1$ components but rather, as we read off from our scheme, of $3+3+3$ or $1+2+3+2+1$ components according as we group with respect to the P- or the D-term. The combination (DF) in the quintet system consists of $3 + 3 + 3 + 2 + 1 = 12$ components, in the septet system it consists of $3 + 3 + 3 + 3 + 3 = 15$ components, and so forth.

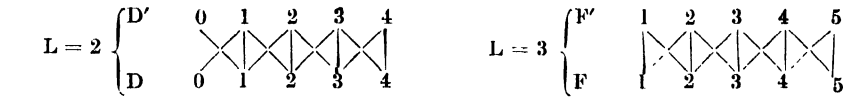
Besides the combinations between terms of the same system intercombinations also occur. These give rise to line-configurations of special structure, the detailed description of which would lead too far here, which may, however, be easily obtained by analogy from the Scheme B. To fix the inner quantum numbers and to recognise the

* His earliest papers: Trans. Roy. Soc., **223**, 127 (1922); Anal. Soc. Esp. Fis. y Quim., **21**, 321 (1923).

term-systems such inter-combinations are of particular significance because we can learn from them the relationship between the inner quanta of the one system to those of the other.

In complex spectra the combinations of the type $\Delta L = 0$ (cf. §§ 3 and 4) become of increasing importance. We give as examples only the groups (DD′) and (FF′) in the quintet system, which are distinguished from one another in a characteristic way in accordance with the supplementary decree which forbids $0 \to 0$:

Scheme D. Quintet



They consist of $2 + 3 + 3 + 3 + 1 = 12$ and $2+3+3+3+2 = 13$ components respectively.

Hitherto we have restricted ourselves to the odd multiplicities. Of the *even multiplicities* we already know the doublet system, $r = 2$. Here the S-term is *simple*, the P-term and all subsequent terms *double*. The same holds for the quartet system : the permanent number of levels is $r = 4$; it is attained at the D-term. Before this, however, the number of levels increases in odd numbers, thus it is 1 for the S-term, 3 for the P-term, and so forth. *In general we have for an even value of r the number of levels* 1, 3, 5, . . . *in the S, P, D,-term and then this number assumes the final permanent value r at the next term.* We must emphasise that this fundamental character of the even term-systems was first deduced from the experimental and theoretical investigation * of the anomalous Zeeman effect of Mn.

If we retain the formula (4) we see immediately that the spin quantum number S is necessarily a *half-integer* when r has an even multiplicity : $S = \frac{1}{2}$ for a doublet system, $S = \frac{3}{2}$ for a quartet system, and so forth. $S = \frac{1}{2}$ evidently corresponds to the occurrence of doublets when there is one valency electron (alkalies, hydrogen), since we should have to assign the spin quantum number

$$S = \tfrac{1}{2}$$

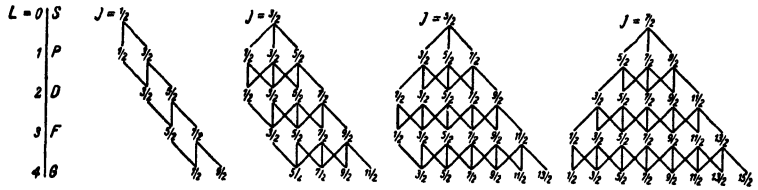
to the individual electron.† In the same way $S = \frac{3}{2}$ corresponds to the addition of *three* spin moments, and so forth. The quantum number L of the revolving motion, however, always retains its *integral* character in the case of the even term-systems : $L = 0$ for the S-term, $L = 1$ for the P-term, and so forth. When L and S are compounded we then get the *half-integral* character of J_{max} and J_{min}

* E. Back, Zeits. f. Phys., **15**, 206 (1923) ; A. Landé, *ibid.*, p. 189.

† Earlier we denoted the spin quantum number of the individual electron by s (cf. p. 330). We shall retain this notation in the sequel for the *individual* electron, so that we might have written above $S = s = \frac{1}{2}$. In general we take S to stand for the quantum number of *several* electrons. Cf. § 3 on this point.

and all the intermediate values of J, in accordance with the equations (5) and (6). In this way we arrive at the following scheme for the *even term-systems :*

Scheme E



The connecting lines in Scheme E again indicate the combinations which are possible according to the selection rule (2). The selection rule (3) obviously does not apply here. The intensity rule holds in the same form as in the case of odd terms. In the higher terms and term-systems multiplets of increasing complexity also occur here. Every $\Delta\nu$ in general occurs twice in them, but in certain circumstances only once. If we consider in particular those multiplets that arise from the combination of the permanent sequences of terms, we see that the " composite doublet," for example (PD), consists of $2 + 1 = 3$ components, the " composite quartet," for example (DF), consists of $3 + 3 + 2 + 1 = 9$ components, the " composite sextet," for example (FG), consists of $3 + 3 + 3 + 3 + 2 + 1 = 15$ components.* The combination (SP) is an ordinary triplet except in the doublet system ; the combination (PD) has the same structure in the sextet and the octet system as, for example, in the quintet system, and only exhibits in the quartet system the peculiar structure that results from the existence of only four D-levels. Two line-configurations which are of similar structure in this way and which belong to different term-systems are distinguishable only by means of the interval rule or the quantitative intensity rule, but most certainly by their Zeeman effects.

The terms of even multiplicity are also distinguished among themselves by having their J-values attached as suffixes to the symbols S, P, . . . and their multiplicity indicated by an index in front of these symbols. Thus the term-expression for the two D-lines is as follows (we use the conventional numbering of the principal quantum numbers 1S, 2P, . . . in the second column and the rational numbering 3S, 3P, which is adapted to the periodic system in the third column) :

	Conventional notation	Rational notation
D_2, $\lambda = 5890$	$\nu = 1^2S_{\frac{1}{2}} - 2^2P_{\frac{3}{2}}$	$\nu = 3^2S_{\frac{1}{2}} - 3^2P_{\frac{3}{2}}$
D_1, $\lambda = 5896$	$\nu = 1^2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$	$\nu = 3^2S_{\frac{1}{2}} - 3^2P_{\frac{1}{2}}$

* In general 6S, also in the case of permanent odd terms.

§ 2. Alternation of Even and Odd Terms in the Periodic System

The alkalies in the first vertical column of the periodic system exhibit the well-known *doublets*, which have contributed in a very particular way to finding order in spectra and which led us to recognise principal series, subsidiary series and so forth. The precious metals Cu, Ag, Au exhibit doublet relationships (as well as quartets). *The alkali earths in the second vertical column have singlet and triplet terms*, and so have the elements Zn, Cd, Hg, so long as we restrict ourselves to their arc spectra. *In the third vertical column* the widely separated *doublets* of Tellurium have long been known; the spectra of B, Al, Ga, In have the same character.

These facts led Rydberg * to suspect a regular alternation of doublet and triplet structure in the periodic system, such that the elements of *odd valency* should exhibit *doublets*, these of *even valency* should exhibit *triplets*. Of the individual series that were known outside the first three vertical columns the triplet series of O, S, Se (Runge and Paschen) confirmed this rule, whereas the so-called triplet series of Mn (Kayser and Runge) appeared to contradict it.

We know nowadays that *Rydberg's Law of Alternation* must be formulated as follows: not the alternation of doublets and triplets but *the alternation of odd and even terms governs the periodic system.* As we saw in the preceding section triplets in the combination (PS) occur not only in the case of odd systems but also in even systems so long as the P-term has not yet become a permanent term in them. This clears up the apparently exceptional position of the Mn-triplet: in spite of its triplet (PS) the Mn-spectrum presents an excellent example of even term structure; it was precisely this example that led Back and Landé (cf. p. 429) to recognise the general scheme of the structure of even terms.

According to our scheme of classification the alternation of even and odd terms simultaneously entails an *alternation between the half-integral and integral nature of the J-values.* In particular it denotes for the spin quantum number S a change by $\pm \frac{1}{2}$ when passing from one element to the next. The indefiniteness of the sign is significant here. When we advance from $S = \frac{1}{2}$ (doublet system) in the first vertical column of the periodic system to $S = 1$ (triplet system) and at the same time to $S = 0$ (singlet system) in the second vertical column, we assert that in general these two transitions $\Delta S = \pm\frac{1}{2}$ are possible in principle. Thence it follows, however, that, on the one hand, the maximum multiplicity $r = 2S + 1$ (Equation (4) on p. 428) of the possible term-systems increases by 1 for each step from left to right in the periodic system, and that, on the other hand, the number of possible term-systems increases by 1 when we pass from an element

* Cf. Kayser, Handb. der Spektr., **2**, 590, No. 464.

TABLE 42

19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn
	Sing.		Sing.		—	—	—		Sing.		*Sing.*
Doubl.	Tripl.	*Doubl.*	*Tripl.*	Doubl.	Tripl.	—	Tripl.	Doubl.	*Tripl.*	*Doubl.*	Tripl.
		Quart.	Quint.	*Quart.*	Quint.	Quart.	*Quint.*	*Quart.*	Quint.	Quart.	
				Sext.	*Sept.*	*Sext.*	Sept.	Sext.			
						Oct.					

of even valency to the next element of odd valency. This step-by-step increase of the maximum and actual number of multiplicities is one of the reasons for the increasing complexity of the spectra as we proceed towards the right-hand end of the periodic system and for the simplicity in understanding the spectra of the first vertical columns. We illustrate this by means of the elements from K to Zn in passing along the first great period. Table 42 exhibits the term-systems so far analysed; those that are yet to be expected are denoted by horizontal strokes.

Among the various term-systems that one is distinguished to which the ground-term, the most stable unexcited state of the atom, belongs. Not only this ground-term but also the excited terms of the same system will in general be represented by having a specially pronounced intensity in the spectrum. This favoured term-system has been shown in italics in our table. In the case of iron, for example, the quintet system is the favoured one. The lines of the septet system are already considerably weaker. The excitation of the nonet system, although possible in principle, would signify an intrusion far into the inner electronic structure of iron; in ordinary excitation this term-system therefore does not occur.

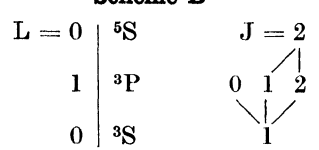
The regular advance of the ground-term which our Table 42 brings into evidence and which is interrupted only at Cr (septet instead of quintet system) may be understood from Pauli's Principle and from the scheme of the periodic system. We shall deal with this in the next section.

Of the two small periods that precede the iron group we shall consider

for the present only the sixth column, that is, the spectra of O and S. There have long been known of them : A, a series system of triplet lines, measured by Paschen and Runge, and B, a system which was described as a doublet system by Paschen and Runge in the case of O.

To determine the structure of these series we have the following data : Paschen and Landé * recognised the oxygen triplet of the system A at $\lambda = 7772$ and $\lambda = 3947$ by their Zeeman effect as members of a *quintet system*. Hopfield † then found series of triplets in the extreme ultra-violet series, which were shown to be combinations of a three-fold P-term of low level with the terms S and D of the so-called doublet system ; the D-term does not appear resolved in them. Finally Hopfield and Birge ‡ ascertained that the same P-term inter-combines with the S-term of the quintet system. From the fact that in this inter-combination one of the three components ($P_J S$) drops out, the J-values of the P-term may be specified from the selection rules for the inner quanta. This is shown in the following scheme B', which is analogous to the scheme B of the preceding section :

Scheme B'



The first-mentioned S-term has as its quintet term $J = S = 2$. The P-term must have $J = 2, 1, 0$, the combination $2 \rightarrow 0$ being forbidden. The S-term, which combines completely with P, then has $S = 1$. Hence $r = 2S + 1$ here becomes equal to 3. The terms SPD of the so-called doublet system thus in reality form a *triplet system*. The complex structure of O, quintet and triplet system, thus accords perfectly with the alternation law. The low-lying P-term is at the same time the ground-term of the oxygen spectrum. The wave-lengths of the ground-triplet PS are $\lambda = 1302, 1305, 1306$ Å.

In sulphur only the so-called triplet (in reality quintet) system was known, according to Paschen and Runge. In addition Hopfield has found lines of the triplet system in the ultra-violet. The *ground-term* of S belongs to the latter system and is again a P-term.

The alternation law holds without exception right down to the beginning of the periodic system, as far as He and H. As we know, hydrogen has a doublet spectrum as a one-electron system, helium

* Zeits. f. Phys., **15**, 189 (1923).

† J. J. Hopfield, Phys. Rev., **21**, 710 (1923) ; Nature, **112**, 437 (1923) ; Astrophys. Journ., **59**, 114 (1924).

‡ J. J. Hopfield and R. T. Birge, Nature, **112**, 790 (1923). Cf. O. Laporte, Naturwiss., **12**, 29 (1924).

has a singulet spectrum (parhelium) and a triplet spectrum (orthohelium) as a two electron system. The spin action of the two electrons can annul or reinforce each other. A doublet system then again follows in the case of univalent lithium. In fact, the assertion of the alternation law is just as general as the first law of atomic structure, according to which the number of extra-nuclear electrons increases by one from element to element, that is, alternates between odd and even.

Our information for judging questions of term structure becomes much richer if we use *spark spectra* as well as arc spectra.

The limit between these two series types is usually not drawn sharply in experimental work. The spark spectra often occur in certain parts of the arc, but are then strengthened in the spark (**enhanced lines**). Many arc lines are vice versa also present as a rule in the emission spectra of sparks.

An unobjectionable *experimental means of distinguishing between spark and arc lines* is given by a canal ray method devised by O. Wien.* According as the canal ray which emits the line is deflected or not in passing through an electric condenser the line belongs to the spark or the arc spectrum respectively. This method confirms the spectroscopic classification in the case of H and Hg (all the Balmer lines and the well-known mercury series lines cannot be deflected); it also shows that certain oxygen lines previously called spark lines are actually O^+-lines, whereas the lines of the Paschen-Runge series, being true arc lines, are not deflected. In a method described by R. Seeliger † spark lines are represented, owing to the potential fall which starts from the cathode in the Geissler tube, as arc lines, in agreement with the distinction between "long" and "short lines" already introduced by Lockyer.

The definition of the spark spectrum of the first and higher order leads directly to the following "displacement law": ‡ *the first spark spectrum of every element is similar in structure to the arc spectrum of the element which precedes it in the periodic system;* it consists of doublets, triplets, or multiplets of precisely the same character as the arc spectrum of the preceding element. *In the same way the spark spectrum of the second, third . . . order is similar in structure to the arc spectrum of the element which lies two, three . . . steps behind in the periodic system.* We have often used this law previously, particularly in § 8 of the preceding chapter, where we compared "corresponding" series of spark lines with one another. In general, spectra and terms belonging to the same electronic arrangement must have a similar structure. We shall illustrate this law by two particularly characteristic and historically interesting examples.

* Ann. d. Physik, **69**, 325 (1922).

† *Ibid.*, **59**, 613 (1919), and in particular (with D. Thaer), *ibid.*, **65**, 423 (1921).

‡ W. Kossel and A. Sommerfeld, Auswahlprinzip und Verschiebungssatz bei den Serienspektren. Verhand. d. D. Phys. Gesellschaft, Jahrg. **21**, 1919.

1. **Alkalies and Inert Gases.**—The doublet system of the alkalies is a typical flame spectrum (sodium "head") or arc spectrum and so, of course, arises from the neutral and not the ionised atom. Through the removal of an electron the alkali atom is subjected to the greatest conceivable change. It joins the rank of the inert gases, that is, it moves from the beginning of one period to the end of the preceding period. For the spectrum this denotes the transition from the simple conditions which rule at the beginning of the period to the complicated conditions which prevail at the end of a period and which involve an abundance of lines.

In accordance with their chemical inertness the outer electrons of inert gases are many times more tightly bound than the chemically particularly active outer electron of the alkalies. The same holds for the alkali ions which are like the inert gases in character. In contrast with the arc spectra the spark spectra of the alkalies should therefore be relatively difficult to excite: and actually, the difference between the energy necessary to excite the arc and the spark spectrum is not as great for any element as for the alkalies.

In 1894 Eder and Valenta * found that Na and, in particular, K if subjected to an intense spark discharge emit besides the series spectrum a new spectrum, very rich in lines, which lies mainly in the ultra-violet. Afterwards Goldstein † succeeded in 1907 in choosing the conditions (matter as finely distributed as possible and current density as high as possible) so that this spectrum, which he called "ground spectrum" (*Grundspektrum*) appeared pure and without the admixture of arc lines.

Goldstein's observations were restricted to the visible region. The abundance of lines, however, which is characteristic of ground spectra, comes into full expression only in the ultra-violet and has since then been noted by many observers.

2. **Alkaline Earths and Alkalies.**—Lorenser,‡ a pupil of Paschen's, had occupied himself even before the Bohr theory had been introduced with the doublet spectra that occur in the alkaline earths. Following on Saunders || he established that Ritz's formula is unsuited to representing these series and he therefore calculated them according to the formula

$$(n, q) = \frac{A}{(n+q)^2}, \quad . \quad . \quad . \quad . \quad (1)$$

which was empirical in the first place; here not only q but also A, which takes the place of R, can be disposed of, that is, given a suitable value. Lorenser found a satisfactory expression, in particular for the

* Denkschr. Wien. Akad., **61**, 347 (1894); cf. also the Beiträge zur Photochemie, etc., p. 109, Vienna, 1904.

† Verhandl. d. D. Phys. Gesellsch., **9**, 321 (1907).

‡ Diss. Tübingen, 1913. || Astrophys. Journ., **35**, 352 (1912).

higher series lines, by assuming values for A which lay more or less near that of $4R = 438948$.

The question was again taken up by Fowler * in 1915 for the case of Mg, this time under the direct influence of Bohr's theory. Fowler gave an exhaustive description of the Mg spark spectrum which had been newly measured by him, and he ordered it into series with the term denominator 4R.

In general this denominator causes the spark terms to be displaced towards the ultra-violet as compared with the corresponding arc terms. In the higher spark spectra we have, of course, instead of 4R, the factors 9R, 16R, and so forth. Examples for the consequent displacements of the spectra into the ultra-violet are given in profusion by Millikan and Bowen's researches on stripped atoms.

We add here a digression on the spectroscopy of the solar and star spectra.

3. **Astrophysical Applications.**—M. N. Saha † has drawn extraordinarily convincing consequences from the differences between the spark and the arc spectra in the case of solar physics. In the sun's spectrum (Fraunhofer spectrum of the photosphere, cf. below) only 36 of the 92 elements found on the earth are represented. For example, Rb and Cs are absent, K is weakly represented and Na very strongly. Are Rb and Cs really not present in the sun ? Saha's answer runs : they *are* present but in the ionised state. Consequently not the characteristic arc lines appear, which we would ordinarily expect, but the spark spectra which, since they lie mainly in the ultra-violet, escape detection by the ordinary methods.

What circumstances favour the appearance of spark lines and increase their intensity relative to that of the arc lines ? We adduce three causes : (1) high temperature, (2) low pressure, (3) low ionisation potential. The first two factors relate to the special circumstances of the sun, the last to the nature of the atom under consideration. A low pressure favours the ionised atomic state as compared with the neutral state in that it renders more difficult the recombination of the ions with free electrons.

In the sun we distinguished three regions of different temperature and pressure conditions : (*a*) the true boundary of the luminous sun's disc, the **photosphere,** whose " effective temperature " is taken as 6000° C. and whose pressure is probably about 10^{-3} atmospheres ; (*b*) the sun's atmosphere, the so-called **chromosphere,** in which the temperature decreases with height to 5000° C. and the pressure diminishes to zero ; and (*c*) the **sun-spots,** whose temperature is taken as 1000° to 2000° lower than that of the photosphere. Whereas

* Phil. Trans. (A), **214** (1914) ; cf. also Proc. Roy. Soc., 1915 ; Bakerian Lecture and Nature, 1915.

† Zeits. f. Physik, **6,** 40 (1921) ; in greater detail, Phil. Mag., **40,** 472 (1920) ; **41,** 809 (1921) ; Proc. Roy. Soc., **99,** 135 (1921) ; cf. also H. N. Russell, Astrophys. Journ., **55,** 129 (1922).

the spectra of the photosphere and the sun-spots are absorption spectra the spectrum of the chromosphere is observed as an emission spectrum during solar eclipses.

We shall first discuss the behaviour of the alkalies: the D-lines are more intense in the sun-spots than in the photosphere; in the chromosphere they vanish entirely above a certain height. The arc lines of Rb occur feebly in sun-spots; they are absent, as already mentioned, in the photosphere and hence, of course, also in the chromosphere. Nor has Cs hitherto been proved to be present in sun-spots. This grading from Na over Rb to Cs corresponds throughout with the grading of their ionisation potentials, cf. Table 38 on p. 382.

A further characteristic is the prominence of the doublet spark spectra of Ca, Sr, Ba in the Fraunhofer spectra of the photosphere, for example, of the two Fraunhofer lines H and K (H.S.-doublet 1S—2P of Ca^+) and the fact that they stretch up into the greatest heights of the chromosphere (14,000 km.). The ground-line of the arc spectrum of Ca, $\lambda = 4226{\cdot}73$, Fraunhofer's g-line (combination of the singlet S with the singlet P-term), reaches only a short way into the chromosphere and distinguishes itself there characteristically from H and K.

Hydrogen, with its relatively high ionisation potential of 13·5 volts is observed not only in the photosphere but also in the uppermost layers of the chromosphere and in the solar protuberances.

Like Saha's theory,* of which we have here sketched only a very small part, also the so-called spectroscopic determination of the parallax according to Kohlschütter and Adams is also based on the intensity ratio of arc and spark lines in the case of stars in which varying conditions of temperature and pressure obtain (of various magnitudes).

4. **Spectroscopic Peculiarities in Astrophysics.**—A particularly beautiful application of atomic theory to the spectra of celestial bodies occurs in the *problem of the lines in nebulæ*. In the spectra of gaseous *nebulæ* there are, in addition to lines of known elements, a large number of lines, some very bright, which could not be identified till quite recently. They were therefore attributed to an unknown element, "nebulium." This assumption had little to support it, for the element would have to be of small atomic weight, since the other lines in gaseous nebulæ arise from elements of atomic number less than 20; there is, however, no place in the periodic system for such an element.

The only escape from this assumption was to regard these lines as belonging to known elements but emitted under conditions that could either not be realised in the laboratory or had not yet been successfully produced. The latter was found to be the case by Bowen †

* Further details may be found in Vol. II of *Astronomy*, Russell, Dugan and Stewart (Ginn & Co.).

† J. S. Bowen, Astrophys. Soc. Pacific, **39**, 205 (1927); Astrophys. Journ., **67**, 1 (1928).

who discovered that the wave-lengths of certain unrecognised lines of the nebulæ coincided with those of lines which had become known through the analysis of the spectra of "stripped atoms," in particular, of the spectra of O II, O III, O IV, N III, N IV, C II, C III. Moreover, the lines identified in this way were always found to be the most intense lines of the spectra in question that were to be expected in the visible region according to the well-known scheme of levels. The fact that the lines of the nebulæ are predominantly spark lines is to be understood as follows, according to Zanstra * and Bowen, from the structure of gaseous nebulæ.

The majority of gaseous nebulæ exhibit in their centre or near it a bright star, the so-called central star. Such nebulæ are called "planetary nebulæ." † It may be shown that the central star has a close relationship with the nebula. In virtue of its high temperature (which averages 40,000° C. according to Zanstra) it emits chiefly ultra-violet light of very short wave-length, which is taken up by the atoms of the surrounding nebula. The layers nearest the central star therefore contain almost only highly ionised atoms. Let us suppose the star to be surrounded, say, by only an oxygen atmosphere and the O-atoms in its vicinity to be so highly ionised that they contain only two outer electrons (O^{4+}-ions, that is, O-atoms that have been ionised four-fold). These ions may then occasionally capture one of the free electrons in the atmosphere of the nebula and so emit the lines of the O IV spectrum. Through the light from the central star, namely that from the part which lies in the extreme ultra-violet, the O^{3+}-atoms again become ionised to O^{4+}-atoms, and so forth. In this way the shortest wave-length part of the light emitted by the star will be used up to a certain extent in emitting the O IV spectrum in the layer nearest the star. The part of longer wave-length will pass through this layer and will lead, further outside, to the ionisation of O^{2+}-atoms and hence (owing to the capture of an electron) to the emission of the O III spectrum. Still further out the O II and lastly the O I spectrum are to be expected. An analogous argument applies, of course, to other atoms present in the gaseous nebula.

In this manner a number of lines of the nebulæ could be identified with spark lines. But the most intense lines, among them the famous green nebulium lines N_1, $\lambda = 5006{\cdot}84$ Å. and N_2, $\lambda = 4958{\cdot}91$ Å., could not be found among the known spark lines. According to Bowen all these uninterpreted lines represented transitions of a particular kind between the lowest terms in the spectra of O II, O III, N II or S II.

We shall take the lines N_1, N_2 as examples. Bowen attributes

* H. Zanstra, Astrophys. Journ., **65**, 50 (1927).

† The following argument applies equally well to nebulæ without a recognisable central star (so-called diffuse nebulæ), if only the temperature is sufficiently high, as appears to be the case with galactic diffuse nebulæ.

them to O III ; according to the laboratory measurements of " stripped atoms " the lowest terms of O III are * : a singlet S-term ^1S, a singlet D-term ^1D and a triplet P-term ^3P, the latter having the term-differences 193 and 116 cm.$^{-1}$. They are shown in Fig. 115 in their correct positions qualitatively. N_1, N_2 are supposed to represent the following transitions :

$$N_1 = {}^3P_2 - {}^1D_2,\ N_2 = {}^3P_1 - {}^1D_2 \qquad (2)$$

and hence

$$N_2 - N_1 = {}^3P_1 - {}^3P_2 = 193 \text{ cm.}^{-1} \qquad (3)$$

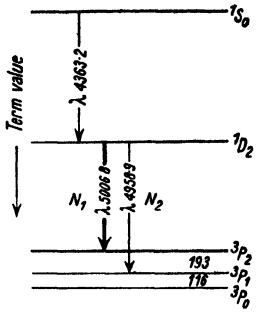


FIG. 115.—The lowest terms of the O III spectrum with the empirically found quadrupole lines, among them the " nebulium " lines N_1, N_2.

Actually N_1, N_2 form a doublet of precisely the given frequency difference, and the wave-number of N_1, N_2 calculated from equation (2) also agrees well with the observed values. In the same way the combination $^1S\,^1D$ gives a line, which occurs in the nebulæ ; its wave-length has been drawn in the figure. We here have a transition $J = 0 \to J = 2$, $L = 0 \to L = 2$, that is, a doubly forbidden process, according to our discussion in § 1 of the present chapter and § 2 of the preceding chapter. We must remark, however, that the formulation on p. 365 is not final but that a more complete formulation, with which we shall become acquainted in the next section, will also contain the assertion that for our case the transitions here under consideration are likewise forbidden, not only the transition $^1S\,^1D$ but also the combinations (2), because all three terms $^1S\,^1D\,^3P$ belong to the same configuration of electrons.

The explanation of this contradiction lies in the fact that we are not dealing with dipole radiation here—to which the selection rules mentioned refer—but to the quadrupole radiation, which is usually much weaker. Rubinowicz † has actually shown that for the quadrupole radiation precisely those transitions in L are allowed for which the dipole radiation is absent, and that in these transitions the quantum number of the total moment of momentum of the electrons changes by 0, $\pm$ 1, $\pm$ 2 (cf. also p. 369). For J we obtain at the same time $\Delta J = 0,\ \pm 1,\ \pm 2$.

It only remains to explain why the quadrupole lines, that must be very weak under earth conditions—it has been possible to produce it in the laboratory in only very few cases—should come out so strongly

* In § 3 we show that these terms are to be expected.

† A. Rubinowicz, Zeits. f. Phys., **65**, 662 (1930). This also contains the intensity formulæ and summation rules for the quadrupole radiation, which correspond to our dipole formulæ in § 9. It is shown that the intensities of the lines in the nebulæ agree well with this theory.

in the case of gaseous nebulæ. The reason is clearly to be sought in the particular physical constitution of these nebulæ. Actually the density of the nebulæ, both of the planetary nebulæ (with their central stars) and of the diffuse nebulæ (without a central star), is extraordinarily small, being of the order of 10^{-17} grm./cm.^{3} or less,* densities such as cannot be realised in the laboratory. This means that the atoms and ions of the nebulæ rarely collide ; the time between two collisions comes out as of the order of many seconds, according to some estimates, of the order of several hours ! We follow Bowen in drawing the following conclusions : the terms that lie closest to the ground-state of the ions are all *metastable* because they all arise from the same electronic configuration as the ground-term itself and because no dipole combinations are allowed between such terms (cf. again § 9). Now, quadrupole combinations occur much more rarely than dipole combinations, that is the " time of relaxation " (*Verweilzeit*) of the ions in such metastable states is much greater (of the order of 10^{-2} to 1 second) than in states from which dipole emission is possible. From the above data about the times between collisions we see that the ions can certainly not be disturbed during their time of relaxation in the metastable states, rather they can fall down to the ground-term at the end of the time of relaxation and so emit the " forbidden " quadrupole radiation. Eddington † has also shown that the radiation that comes from the central star does not disturb the emission of the forbidden lines if it is sufficiently weak,—which is certainly true, on account of the immense extent of the nebulæ. Further, if we take into account that most of the higher terms can combine to give dipole radiation with all the deep terms that come into question, that is, that the metastable states can be much " enriched " by transitions from the higher terms, we see immediately that these " forbidden " lines must appear particularly strongly in the nebulæ.

We have yet to mention that certain " forbidden " iron lines, which have been interpreted by Merrill,‡ occurring in many star spectra, are also to be regarded as quadrupole radiation, as has been shown from their intensities by Rubinowicz.‖

The mystery of the green line of the Northern Lights (Aurora borealis) was also successfully solved by similar considerations.¶ It, too, is a quadrupole line, namely the combination $^1D_2 - {}^1S_0$ in the oxygen arc spectrum. MacLennan and Ireton ** were the first to succeed in producing the line in the laboratory in a mixture of argon

* Cf., for example, the Report by F. Becker and W. Grotrian in the *Ergebnisse der exakten Naturwissenschaften*, Vol. VII. Springer, Berlin.

† A. S. Eddington, Monthly Notices R.A.S., **88**, 134 (1927).

‡ P. W. Merrill, Astrophys. Journ., **67**, 391, 405 (1928).

‖ A. Rubinowicz, *loc. cit.*

¶ J. C. MacLennan, Proc. Roy. Soc., **120**, 327 (1928); R. Frerichs, Phys. Rev., **34**, 1239 (1929); **36**, 398 (1930); F. Paschen, Naturwiss., **18**, 752 (1930).

** J. C. MacLennan and H. J. C. Ireton, Proc. Roy. Soc., **129**, 31 (1930).

and traces of oxygen. The identification was rendered perfect recently by observing the Zeeman * effect of the line, after Rubinowicz † had predicted the Zeeman effect of quadrupole lines wave-mechanically. In the O I spectrum (cf. Fig. 116), besides $^1D\,^1S$ another ground-term combination that is possible is $^1D\,^3P$. The corresponding three lines ($^1D_2\ ^3P_0$ is also allowed here) were found by Paschen ‡ on some old plates taken by Hopfield. All four quadrupole lines are thus obtainable also under earth conditions. Besides being known in the aurora spectrum they are also known in the spectrum of the night sky and the spectra of novæ as well as of certain nebular stars.

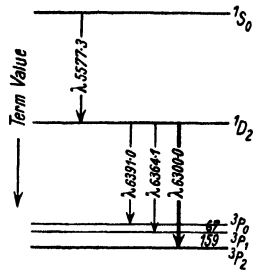


FIG. 116.—The lowest terms of the O I spectrum. The P-term is inverted. The wave-lengths shown are quadrupole lines, among them the green auroral line λ 5577·3 Å.

§ 3. Russell-Saunders Coupling. Term-Systems of Given Configuration containing Two Outer Electrons

The first step towards understanding the rules that underlie multiplets was taken by H. N. Russell and F. A. Saunders || when they subjected alkaline earth terms to a detailed investigation.

The alkaline earths have two outer electrons, while their other electrons are bound in closed shells and may hence be left out of consideration as far as the scheme of terms is concerned. (The proof of this, based on Pauli's Principle, will be given on p. 450.) In the ground-state these outer electrons are in *s*-states (3*s* in Mg, 4*s* in Ca, and so forth, see Tables 7 and 8 on pp. 160 and 162); the corresponding excited terms arise when one of the outer electrons persists in the *s*-state and the other is transferred to a higher *s*-, *p*- or *d*-state. But there is another electronic configuration which is not much less probable than the above. Our attention is directed particularly at Ca. Immediately after Ca the 3*d*-orbits begin to be added, that is, the M-shell begins to be filled up (cf. Table 8). Thence we conclude that in Ca the 3*d*-orbit is approximately as strongly bound as the 4*s*-orbit; cf. also Chapter VII, pp. 401, 406, 409. Hence we expect a second term-system in which one electron is in a 3*d*-orbit and the other in any arbitrary higher state. The two term-systems may be represented diagrammatically as follows:

Ordinary terms	Displaced terms
(4*s*, *nx*)	(3*d*, *nx*)
Limit: Ca^+ 4*s*.	Limit: Ca^+ 3*d*.

* R. Frerichs and J. S. Campbell, Phys. Rev., **36**, 1460 (1930).
† A. Rubinowicz, Zeits. f. Physik, **61**, 338 (1930).
‡ F. Paschen, *ibid.*, **65**, 1 (1930). || Astrophys. Journ., **61**, 38 (1925).

Thus the two-term limits behave exactly as was assumed in Fig. 103, p. 407, to explain the "accented terms"; the term-values of the second system, referred to the limit of the first system, become in part negative, and so forth.

What holds for Ca also holds for Sr, Ba . . . , except that now we must replace $4s$, $3d$ . . . by $5s$, $4d$, . . . But in Mg the corresponding states are $3s$ and $3p$, since after Mg (cf. Table 7) the M-shell becomes completed by the addition of $3p$-orbits. The two types of Mg-terms are therefore diagrammatically:

Ordinary terms	Displaced terms
$(3s, nx)$	$(3d, nx)$
Limit: $Mg^+ 3s$.	Limit: $Mg^+ 3p$.

Summarising all this, we consider two electrons, whose orbital character we shall characterise in general by the quantum numbers l_1 and l_2 (for example, $l_1 = 0$ for an s-orbit, $l_1 = 1$ for a p-orbit, and so forth), and we inquire into the character of the term that results from these two, which we shall denote by a resultant quantum number L. How is L compounded from l_1 and l_2? The answer given by Russell and Saunders is: *L is compounded vectorially and in integral numbers from l_1 and l_2 according to the scheme*

$$\mathrm{L} = \vec{l_1} + \vec{l_2} \text{ in such a way that } l_1 + l_2 \geqq \mathrm{L} \geqq |\, l_1 - l_2 \,| \quad . \quad (1)$$

At the same time we proceed beyond Russell and Saunders by considering the compounding of the spin-vectors s_1 and s_2, which are of course equal to $\frac{1}{2}$ for each individual electron. *The spin-vectors are compounded algebraically thus:*

$$\mathrm{S} = s_1 \pm s_2 = \begin{cases} 1 \text{ triplet} \\ 0 \text{ singlet} \end{cases} \quad . \quad . \quad . \quad (2)$$

The "Russell-Saunders coupling" defined by (1) and (2) is not the only possible coupling but by far the most important coupling of the individual orbital-vectors which leads to resultant term-vectors. We shall deal with other possibilities (for example, a jj-coupling) in § 5. We must first illustrate the Russell-Saunders coupling by examples.

To indicate that the character of the resultant term is given by L we assign the usual symbols S, P, D . . . to the values L = 0, 1, 2 . . . (cf. p. 421). By compounding l_1 and l_2 in accordance with (1) we obtain the following schemes:

A. $l_1 = 0$

L =	0	1	2	3	4
$l_2 = 0$	S				
1		P			
2			D		
3				F	
4					G

B. $l_1 = 1$

$L =$	0	1	2	3	4	5
$l_2 = 0$		P				
1	S	P	D			
2		P	D	F		
3			D	F	G	
4				F	G	H

C. $l_1 = 2$

$L =$	0	1	2	3	4	5	6
$l_2 = 0$			D				
1		P	D	F			
2	S	P	D	F	G		
3		P	D	F	G	H	
4			D	F	G	H	J

In Scheme A we have, on account of $l_1 = 0$ (for example, 4*s* in the case of Ca), that $L = l_2$. Hence the diagonal form of the Scheme A, which corresponds to the ordinary terms (for example, 4*s*, *nx* in Ca). On account of $l_1 = 1$ in the first row ($l_2 = 0$) the Scheme B begins with $L = l_1 = 1$, that is, with a P-term. In the second row ($l_2 = 1$) we have, by equation (1), that $L = \vec{1} + \vec{1} = 0$, 1 or 2, that is, an S-, P- or D-term ; in the third row ($l_2 = 2$) we have $L = \vec{1} + \vec{2} = 1$, 2 or 3, corresponding to a P-, D- or F-term, and so forth. The Scheme C begins, since $l_1 = 2$, with a D-term, $L = l_1 = 2$, and exhibits three terms in the second row ($l_1 = 2$, $l_2 = 1$), in the third and subsequent rows it exhibits five terms,* and so forth.

In the present two-electron case all these terms may, by equation (2), be triplet as well as singlet terms. For the indexing of these terms, that is, for the quantum number J, we now also have

$$S + L \geqq J \geqq |S - L| \quad . \quad . \quad . \quad . \quad (3)$$

Here the selection rule for the J's in general retains its earlier form :

$$\Delta J = \begin{cases} \pm 1 \\ 0 \end{cases} \quad . \quad . \quad . \quad . \quad (4)$$

Actually we applied this rule in the case of the (*pp'*)- and the (*dd'*)-combinations in § 1, to the displaced terms, *p'*, *d'*, equally well as to the ordinary terms *p*, *d*. *The same does not, however, apply to the*

* In passing we must call attention to the analogy between our Schemes A, B, C . . . and the Scheme C on p. 427 for the singlet, triplet, quintet . . . systems. The L-values of our present schemes are identical with the J-values of the earlier schemes. There is a formal reason for this : precisely as the L's are compounded from l_1 and l_2 according to eqn. (1), so the J's are compounded, according to the earlier eqn. (6) on p. 428, from the L's and the S's.

selection rule of the L's. Whereas $\Delta l = 0$ was forbidden earlier, $\Delta L = 0$ is by no means forbidden now, as the just-mentioned combinations show directly.

To arrive at the selection rules we must first revert to the individual Δl_i's. The experimental results so far obtained have obeyed perfectly a rule given by Heisenberg (we enunciate it more generally for any arbitrary number of electrons $i \geqq 2$): *in an allowable transition (dipole-radiation) one electron must change its l-value by* ± 1, *a second electron must change its l, if at all, by* ± 2, *the remaining electrons must retain their l-values unaltered.* In symbols:

$$\Delta l_2 = \pm 1, \quad \Delta l_1 = \begin{cases} 0 \\ \pm 2 \end{cases}, \quad \Delta l_i = 0, \quad i > 2 \quad . \quad . \quad (5)$$

We summarise the two possibilities as follows: " single transitions " (*Einfach-Sprünge*) $\Delta l_1 = 0$, in which case (5) reduces to the well-known selection rule $\Delta l = \pm 1$, and " double transitions " (*Doppel-sprünge*), to which the displaced terms discussed above (see pp. 405 *et seq.*) belong.

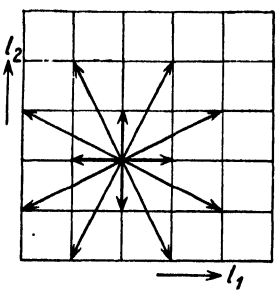


FIG. 117.—Geometrical representation of the selection rule (5), in which l_1 and l_2 are considered as of equal importance. 4 + 8 transitions arise from each term. The number is reduced if transitions occur among them which would lead to negative values of l.

According to O. Laporte,* whose researches on the iron spectrum have formed the foundation for the general form of the selection rules of heteromorphic terms, (5) may be illustrated geometrically by the " star " diagram of Fig. 117.

It had been conjectured earlier † that the rule (5) could be generalised as follows:

$$\Sigma \Delta l_i = \text{odd number} \quad . \quad (5a)$$

Wave-mechanics confirms ‡ this generalisation. Of course the transitions (5) are distinguished among the more general transitions contained in (5*a*) by occurring more often.‖

Supplementary to this selection rule for the l's there is an additional condition for L, namely:

$$\Delta L = 0, \pm 1 \quad . \quad . \quad . \quad . \quad (6)$$

* Handb. der Astrophys., Springer, 1930, Ch. VI, p. 684.

† A. Sommerfeld, *Three Lectures on Atomic Physics*, p. 43 (Messrs. Methuen & Co. Ltd., 1926).

‡ H. Weyl, Gruppentheorie und Quantenmechanik, Hirzel, Leipzig, 2nd edn., 1931, pp. 180, 181.

‖ We can bring the selection rule (5*a*) into a form, which has played a certain part in the older researches on multiplets, if we divide the terms into two classes, " even " and " odd terms," according as Σl_i is even or odd. Then only even terms can combine with odd and vice-versa (Laporte's rule).

which we shall prove in Note 7 (*e*). Exceptions to this last rule occur only if the intervals within a multiplet term become comparable with the intervals made with neighbouring multiplet terms of the same electronic configuration.

We apply this to the Ca terms, Schemes A and C. Within the scope of A every term may combine with its two neighbours, and in the same way with C every term of a row may combine with the neighbouring terms, defined by (6), of the neighbouring rows. All these combinations are *single transitions*. We obtain admissible *double transitions* if we combine, for example, the term P from A with the terms allowed by (6) of the first or the third row of C. Among these combinations there is only one * of the character (*pp'*), since no P-term occurs in the first row. We next inquire into the origin of the (*dd'*)-combinations. They arise when we combine the D-term of the third row of A with the D of the second or of the fourth row of C, whereas the combination with the first, third or fifth row is forbidden. We write down the possible modes of origin, showing at the same time the *detailed term notation* which has become the practice when we wish, to express clearly not only the *structure* but also the origin of the terms *according to atomic theory*:

$$\left.\begin{matrix}(pp')\\(dd')\end{matrix}\right| \begin{matrix}(4snp)\ {}^3P_{012} \rightarrow (3dn'd)\ {}^3P_{012}\\(4snd)\ {}^3D_{123} \rightarrow \begin{cases}(3dn'p)\ {}^3D_{123}\\(3dn'f)\ {}^3D_{123}\end{cases}\end{matrix}$$

Here the *structure* is denoted by the symbol ${}^3P_{012}$ and ${}^3D_{123}$ (we restrict ourselves to triplet structure, as indicated by the upper prefix 3, as we are interested in the line-configuration, cf. pp. 424 and 426; actually, we should also take into account the singlet terms ${}^1P_1$ and ${}^1D_2$). The *origin* of the terms is specified by the preceding symbols (4*snp*), (3*dn'd*), and so forth, for which we shall use the abbreviation *sp*, *dd* or d^2, the latter symbol when both *d*'s belong to the same principal quantum number. Thus in future we shall use the *small* letters, *s*, *p*, *d* . . . only for the state of the *individual* electron, and the *capital* letters, S, P, D, . . . , with upper and lower indices, for the state of the *whole* atom (cf. p. 427). Moreover, the indefinite principal quantum numbers *n*, *n'* in the above symbols indicate that there is not one but a series of terms of the class (*sp*), (*dd*) . . . .

But our diagrammatic schemes require to be supplemented in the case of equivalent orbits, that is, when our two electrons (generally several electrons) belong to the same orbital type n_l, that is when they agree not only in their *l*-values but also in their *n*-values. Here we receive decisive help from Pauli's Principle (p. 154), which states that: *every completely defined quantum-state can be occupied by only* **one**

* Besides this, however, *pp'* may also result as a single transition by a combination of A with B (second row of A with the second row of B).

electron. To define such a state completely we require not only the orbital type (n, l) but also the position of the orbit, which is given by the magnetic quantum numbers m_l and m_s (p. 152). Electrons of the same orbital type are called **equivalent electrons** by Pauli. Pauli's Principle further asserts that: *electrons in the same quantum-state cannot in principle be distinguished from one another;* atomic configurations which become transformed into one another by simply interchanging electrons are fully identical with one another and therefore represent *one* configuration. It is the combination of the Russell-Saunders ideas with Pauli's Principle by F. Hund * that first led to a complete systematic classification of multiplet spectra.

We already know the possible values of the magnetic quantum numbers m_l and m_s for the individual electron from pp. 150 *et seq.* They are determined from

$$l \geqq m_l \geqq -l, \quad s \geqq m_s \geqq -s \quad . \quad . \quad . \quad (7)$$

The values of m_l are integral, like those of l, and those of m_s are half-integral. There are $2l + 1$ values of m_l for a given l. On the other hand, there are only two values of m_s for the individual electron, since $s = \frac{1}{2}$; these values are $m_s = \pm \frac{1}{2}$. We may represent these values graphically by the separate orientation of the orbital-vector l and the spin-vector s in space in a (strong) magnetic field imagined to be present (cf. the analogous Figs. 29 and 30 on pp. 123 and 124; which represented the vector j compounded from l and s).

In the same way we must define the magnetic quantum numbers M_L and M_S for the *resultant atomic state* (L, S). Their possible values are determined from the conditions analogous to (7):

$$L \geqq M_L \geqq -L, \quad S \geqq M_S \geqq -S \quad . \quad . \quad . \quad (7a)$$

The L-vector therefore has belonging to it $2L + 1$ different quantum numbers M_L, which correspond to just as many different positions of the L-vector with respect to the axis of the magnetic field and which may be regarded as projections of L on this axis. In the same manner $2S + 1$ quantum numbers M_S belong to the S-vector, namely, in the cases that come into question here:

Singlet system, $S = 0$, $M_S = 0$.
Triplet system, $S = 1$, $M_S = +1, 0$ or -1

And we have for every electronic configuration

$$M_L = \Sigma m_l, \quad M_S = \Sigma m_s, \quad . \quad . \quad . \quad . \quad (8)$$

where in our case of only two outer electrons the sums are two-fold and extend over any two of the values of m_l and m_s allowed by (7).

* For the interpretation of complicated spectra, in particular of the elements from Sc to Ni, see Zeits. f. Physik, **33**, 345 (1925); also the important text-book: *Linienspektren und periodisches System*, Springer, 1927.

The following remarks may serve to make clear the relationships (8): we start from the imagined limiting case, where the coupling of the electrons and their l, s vectors among themselves is infinitely weak. Then all the vectors will orientate themselves independently of one another in an added imaginary magnetic field, that is, all the m_l's and m_s's will be integral or half-integral. We now allow the coupling its increase in strength but shall at first allow only the l's to combine among themselves and likewise the s's. Interacting moments of momentum then present themselves which alter the individual moments of momentum l and s in time and destroy the quantum-like behaviour of their projections m_l and m_s. The law of sectorial areas then no longer holds for the individual motion of the electrons, but only in the sum for the whole system (here our two electrons, and, by our assumption, separately for the l's and the s's), since the moments of momentum due to the coupling compensate. Hence what previously held for the individual vectors now holds for the sum: the L's and the S's are constant and are quantum numbers of the system; their components M_L and M_S along the magnetic axis are likewise quantum numbers and retain the values they had in the coupling, that is, they may be calculated in the sense of the equations (8) from m_l, m_s. By carrying this line of argument a step further we are able to speak in the next approximation of the coupling of the moments of momentum L and S with the total moments of momentum J; cf. also the remarks at the beginning of § 5.

We pass on to the different cases of "equivalent" states, which present themselves in the case of two electrons according to our Schemes A, B, C on p. 442. We are dealing with the first row of A, the second of B and the third of C and we assume, of course, in each case that the principal quantum numbers are the same ($n_1 = n_2$).

A. $l_1 = l_2 = 0$, both electrons in the s-state. Then the corresponding m_l's are equal to zero, i.e. $m_l = 0$. Thus the first three of the quadruple of numbers

$$n,\ l,\ m_l,\ m_s \qquad . \quad . \quad . \quad . \quad (9)$$

are the *same* for both electrons. Hence, by Pauli's Principle the fourth must be *different* for each. Thus

$$m_{s_1} = +\tfrac{1}{2},\ m_{s_2} = -\tfrac{1}{2},$$

or vice versa. The converse state (also by Pauli's Principle) does not, however, denote a new state. Hence the only possibility is

$$M_L = M_S = 0, \quad L = S = 0.$$

We have a ^{1}S-term; *the ^3S-term is forbidden.* This explains the non-existence of the ortho-helium ground-term, cf. Fig, 92, p. 358, and of all analogous triplet terms in the spectra of Be, Mg, Ca . . . Hg.

Conversely, the non-existence of these terms was the first fact that caused Pauli to formulate his principle.

B. $l_1 = l_2 = 1$, type of carbon and its homologues. We affirm that the more exact expression for the three terms given in the second row of Scheme B should be

$$^1S,\ ^3P,\ ^1D, \quad . \quad . \quad . \quad . \quad (10)$$

that is, that the terms

$$^3S,\ ^1P,\ ^3D \quad . \quad . \quad . \quad . \quad (10a)$$

are forbidden.

To prove this we begin with the D-term, namely with its highest magnetic level, $M_L = 2$. Since m_{l_1} and m_{l_2} cannot be greater than 1 we must write in equation (8) that

$$m_{l_1} = m_{l_2} = 1.$$

The first three figures in (9) are again the same in each case, that is,

$$m_{s_1} = -m_{s_2}, \quad M_S = \Sigma m_s = 0.$$

Hence $S = 0$. Our D-term is a *singlet-term*.

We pass on to $M_L = 1$. This magnetic level arises from

$$m_{l_1} = 1, \quad m_{l_2} = 0 \mid m_{s_1} = \pm \tfrac{1}{2}, \quad m_{s_2} = \pm \tfrac{1}{2}.$$

The converse $m_{l_1} = 0$, $m_{l_2} = 1$ does not, again by Pauli's Principle, denote a new term. There are thus four possibilities, distinguished by the values of

$$M_S = \Sigma m_s = \begin{cases} +1 \\ 0,\ 0 \\ -1 \end{cases}$$

One of the two zero values is used up for a ^1D-term, which has a magnetic level $M_L = 1$ as well as $M_L = 2$. Hence three values $1, 0, -1$ are left over, which belong to the magnetic orientation of a spin-vector $S = 1$, that is, to a triplet-term. Our P-term in the row (10) is therefore in actual fact a *triplet-term*.

We now come to $M_L = 0$. Here we must have either

$$m_{l_1} = m_{l_2} = 0 \mid M_S = 0,$$

or

$$m_{l_1} = -1, \quad m_{l_2} = +1 \mid M_S = +1, 0, 0, -1.$$

The values of M_S on the right-hand side state that: if the two m_l's are equal (first row) the m_s's must be opposite and equal; if the two m_l's are different (second row), the m_s's may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. One of the five M_S-values that arise in this way is a zero, and is used for the ^1D-term. If we strike out the values $M_S = +1, 0, -1$ required for the magnetic level $M_L = 0$ of the ^3P-term, we are left with only $M_S = 0$. The S-term still remaining in (10) is thus a *singlet-term*.

We recognise that our enumeration is complete by noting that it might have been carried out equally well for the negative M_L's.

This may be tested by counting up all the magnetic levels that belong to (10), and also those that belong to (10*a*). In general, we obtain

$$\Sigma(2L + 1)(2S + 1),$$

since $2L + 1$ and $2S + 1$ denote, respectively, the number of M_L's and M_S's for each term. Hence, in the case (10) we obtain

$$1 + 3 \cdot 3 + 5 \cdot 1 = 15,$$

and in the case (10*a*)

$$3 + 3 + 15 = 24.$$

If, on the other hand, we count up the magnetic levels, starting from the m_l's and m_s's, we obtain from $m_l = +1, 0, -1$, $m_s = +\frac{1}{2}, -\frac{1}{2}$

$$3 \cdot 1 + \frac{3 \cdot 2}{2} \cdot 4 = 15.$$

The first product on the left-hand side denotes the combination of two equal terms m_l with opposite values of m_s. The second product corresponds to the combination of two different m_l's, of which $3 \cdot 2$ are present, only half of which count, however, as the electrons cannot be distinguished from each other ; the full number 4 of the m_s-pairs are to be combined with them. The sum 15 agrees with our enumeration of (10), and hence excludes (10*a*).

Before we apply our scheme (10) to the interesting examples of O III and O I, we must develop the *rule of term positions* enunciated by Hund (cf. the reference on p. 446). This rule is an essential constituent of Hund's *theory of the classification of terms*. We give it here as an experimental result. Hund, and in still greater detail Slater,* bases it on general considerations about the strength of the coupling between the different vectors *l*, *s*, similar to those indicated on p. 447. A more rigorous basis, which also allows us to expect *possible exceptions to Hund's rule*, must be left to the next volume (on wave-mechanics).

Among the terms belonging to a definite electron configuration that one is lowest which (a) *has the greatest S and* (b) *has the greatest L among the terms having the same S. In general the positions of the lower terms arrange themselves* (a) *according to the magnitude of S and* (b) *according to the magnitude of L.* The higher terms often exhibit exceptions to this rule.

In our case (electron configuration, p^2) only one term $S = 1$ occurs, namely the ^3P-term. It is the *lowest*. Of the two terms with $S = 0$ the ^1D-term is the *deeper* because it has a *greater* L.

We apply this to the spectra of O III and O I. Oxygen has, accord-

* Phys. Rev., **28**, 291 (1926).

ing to its position in the periodic system, four $2p$-electrons. Hence O^{++} with its two $2p$-electrons falls directly within our scheme. This explains the position of the terms in our Fig. 115 on p. 439. It also makes clear simultaneously why all the nebular lines there shown are *forbidden* lines. For our selection rule (5) demanded that one of the numbers l_1, l_2 should change by ± 1, whereas in combinations within the same electron-configuration $\Delta l_i = 0$ for all i's. This decree, however, applies only to dipole radiation, and not to quadrupole radiation. In the sense of dipole radiation ^1D and ^1S are *metastable* levels. As already mentioned on p. 439, the transitions drawn in Fig. 115 are precisely those that are possible for quadrupole radiation.

But the O I-spectrum also falls within the same term-scheme. To see this, we need Pauli's " Gap Law " (*Lückensatz*).

A direct consequence of Pauli's Exclusion Principle is this : *every closed shell is balanced with respect to moment of momentum*, both as regards *orbital resolutions* and *spin moments of momentum ;* we have $L = 0$ and $S = 0$. Thus the term-state is a $^1S_0$-term. On account of the connexion between moment of momentum and paramagnetism we may also express this as follows : *every closed shell behaves diamagnetically in its ground-state.*

The proof of this law is essentially contained in the enumerations on p. 154. As already emphasised, the closed shell of quantum number l is built up of $2(2l + 1)$-electron ; for example, the $L_{II} + L_{III}$-shell, $l = 1$, consists of $2 \cdot 3 = 6$ electrons. In this way the $2l + 1$ different values of m_l, namely l, $l - 1$, . . . $- l$, and the two different values of m_s, namely $\pm \frac{1}{2}$, are just used up. Hence we obtain for the sums (8) :

$$M_L = 0, \qquad M_S = 0.$$

This is the only term that is possible. It characterises a $^1S_0$-term.

The singlet S-term is familiar to us as the helium ground-term in the completion of the K-shell, as the ground-term of Be, Mg, Ca in the completion of the L_1-, M_1-, N_1-shell. In the same way, $^1S_0$-terms must occur as ground-terms in completing the 8-shells ; that is, in the inert gases Ne, Ar, Kr. . . . (We must note, however, that in these spectra the Russell-Saunders coupling no longer holds, so that, strictly speaking, there is no sense in speaking of L- and S-values. But the characteristic of a closed shell : $J = 0$, remains valid in any sort of coupling) ; the same applies to the completion of the 18-shells (as examples we may give instead of the neutral atoms the corresponding ions Cu^+, Ag^+, Au^+). The same holds for Lu^{+++} as the last stage in the completion of the N-shell.

Pauli's Gap Law is very closely related to Hund's Rule. It states that in a configuration of equivalent orbits the number and character of the possible terms may be counted up just as well on the basis of the electrons that are *missing*, that is, that are required to

complete the shell, as on the basis of the electrons *present* in the configuration.

Let us take as an example O in its neutral state with the configuration $(2p)^4$. To complete the shell we require two $2p$-electrons. The limitations of Pauli's Exclusion Rule apply in choosing these two missing electrons, that is, as regards their quantum numbers m_l and m_s. These restrictions are the same as for two of the existing electrons. Hence the term-number and term-character becomes the same in both cases.

We now understand why Fig. 116 for O I is almost identical with Fig. 115 for O III. " Almost " is to signify : except for the structure of the ^{3}P-term, that is, the sequence of its levels in their dependence on J. We call the structure in Fig. 115 *regular*, that in Fig. 116 *inverted*.* A structure is regular if it corresponds to that of the alkalies or alkaline earths as regards the J-values : *the lowest level has the smallest J, that is, the term-value decreases as J increases.* In the inverted structures the lowest level conversely has the *greatest value for J*, that is, *the term-value increases as J increases.* We shall see in § 10 that the interval-ratios are related to J-values (at least in the case of the Russell-Saunders coupling), namely, *in regular structures the intervals decrease, in inverted structures they increase, as the term-value increases.*

In § 10 we shall be able to make more accurate statements about the occurrence of regular or inverted terms. For the present we formulate the empirical results briefly as follows : *in the first half of each group of equivalent electrons the structures are regular, in the second half they are inverted.* For example, in the iron spectrum all the multiplet structures are inverted, in those of the alkalies and alkaline earths they are regular (with the exception † of certain highly excited terms).

The O I-spectrum $(2p)^4$ takes us into the second half of the group of equivalent $2p$-orbits, the O III-spectrum $(2p)^2$ into the first half. This explains the relative structures of the ^{3}P-term in Figs. 115 and 116 (in Fig. 115 J = 0 is the lowest level, in Fig. 116 J = 2). Otherwise the same applies to Fig. 116 as to Fig. 115. Their lines are forbidden in the sense of dipole-radiation, that is, the S- and the D-terms are metastable. The lines drawn in Fig. 116, the polar line (SD) and the Paschen Combinations (DP) are quadrupole radiations.

From here we return once again to the data on p. 433 concerning the O I-spectrum. The ^{3}P-term discovered by Hopfield is identical

* This distinction was first introduced in the preceding German edition of this book and was illustrated by the spectra of Mn, Fe and so forth.

† According to K. W. Meissner (Ann. d. Phys., **65**, 378 (1920)), the F-terms of cæsium are inverted ; the D-terms of potassium also appear to be inverted, according to F. Paschen (Naturwiss., **2**, 434 (1923)). The analogous terms of Ba^+ and Ca^+ are, however, regular. In the case of Mg^+ and Al^{++} there are inverted D-terms. In the complicated spectra partially inverted terms also occur, in which the term-value increases with J, and then again decreases, or vice versa.

with the ground-term of our Fig. 116. The combination PS with $\lambda = 1302, 1305, 1306$ Å. (cf. p. 433) is the combination of this ground-term with an excited ^{3}S-term, which is to be imagined in Fig. 116 as situated high above the ^{1}S-term. Of the three arrows that pass from this high ^{3}S-term to the three ^{3}P-levels, the two shorter ones are less different between themselves than the two longer ones, on account of the interval ratios in the inverted triplet

$$(P_0P_1 : P_1P_2 \cong 1 : 2, \text{ cf. Fig. 116}).$$

The wave-lengths measured by Hopfield correspond with this: the smaller wave-length difference ~ 1 Å. occurs between the two components of longer wave-length, the greater wave-length difference ~ 3 Å. occurs between the two components of shorter wave-length. Hence we can verify the inverted nature of the ground triplet from these measurements.

C. Lastly we consider the equivalent orbits in our scheme C on p. 443, $l_1 = l_2 = 2$; we are here dealing with d-orbits. We call them, in particular, $3d$-orbits, in view of the iron group, for which system we wish to prepare the ground here. We assert that the terms that result from two $3d$-orbits, which are represented according to their L-character by the third row of the scheme C, are to be specified as regards their S-character by

$$^1S\,^3P\,^1D\,^3F\,^1G \quad . \quad . \quad . \quad . \quad (11)$$

The proof runs as for the analogous term-sequence (10).

We begin with the G-term, $L = 4$, namely with its highest magnetic level $M_L = 4$. Since in the case of our $3d$-electrons $|m_l| \leqq 2$, $M_L = 4$ arises uniquely from

$$m_{l_1} = m_{l_2} = 2.$$

According to Pauli's Exclusion Principle, we must necessarily have $m_{s_1} = -m_{s_2}$, $M_S = 0$; we have one ^{1}G-term.

The magnetic levels $M_L = 3$ arise from

$$m_{l_1} = 1, \quad m_{l_2} = 2 \;|\; m_{s_1} = \pm\tfrac{1}{2}, \quad m_{s_2} = \pm\tfrac{1}{2}.$$

Of the four possibilities one, $M_S = 0$, goes to the ^{1}G-term, the other three characterise a ^{3}F-term.

For $M_L = 2$ there are three modes of origin:

$$\begin{array}{rl|l} m_{l_1} = m_{l_2} = 1 & & m_{s_1} = -m_{s_2} \\ m_{l_1} = 0, & m_{l_2} = 2 & m_{s_1} = \pm\tfrac{1}{2}, \quad m_{s_2} = \pm\tfrac{1}{2} \end{array}$$

We need four of these for ^{1}G and ^{3}F. One remains for the D-term and characterises this, on account of $M_S = 0$, as a ^{1}D-term.

In the next step $M_L = 1$, we have eight possibilities:

$$\begin{array}{rl|l} m_{l_1} = 0, & m_{l_2} = 1 & m_{s_1} = \pm\tfrac{1}{2}, \quad m_{s_2} = \pm\tfrac{1}{2} \\ m_{l_1} = -1, & m_l = 2 & m_{s_1} = \pm\tfrac{1}{2}, \quad m_{s_2} = \pm\tfrac{1}{2} \end{array}$$

After striking out the five M_S-values which are required for ^1G, ^3F and ^1D, we are left with the three values $M_S = +1, 0, -1$, which belong to the ^3P-term.

The last step $M_L = 0$ yields nine possibilities. After striking out the eight M_S-values, which are required for the preceding terms, we are left with an $M_S = 0$, that is, a ^1S-term. The fact that the emuneration is complete may be checked as above in (10).

We may conclude by considering an interesting application of the concept of inverted terms to X-ray spectra. *The X-ray spectra are typical gap spectra* (*Lückenspektra*). For example, the Kα-line can be emitted only if a gap has been made in the K-shell which is filled by an electron from the L_{III}-shell. We therefore expect inverted multiplets in the case of X-ray spectra, or, more accurately, *inverted doublets*. This is actually found to be the case if we start from the view of X-ray spectra already indicated on p. 240.

We may then describe the emission of Kα as follows : " the gap which originally occurred in the K-shell is transferred to the L_{III}-shell." Since the energy of the atom is greatest in the case of K-ionisation (cf. p. 241), in particular greater than if the atom had primarily been ionised in the L_{III}-shell, the gap moves in a Kα-emission *in the sense of decreasing atomic energy*, similarly to the manner in which, in our original mode of expression, the electron moves in the transition $L_{III} \rightarrow K$ *in the sense of decreasing potential energy* (*Fallenergie*). *From the point of view of the total energy of the electron* it would be logical to invert the earlier figures (this possibility was hinted at in using the double arrows in Fig. 66, p. 243). *If we do this the inverted nature of the* (L_{II} L_{III})*-doublet* ($L = 1$, $S = \frac{1}{2}$, $J = \frac{3}{2}$ and $J = \frac{1}{2}$, respectively) *becomes directly evident*, and likewise that of all the other relativistic doublets in the X-ray spectrum. But we shall see in § 5 that in view of the coupling conditions that obtain in the X-ray region the converse view is also logical ; in this view we fix our attention on *the energy of the individual* atomic electron. According to Stoner and Main-Smith it even gives a deeper insight into the method of arrangement of the electrons. From this point of view, it was natural to draw the scheme of X-ray levels as we did earlier, that is, with the K-level lowest.

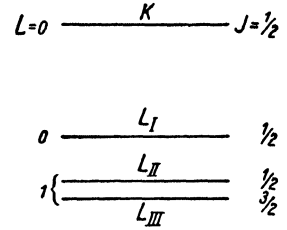


FIG. 118.—Inverted structure of the Röntgen doublets. The L_{III} level with $J = \frac{3}{2}$ lies lower than the L_{II} level with $J = \frac{1}{2}$, because it corresponds to a smaller energy of the whole atom.

§ 4. Configurations of Several Electrons. The Iron Group and the Group of Rare Earths. The Spectra of the Noble Metals compared with the Alkali Spectra. The Iron Spectrum

We proceed to deal in greater detail with the group of equivalent d-electrons and take as an example the $3d$-electrons of the *iron group*. Our results will, of course, apply with very slight changes equally well to the palladium and the platinum group ($4d$- and $5d$-electrons, respectively). But we shall first consider, not the neutral element, but, what is simpler, its *doubly positive ions*, in which the two outer S-electrons, which occur as early as in Ca, are removed. By p. 154 the number of these ions is, since $l = 2$,

$$2(2l + 1) = 10.$$

Ca^{++} is the zero element of the group, and has the configuration of the inert gases (closed M_{II}- and M_{III}-shell). Zn^{++} is the tenth element (closed M_{IV}- and M_V-shell). The middle of the group is representd by Mn with d^5. We emphasise this middle position by placing strokes on both sides of Mn in the following scheme:

TABLE 43

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn^{++}
d^0	d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9	d^{10}
$^1S_0$	$^2D_{3/2}$	$^3F_2$	$^4F_{3/2}$	$^5D_0$	$^6S_{5/2}$	$^5D_4$	$^4F_{9/2}$	$^3F_4$	$^2D_{5/2}$	$^1S_0$
		^3P	^4P				^4P	^3P		

The lower row gives the ground-terms that are to be expected (we shall deal later with the significance of the lowest row). In Ca^{++} and Zn^{++} we have, by the rule on p. 450, singlet S-terms. In Sc^{++} we have an electron outside the closed shell, that is, alkali-character; the term in this case is a ^{2}D-term, and likewise in Cu^{++} by the Gap Law (p. 450). The only difference between these two is in the J-value of the ground-level: $J = \frac{3}{2}$ in Sc^{++} and $J = \frac{5}{2}$ in Cu^{++} because the Cu^{++}-structure is inverted here. The case of two d-electrons that occurs in Ti^{++} and Ni^{++} was treated in detail in the preceding section. Among the terms (11) on p. 452 the term ^{3}F is the ground-term, by Hund's rule on p. 449 (greatest S and greatest L); the ground-level is $^3F_2$ in Ti^{++} ($J_{min} = 2$) and $^3F_4$ in Ni^{++} ($J_{max} = 4$).

To treat the remaining elements, which have three and four electrons present or missing, we adopt the following argument which applies for any l. Suppose we are dealing with an element having z equivalent l-electrons. The maximum value of S is $z/2$. Hence M_S in the highest magnetic level is also equal to $z/2$ and all the m_s's are equal to $\frac{1}{2}$. The m_l's must then all be different. We then obtain the *greatest* value that is possible according to this by forming

$$\sum m_l = l + (l - 1) + \ldots (l - z + 1) = \frac{z}{2}(2l - z + 1). \qquad (1)$$

By equation (8) of the preceding section this is at the same time the maximum value of M_L and hence also of L. Thus we find for the ground-term in the case of z (present or missing) electrons :

$$\left.\begin{array}{l} S = z/2, \quad L = z/2\,(2l - z + 1) \\ J_{min} = |\,L - S\,| = z\,|\,l - z/2\,|, \quad J_{max} = L + S = z(l - z/2 + 1) \end{array}\right\} (2)$$

Equation (2) for L denotes an arithmetic series of the second order if we regard L as a function of the successive z's ; hence

$$\Delta L = L_z - L_{z-1}$$

becomes an arithmetic series of the first order. We obtain

$$\Delta L = l + 1 - z \quad . \quad . \quad . \quad . \quad (3)$$

and hence for $l = 2$ and $z = 1, 2, 3, \quad 4, \quad 5$
we have $\Delta L = 2, 1, 0, -1, -2$

Starting from S ($z = 0$) we thus get in turn for $z = 1, 2 \ldots 5$ the term-character

D, F, F, D, S.

This confirms all the ground-terms given in Table 43.

We apply the same equations (2) and (3) to the case $l = 3$. Here we deal with equivalent 4*f*-electrons, which complete the N-shell in the *group of rare earths*. We again suppose the outer electrons, three in number, cf. Table 9 of p. 163, to be ionised away. As we know the group of rare earths contains

$$2(2l + 1) = 14$$

elements. The middle position is held by gadolinium ($Z = 64$, $z = 7$)• We obtain the following Table 44, which is of fundamental importance for the study of paramagnetism :

TABLE 44

La	Ce	Pr	Nd	Il	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tu	Yb	Lu
f^0	f^1	f^2	f^3	f^4	f^5	f^6	f^7	f^8	f^9	f^{10}	f^{11}	f^{12}	f^{13}	f^{14}
$^1S_0$	$^2F_{5/2}$	$^3H_4$	$^4J_{9/2}$	$^5J_4$	$^6H_{5/2}$	$^7F_0$	$^8S_{7/2}$	$^7F_6$	$^6H_{15/2}$	$^5J_8$	$^4J_{15/2}$	$^3H_6$	$^2F_{7/2}$	$^1S^0$

By (3) the arithmetic series for ΔL now becomes for $z = 1, 2 \ldots$:

$$\Delta L = 3, 2, 1, 0, -1, -2, -3.$$

As in Table 43, so at the beginning, middle and end of Table 44 we have an S-term. This follows directly from the equations (2) for $z = 2l + 1$. In both tables we have just before the middle a term-level whose inner quantum number is zero, which indicates in a certain sense the completion of the shell and diamagnetism. Actually one of the Stoner sub-groups ends at these points, cf. the following section.

We return to the iron group and now consider their *neutral* atoms.

For their lowest terms (that is, in the lowest position) we expect, if we start out from the two-fold ion d^z, the configurations

$$(a)\ d^z s^2, \quad (b)\ d^{z+1} s$$

where d stands for $3d$ and s for $4s$. The two sets of $4s$-electrons already occur actually in Ca and hence are also to be anticipated in the following elements as outer-electrons. Whether the $4s$-electron or the $3d$-electron is more tightly bound, that is, whether the absolutely lowest term appears under the form (a) or (b), will not be discussed here. It is just the rivalry of the $3d$-states with the $4s$-states that favours the elements K and Ca in the periodic system as compared with the iron group. Accordingly we might also consider a third possibility, (c) d^{z+2}, but this is less probable and will be passed over here.

To characterise the resulting terms more clearly we remark that in (a) s^2 forms a closed shell in itself, since two equivalent s-electrons can compound themselves only if their electron-spins are compensated. Hence (a) gives the same ground-term as the ion d^z. Also, (b) is built up on the ground-term of the next ion d^{z+1} and has the same L as the latter (because s belongs to $l = 0$), but an S that differs by $\pm \frac{1}{2}$. Hence when an outer electron $4s$ becomes attached a **branching** (*Verzweigung*) occurs which expresses itself in the increase or decrease of the term-multiplicity.

We consider the examples

$$\text{Fe} \quad z = 6 \qquad \text{and} \qquad \text{Cr} \quad z = 4.$$

From Table 43 we read off that the ground-term of the divalent iron ion is the term ^{5}D. Corresponding to it we have the lower term ^{5}D of neutral Fe, which is of the type (a). From the next successive ion we obtain by branching in the manner just described,

$$^4\text{F} \nearrow {}^5\text{F} \\ \qquad \searrow {}^3\text{F}.$$

In this way we have found the three multiplet terms of the iron spectrum that lie lowest empirically. Their term-position is also in accordance with expectation; they follow one another, from below upwards, in the order

$$^5\text{D}, \ ^5\text{F}, \ ^3\text{F}.$$

This was obtained from the analysis of the multiplets in the Fe-spectrum and its Zeeman effects before the arguments here put forward could be applied.

In Cr we have as a ground-term of type (a), from Table 43, also a ^{5}D-term. The type (b) is built up, on the ^{6}S-term, according to the same table, and gives the branching

$$^6\text{S} \nearrow {}^7\text{S} \\ \qquad \searrow {}^5\text{S}.$$

But experiment shows that the order of sequence of these three terms is

$$^7S,\ ^5S,\ ^5D.$$

With this in mind we again consider Table 42 on p. 432. We now understand the reason for the branching with respect to the term-multiplicities, which increases up to the middle of the group, Mn, and then decreases again. But we also understand a certain irregularity which occurs with respect to the ground-term just at Cr. Beginning from Ca the ground-term (as we see from the italicised words in Table 42) advances continuously to higher multiplicities until Mn is reached from which it again goes to lower multiplicities. This progressive behaviour would be perfectly regular if Cr had the ground-term ^5D as we should have expected at first sight.

In the ground-terms of the Pd-series which is homologous to the iron series, we find the arrangements d^{z+2}, $d^{z+1}s$, $d^z s^2$, as previously obtained except that in the arc spectra it is $d^{z+1}s$ that is now almost always the configuration that yields the ground-term. In the Pt-series $d^z s^2$ appears to predominate, as in the Fe-series. The lowest terms of the arc spectra of the *rare earths* may easily be obtained from Table 44 if we add three more outer electrons to the lowest terms there given for the three-fold ions; by Table 9 on p. 163 we must add two $6s$-electrons and one $5d$-electron or else one $6s$-electron and two $5d$-electrons. For further details cf., for example, the book by Hund * quoted on p. 446.

Before we consider the iron group further, let us turn our attention for a moment to the relation of the *noble metals* to the *alkalies* which stand in the same vertical column of the periodic system. The noble metals follow on the group of ten metals that form the completion of the M-shell or the provisional completion of the N- or the O-shell; together with the 8-shell of the preceding elements they form a so-called "18-shell" (p. 161). But according to general chemical results the completion of the 18-shell is altered by a far less strong binding than that of the 8-shell. Whereas the configuration of the alkalies that follow a closed 8-shell is unique, we shall expect in the noble metals two configurations of the ground-term owing to the rivalry between the s- and the d-term, namely: (a) the attachment of the newly added s-electron to the closed configuration d^{10}, (b) the attachment of two s-electrons to the configuration d^9. The resulting term-character is

$$(a)\ (d^{10}s)^2S, \qquad (b)\ (d^9 s^2)^2D.$$

We see that in (a) we are dealing with a ^2S-term, and in (b) with a

* We there also find the complete tables of *all* terms that correspond to a definite arrangement of equivalent p- or d- electrons. The analogous table of equivalent f-electrons has been worked out by R. C. Gibbs, D. T. Wilber and H. E. White (Phys. Rev., **29**, 790 (1927).)

^{2}D-term following from the fact that d^{10} is a completed shell, and that, on the other hand, d^9 becomes supplemented by a d-electron into a completed shell, whereas s^2 is complete in itself. (a) is the ground-term in all noble metals, but (b) does not lie much higher,—in Cu only about 1200 cm.$^{-1}$. This " low-lying D-term " was already remarked upon and discussed much earlier. A doublet series of alkali-like terms is developed from (a) if the valency-electron is excited. Excitation gives rise to quite different kinds of doublet and quartet terms in the case of (b). We may understand their branching into doublet- and quartet-terms if we start out from the ion d^9s. Its term-character (combination of a missing d-electron with an s-electron) is ^{1}D or ^{3}D. If, for example, we add a p-electron ^{3}D transforms, by vectorial addition of $l = 1$ and algebraic addition of $s = \frac{1}{2}$ into either

$$^2P\,^2D\,^2F,$$

or

$$^4P\,^4D\,^4F.$$

A. G. Shenstone * was the first to disentangle these complicated terms in Cu. He also succeeded in explaining a structure in the Cu-spectrum to which attention had been called long before by Rydberg.†

Precisely as in the Cu-spectrum, so in the Au-spectrum we find, besides alkali-like terms, also similar complicated terms (doublet- and quartet-terms). Why are they so little prominent in the Ag-spectrum that this spectrum exhibits a much clearer and a much more alkali-like character than that of the other two noble metals ?

We may adduce a spectroscopic and a chemical reason for this. The element Pd which precedes Ag has for its lowest level in its arc spectrum a $^1S_0$-term, which indicates the regular completion of the 18-shell, the configuration d^{10}. This configuration is remarkably stable, not only in the case of Ag^+ but also of neutral Pd. The position is different, however, in the case of the elements Ni and Pt, which precede the noble metals Cu and Au. Here the completion of the shell is associated with a weaker binding ; the term $^1S_0$ lies, in the case of Ni, far above the true ground-term, which in Ni and Pt is not d^{10} but d^8s^2.‡ The same result emerges chemically : Ag is typically univalent, Cu may be equally well divalent as univalent (cupric and cuprous salts). Au may be uni-, di-, or tri-valent.‖ Hence in chemical respects silver has more similarity with the alkalies than with copper and gold.

* Phys. Rev., **28,** 449 (1926). The quartet terms were recognised simultaneously by C. S. Beals by means of the Zeeman effect, Proc. Roy. Soc., **111,** 168 (1926). The Cu-spectrum has been investigated in greatest detail by L. A. Sommer, Zeits. f. Physik, **39,** 711 (1926).

† Astrophys. Journ., **6,** 239 (1897).

‡ The ground-term arrangement for Ni is given in the paper : K. Bechert, Ann. d. Physik, **77,** 538 (1925) ; for Pd : K. Bechert and M. A. Catalán, Zeits. f. Physik, **35,** 449 (1925) ; for Pt : J. C. McLennan and A. M. McLay, Trans. Roy. Soc. Canada, **20,** 3 (1926).

‖ This and similar data from the border-lines of spectroscopy and chemistry are given in a paper by H. G. Grimm and A. Sommerfeld, Zeits. f. Physik, **36,** 36 (1926).

We shall now conclude our discussion of the iron group. Since in Table 43 we have given only the absolutely lowest term of the divalent ions, we proceed to search for the other *low terms*. In doing so, we shall maintain for the present the condition for greatest multiplicity, $S = z/2$, $r = z + 1$.

We see directly that no further terms of the same multiplicity can be added to the terms ^6S and ^5D, $z = 5$ and 4 (or 6, respectively). Since such terms would necessarily belong to a smaller L, a further term is obviously out of the question for ^6S ($L = 0$). But it is easy to prove the same for ^5D. By equation (1) the highest M_L-level of the ^5D-term arose from the sum

$$M_L = \sum m_l = 2 + 1 + 0 + -1 = 2,$$

that is, we omit $m_l = -2$. By omitting instead of this one of the numbers -1, 0, $+1$, $+2$, we obtain $M_L = 1, 0, -1, -2$, that is, only those M_L-values that we required for the D-term.

The case is different with $z = 3$. We arrived at the ^4F-term by (1) from the sum

$$M_L = \sum m_l = 2 + 1 + 0 = 3.$$

Instead of this, we may also form

$$\begin{matrix} M_L = 2, 1, 0 \\ \qquad\quad 1, 0, \end{matrix}$$

if we systematically omit *two* of the possible m_l-values (it is not necessary first to write down the negative values of the resulting sums). We require the first three M_L-values for the complete magnetic scheme of the already known ^4F-term. The last two values constitute a P-term, namely a ^4P-term, since our argument is concerned only with the highest multiplicity in question. This term has been added in the lowest row of Table 43 at d^3 and d^7, as the sole additional term of highest multiplicity. In d^2 and d^8, also, there is only one such additional term, namely, by (11) of the preceding section, the term ^3P. Thus the lowest row of Table 43 is verified.

As we shall see from the example of the iron spectrum, these few ground-terms are in general sufficient to unravel the spectra. But to illustrate our method of enumeration further we shall calculate the terms with the greatest L and *second greatest multiplicity*. Following on equations (1) and (2) we now write

$$S = \frac{z}{2} - 1, \quad L = l + \{l + (l - 1) + \ldots (l - z + 2)\}.$$

For we obtain the greatest L if we use the greatest $m_l = l$ twice, so that the smallest m_l becomes greater by one unit than in equation (1). Using $m_l = l$ twice is allowed by Pauli's Principle, since now not all

m_s's are equal to $+\frac{1}{2}$ but an $m_s = -\frac{1}{2}$ also occurs. Working out the arithmetic series { }, we obtain

$$L = l + \frac{z-1}{2}(2l - z + 2) \quad . \quad . \quad . \quad (4)$$

and hence

$$\Delta L = L_z - L_{z-1} = l + 2 - z = 4 - z \quad \text{for} \quad l = 2 \quad . \quad (5)$$

Since S becomes meaningless (negative) for $z = 1$, we begin with $z = 2$ and calculate with $l = 2$ from (4) that $L = 4$ and we obtain successively from (5) for $z = 3, 4, 5$ that

$$\Delta L = 1, 0, -1.$$

Hence we obtain, as a supplement to Table 43, for the terms of second highest multiplicity with the greatest L (the multiplicity written alongside the term symbols is, of course, obtained from $S = z/2 - 1$, and comes out as $r = z - 1$) :

d^1	d^2	d^3	d^4	d^5	d^6	d^7	d^8	d^9
	^1G	^2H	^3H	^4G	^3H	^2H	^1G	

The complete term-scheme of the configuration d^z has been calculated by Hund (*loc. cit.*).

We concentrate our attention further on the *iron spectrum* as the most famous example of complex-structures and as the most used comparison spectrum. We already know its ground-terms from p. 456. We repeat them here in a more complete form :

Fe^{++}	$3d^6$	^5D	$3d^7$	^4F	^4P
Fe^{+}	$3d^6 4s$	$^6D\,^4D$			
Fe	$3d^6 4s^2$	^5D	$3d^7 4s$	$^5F\,^3F$	$^5P\,^3P$

The greater completeness consists in our having taken into account in the configuration $3d^7$ of Fe^+ besides the lowest term,* ^4F, also the second lowest term ^4P (cf. Table 43), from which the terms ^5P and ^3P follow by the addition of an s-electron (unchanged L, multiplicity changed by ± 1), as described earlier. All these ground-terms are " even terms " in the sense of footnote on p. 444. Hence they may

* The ground-term of Fe^+ is the term $^6D(d^6s)$. In an analogous way the other *first* spark spectra of the Fe-series exhibit as ground-terms mostly $d^z s$ or d^{z+1}. The arrangement $d^{z-1}s^2$ is less stable here. The *two-fold* ions of the Fe-series all have d^z as the ground-term. This means that as the nuclear charge increases the configurations of the " ideal system " of the elements (cf. p. 156) become more stable ; we obtain the natural order of sequence of the building in of electrons. The same conclusion was drawn on p. 415 from the " stripped spectra." In our example $3d$ comes first when the nuclear charge is high ; $4s$-orbits occur only when the $3d$-shell is fully occupied. The same statements must hold qualitatively for the spark spectra of the Pd- and the Pt-series, of which only a part has hitherto been analysed. For further details see, for example, the report by O. Laporte quoted on p. 444.

combine only with "odd" terms. The lowest and strongest odd terms will be obtained if we replace an s-electron by a p-electron in the ground-terms, so that Σl_1 becomes increased by 1 or, as we may say more simply, if we add a $4p$-electron to the different ground-configurations of Fe^+. In this process L changes to L + 1, L or L − 1, and S to S ± 1 :

From $3d^64s^6D$ we obtain $^{7,5}F$, $^{7,5}D$, $^{7,5}P$ } Config. $3d^64s4p$.
,, $3d^64s^4D$,, ,, $^{5,3}F$, $^{5,3}D$, $^{5,3}P$ }
,, $3d^7\,^4F$,, ,, $^{5,3}G$, $^{5,3}F$, $^{5,3}D$ } Config. $3d^74p$.
,, $3d^7\,^4P$,, ,, $^{5,3}D$, $^{5,3}P$, $^{5,3}S$ }

Finally, if we add a $5s$-electron to $3d^64s$ and to $3d^7$ we obtain a third layer of terms which apparently form the second series term of the arrangement $3d^64s^2$ and $3d^74s$, respectively :

From $3d^64s^6D$ we obtain $^{7,5}D$ } Config. $3d^64s5s$.
,, $3d^64s^4D$,, ,, $^{5,3}D$ }
,, $3d^7\,^4F$,, ,, $^{5,3}F$ } Config. $3d^75s$.
,, $3d^7\,^4P$,, ,, $^{5,3}P$ }

These term-groups have actually, for the most part, been shown to exist, as Fig. 119, taken from Hund, shows. The terms that belong to

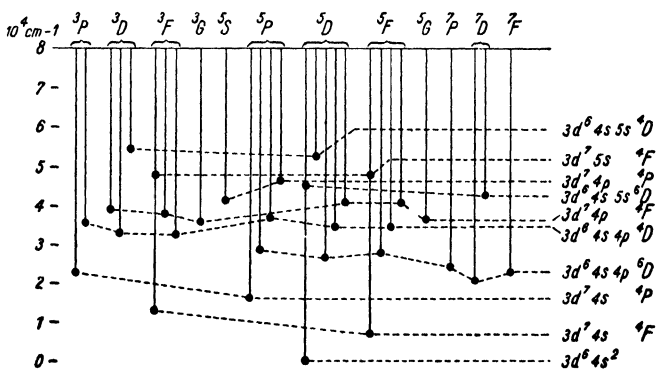


FIG. 119.—Scheme of levels of the iron spectrum. The scale of term-values is numbered upwards from the lowest term, whose magnitude is arbitrarily put equal to zero. Terms of similar electronic arrangement are connected by dotted lines. The electronic arrangement is given on the right, together with the spark term which goes to form the arc terms lying on the respective vertical lines.

the same configuration have been connected together. We see how the ground-terms are overlapped by a layer of higher terms, which arise from them by the addition of a $4p$- or a $5s$-electron. The terms of the same configuration are at approximately the same distance from the zero-level. This is plausible, since they do not differ in their structure but only in the way in which their s-, p-, d-elements are conjointly assigned to different L- and S-values. Terms bearing the same

symbol, in particular ^{5}D- and ^{5}F-terms, arise several times from different origins and hence are also at somewhat different levels. All these terms are ultimately built up on the ^{5}D-state of the configuration d^6 in Table 43. The triplet-states (cf. the table on p. 460) have not even been required to explain the most important lines of the iron arc.

Our mode of derivation brings out clearly the origin of the septet-system, whose existence had already been noted in Table 42 on p. 432. The reason that it is not represented in the ground-terms is to be found in Pauli's Principle. But in the higher layers Pauli's Principle loses face on account of the addition of the non-equivalent $4p$- or $5s$-electron.

The occurrence of the terms with a large L, for example, of F- and G-terms (" Bergmann " and " ultra-Bergmann " terms) here has quite a different meaning than with the alkalies. With the latter it denoted high excitation of the radiating electron and hence occurred relatively rarely. In the case of iron, however, it signifies only the successive addition of several relatively small l_i's. The elementary states from which such terms result are not highly excited, but are simple s-, p- and, in particular, d-states ; the d-states occur on account of the position of the iron group in the periodic system. The contrast with the alkalies comes out in the following point. Whereas in the atoms K and Ca, which stand in the same horizontal row, the normal (" unaccented ") D-terms are only very little resolved and the F-terms not at all (experimentally), the F- and the G-terms of iron exhibit resolutions of the same magnitude as the P-terms. The reason is obviously that a high L here no longer denotes weak coupling with the atomic core. We shall deal in greater detail in § 10 with the magnitude of the multiplet resolutions.

The rich abundance of lines in the iron spectrum is caused not only by the great number of the terms, but also by the high multiplicities (quintet-, septet-system). By combining and inter-combining these multiplicities configurations with a considerable number of lines result. We shall illustrate this at the end by a number of examples which may also serve as a model for the characteristic manifested in other complex spectra. At the same time, those examples will prepare the ground qualitatively for studying the intensity-distribution in multiplet lines, the quantitative aspect of which will occupy our attention in § 9.

The most important system in the iron spectrum is the *quintet*-system, because it contains the ground-term.* Its combinations (SP), (PD), (DF), (FG) . . . contain, respectively,

3, 9, 12, 12, . . .

* For literature dealing with the Fe-spectrum we may quote : F. M. Walters, Journ. Opt. Soc. Amer., **8**, 245 (1924) ; M. A. Catalán, Nature, **113**, 889 (1924) ; O. Laporte, Zeits. f. Physik, **23**, 135 ; **26**, 1 (1924) ; W. F. Meggers, Astrophys. Journ., **60**, 60 (1924) ; O. Laporte, Proc. Wash. Nat. Ac., **12**, 496 (1926) ; M. A. Catalán, An. Soc. Esp. Fis. y Quim., **22**, 398 (1924) ; C. E. Moore and H. N. Russell, Astrophys. Journ., **68**, 151 (1928) ; M. A. Catalán, An. Soc. Esp. Fis. y Quim., **28**, 1239 (1930).

components, as we see from the scheme of inner quantum numbers given on p. 427.

The constancy of the number of components 12 after the combination (DF) denotes that the permanent number of levels 5 has been reached at the D-term. We show here the 12-component multiplet (DF) formed from the ground-term D of the iron spectrum (electron arrangement $3d^6 4s^2$) and the lowest F-term of the higher term-group (arrangement $3d^6 4s 4p$). The diagonal terms are the strongest, since they correspond to the transition $J \to J - 1$, which runs parallel with the transition $L \to L - 1$ (cf. our qualitative intensity rule on p. 422). Inside the diagonals the intensities decrease from left above to the right below. Cf. the numbers written in brackets above the wave-numbers (these numbers have been estimated by King); R and *r* denote reversal owing to absorption, R denoting complete and *r* partial self-reversion. Starting from the diagonal, the intensities graduate themselves to the right and downwards, corresponding to the transitions $J \to J$ and

			^5F			
J		5	4	3	2	1
	$\Delta\nu$	292·29	227·86	164·89	106·77	
^5D 4		(300 R) 26,874·53	(100 R) 27,166·82	(20 *r*) 27,394·67		
	415·92		(200 R) 26,750·88	(100 R) 26,978·76	(20 *r*) 27,143·66	
3	288·08			(150 R) 26,690·69	(100 *r*) 26,855·57	(20*r*) 26,962·43
2	184·11				(125 R) 26,671·45	(80 R) 26,778·22
1	89·91					(80 R) 26,688·31
0						

$J \to J + 1$. We have not written down the wave-lengths in our scheme. They range from $\lambda = 3649$ to $\lambda = 3748$ Å. The wave-number differences $\Delta\nu$ have been written down above and on the left; in general each $\Delta\nu$ occurs twice; the agreement in the $\Delta\nu$'s is excellent, as we see from the scheme; the fluctuations do not exceed the errors of observation. Our scheme is, so to speak, a continuation to the left above of the (*pd*)-triplet scheme on p. 425.

The general occurrence of self-reversed lines indicates that the ground-state of the iron atom participates in this multiplet. This state must, of course, be the *final state* of the emission process. If D were a *regular* term the ν's would have to *increase* within a vertical of our scheme from above downwards. Since in reality they decrease, we must conclude that the D-term is *inverted*. The same holds of the F-term, since the ν's increase from left to right within the horizontal rows, and the same holds for *all terms of the iron spectrum*, as already

emphasised on p. 451. In particular, we remark that the absolutely lowest energy level of the iron spectrum is our D_4-level with $J = 4$; this will be found to be important when we calculate the number of magnetons in the Fe-atom.

The combination (FG), with likewise 12 components, has the same structure as (DF).

The inter-combination $^5D\ ^7D$ has the same structure as D^5F^5. For the septet-term is not only, like the quintet F-term, a five-fold term but, by p. 427, it also has the same inner quanta $J = 5, 4, 3, 2, 1$. In virtue of these same J's we therefore get the same combinations as in our scheme ($^5D\ ^5F$), but with one difference: it is not the intensities of the diagonal series that is emphasised but those of the parallel line on the right, because this belongs to the transition $J \rightarrow J$ and because we are now dealing with a transition $L \rightarrow L$.

We consider as the next multiplet-type the combination ($^5D\ ^5D$) between the ground-term D of the quintet system and a quintet D-term of the higher term group (arrangement $3d^6 4s 4p$) which we distinguish by drawing a bar over the ground-term. This combination contains one of the strongest lines of the whole iron spectrum, $\lambda = 3860$ Å.

	J		$^5\overline{D}$				
			4	3	2	1	0
		$\Delta\nu$	240·20	199·53	139·73	71·12	
^5D	4		25,900·00	26,140·19			
		415·96					
	3		25,484·03	25,724·24	25,923·77		
		288·10					
	2			25,436·14	25,635·67	25,775·35	
		184·17					
	1				25,451·45	25,591·23	25,662·35
		89·92					
	0					25,501·31	

The diagonal members of the scheme which correspond to the transition $J \rightarrow J$ are the strongest; the absolutely strongest component is the line $\lambda = 3860$ Å, $\nu = 25{,}900$, already mentioned. If we cover up the two upper rows and the two rows on the left, we get the triplet scheme of p. 425. As in that scheme so here the absence of the combination $0 \rightarrow 0$ in the right-hand bottom corner is characteristic.

($^5F\ ^5F$) distinguishes itself from the combination ($^5D\ ^5D$) essentially only in not being without the transition $1 \rightarrow 1$ between the smallest inner quantum numbers of both terms. Consequently the multiplet ($^5F\ ^5F$) consists of 13 and not, like ($^5D\ ^5D$), of 12 components. These

13 components resolve into groups of 2 + 3 + 3 + 3 + 2 lines. But for the eye here as everywhere in the Fe-multiplets, no such separation into groups is apparent; this, of course, renders it more difficult to recognise them. This is evident in the following graphical representation (Fig. 120).

The length of the lines gives an approximate measure of their intensities. The arraying into the order of the $\Delta\nu$'s of the higher F-term is explained at the foot of the diagram. The sequence of five lines that begins with the most intense line and decreases towards the right-hand side corresponds to the diagonal column of the scheme; the other lines partially overlap with this sequence. The combination (^{7}D ^{7}D) in the septet system, $\lambda = 4187$ to 4299 Å. has the same structure as (^{5}F ^{5}F), since the (five-fold) ^{7}D-term has the same J-values as the ^{5}F-term. In spite of this we shall illustrate the combination (^{7}D ^{7}D) by an example, because it exhibits a striking anomaly in respect of intensity. For this we choose (see the following table) the combination between the ^{7}D-term of the middle term-group $3d^64s4p$ and the ^{7}D-term of the arrangement $3d^64s5s$, which represents the second series term to the ground-term $3d^64s^2(^5\mathrm{D})$.

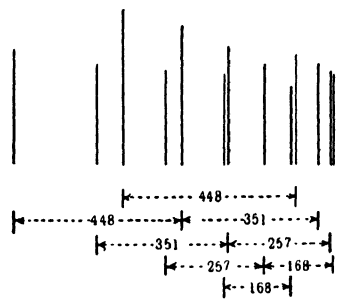


FIG. 120.

J		^{7}D				
		5	4	3	2	1
	$\Delta\nu$	347·48	271·31	198·91	130·42	
^{7}D 5	211·58	23,464·90	23,812·39			
^{7}D 4	194·58	23,253·33	23,600·81	23,872·11		
^{7}D 3	155·46		23,406·22	23,677·54	23,876·44	
^{7}D 2	107·15			23,522·07	(23,720·99)	23,851·42
^{7}D 1					23,613·85	23,744·26

The line which corresponds to the combination ($^7\mathrm{D}_2$ $^7\mathrm{D}_2$), to which the wave-number 23,720·99 cm.$^{-1}$ corresponds, has not been observed although it belongs to the transitions $\Delta J = 0$, which should be the strongest in this triplet, for which $\Delta L = 0$, according to our qualitative intensity rule. In § 9 we shall be able to prove by means of a

more rigorous intensity rule, that the line $^7D_2{}^7D_2$ is forbidden theoretically ; its intensity becomes exactly equal to zero.

In the *septet-systems* combinations ($^7S^7P$), ($^7P^7D$), ($^7D^7F$), ($^7F^7G$) . . . have respectively

$$3,\ 9,\ 15,\ 18,\ \ldots$$

components, as may easily be read off from the septet scheme of the inner quanta on p. 427. In Fig. 121 we show the combination ($^7D\,^7F$) which is particularly rich in lines. According as the multiplet is arrayed according to the term ^7D or ^7F it divides into groups of

$$3+3+3+3+3 \qquad = 15$$

or of

$$1+2+3+3+3+2+1 = 15$$

lines. Our little scheme at the foot of the figure represents the first type of resolution.

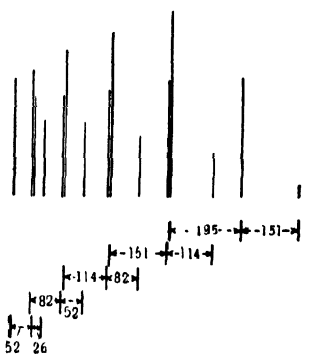


Fig. 121.

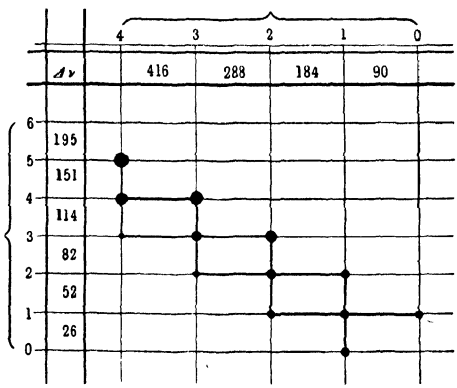


Fig. 122.—Intercombination between quintet and septet-systems ($^5D^7F$). Fe-spectrum $\lambda = 4326$ to 4490 Å.

The combination ($^5D\,^7F$) between the quintet- and the septet-system is interesting ; we shall describe it symbolically by means of a point-scheme (Fig. 122). It consists of $1+2+3+3+3+1 = 13$ lines ; the level $J = 6$ of the ^7F-term does not combine at all and the combination $0 \rightarrow 0$ is forbidden.

As a last example we give, also in the form of a point-scheme, an inter-combination between a quintet- and a triplet-system, namely $^5F\,^3G$, which consists of strong lines (Fig. 123). As in the above combination ($^5D\,^7F$) one of the term-levels, namely $^5F_1$, is not capable of combining at all. The group consists of $2 + 3 + 3 = 8$ components.

In Fig. 124 we show a section out of the atlas of the iron spectrum prepared by Fabry and Buisson ; the region is from $\lambda = 3600$ to 3900 Å and the connected multiplets are written below. We observe

how peculiarly they overlap and how little they appear separated from each other at a first glance. The two multiplets ($^5D\,^5F$) and $^5D\,^5D$, whose number-schemes have been given above, lie within the spectral region shown.

The figure shows that in this region *all the strong iron lines* have been ordered into multiplets; the same applies to the other parts of the spectrum.

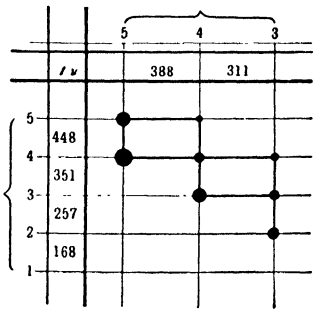


Fig. 123.—Intercombination between quintet- and triplet-systems ($^5F\,^3G$). Fe-spectrum, λ = 3467 to 2570 Å.

It has been found possible to reduce to order not only the iron spectrum but also a large number of other spectra.* The results obtained form the sure foundation of the theoretical atomic model. We do not go too far when we assert that the researches on multiplets, which has been developed to an astounding degree of perfection in the last decade, has not only been of importance for getting an insight into atomic structure, but together with the study of the Zeeman effect it has

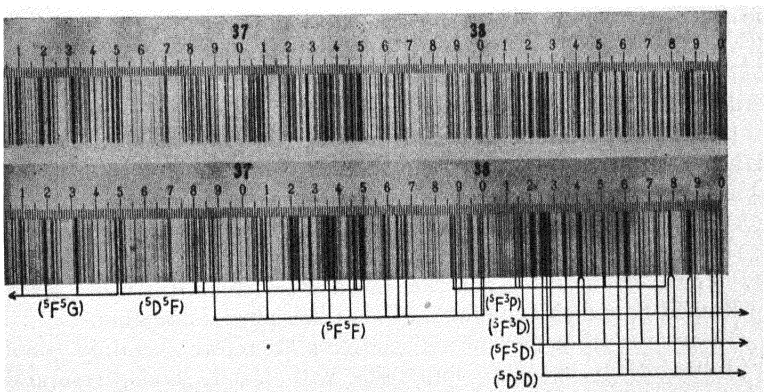


Fig. 124.—Part of the iron spectrum taken from Fabry and Buisson's atlas. The numbers denote wave-lengths in Å. (37, for example, denotes 3700 Å.) Below are some of the Fe multiplets bracketed together.

formed the framework for the discovery of the spinning electron and the subsequent structure of relativistic wave-mechanics.

§ 5. Other Couplings

The Russell-Saunders coupling of quantum vectors, which we have treated in the preceding sections, represents only one of the possible

* References are given in the report by Laporte quoted on p. 444.

limiting cases of real coupling conditions. Actually we assumed that the l_i's of the individual electrons were to compound into a resultant L, the s_i's to a resultant S. By vectorial addition of L and S we finally obtained J, the quantum number of the total moment of momentum. This clearly denotes that there is a strong (magnetic) interaction between the l_i's and likewise between the s_i's among themselves. To a first-approximation the interaction or mutual action $(l_i s_i)$ does not come into consideration at all; if we were to neglect it altogether the moment of momentum vectors L and S would be strictly constant in magnitude and direction. For a second approximation we take into account the mutual action (L, S) which we suppose to be compounded of the individual actions of the kind just mentioned, namely of the interactions $(l_i s_i)$. This causes the L and S to perform a precession about the fixed direction of J, whose velocity is, by our assumptions, small compared with the precessional velocity of the l_i's about L and the s_i's about S.

By means of the Correspondence Principle these statements may easily be translated into the language of term schemes (cf. the analogous remarks in Chap. VI (§ 5, p. 337)). We suppose a definite configuration of electrons to be given and the corresponding L, S to be written down. Then the rapid precession about L and S, respectively, denotes great intervals between terms having different L's and S's, respectively. In the same way we infer from the slow motion about J that the distances between levels having different J's (L and S being kept fixed) must be small compared with the L- and S-intervals just mentioned. In other words, we obtain a clear separation of the terms according to L and S; the terms (L_1, S_1) are separated from (L_2, S_1), (L_1, S_2), (L_2, S_2), and so forth. Every term L, S is then still further sub-divided into levels having different J's.

This type of term arrangement holds, as we know from experiment, for the deep terms of most known spectra; it is therefore called the *normal term arrangement*, and the coupling on which it is based is called the **Russell-Saunders coupling** and also the **normal coupling.**

Departures from the normal coupling therefore certainly occur if the J-resolutions become comparable with the L- and S-resolutions. This is the case with the heavy atoms and in the last vertical columns of the periodic system (for example, Ni, Pd, Pt). The J-resolutions there increase enormously (up to several thousand $cm.^{-1}$). In the deeper terms of the Fe-spectrum we still essentially use the Russell-Saunders coupling, whereas in Ni even the deeper terms overlap apparently quite irregularly.

In the vector model this denotes that the mutual action (LS) becomes of the same order of magnitude as that between the l_i's and the s_i's respectively. The moments of momentum L, S may then no longer be regarded to a first approximation as fixed and constant; they lose their significance because the l_i's and s_i's will compound in some

other way. On the other hand, the total moment of momentum J of all the electrons remains constant now as before, since the law of sectorial areas is generally applicable in a closed mechanical system : *in the case of general coupling conditions only J retains its mechanical significance.* Actually it has always been possible, even in the case of the most complicated spectra, to ascribe to the term-levels J-values for which the selection rule $\Delta J = 0, \pm 1$ holds.

Among these general coupling schemes there are limiting cases for which certain of the mutual actions may become small compared with the remaining ones. The Russell-Saunders coupling itself is one of these limiting cases. We may represent it by the symbol

$$[(l_1 l_2 \ldots)(s_1 s_2 \ldots)] = [\mathrm{LS}] = \mathrm{J}. \quad . \quad . \quad (1)$$

Another limiting case may be illustrated by a simple example. We consider the configuration $[np, n's]$, that is, $l_1 = 1$, $l_2 = 0$. In the limiting case of normal coupling we obtain the terms $^{3,1}\mathrm{P}$ from it. If we now keep n fixed and allow n' to increase a series of terms results ; the s-electron becomes more and more removed from the atomic core. For sufficiently great values of n' the two electrons will act only weakly on one another ; to a first approximation we may regard them as independent of one another so that the l_i's, s_i's of each electron for itself will compound into a resultant j_i. To a second degree of approximation j_1 and j_2 together form the resultant J. The vector j here clearly denotes the total moment of momentum of the individual electron. The symbolic appearance of this new kind * of coupling—the so-called (jj)-coupling, written for several electrons, is as follows :

$$[(l_1 s_1)(l_2 s_2) \ldots] = [j_1 j_2 \ldots] = \mathrm{J}. \quad . \quad . \quad (2)$$

It is generally characterised by having the electrons independent of one another to a first degree of approximation.

In our example only the first electron remains when the second electron has been completely removed from the atom, that is, the term $(l_1 s_1) = j_1$; this is, for $l_1 = 1$, $s_1 = \frac{1}{2}$, the term $^2\mathrm{P}$ of the spark spectrum. Hence it follows that in the neighbourhood of the series limit the arc terms divide into groups whose distance apart is given in order of magnitude by the resolutions of that *spark-term* towards which the series converges. In our example two groups will form whose distance apart is approximately equal to the resolution $^2\mathrm{P}_{\frac{1}{2}} - {}^2\mathrm{P}_{\frac{3}{2}}$ of the spark-term. It is also easily possible to specify which J-levels of the arc terms $^{3,1}\mathrm{P}$ converge to $^2\mathrm{P}_{\frac{1}{2}}$ and which converge to $^2\mathrm{P}_{\frac{3}{2}}$. We have $j_1 = \frac{1}{2}, \frac{3}{2}$ and $j_2 = \frac{1}{2}$ (on account of $l_2 = 0$). By adding j_1 and j_2 vectorially in accordance with (2) we obtain

$$\left.\begin{array}{l} \text{from } j_1 = \frac{1}{2}(^2\mathrm{P}_{\frac{1}{2}}) : \ \mathrm{J} = \frac{1}{2} \pm \frac{1}{2} = 1, 0 \\ \text{,, } \ j_1 = \frac{3}{2}(^2\mathrm{P}_{\frac{3}{2}}) : \ \mathrm{J} = \frac{3}{2} \pm \frac{1}{2} = 2, 1 \end{array}\right\} \quad . \quad . \quad (3)$$

* There are also other conceivable limiting cases such as $[((l_1 s_1) l_2) s_2] = [(j_1 l_2) s_2] = \mathrm{J}$. Like the coupling (2) they also lead to a grouping according to the levels j_1 of the spark-term (cf. below in the text). They do not appear to occur in the spectra.

If we assume that the Russell-Saunders coupling holds for the first terms of our series [np, $n's$], as is the case in most spectra, the levels $^3P_{2,\,1,\,0}$ lie close together, and $^1P_1$ lies at a greater distance away. At the series limit, however, the terms become torn apart by (3), their J-values remaining unchanged. $^3P_2$ moves over to a limit other than that to which $^3P_0$ goes; the former goes to $^2P_{\frac{3}{2}}$, the latter to $^2P_{\frac{1}{2}}$ (cf. Fig. 125). We can say nothing about $^3P_1$ from (3), because J = 1 occurs twice and at different limits.

We shall not enter into the question of the unique allocation of the L- and S-values to the series limits, that is, into the question as to which series limits the Russell-Saunders terms of the beginning of the series converge.*

Equation (3) is an illustration of the rule that the J-values that belong to a given configuration n_i, l_i must be the same for all couplings, corresponding to the adiabatic invariance of J. For we found in the case of the jj-coupling that J = 2, 1, 1, 0; these are the same values as are obtained according to the Russell-Saunders coupling. For in the latter case we have to compound L (in our example, L = 1) with S (here = 0 and 1) and so obtain J = 2, 1, 0 for the ^3P-term, and J = 1 for the ^1P-term.

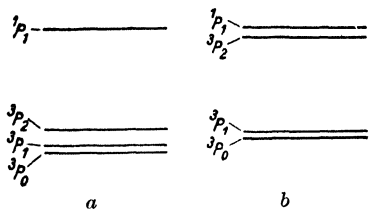


FIG. 125.—The terms of the electronic arrangement $npn's$ (n' variable, n fixed) according to the Russell-Saunders coupling (Fig. a) and according to the (jj)-coupling (series limit, Fig. b) shown diagrammatically. In the latter case the distance apart of the two groups of terms is about the same as the doublet separation of the arrangement $np(^2P)$ of the spark spectrum.

Our example [np, $n's$] holds for, say, an element of the fourth vertical column. In the case of Si, for example, we have the ground-term arrangement $3S^2 3p^2$ (outside the neon shell). If we place one of the p-electrons in the $4s$-orbit, we obtain the first member of our series [np, $n's$], which would here be called [$3p$, $n's$].

As an opposite example to this we shall consider the series [$ns\ n'p$], such as occurs in the alkaline earths, as in Ca. As in the previous example we have, for the Russell-Saunders coupling (that is, for the first members of the series), the terms ^3P, ^1P. But now the p-electron moves and the series converges to the state ns of the ion ($4s$ in the case of Ca); this is the ^2S-term of the spark spectrum. It is simple; we obtain no grouping in various levels, all four levels of ^3P ^1P converge to the same limit. It corresponds with this in the model that, on account of $l_1 = 0$, no mutual action ($l_1 s_1$) occurs. This simple

* It may be answered by means of wave-mechanics or by the methods developed by Hund from the vector model, Zeits. f. Physik, **52**, 601 (1928).

type of series, where all terms of a configuration move to the same limit, is clearly always obtained when the series limit corresponds to a simple term of the spark spectrum, in particular, to an S-term. All " non-displaced " terms of the alkaline earths and all terms of the alkalies belong here. For the latter converge towards the $^1S_0$-term * of the closed inert gas shell of the alkali-ion. The " displaced terms " of Ca, Sr, Ba (configuration $[nd, n'x]$ and so forth) move towards the double ^2D-terms of the spark spectrum (cf. Ch. VII, § 7), that is, belong to the more general type of series terms first discussed.

Numerous other examples of terms with multiple series limits may be taken from the spectra treated in previous sections. Let us choose, say, the series $3d^64sn's$ of the iron spectrum. All Fe-terms of this arrangement that are built up on the Fe^+-term $^6D(3d^64s)$ converge towards this five-fold term ^6D of Fe^+. The deepest term that belongs to these series terms is the ground-term ^5D of the iron spectrum, and also the terms $^{7,5}D$ of the highest layer of terms in Fig. 119. The terms of the arrangement $3d^64sn'p$ also go to the same five-fold limit ^6D, in so far as they are built up on ^6D. These are the terms $^{7,5}F$, $^{7,5}D$, $^{7,5}P$ that lie lowest in the middle layer of terms in Fig. 119.

Thus in complicated spectra we obtain theoretically a great number of series limits. In Chapter VII, § 7, we have already become acquainted with two cases where the series may also be followed exactly empirically. The one case was that just mentioned of the " displaced " terms of the alkaline earths, the second that of the neon spectrum. On the other hand, series are only incompletely known in the case of spectra described as *serienlos* (devoid of series), for example, in the Fe-group.† They consist for the most part of two or three terms, so that the predictions of the theory cannot be accurately tested by them.

Historically the neon-spectrum was the first in which series of terms with different limits were found.‡ The ground-term of the spectrum, which corresponds to the closed shell $2p^6$, is, on account of Pauli's Principle, a (simple) term $J = 0$; if the coupling were normal this term would be denoted by $^1S_0$. But normal coupling does certainly not occur in most terms of the Ne-spectrum. Their resolutions are so great that the terms with different L's and S's overlap very largely. If we take one of the p-electrons out of the shell $2p^6$ and transport it to higher orbits, all the series that result in this way clearly converge to the configuration $2p^5$, which corresponds to a doublet P-term. It is double, that is, the Ne arc-terms have two series limits,

* Cf. the remarks on page 472.

† In the iron-spectrum series were first given by H. Gieseler and W. Grotrian (Zeits. f. Physik, **25**, 165 (1924)). For other elements see H. N. Russell, Astrophys. Journ., **66**, 233 (1927).

‡ F. Paschen, cf. the reference in Chap. VII, § 7.

whose interval is equal to the doublet resolution of this ^{2}P-term of Ne^+ or, as we showed on p. 404, equal to the difference $L_{II}\ L_{III}$ of the X-ray spectrum of neon; in fact, $^2P_{\frac{1}{2}}$ corresponds to the level L_{II} and $^2P_{\frac{3}{2}}$ to the level L_{III}.

We now consider the higher terms of Ne individually. The arrangement $2p^5 3s$ gives J = 2, 1, 1, 0 (cf. our first example in this section). In the case of normal coupling these levels would have to be denoted by ^{3}P ^{1}P. From energy considerations they are to be expected as the first group above the ground-level $2p^6$; the ground-term itself lies extraordinarily low as in the case of all inert gases, and this is the spectroscopic expression for the great chemical stability (inactivity) of the inert gases. Ground-term combinations are thus to be expected only in the far ultra-violet. In an investigation in the visible region, such as was undertaken by Paschen, one obtains as the apparently lowest (deepest) terms the four levels just mentioned of the arrangement $2p^5 3s$. Actually, Paschen found four terms that were lowest, which he called s-terms (s_2, s_3, s_4, s_5). They form the beginning of a series of four terms which converge to two different series limits, as should be, according to our argument. The combinations of the four "s-terms" found by Paschen may be explained by means of the four inner quantum numbers given above.

We expect the next highest groups of neon-terms from the arrangement $2p^5 3p$; this forms the second series member of the ground-term arrangement $2p^6$ and gives J = 3, 2, 2, 2, 1, 1, 1, 1, 0, 0, that is, ten levels. With normal coupling they would be called ^{3,1}D ^{3,1}P ^{3,1}S. Four of them, namely J = 2, 1, 1, 0 go theoretically to $^2P_{\frac{1}{2}}$, the other six to $^2P_{\frac{3}{2}}$. The proof is fully analogous to the discussion given in connection with equation (3), p. 469. Experimentally Paschen discovered as the second term-group exactly ten levels (his p-terms, p_1 to p_{10}), to which the same inner quanta are to be assigned as were just now specified and which distribute themselves in the manner given over the two series limits of Ne. Further terms would result from $2p^5 3d$, but we shall content ourselves with the indications so far given.

We have still to make some remarks about the coupling conditions in the X-ray spectra. If the atomic number Z of the element is not too small the high nuclear charge certainly predominates in the interior of the atom over the mutual action between the electrons. To a first approximation we may regard the electrons as independent of each other, so that we have (jj)-couplings. The vectors l_i, s_i of each electron form a resultant j_i in each individual case. Hence we may order the inner electrons within a shell of given n, l according to the j's because j now has a real physical meaning in the model. In the Russell-Saunders coupling, however, we should be able to order the individual electrons only according to n, l because the l_i's and s_i's do not combine into j_i's in that case.

In the shell n, l we have $j = l + \frac{1}{2}$ or $l - \frac{1}{2}$. One part of the electrons has $j = l + \frac{1}{2}$, the other part $j = l - \frac{1}{2}$. The number in each case is determined by Pauli's Principle. To fix an electron quite definitely we require four quantum numbers; in our case the numbers having a physical meaning are n, l, j. To do away with the direction degeneracy we imagine a magnetic field superimposed, which may not, however, be so great as to disturb the mutual action (ls) of the individual electrons, as otherwise j would lose its meaning. We call the projection of j on the field direction m_j; our four quantum numbers are then n, l, j, m_j. In virtue of directional quantising there are $(2j + 1)$ values of the quantum number m_j for each $n\,l\,j$; that is, by Pauli's Principle, there are $(2j + 1)$ electrons. Accordingly, for $j = l - \frac{1}{2}$ we have $2l$ electrons and for $j = l + \frac{1}{2}$ we have $2l + 2$. *The shell n, l may be divided into two sub-groups with the quantum numbers $j = l \pm \frac{1}{2}$ and the occupation numbers (Besetzungszahlen) $2l + 2$ and $2l$, respectively.* This sub-division was first deduced from X-ray spectra by Stoner * and Main Smith.†

The total occupation number of the shell n, l comes out, of course, as $(2l + 2) + 2l = 4l + 2 = 2(2l + 1)$, as has already been found on p. 154 on the basis of another method of counting quantum states.

The electrons with $j = l - \frac{1}{2}$ are *more tightly* bound than those with $j = l + \frac{1}{2}$. We may derive this directly from the position of the alkali levels, where the term with $j = l - \frac{1}{2}$ is the *lower* (deeper) one. The reason that we may here and in general take over the (jj)-coupling from the discussion on the alkalies is simply because on account of the vanishingly small mutual action each electron behaves like an alkali-electron. *From the point of view of the individual electron* the position of the energy-levels is *regular*, as in the alkalies. This does not contradict our statement on p. 453 that the X-ray terms, *regarded from the point of view of the whole atom*, are *inverted*. Actually in order to produce the observed X-ray spectra it is necessary to make a gap in one of Stoner's sub-groups. For the gap in $j = l - \frac{1}{2}$ we require more energy than for $j = l + \frac{1}{2}$. The total energy of the atom in the first case becomes greater than in the second case and the position of the energy-levels for the whole atom becomes the reverse of that for the individual electron.

For lighter elements, as say, Li, and for X-ray levels, which arise in the outermost shells of the atom the (jj)-coupling may no longer remain valid, owing to the decreasing nuclear charge and the increased screening.

* E. C. Stoner, Phil. Mag., **48**, 719 (1924).

† J. D. Main Smith, *Chemistry and Atomic Structure*, D. van Nostrand Co. New York, 1924.

§ 6. Anomalous Zeeman Effect of the Multiplets

The normal Zeeman effect occurs only in the case of singlet lines (Ch. 6, § 4); in the case of multiple lines and even in those of hydrogen (Ch. 6, § 5) *anomalous Zeeman effects* occur. Anomalous resolutions intruded themselves even in the first discovery of the phenomenon (1896). What Zeeman first observed was a *broadening* of the image of the D-lines observed in the spectroscope, combined with a characteristic *polarisation* of the light at the broadened edges. As we saw in Figs. 87 and 88, p. 336, the D_1-line gives a quartet, the D_2-line a sextet of lines polarised partly in the parallel and partly in the perpendicular direction. Zeeman was able to prove the polarisation of the outer edge of the broadening in this complicated line configuration only because in this case as in that of the normal triplet the perpendicularly polarised components are situated more towards the outside, the parallel polarised components are situated more towards the middle of the resolved pattern. Whereas the deviations from the theory of the normal Zeeman effect at first appeared discouraging for quantitative investigation, it is now precisely these deviations that are of greatest interest.

Historically there are two rules that opened up the way to the anomalous Zeeman effect, Preston's rule * and Runge's rule.†

Preston's rule (cf. also p. 334) states that related lines, that is, lines which are composed of *terms of the same kind* have the same Zeeman effect. Terms of the same kind are those which *have the same multiplicity* and *the same quantum numbers* for L and J. The Zeeman type is, however, independent of the principal quantum number n and the chemical nature of the element.

Runge's rule states that the line resolutions that occur in the anomalous Zeeman effects are, if measured in wave-numbers (*not* in wave-lengths) rational multiples of the normal Lorentz resolution,

$$\Delta\nu = \frac{q}{r}\Delta\nu_{norm} \quad . \quad . \quad . \quad . \quad (1)$$

where r is a number which we shall call the **Runge denominator.**

Let us consider from the point of view of these two rules the resolution patterns of the type represented by the D-lines, Figs. 87 and 88, in the way in which they were analysed almost simultaneously in 1898 by Zeeman and Cornu. The distances of the components of the resolution from the original line are all multiples of $\frac{1}{3}$ of the normal Lorentz resolution (Tables 33 and 34 on p. 335). *The "Runge denominator" is equal to* 3. The intensity, like the line-distribution, is, if perturbations are not acting (see § 7), symmetrical with regard to the middle.

* Cf. Kayser's Handbuch, **2**, 619.

† Phys. Zeits., **8**, 232 (1907); enunciated on the basis of the particularly abundant Zeeman types of neon.

As is demanded by Preston's rule this type of resolution-pattern occurs not only in the D-lines but also in all combinations (SP) and (PS) in the Principal Series and in the second Subordinate Series of the alkalies and the noble metals. It also characterises the doublet terms of similar composition in the earths, Al, Ga, In, Tl, and not these alone but also the spark spectra of the alkaline earths and of the elements Zn, Cd, Hg, and so forth.

Fig. 126 represents as the second most important case the resolution-pattern of the II N.S. of the triplet-systems, as was first observed by Runge and Paschen * in the case of Hg. The wave-lengths written down on the right-hand side refer to Hg; the highest is the "green mercury line." All the intervals between the components and the original lines are *half-integral* multiples of the normal resolution $\Delta\nu$; *the Runge denominator is equal to* 2 *in this case.*

The same resolution-pattern occurs not only in the triplet lines of Hg shown in the figure but also in all similarly constructed com-

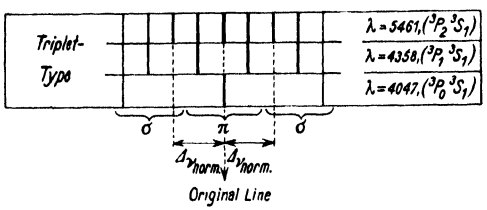


FIG. 126.—Anomalous Zeeman effect of the combination $^3P^3S$ (Hg).

binations of Hg, Cd, Zn, as well as in the alkaline earths, and also in the spark spectra of the earths and so forth. A large group of apparent contradictions to Preston's rule is explained by the Paschen-Back effect (§ 7).

The most general point of view in the theory of spectra is that opened up by the *Combination Principle.* This must doubtless also hold for the anomalous Zeeman effects.† The magnetic field influences the energy of the initial and the final configuration separately; the Zeeman effect of the lines is therefore compounded from the Zeeman effect of the initial term and of the final term

$$\Delta\nu = \Delta\nu_1 - \Delta\nu_2. \quad . \quad . \quad . \quad . \quad (2)$$

* Berlin Academy, Feb., 1902.

† T. van Lohuizen, Amsterdam Academy, May, 1919; A. Sommerfeld, Naturwiss., Jan., 1920, and Ann. d. Phys., **63**, 121 (1920). The "rule of magneto optical resolution" discussed in the last two papers deduced from the combination principle the arithmetic law that the Runge denominator of the term combination may be separated into the product of the Runge denominator of the two terms in question. But since this law was soon surpassed by the papers on the same subject by Landé we need not here discuss it further.

Hence we shall be concerned in the sequel with the *Zeeman effect of the terms* which is simpler than the *Zeeman effect of the lines.*

Extending the arguments and formulæ given in Chapter VI, § 5, we start from the following points of view. The resolution of the individual term depends on its J-value, that is, on its total moment of momentum. In the magnetic field $\vec{J}$ arranges itself in such a position that its projection M in the direction of the magnetic field becomes integral or half-integral with J. Moreover, since the absolute value of M, the projection of J, can be at most equal to J, we obtain the following $2J + 1$ possible values for M:

$$M = J,\quad J-1,\quad J-2,\ \ldots\ -J+2,\quad -J+1,\quad -J. \qquad (3)$$

The values $M = \pm J$ correspond to the position *parallel* or *anti-parallel* to the magnetic lines of force. The value $M = 0$, *that can occur only for integral values of J*, that is, *in odd term-systems*, denotes the position perpendicular to the magnetic field. Precisely as in Figs. 29 and 30 on pp. 123-124 we must picture to ourselves that if the arrow of the moment of momentum J is appropriately inclined to the magnetic field there will be a precession around the direction of the lines of force.

Corresponding to the *mechanical moment of momentum* M_{mech} defined by J there is a *magnetic moment* M_{mag}. In the Russell-Saunders coupling this magnetic moment is composed of the magnetic moment of the resulting orbital moment of momentum L and of the resultant spin moment of momentum S. If $S = 0$, that is, for a singlet system, M_{mag} is given by the mathematical relationship, equation (2) on p. 331. The Zeeman effect is then normal. The anomalous behaviour of the Zeeman effect consists in the addition of the spin moment of momentum and its magnetic anomaly, equation (3) on p. 332.

On account of the precession of the magnetic moment about $\vec{J}$ (cf. Fig. 86, p. 331) only its component parallel to $\vec{J}$ comes into question. It is given by equation (4) on p. 332 (if we exchange l, s, j for L, S, J). Hence we may draw the same conclusions about them as on pp. 333-334. They lead to **Landé's splitting factor:**

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)} \qquad (4)$$

and to the *expression for the term resolution*, calculated in terms of the normal Lorentz resolution:

$$\Delta W = h\Delta\nu = Mg. \qquad (5)$$

As a matter of historical interest we must observe that the bold inductive process which led Landé to equation (4) was based on the masterly Zeeman-measurements carried out by E. Back. The measure-

ment and the theoretical interpretation occurred in two steps, first for the ordinary doublet and triplet systems * and then for that class of multiplets † which we nowadays call multiplets of pure Russell-Saunders coupling. The equations (4) and (5) determine completely the resolution-pattern of the terms of such multiplets: *there are* $2J + 1$ *equidistant magnetic term-levels at a distance g from one another, symmetrically placed with respect to the zero, the zero itself representing a term-level in the case of odd terms but not in the case of even terms.* In Table 45 we give a complete list of the g-values. Attention must be called to several characteristic points.

A. $g = 2$ for the S-state of every term-system. This is obvious, since for every S-term $L = 0$, that is, $\vec{J} = \vec{S}$. But then the magnetic moment and at the same time its component parallel to $\vec{J}$ becomes equal to the magnetic moment of the spin moment of momentum S and this (cf. eqn. (4) on p. 332) is equal to 2S, as measured in Bohr magnetons. The value $g = 2$ denotes nothing else than the magnetic anomaly of the spin.

B. *For every term* with $J = J_{max} = L + S$ (the boundary on the right-hand side running down obliquely in every field of our scheme) we have

$$Jg = 2S + L. \quad . \quad . \quad . \quad . \quad (6)$$

To prove this it is convenient to transform the expression (4) into the identical expression

$$g = \tfrac{3}{2} + \tfrac{1}{2}\frac{(S - L)(S + L + 1)}{J(J + 1)}. \quad . \quad . \quad . \quad (7)$$

If we here set $J = S + L$ the factor $J + 1$ in the denominator cancels out with the factor $S + L + 1$ in the numerator and we obtain

$$g = \tfrac{3}{2} + \tfrac{1}{2}\frac{S - L}{S + L} = \frac{2S + L}{S + L}$$

which agrees ‡ with (6).

C. For $L \gg S$ (lowest row, particularly in the first fields of our scheme) g *approaches the value* 1. Actually when $L \gg S$ we also

* E. Back, Dissertation, Tübingen, 1921; A. Landé, Zeits. f. Phys., **5**, 231 (1921).

† E. Back, Zeits. f. Phys., **15**, 206 (1923); A. Landé, *ibid.*, p. 189.

‡ We might be tempted to interpret eqn. (6) in an elementary way: if L, S and J were in the "parallel position" with respect to $\vec{H}$ the magnetic moment in the direction $\vec{H}$ would on the one hand be $2S + L$, and on the other Jg. But we should then be leaving out of account the wave-mechanical difference, emphasised on p. 333, between the absolute value of a quantum vector and its quantum number. The incorrectness of this elementary line of argument is shown when we pass over to the "anti-parallel position" $J = |L - S|$ for which we by no means have: $Jg = |2S - L|$.

have $J \cong L$. Consequently the second term in the right-hand side of (7) approaches the value $-\frac{1}{2}$. We then have *an asymptotic normal*

TABLE 45

		J = 0	1	2	3	4	5	6	7											= J		
										$\frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$	$\frac{13}{2}$	$\frac{15}{2}$				
L=0	S	$\frac{0}{0}$							Singlet	2								Doublet	S	0=L
1	P		1						S = 0	$\frac{2}{3}$	$\frac{4}{3}$							S = $\frac{1}{2}$	P	1
2	D			1							$\frac{4}{5}$	$\frac{6}{5}$							D	2
3	F				1							$\frac{6}{7}$	$\frac{8}{7}$						F	3
4	G					1							$\frac{8}{9}$	$\frac{10}{9}$					G	4
0	S		2						Triplet		2							Quartet	S	0
1	P	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$					S = 1	$\frac{8}{3}$	$\frac{26}{15}$	$\frac{8}{5}$						S = $\frac{3}{2}$	P	1
2	D		$\frac{1}{2}$	$\frac{7}{6}$	$\frac{4}{3}$					0	$\frac{6}{5}$	$\frac{48}{35}$	$\frac{10}{7}$						D	2
3	F			$\frac{3}{2}$	$\frac{13}{12}$	$\frac{5}{4}$					$\frac{2}{5}$	$\frac{36}{35}$	$\frac{78}{63}$	$\frac{4}{3}$					F	3
4	G				$\frac{3}{4}$	$\frac{21}{20}$	$\frac{6}{5}$					$\frac{4}{7}$	$\frac{62}{63}$	$\frac{116}{99}$	$\frac{14}{11}$				G	4
0	S			2					Quintet			2						Sextet	S	0
1	P		$\frac{5}{2}$	$\frac{11}{6}$	$\frac{5}{3}$				S = 2		$\frac{12}{5}$	$\frac{66}{35}$	$\frac{12}{7}$					S = $\frac{5}{2}$	P	1
2	D	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$				$\frac{10}{3}$	$\frac{28}{15}$	$\frac{58}{35}$	$\frac{100}{63}$	$\frac{14}{9}$					D	2
3	F		0	1	$\frac{5}{4}$	$\frac{27}{20}$	$\frac{7}{5}$			$-\frac{2}{3}$	$\frac{16}{15}$	$\frac{46}{35}$	$\frac{88}{63}$	$\frac{142}{99}$	$\frac{16}{11}$				F	3
4	G			$\frac{1}{3}$	$\frac{11}{12}$	$\frac{23}{20}$	$\frac{19}{15}$	$\frac{4}{3}$			0	$\frac{6}{7}$	$\frac{8}{7}$	$\frac{14}{11}$	$\frac{192}{143}$	$\frac{18}{13}$		G	4
0	S				2				Septet				2					Octet	S	0
1	P			$\frac{7}{3}$	$\frac{23}{12}$	$\frac{7}{4}$			S = 3			$\frac{16}{7}$	$\frac{122}{63}$	$\frac{16}{9}$				S = $\frac{7}{2}$	P	1
2	D		3	2	$\frac{7}{4}$	$\frac{33}{20}$	$\frac{8}{5}$				$\frac{14}{5}$	$\frac{72}{35}$	$\frac{38}{21}$	$\frac{56}{33}$	$\frac{18}{11}$				D	2
3	F	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{3}{2}$		4	2	$\frac{12}{7}$	$\frac{34}{21}$	$\frac{52}{33}$	$\frac{222}{143}$	$\frac{20}{13}$			F	3
4	G	$-\frac{1}{2}$	$\frac{5}{6}$	$\frac{7}{6}$	$\frac{13}{10}$	$\frac{41}{30}$	$\frac{59}{42}$	$\frac{10}{7}$		$-\frac{4}{3}$	$\frac{14}{15}$	$\frac{44}{35}$	$\frac{86}{63}$	$\frac{140}{99}$	$\frac{206}{143}$	$\frac{284}{195}$	$\frac{22}{15}$		G	4

resolution of the terms, as is to be expected on the basis of the correspondence principle.

D. Within every horizontal row of our table a remarkable summation rule holds: *the mean value* $\bar{g}$ *of* g, *that is, the sum of all the* g's *divided by the number of levels, is equal to* 1 *or* 2 *according as we are dealing with a term sequence with the permanent number* r *of levels or with the incomplete number* $< r$ *of levels.* To prove this we keep L and S constant, as demanded by our rule and sum up over all J's from $J_{min} = |S - L|$ to $J_{max} = S + L$ and divide by $J_{max} - J_{min} + 1$, that is, by the number of terms between J_{min} and J_{max}. In this way we obtain from (7)

$$\bar{g} = \tfrac{3}{2} + \tfrac{1}{2}\frac{(S-L)(S+L+1)}{J_{max} - J + 1_{min}} \sum_{J_{min}}^{J_{max}} \frac{1}{J(J+1)} \quad . \quad . \quad (8)$$

This summation may be effected quite generally. It is analogous to the integral

$$\int_a^b \frac{dx}{x^2} = -\frac{1}{x}\Big|_b^a = \frac{1}{a} - \frac{1}{b},$$

where we replace the infinitely small difference by the finite difference 1. For we have

$$\sum \frac{1}{J(J+1)} = \sum \frac{1}{J} - \sum \frac{1}{J+1} = \frac{1}{J_{min}} - \frac{1}{J_{max}+1}, \quad . \quad (9)$$

since in the middle term of this equation all the other members of the two partial sums cancel out in pairs and only the lower limit of the first and the upper limit of the second partial sum remain. In contrast to this $1/J^2$ would be no "perfect difference" and hence could not in general be "summed up." This shows that the replacement of J^2 by $J(J+1)$ in wave-mechanics, that is, the transition from f to g on p. 333, corresponds in a certain sense to the transition from the differential calculus to the calculus of finite differences.

If we substitute (9) in (8) the factors in front of the summation sign cancel out and we are left with

$$\bar{g} = \tfrac{3}{2} \mp \tfrac{1}{2}. \quad . \quad . \quad . \quad . \quad (10)$$

The upper sign applies here when $J_{min} = L - S$, that is, when the number of levels is "permanent"; the lower sign when $J_{min} = S - L$, that is, when the number of levels is incomplete. This proves our summation rule; it may be confirmed by the numerical values given in the table.

E. In the case of the odd terms that horizontal row of the table is distinguished for which $L = S$, that is, in which the permanent number of levels is attained for the first time. *As follows directly*

from equation 7, $g = \frac{3}{2}$ *for it.* It is only when the factor J in the denominator vanishes simultaneously with L − S that the fraction in (7) becomes indeterminate. In this case we follow Landé in writing $\frac{0}{0}$ for the value of g (cf. the first vertical column of the table).

Moreover, it would be better in this case to speak, not of the quantity g, which arises in the course of the calculations, but of the moment Mg, which has an immediate physical significance. On account of $J = M = 0$ the latter quantity has the definite value zero. The corresponding term is thus *unable to be resolved magnetically.* According to our table there are also terms in the even systems that are unable to be resolved magnetically, for example, in the ^{4}D-term for $J = \frac{1}{2}$.

We now pass on from the terms to the lines. First we recall the selection rule for the magnetic quantum number, given on p. 335. It simultaneously acts as a polarisation rule. For the transition $1 \rightarrow 2$ we now write in our present notations (M instead of m)

$$M_1 - M_2 = \begin{cases} \pm 1 \ldots \sigma\text{-components} \\ 0 \ldots \pi\text{-components} \end{cases} \quad . \quad . \quad (11)$$

All transitions greater than 1 *are forbidden.* The polarisation data refer to the transverse effect; when observed longitudinally the σ-components, as explained on p. 323, appear circularly polarised, the π-components are absent.

To this general selection rule we must add an *additional decree* for the case where the line arises from the transition $J \rightarrow J$, namely the transition $0 \rightarrow 0$ is forbidden, that is,

$$M_1 = M_2 = 0. \quad . \quad . \quad . \quad . \quad (11a)$$

An immediately obvious example occurs in Fig. 126. Here the middle π-component, which corresponds to the transition from $M_1 = 0$ to $M_2 = 0$, is present in (P_2S) and (P_0S), but is absent in (P_1S). Actually this line denotes a transition $J \rightarrow J$, since both for the P_1- and for the S-term $J = 1$. We shall give the basis in which this additional decree is founded and also the general selection rule for M in Note 7 (under *f*).

To check the resolution pattern of Fig. 126 further we shall proceed as on p. 336 for the D-lines. Using the triplet g-values we write down the following tables from Table 45; they correspond successively to the three term-combinations $^3P_2\,{}^3S_1$, $^3P_1\,{}^3S_1$, $^3P_0\,{}^3S_1$, in the triplet system. We obtain the π-components, bracketed, as the differences of the numbers vertically below each other in the table, the σ-components, which are not bracketed, are the differences between the numbers diagonally neighbouring on the right or the left-hand side. The result is reduced to the common "Runge denominator," which is 2 in the present case.

TABLE 46 ($^3P_2\ ^3S_1$)

	M	−2	−1	0	1	2
L = 1, J = 2	Mg	−3	$-\frac{3}{2}$	0	$\frac{3}{2}$	3
L = 0, J = 1	Mg		−2	0	2	

$$\pm\frac{(0)\ (1)\ 2,\ 3,\ 4}{2}$$

TABLE 47 ($^3P_1\ ^3S_1$)

	M	−1	0	1
L = 1, J = 1	Mg	$-\frac{3}{2}$	0	$\frac{3}{2}$
L = 0, J = 1	Mg	−2	0	2

$$\pm\frac{(1)\ 3,\ 4}{2}$$

TABLE 48 ($^3P_0\ ^3S_1$)

	M	−1	0	1
L = 1, J = 0	Mg		0	
L = 0, J = 1	Mg	−2	0	2

$$\pm\frac{(0)\ 4}{2}$$

Our remark E explains the frequent occurrence of the $\frac{3}{2}$ of the normal resolutions. Let us consider, for example, the combination (PP′) in the triplet system, which we discussed on p. 424, and let us choose, say, the component P_2P_1 in it. The resolution-pattern for P_2P_1 is clearly :

TABLE 49

M =	−2	−1	0	1	2	
$^3P_2$	−3	$-\frac{3}{2}$	0	$\frac{3}{2}$	3	$\frac{(0),\ 3}{2}$
$^3P_1$		$-\frac{1}{2}$	0	$\frac{1}{2}$		

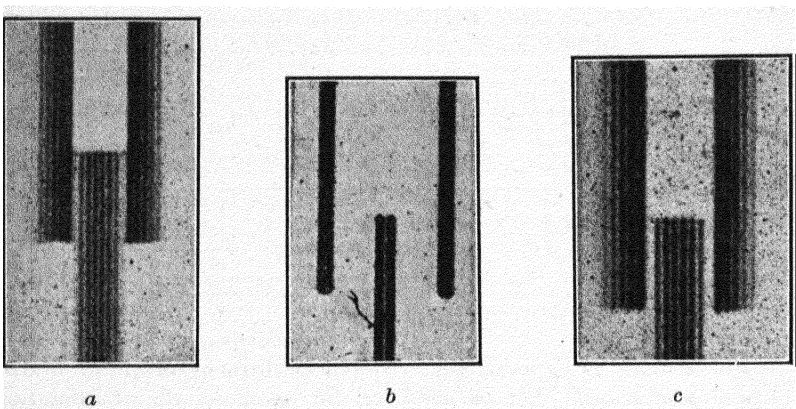
All the other components of (PP′) behave in the same way, and also the combinations (DD′) in the quintet system, (FF′) in the septet system and so forth, together with all their components.

We now consider Fig. 127, which represents the ground-triplet in the octet system of Mn. It is magnified fourteen times from the original photograph (in the second order) by M. Back and has kindly

been placed at the disposal of the author. The π-components are displaced downwards, owing to the optical arrangement, as compared with the σ-components, because the line in question was photographed once in the π-position of the analyser and again in the σ-position and in each case a part of the picture was covered over. Fig. 127 *a* represents the line $\lambda = 4823$ ($^8S_{\frac{7}{2}}$, $^8P_{\frac{9}{2}}$). The resolution factors are 2 and $\frac{1}{9}$. A table similar to that above gives the following scheme for the components :

$$\pm \frac{(1)\ (3)\ (5)\ (7)\ 9,\ 11,\ 13,\ 15,\ 17,\ 19,\ 21,\ 23}{9}.$$

The figure correspondingly shows eight π-components and, on both sides, eight σ-components. At the same time it shows that the



a *b* *c*

FIG. 127.—Anomalous Zeeman effect of the combination $^8S^8P$ (Mn) according to Back. The σ-components are given above, the π-components below. On the left (*a*) is the line $^8S_{\frac{9}{2}}{}^8P_{\frac{9}{2}}$, in the middle (*b*) the line $^8S_{\frac{7}{2}}{}^8P_{\frac{7}{2}}$, on the right (*c*) the line $^8S_{\frac{7}{2}}{}^8P_{\frac{5}{2}}$.

intensity of the π- and the σ-components decreases from the centre outwards : the line of greatest intensity is the σ-component of normal resolution $\frac{9}{9}$; the three outermost σ-components are hardly recognisable owing to their very feeble intensity. Fig. 127*b*, $\lambda = 4783$, is the combination ($^8S_{\frac{7}{2}}$ $^8P_{\frac{7}{2}}$). The splitting factor of the P-term is $\frac{1,2,3}{6,3}$ (cf. Table 45). Hence we obtain the theoretical resolution pattern

$$\pm \frac{(2)\ (6)\ (10)\ (14)\ 112,\ 116,\ 120,\ 124,\ 128,\ 132,\ 136}{63}.$$

In the reproduction the seven σ-components are not separated ; the π-components exhibit the absence of the zero (white centre of the picture) which is characteristic of all even terms. Fig. 127 *c*, $\lambda = 4754$,

is the combination $(^8S_{\frac{7}{2}}\ ^8P_{\frac{5}{2}})$. We have $g = \frac{13}{7}$ for this P-term according to our table. The resolution-pattern is

$$\frac{(1)\ (3)\ (5)\ 9\ 11\ 13\ 15\ 17\ 19}{7}.$$

In accordance with the small Runge denominator the separation of the lines is complete. The gap at the position of normal resolution, between the π- and the σ-components, is very striking. Of the six σ-components which occur on both sides those on the outside are difficult to see on account of their feeble intensity.

As a last example we show a resolution-pattern of particular beauty kindly produced by Mr. P. Zeeman for the purpose of this

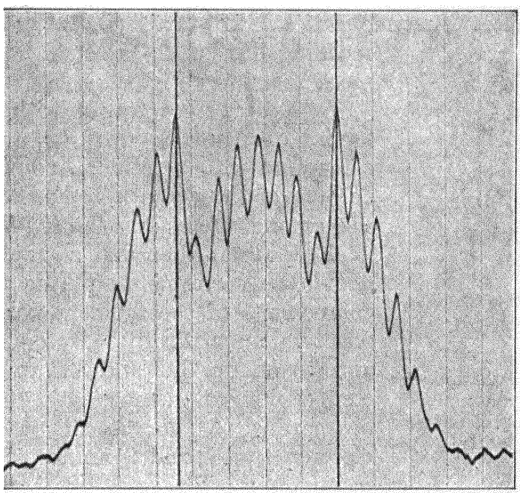


FIG. 128.—Photometer curve of the anomalous Zeeman effect of the combination $^7S_3\,^7P_4$ (Cr) according to Zeeman. In the absence of a field the line would be in the middle. The vertical lines denote the positions of normal separation reckoned from the field-free line.

book. The line in question is the strongest line $\lambda = 4254$ of the ground-triplet ($^7S\,^7P$) of Cr, that is, the combination $(^7S_3\,^7P_4)$. The resolution-pattern consists of the seven π-components,

$$(0, \pm\tfrac{1}{4}, \pm\tfrac{2}{4}, \pm\tfrac{3}{4})\Delta\nu_{norm}$$

and the seven σ-components which occur on both sides,

$$\pm(\tfrac{1}{4}, \tfrac{5}{4}, \tfrac{6}{4}, \tfrac{7}{4}, \tfrac{8}{4}, \tfrac{9}{4}, \tfrac{10}{4})\Delta\nu_{norm}.$$

All these components are beautifully resolved in the photometric curve (Fig. 128), which represents the original photographic record magnified thirty-six times automatically*; only the extreme

* For the technique of working out these photographic densities photometrically see a report by P. Zeeman, Amsterd. Akad., Dec., 1924.

σ-components $\pm \frac{1}{4}$ become lost in the maze of the granules of the plate. The normal resolutions are made recognisable on both sides by vertical strokes. The π-components lie between them and the σ-components are on either side. The strongest π-component which is in the middle is situated in the position of the original line.

Hitherto we have assumed *pure Russell-Saunders coupling*. We shall now consider the extreme counterpart in the form of a *pure (jj)-coupling* (cf. p. 469). This gives us information about the Zeeman effect at the series limit. In general the Zeeman effect changes as soon as the coupling changes appreciably.

In the case of (*jj*)-coupling, Fig. 86 on p. 331 holds for the individual electron, but we must not replace, as was done at the beginning of this section, the l, s of the figure simply by the resultants L, S of the electron configuration. The latter (L, S) lose their physical meaning altogether. Rather, we must supplement Fig. 86 by Fig. 129.

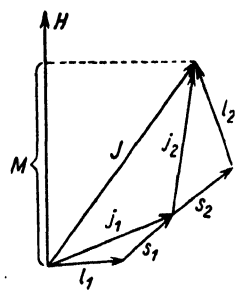


FIG. 129.—Vector model of the anomalous Zeeman effect of two electrons with (*jj*)-coupling.

Suppose we are dealing with two electrons having quantum numbers $l_1 s_1$ and $l_2 s_2$, which compound into j_1 and j_2, respectively. On account of the strong coupling of the l_i's and s_i's among themselves both vector models (*Vektorgerüste*) describe a rapid precession about the corresponding j, so that only the components of the moment parallel to j are effective magnetically. By equations (4), (5) and (9) on pp. 332 and 333 we calculate the components of the magnetic moment which are parallel to j for the first and the second electron ($i = 1$ and 2) in terms of the Bohr magneton :

$$\mathrm{M}_{i\|} = |\, l_i \,| \cos(l_i, j_i) + 2\,|\, s_i \,| \cos(s_i, j_i) = |\, j_i \,|\, g(j_i), \quad . \quad (12)$$

where $g(j_i)$ denotes the Landé splitting factor for the one-electron system (doublet system, $s_i = \frac{1}{2}$) and $|\, l_i \,|$, $|\, s_i \,|$, $|\, j_i \,|$ denote the wave-mechanical magnitudes of the vectors in question ; for example, by p. 333,

$$|\, j_i \,| = \sqrt{j_i(j_i + 1)}.$$

But j_1 and j_2 are also coupled with J. On account of the precession of the vector model ($j_1 j_2$) about J only the component parallel to J comes into question for the magnetic moment of the whole atom. This becomes

$$\mathrm{M} = \Sigma \mathrm{M}_{i\|} \cos(j_i, \mathrm{J}) = |\, \mathrm{J} \,|\, . g, \quad . \quad . \quad . \quad (13)$$

where g is defined by the last term of this equation and denotes *the splitting factor* (not Landé's) *for the (jj)-coupling*.

But we have (cf. Fig. 129)

$$\cos(j_1, J) = \frac{|J|^2 + |j_1|^2 - |j_2|^2}{2|j_1||J|}, \quad \cos(j_2, J) = \frac{|J|^2 + |j_2|^2 - |j_1|^2}{2|j_2||J|} \quad (14)$$

Substituting (12) and (14) in (13) we obtain *

$$g = \frac{M}{|J|} = \sum g(j_i) h(j_i) \quad . \quad . \quad . \quad (15)$$

where we have used the abbreviation

$$h(j_1) = \frac{|J|^2 + |j_1|^2 - |j_2|^2}{2|J|^2} = \frac{J(J+1) + j_1(j_1+1) - j_2(j_2+1)}{2J(J+1)} \quad (15a)$$

and the corresponding expression for $h(j_2)$ obtained by interchanging indices. The following relationship, which is analogous to equation (3) on p. 443, holds between j_1, j_2, and J :

$$j_1 + j_2 \geqq J \geqq |j_1 - j_2| \quad . \quad (16)$$

The extension to systems of more than one electron for pure (jj)-coupling will now be briefly sketched. Whereas the equations (12) and (13) obviously remain standing the definition of the cosines in equation (14) must be modified. For example, in Fig. 130 we consider the case of three electrons and denote the diagonals (dotted in the figure), which supplement the j_i's to form J, by $\bar{j}_i$ (where we find the supplementary vector $\bar{j}_2$ which belongs to j_2 by the auxiliary figure given on the left-hand side of J). Then (14) becomes replaced by

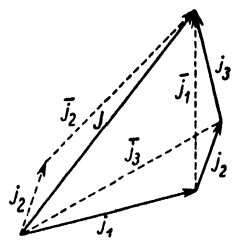


FIG. 130.—(jj)-coupling of three electrons on the assumption of vanishingly small mutual action between the electrons. In these circumstances the vectors $\bar{j}_i$, which, with the j_i form J, remain constant to a first approximation, and the polygon of the j_i precesses as a whole round J.

$$\cos(j_i, J) = \frac{|J|^2 + |j_i|^2 - |\bar{j}_i|^2}{2|j_i||J|}$$

if we suppose the $\bar{j}_i$'s to be given as well as the j_i's. And in place of (15a) we have

$$h(j_i) = \frac{J(J+1) + j_i(j_i+1) - \bar{j}_i(\bar{j}_i+1)}{2J(J+1)} \quad . \quad . \quad (15b)$$

The splitting factor g is then given accurately by equation (15) if the sum is taken over all values of i that come into question.

* First derived by Goudsmit; cf. Goudsmit and Uhlenbeck, Zeits. f. Physik. **35**, 618 (1926).

The reason that, with more than two electrons, we assume the $\overline{j}_i$'s to be given as well as the j_i's and the J is that otherwise the polygon of the j_i's and hence also the position of the energy-levels in question would be undetermined. Our diagonals $\overline{j}_i$ stiffen the polygon, so to speak, so that it precesses as a rigid configuration about the J-axis. This corresponds to a definite kind of coupling between the j_i's and J. With any other kind of coupling the polygon of the j's would not move as a whole, so that other formulæ would result for the splitting factor g.

Pure (jj)-coupling hardly occurs except in the X-ray spectra of atoms of rather high atomic number. In the neon spectrum (cf. p. 471) the coupling is intermediate between the Russell-Saunders and the (jj)-coupling, the higher series term approximating to (jj)-coupling and the lower terms to the normal Russell-Saunders coupling.

What happens in the transition from one kind of coupling to another? The quantum numbers L, S which distinguish the individual multiplets from each other in normal couplings, lose their physical meaning; the quantum numbers j acquire a physical meaning only in the limit when pure (jj)-coupling is reached. The quantum number J alone has a physical meaning throughout as the total moment of momentum of the atom. Together with the L's and S's so also the Landé g-factor loses its validity in the transition stage; simultaneously with the j_i's our g-factor of equation (15) becomes valid only in the limit of this transition. But during the whole transition *the sum of all the g's that belong to the same J retain*, together with J, *their meaning*, no matter whether we calculate J by Landé's formula or by formula (15). This "g-sum rule" thus states that if J is kept fixed the sum of the g's is quite independent of the type of coupling, and for this we may take into consideration, instead of the limiting cases so far considered, any other arbitrary allocations of the individual vectors l_i, s_i. Our g-sum is adiabatically invariant with respect to any changes of coupling whatsoever, exactly as by the law of sectorial areas in mechanics, the total moment of momentum J, to which the g-sum is allocated.

This law may be proved quite generally only by means of wave-mechanics. We shall do no more here than verify it in the case of neon by calculating the g-sums both according to Landé and according to equation (15) and then comparing the results with those of experiment.

We first consider the Paschen s-terms (cf. p. 472). They correspond to the configuration $2p^5 3s$ (simple excitation state of the complete L-shell), for which we shall write, by the Gap Law,

$$2p3s.$$

Thus we calculate with

$$l_1 = 1,\ s_1 = \tfrac{1}{2};\ l_2 = 0,\ s_2 = \tfrac{1}{2}. \quad . \quad . \quad (17)$$

With Russell-Saunders coupling there would follow from this (cf. p. 472 of the previous section) a ^{3}P- and a ^{1}P-term with

$$J = 2, \underbrace{1, 1}, 0. \quad . \quad . \quad . \quad . \quad (18)$$

The 1 occurs twice. The corresponding g-values or g-sums, respectively, are, by the table on p. 478,

$$g(2) = \tfrac{3}{2}, \quad \Sigma g(1) = 1 + \tfrac{3}{2} = \tfrac{5}{2}, \quad g(0) = \tfrac{0}{0}. \quad . \quad . \quad (19)$$

On the other hand, we have, by (17), in the case of (jj)-coupling,

$$j_1 = 1 \pm \tfrac{1}{2} = \begin{cases} \tfrac{3}{2}, \\ \tfrac{1}{2}, \end{cases} \quad j_2 = 0 + \tfrac{1}{2} = \tfrac{1}{2},$$

and from these values, as should be, the same J-values as in (18). We next calculate for the two J = 1 that occur the corresponding h's from (15a):

$$J = 1 \begin{cases} j_1 = \tfrac{3}{2}, \quad j_2 = \tfrac{1}{2}, \quad h(j_1) = \tfrac{5}{4}, \quad h(j_2) = -\tfrac{1}{4} \\ j_1 = \tfrac{1}{2}, \quad j_2 = \tfrac{1}{2}, \quad h(j_1) = \tfrac{1}{2}, \quad h(j_2) = \tfrac{1}{2} \end{cases}$$

and combine them with the $g(j_i)$'s out of Table 45 [doublet system $g(j_1) = \frac{4}{3}$ and $\frac{2}{3}$, $g(j_2) = 2$]. By (15) there results

$$g = \begin{cases} \tfrac{4}{3} \cdot \tfrac{5}{4} - 2 \cdot \tfrac{1}{4} = \tfrac{7}{6} \\ \tfrac{2}{3} \cdot \tfrac{1}{2} + 2 \cdot \tfrac{1}{2} = \tfrac{4}{3}. \end{cases}$$

Hence

$$\Sigma g(1) = \tfrac{7}{6} + \tfrac{4}{3} = \tfrac{5}{2}, \quad . \quad . \quad . \quad (20)$$

that is, the same value as in (19).

TABLE 50

	J	Obs.	R.S.-Coupling	(jj)-Coupling
s_3	0	$^0/_0$	$^0/_0$	$^0/_0$
s_2	1	1·034 | 2·498	1 | $^5/_2$	$^4/_3$ | $^5/_2$
s_4	1	1·464 |	$^3/_2$ |	$^7/_6$ |
s_5	2	1·503	$^3/_2$	$^3/_2$

It is easy to see why the two individual g-values, namely $g(2)$ and $g(0)$, comes out in the (jj)-coupling exactly as in (19). The value $\frac{0}{0}$ for $g(0)$ follows directly from $h(j_1) = h(j_2) = \frac{0}{0}$; the value $\frac{3}{2}$ for $g(2)$ comes out from (15) and (15a) from the data that are given:

$$g(2) = \tfrac{4}{3} \cdot \tfrac{3}{4} + 2 : \tfrac{1}{4} = \tfrac{3}{2}.$$

We compare with these results the experimental results obtained by Back.* In the preceding table we have on the left-hand side the original symbols of Paschen and alongside them the observed

* Ann. d. Phys., **76**, 317 (1925).

and the calculated values. In the case of the g-sum the agreement between theory and experiment is perfect.

We also consider the Paschen p-terms, ten in number, which correspond to the configuration $2p^5 3p$ (cf. p. 472). By the Gap Law it is equivalent to the configuration $2p3p$. Hence we have

$$l_1 = 1, \quad s_1 = \tfrac{1}{2}; \quad l_2 = 1, \quad s_2 = \tfrac{1}{2}$$

and calculate from these values for the two types of coupling:

R.S.-Coupling	(jj)-Coupling
L = 2, 1, 0 S = 1, 0	$j_1 = {}^3/_2, {}^1/_2$ $j_2 = {}^3/_2, {}^1/_2$
J = 3, 2, 1, 2, 1, 0 1 2, 1, 0	J = 3, 2, 1, 0 2, 1 2, 1 1, 0

In the case of Russell-Saunders coupling the first three rows of the J-values correspond to the ^{3}D, ^{3}P, ^{3}S-term, the last to the ^{1}D, ^{1}P, ^{1}S-term. In the (jj)-coupling the four rows of the J-values arise, by equation (16), from the respective combinations:

$$(\tfrac{3}{2}, \tfrac{3}{2}), \quad (\tfrac{3}{2}, \tfrac{1}{2}), \quad (\tfrac{1}{2}, \tfrac{3}{2}), \quad (\tfrac{1}{2}, \tfrac{1}{2}).$$

By Table 45 on p. 478 we obtain in the case of the Russell-Saunders coupling:

$$\Sigma g(2) = \tfrac{7}{6} + \tfrac{3}{2} + 1 = {}^{11}/_3,$$
$$\Sigma g(1) = \tfrac{1}{2} + \tfrac{3}{2} + 2 + 1 = 5.$$

On the other hand, we obtain in the case of the (jj)-coupling from equation (15):

$$\Sigma g(2) = \tfrac{4}{3} + \tfrac{7}{6} + \tfrac{7}{6} = {}^{11}/_3,$$
$$\Sigma g(1) = \tfrac{4}{3} + \tfrac{3}{2} + \tfrac{3}{2} + \tfrac{2}{3} = 5.$$

The following table, which is arranged like the preceding one, shows how the results agree with those of observation:

TABLE 51

	J	Obs	R.S.-Coupling	(jj)-Coupling
p_1	0	0/0	0/0	0/0
p_3	0	0/0	0/0	0/0
p_2	1	1·340	2, 3/2, 1, 1/2	3/2, 3/2, 4/3, 2/3
p_5	1	0·999	5	5
p_7	1	0·699		
p_{10}	1	1·984		
p_4	2	1·301	3/2, 7/6, 1	4/3, 7/6, 7/6
p_6	2	1·229	11/3	11/3
p_8	2	1·137		
p_9	3	1·329	4/3	4/3

The g-sums are seen to be in complete agreement here, too, whereas the individual g's exhibit considerable departures from the values obtained experimentally.

Both the original ordering of the neon series by Paschen and the measurement of the g-values by Back were supreme achievements of spectroscopic accuracy; this receives particular emphasis in the g-sum law.

§ 7. Paschen-Back Effect

In weak fields the Zeeman type of every line of a multiplet can form itself undisturbed by the Zeeman type of neighbouring lines. In increasing fields the resolution patterns would overlap. But before this happens the Zeeman types begin to influence each other mutually. In strong fields (magnetic resolution $\Delta\nu$ great compared with the original frequency differences in the multiplet) every line configuration finally behaves approximately as a single line and *exhibits the normal Zeeman effect*. This is what was proved by Paschen and Back in the case of a number of narrow doublets and triplets, for example, the oxygen triplet $\lambda = 3947$, p. 433. It is already implied in our definition of strong fields that for a single line even the weakest magnetic field must be regarded as "strong." In the case of the D-lines of Na (initial separation 6 Å) it is only when we have a field of 180,000 gauss that the full Paschen-Back effect would show itself. The first stages of the change and the effect exerted by D_1 on D_2 and vice versa manifest themselves even at 30,000 gauss.* In the magneto-optical investigation of the corresponding lithium line $\lambda = 6708$, however, whose components are separated only by 0·13 Å., we arrive very quickly at the conditions for the Paschen-Back effect; the transformation may be followed right up to the final result of the normal triplet.† Compared with the other alkalies lithium formerly appeared to form an exception to Preston's rule. The discovery of the Paschen-Back effect explained this exception as well as many others.

We have already dealt with the Paschen-Back effect of hydrogen in Chapter VI, § 5. The most careful measurements have been carried out by K. Försterling and G. Hansen ‡ by means of a Lummer plate.

Besides the "total" Paschen-Back effect we must also consider the "partial" Paschen-Back effect. By this we mean, for example, the case where in the combination (PD) the magnetic field is strong compared with the small D-difference but weak compared with the larger $\Delta\nu$ of the P-difference. Further details are given at the end of the chapter.

The Paschen-Back effect, of course, only couples together lines

* Cf. E. Back in his dissertation quoted on p. 477.

† Cf. Kent, Astrophys. Journ., **40**, 343 (1914).

‡ Zeits. f. Physik, **18**, 26 (1923). With regard to the theoretical interpretation of their results, cf. A. Sommerfeld and A. Unsöld, *ibid.*, **36**, 259 (1926).

that belong to the same multiplet. Two lines that do not belong together do not disturb one another magneto-optically, no matter how close they are.

We now consider an instructive photograph * of the narrow chromium triplet (SP), $\lambda = 5204, 5206, 5208$ in the quintet system for $H = 38{,}000$ gauss. The π-components of $\lambda = 5208$ (on the right-hand side below) appear undistrubed: five components are at $\frac{1}{3}$ of the normal distance from each other; of the σ-components those of short wave-length (which follow above on the left) are much stronger than those of longer wave-length. The central line $\lambda = 5206$ is disturbed quite unsymmetrically; its short wave-length σ-components are fused with the long-wave components of $\lambda = 5204$. The triplet is still far from having reached the final magnetic state. This would consist (except for finer details, see below) of *one* π-component at the centre of gravity of the triplet lines and of one σ-component on each side at a distance $\Delta\nu_{norm}$. The final state is to be expected only in a field of $H > 150{,}000$ gauss.

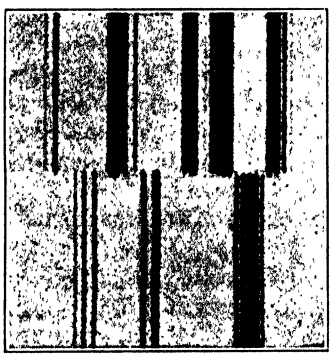


Fig. 131.—Paschen-Back effect of the chromium triplet $^5S^5P$, $\lambda = 5204, 5206, 5208$. The σ-components are shown above, the π-components below. λ increases from left to right. $H = 38{,}000$ gauss.

It is only in the case of doublet-lines that we are able, without the services of wave-mechanics, to trace the transition from weak to strong fields, that is, from the anomalous Zeeman effect of the D-line type to the normal triplet of the Paschen-Back effect quantitatively. We base our remarks on Voigt's theory.†

Like Lorentz in his theory of the normal Zeeman effect Voigt assumes quasi-elastic electrons, which are capable of vibrating, and, in agreement with the intensity ratio $D_1 : D_2$, he assumes one electron having the original frequency of D_1 and two electrons with that of D_2. The motions of all three electrons are imagined coupled together in some peculiar way in virtue of the magnetic field.

Just as Lorentz's theory in Chapter VI, § 4, was re-interpreted in terms of the quantum theory, so also the results of Voigt's theory may be translated into the language of the quantum theory.‡ We shall present it here at once in the latter form, that is, we give the

* H. Gieseler, Zeits. f. Physik, **22**, 228 (1924); the magnified copy of the original here shown was kindly presented to the author by Mr. Back.

† W. Voigt, Ann. d. Phys., **41**, 403 (1913); **42**, 210 (1913). Cf. also the author's simplification of Voigt's theory given in Göttinger Nachr., March, 1914. Voigt deals with the absorption process, the author with the emission process.

‡ A. Sommerfeld, Zeits. f. Physik, **8**, 257 (1922).

magnetic resolutions $\Delta\nu$ not for the term-combinations but for the terms themselves and shall generalise then for arbitrary terms having the azimuthal quantum L.

In the doublet system two terms belong to the azimuthal quantum L, which are distinguished by the two values $J = L \pm \frac{1}{2}$; each of these terms splits up in the magnetic field, as we know, into $2J + 1$ magnetic levels, which for their part are again distinguished by the magnetic quantum number M. We express the magnetic resolution $\Delta\nu$ of the individual level in fractions of the normal resolution $\Delta\nu_{norm}$ and measure it from the middle (not from the centre of gravity) of the original doublet distance $\Delta\nu_0$ which obtains when no field is acting. $\Delta\nu$ then depends not only on the magnetic field H but also on the three quantum numbers L, J and M. In contrast to L and M, however, J will not occur explicitly in our formula but will be described by the occurrence of the double sign in the square root of the following equation (2), the upper sign corresponding to the value $J = L + \frac{1}{2}$, the lower to the value $J = L - \frac{1}{2}$. Nor will the field-strength H enter explicitly into our formula, but will be expressed by the ratio

$$v = \frac{\Delta\nu_0}{\Delta\nu_{norm}}. \qquad . \quad . \quad . \quad . \quad (1)$$

Since $\Delta\nu_{norm}$ is proportional to H, v gives an inverse measure of the magnetic field-strength. Great values of v then denote "weak" fields, small values "strong" fields.

Our formula, which comprehends Voigt's theory in an extended form, then runs *

$$\Delta\nu = \left\{M \pm \tfrac{1}{2}\sqrt{1 + \frac{2Mv}{L + \frac{1}{2}} + v^2}\right\}\Delta\nu_{norm}. \quad . \quad . \quad (2)$$

If we do not wish to use wave-mechanical arguments we must use experimental data as a basis for this formula; cf., for example, Kent, *loc. cit.* p. 530. We verify it here by showing that for *weak fields* we again arrive at the results of § 6.

So we assume $v \gg 1$ and expand the square root in (2):

$$\sqrt{1 + \frac{2Mv}{L + \frac{1}{2}} + v^2} = v\left(1 + \frac{M}{L + \frac{1}{2}}\frac{1}{v} + \ldots\right) = v + \frac{M}{L + \frac{1}{2}}.$$

Instead of (2) we may write, in view of (1),

$$\Delta\nu \mp \tfrac{1}{2}\Delta\nu_0 = M\left(1 \pm \frac{1}{2L + 1}\right)\Delta\nu_{norm}. \quad . \quad . \quad (3)$$

* The signs $\pm$ refer to the case of weak fields ($v \gg 1$). If as the field increases (v decreases) the square root passes through zero, the sign naturally reverses. As C. Runge has pointed out, this must be borne in mind in the case $-M = L + \frac{1}{2}$ (lowest magnetic level of the term $J = L + \frac{1}{2}$; no such level occurs in the case of the term $J = L - \frac{1}{2}$). We then have

$$+\sqrt{1 + \frac{2Mv}{L + \frac{1}{2}} + v^2} = \sqrt{(v - 1)^2} = v - 1,$$

which is positive for $v > 1$ and negative for $v < 1$.

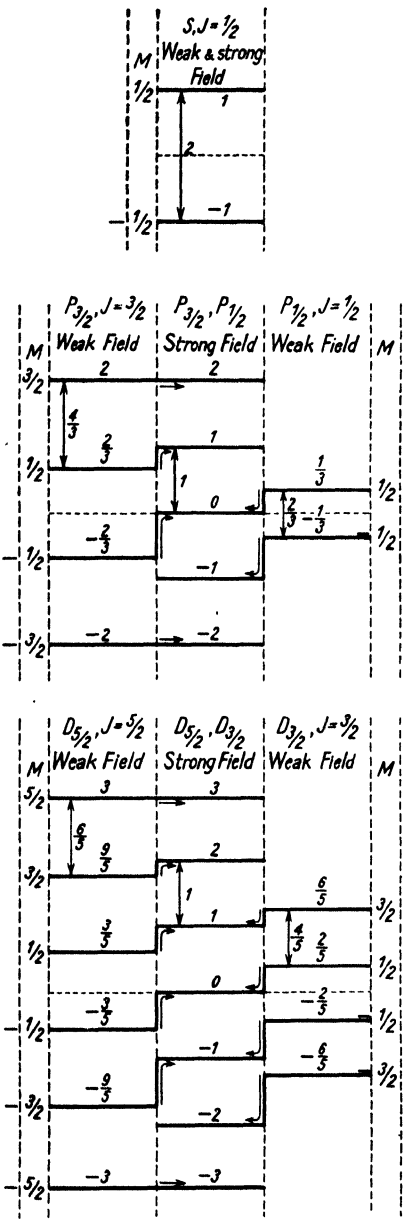


FIG. 132.—Relation between the energy-levels of doublet terms in weak and strong fields. The separations are expressed in terms of $\Delta\nu_{norm}$ as unity.

Since $\Delta\nu$ was to be counted from the middle of the doublet distance $\Delta\nu_0$ the left-hand side denotes, according to its sign, the magnetic resolution of the upper or the lower doublet term $J = L \pm \frac{1}{2}$. Thus the brackets on the right-hand side of (3) are to represent the splitting factor g for our two doublet terms. It agrees, in fact, with our Table 45 on p. 478 or with our special calculation in the equations of p. 334 (small letters instead of capitals).

If we now consider the converse case of passing to the limit of *strong fields*, $v = 0$, then equation (2) gives

$$\Delta\nu = \{M \pm \tfrac{1}{2}\}\Delta\nu_{norm} \qquad (4)$$

(For a more accurate approximation, cf. equation (6) below.)

Since M is a half-integral number $M \pm \frac{1}{2}$ *is an integer. Hence in the case of strong fields the magnetic resolution pattern becomes normal.* The magnetic levels follow each other according to (4) at intervals of $\Delta\nu_{norm}$.

Fig. 132 illustrates how the anomalous energy-levels of the weak fields are assigned to the normal levels of the strong fields. The two outer columns correspond to weak fields, the middle column to strong fields. It must be noted that in weak fields the resolutions $\Delta\nu$ which are written down in the figure are counted in each case from the original position of the energy-levels, when no field is present, but in strong fields from the middle (see below) or from their centre of gravity. The arrows in the figure indicate in

what direction the anomalous levels must be displaced in order to be normal eventually. A glance at the figure shows that the Paschen-Back effect is nothing else than a rearrangement, mostly very trivial, of the energy-levels. Those levels which were originally normal remain normal; these are the two levels of the S-term and the outermost levels of the terms $P_{\frac{3}{2}}$ and $D_{\frac{5}{2}}$. Both terms contribute to individual members of the normalised levels.

Having now studied the final magnetic position of the term-levels we may now specify how the individual line-components of the Zeeman pattern becomes displaced as the field increases. We depict this for the combination (SP), the D-line type, in Fig. 133. The original doublet has been strongly marked on the upper edge of the figure. Below this the anomalous type of Zeeman resolutions is indicated, the quartet and sextet from Figs. 87 and 88; the type of polarisation

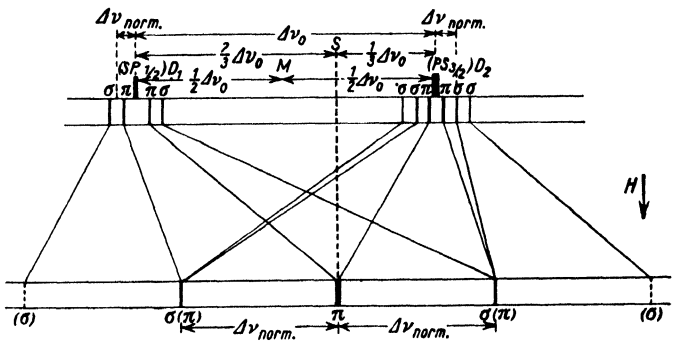


FIG. 133.—Zeeman effect of the combination (SP) of a doublet system (D-line type) in a weak field (above) and a strong field (below). The connecting lines between the two diagrams indicate how the components are displaced with increasing field.

is also indicated by π and σ. In the lower edge of the figure we see the scheme of the normal triplet $\Delta\nu_{norm}$ drawn on an arbitrarily magnified scale. The figure shows the strange and unsymmetrical way in which the original Zeeman components (ten in number in all) which are present in weak fields melt together into the final Paschen-Back components in strong fields. The figure also shows that on both sides one of the original components strives towards the position of twice the normal resolution, its intensity, however, decreasing asymptotically to zero. We indicate the latter result in the figure by writing (σ); in the same way (π) denotes that certain lines also contribute to the σ-components in question, which are polarised in a parallel direction, but whose intensity decreases asymptotically to zero in proportion as they approach their final position in the Paschen-Back effect. Voigt's theory enables us to calculate here and in general for doublet systems the intensities of the components

in complete agreement with the formulæ which the wave-mechanical calculation gives for this case (cf. the papers quoted on p. 499). But we may also find a reason for the vanishing of the bracketed components in the limiting case of a very strong field by using the correspondence argument given in Chapter VI, § 5, pp. 338 and 339. There we deduced generally the resolution-pattern of the normal Lorentz triplet for doublet combinations in strong fields from the selection and polarisation rules: a π-component and two pure σ-components at the normal distance from it, that is, no admixture of π-polarisation.

The arguments there developed may clearly be applied generally to arbitrary multiplicities. If we replace the l by L there and the s by S we may formulate *the selection and polarisation rules of the Paschen-Back effect* (cf. Note 7 (f)) as follows: only those components occur for which $\Delta M_S = 0$ and $\Delta M_L = 0, \pm 1$; $\Delta M_L = 0$ gives π-components, $\Delta M_L = \pm 1$ σ-components. The resolution-pattern of any arbitrary combination therefore assumes as before (equation (14) and (15), p. 338) the form

$$\Delta\nu_1 - \Delta\nu_2 = 2M_{S_1} - 2M_{S_2} + M_{L_1} - M_{L_2} = 0, \pm 1$$

(where the term-resolution $\Delta\nu$ is expressed in units of $\Delta\nu_{norm}$). In other words: *any arbitrary combination of any multiplicity whatsoever gives a normal Lorentz triplet in a strong field.* We repeat once again that in general

$$\Delta\nu = M_L + 2M_S \quad . \quad . \quad . \quad . \quad (5)$$

holds for the resolution of the terms in the strong field.

We revert to the doublet system and to Fig. 133. We have yet to explain why, in Fig. 133, we have allowed the π-component of the Paschen-Back effect to coincide with the centre of gravity S and not with the middle M of the two D-lines. The latter would be indicated by equation (4) since here $\Delta\nu$ is counted from the middle. We easily see, however, that this equation must be replaced by

$$\Delta\nu = \left\{M \pm \tfrac{1}{2}\left(1 + \frac{Mv}{L + \frac{1}{2}}\right)\right\}\Delta\nu_{norm} \quad . \quad . \quad (6)$$

if we make the proper approximation for the square root in (2) for the limit $v = 0$. From the significance of v in (1) we obtain for this

$$\Delta\nu + \frac{M}{2L + 1}\Delta\nu_0 = (M \pm \tfrac{1}{2})\Delta\nu_{norm}. \quad . \quad . \quad (7)$$

We apply this formula to the D-lines, that is, to the combination SP. If we imagine equation (7) written down for the P-term then the upper sign holds for the quantum numbers $M = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}$ of the $^2P_{\frac{3}{2}}$-term, according to the remarks on p. 491 and the footnote on the same page; the lower sign holds for $M = \frac{1}{2}, -\frac{1}{2}$ of $^2P_{\frac{1}{2}}$ and for

$M = -\frac{3}{2}$ of $^2P_{\frac{3}{2}}$. In the case of the S-term $\Delta\nu_0 = 0$, and the upper sign in (7) applies for $M = \frac{1}{2}$, the lower for $M = -\frac{1}{2}$.

We shall determine the position of the middle π-component of Fig. 133 (below); to do this we must form the difference of equation (7) for the P- and the S-term; M must have the same value in both cases and must be so chosen that the difference of the factors of $\Delta\nu_{norm}$ becomes equal to zero. We then deduce from the allocation of the signs given above or, more simply, from Fig. 132, that then we must have $M = \frac{1}{2}$ for the upper sign and $M = -\frac{1}{2}$ for the lower sign. The difference of the equations for the P- and the S-term then gives

$$\Delta\nu_P - \Delta\nu_S = +\frac{\Delta\nu_0}{6}, \quad . \quad . \quad . \quad (8a)$$

where $\Delta\nu_0$ denotes the natural interval of resolution of the P-term. Since we count $\Delta\nu$ from the middle of the term the above equation states that the π-component is displaced by the amount $\Delta\nu_0/6$ from the centre of the original doublet-line as compared with the D_2-line, that is, that it actually coincides with the centre of gravity S of the natural resolution, as indicated in Fig. 133. Both possible modes (namely, $M = +\frac{1}{2}$ and $M = -\frac{1}{2}$) give exactly the *same* line in *this* case.

Equation (7) also leads to an interesting refinement in the case of the σ-components. We are concerned only with those σ-components which lie at the normal distance (as far as quantities of the order $\Delta\nu_0$) from the π-component just considered, because the other σ-components vanish in a strong field according to the discussion on the preceding page. In forming the difference of two equations of the form (7) for a P- and an S-term only ± 1 may therefore remain as a factor of $\Delta\nu_{norm}$; here we may combine together the highest levels in the middle and highest drawings of Fig. 132. Hence we have $M = \frac{3}{2} \rightarrow M = \frac{1}{2}$, and the upper sign of (7) holds in both cases. This gives

$$\Delta\nu_P - \Delta\nu_S = \tfrac{3}{2} \cdot \tfrac{1}{3}\Delta\nu_0 + \Delta\nu_{norm}. \quad . \quad . \quad . \quad (8b)$$

Or we may combine the level 0 of the P-term with the level -1 of the S-term; this corresponds with the transition $M = \frac{1}{2} \rightarrow M = -\frac{1}{2}$. In both these cases the lower sign of (7) then applies. In this way we obtain

$$\Delta\nu_P - \Delta\nu_S = -\tfrac{1}{2} \cdot \tfrac{1}{3}\Delta\nu_0 + \Delta\nu_{norm}. \quad . \quad . \quad (8c)$$

Thus we find not one but *two* σ-components, which are separated by a distance

$$\Delta\nu_0(\tfrac{1}{2} + \tfrac{1}{6}) = \tfrac{2}{3}\Delta\nu_0 \quad . \quad . \quad . \quad . \quad (9)$$

and have at their centre the point of exact normal resolution, measured from the central π-component. These two components are close neighbours only in that we assumed that for strong fields $\Delta\nu_{norm} \gg \Delta\nu_0$, so that in Fig. 133 they may be replaced by a single line. The

σ-component on the other side (factor of $\Delta\nu_{norm} = -1$) lie symmetrically to the σ-components just considered with respect to the central π-component. In this way we have completely justified Fig. 89 on p. 340.

Analogous considerations also apply to other multiplicities. Whereas we have hitherto described the final result for infinitely strong fields as a normal triplet with *simple* lines, we must be prepared to find the Paschen-Back components *double* or even *multiple* at distances of the same order of magnitude as the original resolutions when no field is present (cf. also Note 12, 2). Observations in the case of lithium has completely confirmed this consequence of the theory which seems so strange at first sight.

We now know the resolution of the terms in a weak (§ 6) and in a strong field for arbitrary multiplicities. But we can make predictions about the transition from weak to strong fields only in the case of doublet terms. Wave-mechanics also gives the solution for the general problem (cf. the references on p. 499); we restrict ourselves here to stating a rule which was first enunciated by W. Pauli * *before* the advent of wave-mechanics and which was confirmed by him (see p. 502); according to this rule the magnetic levels are to be allocated in the case of weak fields to the normalised levels in the case of strong fields.† If the former are characterised by the quantum numbers M and J, then according to Pauli the latter are given by

$$\frac{\Delta\nu}{\Delta\nu_{norm}} = \begin{cases} M + J - L \;\ldots\; M \geqq S - L \\ 2M + J - S \;\ldots\; M \leqq S - L \end{cases} . \qquad (10)$$

Concerning (10) we add the following remarks :—

1. For $M = S - L$ the right-hand sides of the two formulæ (10) become identical, namely, equal to $J + S - 2L$.

2. Both formulæ give *integral* values, that is, *normal* term-resolutions not only for odd but also for even multiplets (M, J and S half-integral), as should be.

3. For doublet systems $S = \frac{1}{2}$, $J - L = \pm\frac{1}{2}$ according as we are dealing with a greater or a smaller J. Thus the first row of (10) gives $\Delta\nu = \{M \pm \frac{1}{2}\}\,\Delta\nu_{norm}$, in agreement with (4); the second row comes into force owing to the condition $M \leqq S - L$ only for the lowest level $M = -J$ of the term $J = L + \frac{1}{2}$ and here gives $\Delta\nu = -(L + 1)\,\Delta\nu_{norm}$, in agreement with Fig. 132. We may therefore regard (10) as a generalisation of what we ascertained for doublet systems.

4. For " inverted terms " the signs of $\Delta\nu$ and M must be reversed in the equations and inequalities (10).

We write down the content of formula (10), for example, for the triplet terms ($S = 1$) in the following scheme :

* Zeits. f. Physik, **16**, 155 (1923).

† We shall again disregard in the sequel the *fine* resolution of the normalised levels, which we have discussed just above.

TABLE 52

	M =	−4	−3	−2	−1	0	1	2	3	4
S	. .				−2	0	2			
P_2	. .			−3	−1	1	2	3		
P_1	. .				−2	0	1			
P_0	. .					−1				
D_3	. .		−4	−2	0	1	2	3	4	
D_2	. .			−3	−1	0	1	2		
D_1	. .				−2	−1	0			
F_4	. .	−5	−3	−1	0	1	2	3	4	5
F_3	. .		−4	−2	−1	0	1	2	3	
F_2	. .			−3	−2	−1	0	1		

The symmetry of the scheme strikes us immediately: in every term-group (for example, $D_1D_2D_3$) the individual normalised level occurs equally often with a positive and a negative sign but in general arises from different terms (for example, + 2 from D_3, D_2, and − 2 from D_3, D_1). For the individual term, that is, in one and the same horizontal row, the numbers of the scheme first decrease by one unit each as we come from the right-hand side until we reach the place where M = S − L, after which they decrease by two units. Thus whereas the individual term resolves unsymmetrically in this way, the terms of a group that belong together supplement each other so as to form a completely symmetrical resolution-pattern. The schemes of the higher multiplet systems have the same character.

A remarkable feature is that the normalised levels do not in general bear the magnetic quantum number that corresponds to their resolution. For example, the normal level + 2 of the D-term arises not only from the level M = 2 but also from M = 1 and hence bears *both* these quantum numbers. Actually we may suppose the transition from weak to strong fields to be made adiabatically, so that in principle the quantum numbers remain conserved. The same may be read off from the doublet Figure 132, for example, the three middle levels of the resolution of the D-term. *The levels of the multiple terms normalised by the Paschen-Back effect are thus in general multi-valued as regards their multiple terms and are displaced as compared with originally normal levels such as would be associated with simple terms.*

We recognise a confirmation of this peculiar displacement in the "partial Paschen-Back effect" (cf. p. 489), which has been observed by Back,* for example, in the I N.S. of Mg. The D-differences are so small in the case of Mg that every appreciable magnetic field measured in comparison with them must be regarded as "strong." Accordingly we write the formula of the Mg-lines in question, λ = 3838, 3832, 3830, in the form $\nu = 2P_J - 3D$. In the following table we see

* Naturwiss., **12**, 200 (1921), and Zeits. f. Physik, **33**, 579 (1925).

under the M-values of the upper row the resolutions of the terms P_J in a weak field, in the three following rows those of the three D-terms in strong fields, the latter being taken from the preceding scheme and the former from Table 45 on p. 478. The brackets over the table indicate that the P_2-term consists of five, the P_1-term of three levels, the term P_0 of only the one zero-level. The magnetic levels of the D-terms are all integral (normal), but in general they are displaced as compared with the scale of the M's (the levels of an original simple term). We exhibit the effect of this in the resolution-patterns of the individual combinations (P_JD).

Let us first consider (P_0D). The

$$\pi\text{-components}: \ 0, \pm 1$$

arise from the zero-level of P_0 taken together with the D-levels, 1, 0, -1 which stand vertically under them. If, however, we go from the same zero-level to the D-level which lies to the right or to the left of the middle, we get the

$$\sigma\text{-components}: \ 0, \pm 2, \pm 2.$$

This is precisely the resolution-pattern that was observed by Back.

TABLE 53

		P_4						
			P_1					
				P_0				
	M =	-3	-2	-1	0	$+1$	$+2$	$+3$
D	P_J		-3	$-\frac{3}{2}$	0	$+\frac{1}{2}$	$+3$	
	D_3	-4	-2	0	$+1$	$+2$	$+3$	$+4$
	D_2		-3	-1	0	$+1$	$+2$	
	D_1			-2	-1	0		

Accordingly in the combination (P_1D) we obtain from the three middle rows of the scheme

$$\pi\text{-components}: \ (0), \pm \tfrac{1}{2}, \pm 1, (\pm \tfrac{3}{2}),$$

and by connecting together the neighbouring rows on the left and on the right we obtain the

$$\sigma\text{-components}: \ 0, \ \pm \tfrac{1}{2}, \ (\pm 1), \ \pm \tfrac{3}{2}, \ \pm 2, \ (\pm \tfrac{5}{2}).$$

This type, too, agrees as regards the drawing closer together of the π- and σ-components with the observations of Back; only the bracketed components are absent in the observations.

Lastly, the combination (P_2D) gives the

$$\pi\text{-components}: \quad 0, \ \pm\tfrac{1}{2}, \ \pm 1, \ (\pm\tfrac{3}{2})$$

and the

$$\sigma\text{-components}: \quad 0, \ \pm\tfrac{1}{2}, \ \pm 1, \ \pm\tfrac{3}{2}, \ \pm 2, \ (\pm\tfrac{5}{2}), \ (\pm 3).$$

This also agrees with observation except for the bracketed components.

The combination (P_0D) is particularly instructive. Although we here connect the normal zero-level of P_0 with the normalised levels of the D-term, it is not the normal triplet $0(\pi), \pm 1(\sigma)$ that arises, but the quintet $0(\pi, \sigma), \pm 1(\pi, \sigma) \pm 2(\sigma)$. This is merely a result of the displacement of the normalised levels as compared with their natural position. Concerning the omitted components (bracketed here) in the combinations (P_1D) and (P_2D) Lucy Mensing * proves by quantum-mechanics that they should actually have zero intensity. This was confirmed by van Geel † by quantitative measurements of the intensity.

The circumstances are quite similar in the partial Paschen-Back effect of doublet systems, for example,‡ Na : $\nu = 2P_J - 4D$, $\lambda = 5688$ and 5683.

We may also draw another conclusion of a very general character from Table 52.

We first note that in those vertical columns of the table, which are filled up (for example, the sequence $M = 0$ for the P-terms, the sequence $M = -1, 0, 1$ for the D-terms, and so forth), the sum of the resolutions shown in the table becomes exactly equal to AM, where A (here = 3) denotes the number of levels in question. On the other hand, the same sum for weak fields is $AM\bar{g}$, where we take $\bar{g}$, as on p. 479, to stand for the mean value of all g-values for a given L and variable J. But we showed there that $\bar{g} = 1$ in the case of a permanent term-number. *Thus the two sums for strong and weak fields agree.* We may easily convince ourselves that the same holds for not completely filled columns.

This leads us to a general law which is valid not only for strong and weak fields but also for medium fields, not only for triplet systems but also for any arbitrary multiplet system ; this is the " Permanence Law of g-Sums " formulated by Pauli (*loc. cit.* p. 496). It states that : *the sums of the resolutions measured in terms of* $\Delta\nu_{norm}$ *and taken over all J's while M and L are kept constant, is constant, that is, independent of the field.*

* Zeits. f. Physik, **39**, 24 (1926). Cf. also the general investigation by C. G. Darwin, Proc. Roy. Soc., London (A) **115**, 1 (1927) ; K. Darwin, *ibid.*, **118**, 264 (1928).

† Zeits. f. Physik, **39**, 877 (1926).

‡ E. Back, Ann. d. Phys., **70**, 370 (1923). Cf. also S. Frisch, Journ. d. russ. phys. chem. Ges., **56**, 525 (1924), as well as the theoretical paper by L. Mensing, *loc. cit.*

To produce the proof (which is not contained in Pauli's paper) for the two limiting cases of weak and strong fields (the proof is only possible with the help of wave-mechanics in the case of medium fields) we form for the weak field :

$$M\Sigma g\,(J) \quad \ldots \text{ summation over J} \qquad . \qquad . \qquad (11)$$

and for the strong field :

$$\Sigma(2M_S + M_L) \quad \ldots \quad \begin{cases} \text{summation over } M_L \text{ or } M_S \text{ while} \\ M = M_L + M_S \text{ is kept fixed.} \end{cases} \qquad (12)$$

To explain this process we make the following preliminary remarks : in weak fields L and S are coupled to J, and M is the projection of the J-vector in the direction of the magnetic field. As the magnetic field increases J loses its physical meaning, the coupling between L and S becomes released, and L and S adjust themselves individually in the magnetic field, and have the projections M_L and M_S in the direction of the field. Expressed in terms of mechanics this means : the law of sectorial areas on which the existence of the quantum number J depends when the field is vanishingly small loses its general validity as the field increases. It then holds only for the direction of the magnetic field and establishes the permanent physical meaning of the quantum number M, that is, of the moment of momentum in the direction of the field ; this is invariant if the field is imposed adiabatically. Hence we have

$$M \text{ (weak field)} = M_L + M_S \text{ (strong field)}$$

for the whole stage of the transition. Our present procedure therefore corresponds entirely with that described in the previous section on p. 486, where we summed over those quantities that lose their physical meaning in the transition, while we keep those quantities fixed which retain their meaning (J previously, now M). We must yet remark that we must not increase the field so far that L and S lose their significance, as this would correspond with a blurring of the multiplets among themselves ; this would, however, occur only with fields that are generally beyond the realm of practical realisation.

We begin by evaluating (12), and, in agreement with the inequalities

$$L \geqq M_L \geqq -L, \quad S \geqq M_S \geqq -S,$$

we build up the numbers M_L and M_S in Figs. 134*a* and 134*b* as a rectangular lattice. (It is immaterial whether S is integral or half-integral ; in the latter case the axis $M_S = 0$ would not be occupied by lattice-points as in the figure but would run mid-way between two straight lines occupied by lattice-points.) The straight line $M = M_L + M_S$ is inclined at an angle of 45° to the axis of the lattice. We distinguish two sets of three cases, corresponding to the two figures 134*a* and 134*b*.

(*a*) $M \geqq L - S$,	$M \geqq S - L$,
(*b*) $L - S \geqq M \geqq S - L$,	$S - L \geqq M \geqq L - S$,
(*c*) $S - L \geqq M$,	$L - S \geqq M$.

The region for the case (*b*) is shaded in both figures.

Instead of (12) we write, on account of $M = M_S + M_L$,

$$M\Sigma 1 + \Sigma M_S. \quad . \quad . \quad . \quad (13)$$

$\Sigma 1$ denotes the number of lattice-points that are cut out of our rectangle by the straight line M. In our three cases it is (cf. the summation-limits of M_S written down in Figs 134 *a* and *b*):

(*a*) $S + L - M + 1$,
(*b*) $2S + 1$ and $2L + 1$, respectively,
(*c*) $S + L + M + 1$.

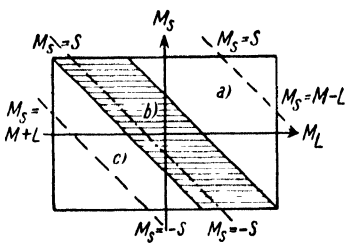


FIG. 134*a*.—L > S.

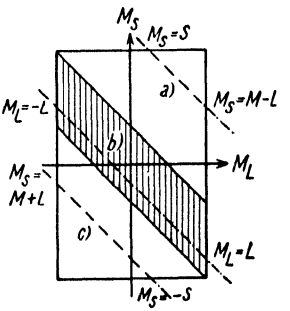


FIG. 134*b*.—S > L.

Evaluation of the M_S values which can belong to a given $M = M_L + M_S$ for fixed values of L and S. For each of the cases *a*, *b*, *c* (see text) a chain line for M = constant has been drawn. The region *b* is shaded.

Similarly, we obtain by forming ΣM_S by summing up an arithmetic series between the same limits as for $\Sigma 1$:

$$(a) \quad (S + L - M + 1)\frac{S + M - L}{2},$$

$$(b) \quad 0 \quad \text{and} \quad 0,$$

$$(c) \quad (S + L + M + 1)\frac{L + M - S}{2}.$$

By (13) the sum of the magnetic resolutions is therefore

$$\left.\begin{array}{ll} (a) & (S + L - M + 1)\dfrac{S + 3M - L}{2} \\ (b) & 2S + 1 \quad \text{and} \quad 2L + 1 \\ (c) & (S + L + M + 1)\dfrac{L + 3M - S}{2} \end{array}\right\} \quad . \quad . \quad (14)$$

We now proceed to weak fields, that is, to equation (11). Concerning the limits of J we now distinguish two cases:

$$(a),\ (c)\ \ |M| \geqq |L-S|,\quad J_{max} = L+S,\quad J_{min} = |M|,$$
$$(b)\ \ |M| \leqq |L-S|,\quad J_{max} = L+S,\quad J_{min} = |L-S|.$$

The values of J_{max} and J_{min} here given follow from the two inequalities:

$$|L-S| \leqq J \leqq L+S,\ |M| \leqq J,$$

and bound the J-region common to the two inequalities. Hence the number of J-values is

$$\text{Case } (a),\ (c):\ L+S-|M|+1.$$
$$\text{,,}\quad (b):\ L+S-|L-S|+1.$$

For $\sum g$ we use in equation (11) an expression analogous to (8) in p. 479, namely:

$$(a),\ (c):\ \tfrac{3}{2}(L+S-|M|+1)+\tfrac{1}{2}(S-L)(S+L+1)\sum_{|M|}^{L+S}\frac{1}{J(J+1)},$$

$$(b):\ \tfrac{3}{2}(L+S-|L-S|+1)+\tfrac{1}{2}(S-L)(S+L+1)\sum_{|L-S|}^{L+S}\frac{1}{J(J+1)}.$$

The summation over J is performed as in equation (9) on p. 479, and, after simple reductions and the addition of the factor M from (11), gives

$$\left.\begin{aligned}(a),\ (c):\ &\frac{M}{|M|}(L+S-|M|+1)\frac{3|M|+S-L}{2}\\ (b):\ &(L+S-|L-S|+1)\frac{3|L-S|+S-L}{2|S-L|}\end{aligned}\right\}. \qquad (15)$$

The first expression resolves, according as $M > 0$ or $M < 0$, into the two values (a) and (c) of equation (14); in the same way the second expression resolves, according as $L > S$ or $L < S$, into the two values (b) of equation (14). This proves the permanence of the magnetic resolutions for weak and strong fields.

With the help of Figs. 134 *a* and *b* the allocation of terms in strong and weak fields given by Pauli in p. 496 may be reduced to the wave-mechanical formulation of this allocation. Wave-mechanics asserts that terms which belong to the same M-value do not intersect when we pass from weak to strong fields. We can now show that we may derive Pauli's allocation from the postulate of non-intersection. Let us consider the case of a regular term. In the field-free term the levels then lie above each other in the order of increasing J's, so that the smallest J-value lies lowest. Consequently, in *weak* fields the levels having a fixed M are similarly arranged: the level that belongs to the smallest J-value that is possible for a given M, lies lowest. In

a *strong* field the resolutions are given by $\Delta\nu/\Delta\nu_{norm} = 2M_S + M_L$ for a fixed M. Now, $2M_S + M_L = M + M_S$, hence the terms here lie above each other in the order of increasing M_S. If no intersections are to occur we must assign the lowest level in the weak field to the lowest in the strong field and so on in the sequence of levels. We assume the allocation to be linear and therefore write

$$M + M_S = \alpha M + \beta L + \gamma S + \delta J, \quad . \quad . \quad (16)$$

where the resolution in the strong field stands on the left-hand side and all those quantum numbers are introduced on the right-hand side, on which the resolution in a weak field depends. We now consider the different cases that we already know from Figs. 134 *a*, *b*:

1. $L > S$. (*a*) $M \geqq L - S$; (by Fig. 134*a*) $M + M_S$ here goes from $2M - L$ to $M + S$ and J from M to $J_{max} = L + S$, M remaining fixed.

If we substitute these associated limiting values of M_S and J in (16) we obtain $\alpha = \delta = 1$, $\beta = -1$, $\gamma = 0$. Equation (16) then runs like Pauli's equation (10):

$$\Delta\nu/\Delta\nu_{norm} = M + J - L.$$

(*b*) $L - S \geqq M \geqq S - L$; $M + M_S$ goes from $M - S$ to $M + S$, J from $L - S$ to $L + S$. The determination of α, β, γ, δ gives the same as under (*a*).

(*c*) $S - L \geqq M$; $M + M_S$ goes from $M - S$ to $2M + L$, J from $|M| = -M$ to $L + S$. The corresponding calculation of the factors α, β, γ, δ now gives: $\Delta\nu/\Delta\nu_{norm} = 2M + J - S$.

2. $L < S$. (*a*) $M \geqq S - L$ gives the same as 1*a*,
(*b*) $S - L \geqq M \geqq L - S$, and
(*c*) $L - S \geqq M$ give the same as 1*c*.

Hence, recapitulating we have

if $M \geqq S - L$, we obtain $\Delta\nu/\Delta\nu_{norm} = M + J - L$,
and if $M \leqq S - L$, we obtain $\Delta\nu/\Delta\nu_{norm} = 2M + J - S$,

that is precisely Pauli's allocation.

We may apply an analogous argument to inverted terms and likewise obtain the allocation already given on p. 496.

We must next mention an attractive application of the Permanence Law made by Pauli, namely: *to calculate the g-values in weak fields from the resolution-sums in strong fields.* This will be illustrated for the case of the triplet D-terms, in which case we may derive the resolution-sums directly and simply from Table 52 instead of from eqns. (14) and (15).

Denoting the g's that belong to the terms D_J by g_J and hence the

resolutions by Mg_J, we deduce successively from the vertical columns of the Table 52, proceeding from right to left:

$M = 3$	$3g_3 = 4$	$g_3 = \frac{4}{3}$
$= 2$	$2(g_3 + g_2) = 5$	$g_2 = \frac{7}{6}$
$= 1$	$1(g_3 + g_2 + g_1) = 3$	$g_1 = \frac{1}{2}$
$= 0$	$0(g_3 + g_2 + g_1) = 0$	. . .
. . .	. . . . .	. . .

These are the same g_J's as were given in Table 45 on p. 478 for the triplet D-terms. We may verify the other data in this table in the same way.

Lastly, we must discuss the beautiful observations, already made use of in p. 337, which Paschen and Back made in the case of medium fields. They arose in the effort to discover the selection principle of the inner quantum numbers and its possible transgression.*

We know that an external *electric* field must be acting if the selection principle of the azimuthal quantum number L is to be transgressed, namely, if the forbidden combinations † $\Delta L = 0$ and $|\Delta L| > 1$ are to be realised. Such a field is, however, found to be ineffective in the case of the selection principle of the inner quantum number. Paschen and Back show us that a *magnetic* field is able to make this transgression possible, but only in the course of the transformation which leads from the anomalous Zeeman effect in weak fields to a partial Paschen-Back effect in fields which are to be regarded as strong compared with the less resolved term-difference. Cf. the discussion based on the Correspondence Principle given in Chap. VI, § 5, which may be applied to any arbitrary multiplicities.

Let us consider the PD-combinations in the triplet spectrum of Ca. In addition to the principal lines (P_2D_3), (P_1D_2), (P_0D_1) and the satellites (P_2D_2), (P_1D_1), (P_2D_1) of the composite triplet we have the forbidden combinations:

(P_1D_3), (P_0D_2) with $\Delta J = 2$,
(P_0D_3) with $\Delta J = 3$.

Taken together with the allowed combinations, they form an organic complex: whereas they have the intensity zero in weak fields and merge into the state of the partial Paschen-Back effect in strong fields, they have a transitory existence in medium fields. They do not, of course, occur in their original field-less position, but in a magnetically influenced position; it is possible, however, to extrapolate the former

* *Liniengruppen magnetisch vervollständigt.* Zeeman Jubilee Number of Physica, 1st series, Oct., 1921, p. 261.

† $\Delta L = 0$ is forbidden only for one-electron systems (cf. Note 7(*e*), because in this case L becomes identical with the l of the electron, for which $\Delta l = \pm 1$ holds. For systems with more than one electron $\Delta L = 0$ is allowed. cf. p. 444. But $|\Delta L| > 1$ is of course also forbidden for systems with more than one electron.

linearly from the latter, and to identify the forbidden components as such.

This phenomenon was shown to occur not only in Ca, but also in the case of (PD)-triplets of Zn and Cd as well as in (PD)-doublets of Al and Ca^+. It is very characteristic that the, so to speak, doubly forbidden combinations (P_0D_3), $\Delta J = 3$, are much harder to produce, that is, require stronger fields and occur only over a smaller range, than the simply forbidden combinations, $\Delta J = 2$.

Accordingly, the observations of Paschen and Back in question provide a suitable means of shedding light on the magnetic origin of the complex structure and of exhibiting its relationship to electron spin. We quote two passages from their paper: "Only the general arrangement of series is electrically sensitive in so far as combinations of a forbidden type may be forced to appear by means of electric fields. On the other hand, the term-differentiation is to be influenced by magnetic forces, as is proved by the anomalous Zeeman types and the magnetic transformation phenomenon." "The forbidden lines appear if the D_J-differences are shattered magnetically; they become brighter as the magnetic perturbation increases and then disappear in the subsequent magnetic transformation. The effect is the swan-song of the configuration before its magnetic annihilation."

§ 8. Theory of the Magneton

Of the various routes which lead to the determination of the elementary magnetic moment of an atom, we shall first discuss the fundamental experiment of Stern and Gerlach, because this is performed under the conditions which are theoretically simplest and clearest; secondly we discuss the magneto-chemical measurements which concern the number of magnetons in ions and compare them with the "spectroscopic number of magnetons." We then report on the magneto-mechanical experiments which are associated with the names Barnett, Einstein and de Haas, Sucksmith and so forth. All these ways are closely connected with the theory of the anomalous Zeeman effect.

(*a*) The Stern-Gerlach Experiment

In Fig. 31, p. 124, we have already described diagrammatically the arrangement, and in Figs. 32 and 33 the result of the experiment with the atomic rays of silver and hydrogen. The theory of the experiment which we sketched very incompletely before (cf. the footnote on p. 128) may now be given rigorously. The ground-orbit of the Ag-atom and of the H-atom is, as in the case of the alkali metals, an S-orbit. Its inner quantum number is $J = \frac{1}{2}$, its magnetic moment in the direction of the field is, by p. 476, $\mu = \frac{1}{2} \cdot 2 = 1$, that is, equal to a Bohr magneton. *Stern and Gerlach have confirmed this moment* $\mu = 1$ *in their*

experiment (cf. p. 129). The first Fig. 30 on p. 124 decides the spatial orientation in the magnetic field. The magnetic moment sets itself either parallel or anti-parallel to the magnetic lines of force. Hence, in Fig. 31 the atom will be deflected either to the right or to the left-hand side. The middle of the picture in Figs. 32 and 33 remains completely free, because *the magnetic zero-levels is missing in all even terms* (and not only in the S-state). What has already been said is enough to show how such experiments are in general to be interpreted, and what results are to be expected from them. For every atom they give us the *magnetic resolution of the ground-term*, and indicate what and how many positions the axis of the magnetic moment assumes in the field. For example, in Mn (ground-state sextet-S-term) we expect six deflection traces, the two outermost corresponding to the parallel and anti-parallel orientation of μ in the magnetic field, the inner ones corresponding to more or less oblique orientations. In Cr (ground-state septet-S-term) we expect a deflection picture consisting of seven traces, the two outermost corresponding to the two parallel positions, the middle undeflected one corresponding to the position perpendicular to the magnetic field. Actually the deflection is proportional to $\mu \cos(\mu, H)$, precisely like the magnetic resolution of terms in the Zeeman effect. The number of traces is in general equal to $2J + 1$, namely, equal to the number of magnetic term-levels ; every trace can be characterised by a definite value of the magnetic quantum number M. The distance between two neighbouring traces is equal to 2, if we are dealing with an S-state, as this corresponds to the splitting-factor $g = 2$; that is, the difference between the values of $\mu \cos(\mu, H)$ which are effective in the deflection amounts to two magnetons in each case.

Tellurium presents an instructive example. The ground-term is the $P_{\frac{1}{2}}$-doublet term. Hence, in Tl we expect two traces as in the case of Ag, but at a third of the former distance, because by Table 45 on p. 478, the g-value of the $^2P_{\frac{1}{2}}$ term amounts to two-thirds, and not to two, as in the S-term. The results of observation * are in good agreement with this : the deflection-picture comes out broadened as compared with the trace when no field is present, but it was not possible to resolve it into two separate traces.†

Stern found no signs of a deflection in Zn, Cd, Hg : the ground-state here is the S-term with $J = 0$, $\mu = 0$. The absence of the deflection is not due to the perpendicular position, but to the diamagnetic character of the ground-state. (On the other hand, the excited states of these atoms would have to behave para-magnetically.) The deflection zero is also exhibited by Pb, according to Gerlach. The ground-

* W. Gerlach, Ann. d. Phys., **76**, 113 (1925) ; A. Lew, Zeits. of Physik, **41**, 551 (1927).

† We have here disregarded the nuclear moment, cf. § 10. This should change the resolution-pattern slightly. Cf. a paper by E. Fermi which will shortly appear.

state of Pb was discovered by Grotrian * ; it corresponds to a term with J = 0. This J-value predicts diamagnetic behaviour, and the absence of a deflection. The same applies to Sn.

Gerlach has found that Cu and Au behave exactly like Ag. It was to be expected that the alkali metals, as Stern has confirmed, would exhibit the same deflection pattern as Ag. The observed deflection pattern of Co and Ni consists of more than two traces. According to more recent and as yet unpublished papers, Gerlach obtained in the case of Fe one blurred trace which is probably composed of a fairly large number of individual lines which overlap owing to the non-homogeneity of the individual lines. For a comparison, we may take the theoretical deflection pattern of the Fe-atom. In the ground-state of Fe, inverted ^{5}D-term (cf. p. 463), we have J = 4, $g = \frac{3}{2}$. Here, then, we should have nine traces at a distance from each other corresponding to a difference of $\frac{3}{2}$ magnetons.

Reverting to the silver atom, we are led to ask : why do the two traces in Fig. 32*b* appear equally intense, seeing that the one trace corresponds to an apparently unstable position of the atom ? Whence does the atom, which was originally orientated arbitrarily, derive the energy to enable it to adjust itself into this higher position as regards energy ?

The answer to the second question is doubtless : the energy is derived from the external field H. Whereas the adjustment into the position parallel to, and in the same sense as, the field is associated with loss of energy to the field (possibly as radiation ultimately), the adjustment into the position anti-parallel to the field must occur with the acquisition of energy from the field. We must bear in mind that the passage of the atom from the field-free space into the field is very slow (adiabatic) in view of the relatively slow speed of the atomic ray.

Concerning the first question, the instability of the atom, we must emphasize that the para-magnetic atom is to be compared not with a *magnet needle*, but rather with a *top*. The magnetic needle with its north pole directed towards the south is certainly *unstable ;* but the top with its centre of gravity in an elevated position is, as we know, *stable* if the moment of momentum is sufficient.

It may easily be calculated from the data given on p. 513, that the general statistics of Boltzmann leads to the opposite orientations occurring with appreciably equal probabilities.

(*b*) Magneto-chemical Measurements

The interpretation of para-magnetic observations is in general based on Langevin's theory, which states that the Curie constant C,

* Zeits. f. Physik, **18**, 196 (1923) ; the term was conventionally called the $^2p_4$ term at that time.

that is, the product of the absolute temperature with the susceptibility calculated for a mol of the gas, is given by

$$C = \chi T = \frac{M^2}{R}\,\overline{\cos^2\theta}. \qquad . \quad . \quad . \quad (1)$$

M is the magnetic moment per mol (macro-unit of the atomic or, respectively, the molecular moment, cf. p. 128 above); R is the gas constant per mol, θ the inclination of the axis of the moment to the direction of the magnetic field; the horizontal bar denotes that the average is taken over all possible angles of inclination. Langevin's theory, which preceded the quantum theory of course assumed θ to be continuously variable and all positions to be equally probable (we may reasonably discard the possibility of the direction of the magnetic lines of force being favoured for the adjustment, since this causes only a correction proportional to the field-strength). Hence Langevin set

$$\overline{\cos^2\theta} = \tfrac{1}{3}, \qquad . \quad . \quad . \quad . \quad (2)$$

that is, equally great for the direction of the lines of force as for two axes perpendicular to it. *But, on account of spatial quantising, this is no longer admissible.*

If we substitute (2) in (1), we obtain

$$M = \sqrt{3RC}. \qquad . \quad . \quad . \quad . \quad (2a)$$

The natural unit for M is the Bohr magneton M_B, of eqn. (14), on p. 128, which is given by the quantum theory. But since the measurements are given throughout as multiples p of the Weiss unit M_W, of eqn. (15) on p. 128, we must use the conversion factor

$$\frac{M_B}{M_W} = 4{\cdot}97$$

in the sequel and specify the number of Bohr magnetons by

$$\frac{p}{4{\cdot}97}$$

In a note dating back to 1920, W. Pauli * used that kind of spatial quantising which led to the *normal Zeeman effect*, and which was at that time (erroneously) applied to the hydrogen atom. Pauli chose as his examples the paramagnetic gases NO and O_2 as he had doubts about extending his calculation to solutions or solid bodies.

The latter step was taken by P. S. Epstein † and W. Gerlach,‡ who extended Pauli's calculation to atomic ions, in particular, to those of the Fe group.

* Phys. Zeits., **21**, 615 (1920).
† Science, **57**, 532 (1923).
‡ Phys. Zeits., **24**, 275 (1923), and Vol. II. of "Ergebnisse der exakten Naturwissenschaften."

As early as 1916 Kossel * had recognised that in the Fe group, ions having the same number of electrons, for example, Fe^{+++}, Mn^{++}, or Mn^{+++} and Cr^{++}, have the *same number of magnetons* (" magnetic displacement law "), and that in the above-mentioned examples the removal of an electron causes p to diminish by, say, 5 units, which would indicate that one Bohr magneton must be assigned to the individual electron in each case.

The calculation according to the rules of the normal Zeeman effect is not correct for most atoms. Rather, we have in general to apply the rules of the anomalous Zeeman effect. According to these rules the moment M in the direction of the field is given by

$$M = Jg M_B \quad (g = \text{Landé's splitting factor}). \qquad (3)$$

In general the moment does not lie in the direction of the field, but inclined to it in such a way that the projection of J in the direction of H, which we shall call m in the sequel, becomes integral or half-integral simultaneously with J :

$$m = J, \quad J - 1, \quad J - 2, \ldots - J + 1, \quad -J.$$

Thus, corresponding to every term-level there are in general $2J + 1$ positions which are respectively inclined at the angle given by $\cos\theta = m/J$. Every position is given the weight 1 ; the total weight of the term is $2J + 1$.

To calculate the susceptibility χ we must form, analogously to (1),

$$\overline{\cos^2\theta} = \frac{1}{J^2}\sum_{-J}^{+J}\frac{m^2}{(2J+1)} = \frac{J(J+1)}{3J^2}. \qquad (4)$$

Hence by (3)

$$\overline{\cos^2\theta}\, M^2 = \frac{J(J+1)}{3} g^2 M_B^2 \qquad (4a)$$

and by (1)

$$\chi = \frac{J(J+1)}{3RT} g^2 M_B^2 \qquad (5)$$

If we assume an equal distribution over all directions in the sense of eqn. (2), we immediately obtain from (1) and (3)

$$\chi = \frac{J^2 g^2}{3RT} M_B^2. \qquad (5a)$$

It is very remarkable that (5a) changes into (5) if we merely replace J by $J(J + 1)$. This lends us to conclude that this rule, well-known to us in wave-mechanics, is in a certain sense equivalent to our spatial quantising. We must remark at the same time, however, that the

* Ann. d. Phys., **49**, 229 (1916) ; cf. in particular p. 261. See also the following Fig. 136, where ions having the same number of electrons are represented by the same point on the axis of abscissæ.

complete wave-mechanical calculation of the susceptibility in Dirac's sense (for hydrogen or more generally for doublet spectra) yields not only this factor $J(J+1)$ but also the factor g^2 quite spontaneously, and without having recourse either to experimental results or to the vector-spin model.

The ideally simple example of direction quantising is given by the vapours of the alkali metals. The ground-term of the alkali metals belongs to $J = \frac{1}{2}$, $g = 2$. Here there are two possible positions of adjustment (as the Stern-Gerlach experiment shows directly), namely, that parallel and anti-parallel to the magnetic field.

Hence $$\overline{\cos^2\theta} = \frac{1^2 + (-1)^2}{2} = 1, \quad \overline{\cos^2\theta}\, J^2 = \tfrac{1}{4}$$

$$\overline{\cos^2\theta}\, J^2 g^2 = M_B^2.$$

Hence we obtain for the alkali metals simply

$$\chi = \frac{M_B^2}{RT}. \qquad (6)$$

The same result follows naturally from the general eqn. (5) with $J = \frac{1}{2}$, $g = 2$.

On the other hand, according to Langevin, that is, if we assume equi-distribution over all directions, we should expect a value of χ that is three times smaller, if we regard the magnetic moment $M = M_B$ as given by the Stern-Gerlach experiment. Observations by Gerlach * for K-vapour, which confirm (6), thus exhibit directly the preferential adjustment of the magnetic axes.

It is usual to calculate paramagnetic measurements according to Langevin's theory, the Weiss unit M_W being taken as the basis. Thus in (1) we substitute $M = pM_W$ and obtain, in view of (2),

$$\chi = \frac{p^2 M_W^2}{3RT}.$$

A comparison with (5) gives

$$pM_W = \sqrt{J(J+1)}\, g M_B$$

or

$$\frac{p}{4{\cdot}97} = \sqrt{J(J+1)}\, g. \qquad (7)$$

In the complete analysis of a spectroscopic term (in paramagnetic measurements we are of course always concerned with the ground-term of the atom or ion in question) we know in this formula not only J, but also the quantum numbers L and S, which enter into g. We may therefore calculate the number p of magnetons by spectroscopic

* Como Congress, 1927.

means. This scheme, suggested by the author,* of "spectroscopic magneton numbers," which is beset with difficulties in the Fe group, leads, as F. Hund † has shown, to complete success in the case of the ions of the rare earths, which are better defined and better screened from the outside. In the sequel we shall go further than Hund ‡ by representing the sequences of magneton numbers by means of a formula, or, more accurately expressed, by means of two such formulæ, one of which holds in the first the other in the second of the Stoner sub-groups (cf. p. 473), into which the total group of rare earths resolve.

As we know, in the case of the rare earths we are concerned with the filling up of the N-shell ($n = 4$) by f-electrons, that is, by electrons of azimuthal quantum number $l = 3$ (in the Fe group we should correspondingly be concerned with d-electrons, $l = 2$). Since we are interested throughout only in the triply positive ions of the rare earths the electrons of the O-shell that still remain after the triple ionisation do not come into question, because they form a closed 8-shell (cf. Table 9 on p. 163). The total number of f-electrons in the complete shell is, by Pauli's Principle, $2(2l + 1) = 14$. We use z to denote the number of f-electrons in each ion and z' to denote the number of missing f-electrons required to complete the 14-group, so that

$$z + z' = 2(2l + 1) = 14.$$

z and z' are the independent variables, with which we shall construct our curve of magneton numbers.

On p. 455 we determined the ground-terms of these ions and also their ground-levels ($J = J_{min}$, regular terms, in the first half of the group; $J = J_{max}$ inverted terms, in the second half of the group). From the equations (2), p. 455, we obtain for the J which enters into our present equation (7):

$$\left.\begin{array}{llllll} z < 2l+1, & J = J_{min} & L & S & \frac{z}{2}(2l & z) \\ z \geqq 2l+1, & J = J_{max} & L+S & & \frac{z'}{2}(2l & z'+2) \end{array}\right\} \quad . \quad (8)$$

On the other hand, the factor g which enters into (7) (cf. (7) on p. 477) stands for

$$g = \tfrac{3}{2} + \tfrac{1}{2}\frac{(S-L)(S+L+1)}{J(J+1)}.$$

By substituting from equation (2) on p. 455 we easily obtain

$$\left.\begin{array}{l} z < 2l+1,\ g(J+1) = \frac{z}{2}(2l - z - 1) + 1 \\ z \geqq 2l+1.\ gJ = \frac{z'}{2}(2l - z' + 3) \end{array}\right\} \quad . \quad (8a)$$

* Phys. Zeits., **24**, 360 (1923); Zeits. f. Physik, **19**, 221 (1923).
† *Ibid.*, **33**, 855 (1925).
‡ Cf. a note by the author given in the Wiener Akademie, 30 Jan., 1930.

Hence on account of (8) and (8*a*) we obtain from (7)

$$z < 2l+1,\ \frac{p}{4\cdot 97} = \sqrt{\frac{z(2l-z)}{z(2l-z)+2}}\left\{\frac{z}{2}(2l-z-1)+1\right\} \qquad (9a)$$

$$z \geq 2l+1,\ \frac{p}{4\cdot 97} = \sqrt{\frac{z'(2l-z'+2)+2}{z'(2l-z'+2)}}\ \frac{z'}{2}\{2l-z'+3\} \qquad (9b)$$

By (9*a*) we have $p = 0$ for $z = 0$, La, and for $z = 2l$, Eu, and p attains a maximum between these elements; for $z > 2l$ p becomes imaginary. In Fig. 135 we therefore break off this branch of the curve at $z = 2l$. By (9*b*) $p = 0$ for $z' = 0$, Lu; for $z' = 2l+1$, Gd, the right-hand side of (9*b*) becomes equal to $\sqrt{(2l+1)(2l+3)} = \sqrt{63}$, after having previously attained a maximum between Dy and Ho. Beyond $z' = 2l+1$ we have dotted the extension of the curve to indicate that it is no longer valid here.

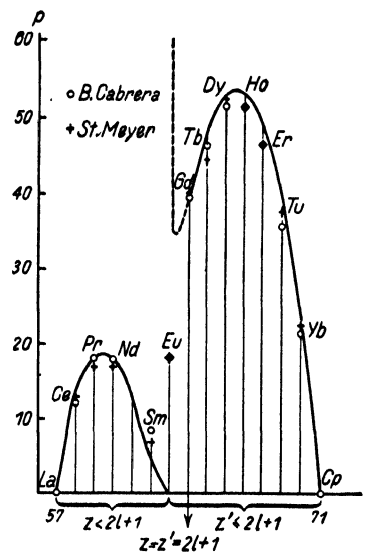


FIG. 135.—The magneton numbers of the triply ionised atoms of the rare earths (in Weiss units) as a function of the atomic number.

The agreement with the observations of Stefan Meyer and Cabrera is satisfactory throughout, as Hund has pointed out, except in the case of Sm and Eu. A wave-mechanical refinement of the theory (by van Vleck) has also given approximate agreement between theory and experiment in the case of these elements. At anyrate the subdivision of the curve into two parts, which corresponds with Stoner's two subgroups, is very characteristic; there can be no doubt that spectroscopic theory explains the essential features in the case of the rare earths.

It might be expected that the same laws (with $l = 2$ instead of 3) would apply in the iron group. The reason for this not being so is in the first place due to the following differences: the multiplets of the rare earths are *widely separated:*

$$h\Delta\nu \gg kT,$$

those of the iron group are only *slightly separated:*

$$h\Delta\nu < kT \quad \text{or} \quad \sim kT.$$

That is why we were justified in assuming in the case of the rare earths that only the lowest multiplet-level came into question in calculating

the susceptibility, whereas in the iron group several or all levels may contribute to the susceptibility.

Clearly the distinction between widely separated and close levels is meant relatively to the temperature at which observations are made. Instead of saying a great or a small $\Delta\nu$ we may also say a small or a great T.

Laporte and the author,* adopting this point of view, have endeavoured to get an understanding of the magneton numbers of the iron group. The first feature that strikes us is that in the middle of the group $z = 2l + 1 = 5(Fe^{+++}$ or $Mn^{++})$, where by Table 43 on p. 454 a ^{6}S-term occurs, the observed and the calculated value agree well † (cf. Fig. 136). Actually the distinction between widely separated and close multiplets does not arise for S-terms since an S-term is always simple. Consequently we are inclined to blame deviations which occur at other points of the iron group on to the multiplicity of the terms.

Assuming that every term-level J is occupied by

$$N_J = (2J + 1)e^{-\frac{h\nu}{kT}}$$

ions, corresponding to the Boltzmann factor ($2J + 1$ = statistical weight, cf. p. 509; $\nu = \nu_J$ as the vibration number of the J-level in question), we obtain instead of (5)

$$\chi = \frac{\Sigma_{(J)} N_J J(J+1) g^2}{\Sigma_{(J)} N_J} \frac{M_B^2}{3RT},$$

and accordingly instead of (7),

$$\frac{p}{4{\cdot}97} = \sqrt{\frac{\Sigma N_J J(J+1) g^2}{\Sigma N_J}}. \quad . \quad . \quad . \quad (10)$$

The summation here and in the sequel is to be performed over the range from $J = |L - S|$ to $J = L + S$. If we divide numerator and denominator by the Boltzmann factor of the ground-level and measure the distances $\Delta\nu$ from it, using for convenience wave-numbers instead of frequencies (factor c) we must now take N_J as standing for

$$N_J = (2J+1)e^{-\frac{hc\Delta\nu}{kT}}. \quad . \quad . \quad . \quad (10a)$$

In the case of very widely separated multiplets (10) naturally passes over into (7), since all N_J's vanish except the N_J of the ground-level, which cancels in the numerator and denominator. In the case of

* Zeits. f. Physik, **40**, 333 (1926). Cf. also a criticism of this view by O. Laporte, *ibid.*, **47**, 761 (1928).

† We obtain by calculation [most simply from eqn. (7) with $J = \frac{5}{2}$, $g = 2$] $p = 4{\cdot}97 \cdot \sqrt{35} = 29{\cdot}5$.

very narrow multiplets we may conversely set all exponential factors equal to 1 and obtain

$$\frac{p}{4{\cdot}97} = \sqrt{\frac{\Sigma(2J+1)J(J+1)g^2}{\Sigma 2J+1}}. \quad . \quad . \quad (11)$$

The two extreme cases (7) and (11) are shown in Fig. 136; we shall presently discuss the significance of the line (13). (7) has the same character as in the rare earths and is *unsymmetrical* with respect to the middle; (11) is *symmetrical* because the reason for the lack of symmetry (regular terms in the first, inverted terms in the second half) is disposed of by the summation over J. In consequence of this symmetry (11) approaches the observed values which, in the iron group, show no sign of the division into the two Stoner sub-groups and lie at least approximately symmetrical with respect to the middle. According to our line of reasoning we should expect that the observed points would lie between the two limiting curves (7) and (11). This is so in the first half, *but not in the second* (cf. Ni^{++}, Cu^{++}).

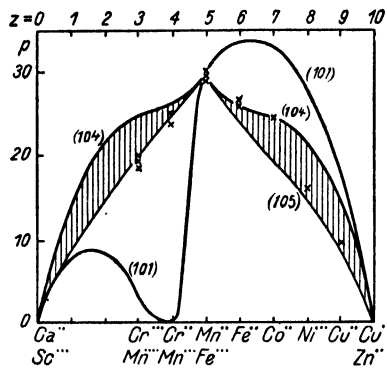


FIG. 136.—The magneton numbers of the ions of the iron group in Weiss units. The figures along the top denote the number of *d* electrons for the ions given along the bottom. The degree of ionisation of these is indicated by dots instead of, as is usual, by crosses.

In deriving (11) we assumed that the "normal coupling" of L and S with J held and that J orientated itself in the magnetic field in accordance with the quantum theory. In the case of very narrow multiplets, it suggests itself to assume that the coupling between L and S is released, and that L and S therefore may orientate themselves individually in the magnetic field. On this last assumption we obtain instead of (11) the simpler expression

$$\frac{p}{4{\cdot}97} = \sqrt{4S(S+1) + L(L+1)}. \quad . \quad . \quad (11a)$$

The proof runs as follows. Corresponding to the moment of momentum S and L we have, respectively, the magnetic moment

$$2SM_B \quad \text{and} \quad LM_B.$$

By projecting on the direction of H we obtain

$$M_H = (2S\cos\theta_S + L\cos\theta_L)M_B. \quad . \quad . \quad (12)$$

To calculate the susceptibility we have to form, as in (1) and (4),

$$\overline{M_H^2} = (4S^2\,\overline{\cos^2\theta_S} + 4S\,\overline{\cos\theta_S}\,L\,\overline{\cos\theta_L} + L^2\,\overline{\cos^2\theta_L})M_B^2. \quad (12a)$$

But we have

$$S\cos\theta_S = m_S, \quad L\cos\theta_L = m_L,$$

where the magnetic quantum numbers m_S, m_L run through all values between $-S$ and $+S$, and $-L$ and $+L$ with integral differences. Hence

$$\overline{M_H^2} = \Big(4\sum_{-S}^{+S}\frac{m_S^2}{2S+1} + \sum_{-L}^{+L}\frac{m_L^2}{2L+1}\Big)M_B^2. \quad . \quad . \quad (12b)$$

We have already omitted the middle term, since both $\overline{\cos\theta_S}$ and $\overline{\cos\theta_L}$ vanish. But precisely as in (4) so

$$\sum_{-S}^{+S}\frac{m_S^2}{2S+1} = \frac{S(S+1)}{3}, \sum_{-L}^{+L}\frac{m_L^2}{2L+1)} = \frac{L(L+1)}{3}$$

holds. Accordingly

$$\overline{M_H^2} = [4S(S+1) + L(L+1)]\frac{M_B^2}{3}.$$

This is equivalent to (11a), since the factor 3 cancels with the 3 in Langevin's formula, which serves to define p.

Van Vleck * has shown numerically that the difference between (11) and (11a) is very small. Consequently, we may use our curve (11) in Fig. 136 also to represent (11a). It is remarkable that in the case of very close multiplets wave-mechanics yields (11a) directly without any particular assumptions about the type of coupling being necessary.

The application of the $\Delta\nu$ calculated for the vapour-state to solutions and crystals appears precarious. Joos † emphasises that the colour of solutions in the iron group which were originally brought into connection with paramagnetic properties remains unintelligible from the point of view of the vapour-state of the ions. For the spark spectra in question contain no absorption line in the visible ; the λ's in question are all < 1700 Å. Hence Joos concludes that the colour must have its origin in complex compounds in which loose bonds occur.

Bethe, however, has shown by an analysis of the crystallised state and of its electric fields (in a paper which will shortly be published) that the susceptibility, averaged over all directions as is observed in the case of a crystalline powder, is the same as a free ion so long as the temperature is not extremely low. Bethe ‡ had already shown earlier that through the interaction with the neighbouring atoms of the crystals the moments of momentum are more disturbed (fixed in the

* Phys. Rev., **29**, 727 (1927) ; **30**, 31 (1927) ; **31**, 587 (1928).
† Ann. d. Phys., **81**, 1076 (1926). ‡ *Ibid.*, **3**, 133 (1929).

crystal lattice) than the spin moments of momentum, which is of importance for the discussion by Stoner which follows below. This result is confirmed by the character of the Zeeman effect of gadolinium sulphate (J. Becquerel). On the other hand, Saha * points out that in the salts of the so-called *Umordnungsgruppen* (for example, the iron group) transitions may occur, in the crystal and in solutions under the influence of incident light, between the deepest levels of the ions in the form of quadrupole-radiation ; these transitions are forbidden in the case of free ions. The wave-lengths of such transitions correspond in order of magnitude to the colour of these salts.

To the distinction between *widely separated* and *narrow* multiplets E. S. Stoner † adds the distinction between *slightly and greatly perturbed multiplets*. The energy-levels of the rare earths are not only *widely separated*, but are also *slightly perturbed*, since their magnetically active electrons belonging to the N-shell is shielded towards the outside by the completely developed and magnetically inactive 8-group of the O-electrons. It is different with the iron group, where the M-shell is magnetically unsaturated and the two electrons of the N-shell, which become added on the outside from Ca onwards, are absent in the ions of the subsequent elements. Hence here the perturbation of the magnetically active electrons by the surroundings is *marked*. If we could observe the ions of the iron group in the vapour-state we should presumably find the magneton numbers determined above, that is, for widely separated multiplets, points of the curve (7) in Fig. 136. Stoner assumes that this perturbation will essentially affect the orbital moments of momentum l, and not the electronic moments of momentum s, and that they will express themselves in a diminution of the resultant quantum number L. Hence he makes $L = 0$ for extremely strong interaction with the neighbourhood in equation (11a) which, as remarked, is essentially identical with (11). Hence whereas (11a) is retained for *slightly separated* and *slightly perturbed* multiplets the following is to hold instead of (11a) for *slightly separated* and *greatly perturbed* multiplets :

$$\frac{p}{4{\cdot}97} = \sqrt{4S(S+1)}. \quad . \quad . \quad . \quad (13)$$

In the first and the second half of the period $S = z/2$ and $z'/2$, we may also write, respectively,

$$\frac{p}{4{\cdot}97} = \left\{\begin{matrix} \sqrt{z(z+2)} & z \\ \sqrt{z'(z'+2)} & z' \end{matrix}\right\} < 2l+1. \quad . \quad . \quad (13a)$$

The new boundary curve which results in this way is like the earlier equation (11) symmetrical with respect to the middle. The region

* M. N. Saha, Nature, **125**, 163 (1930) ; cf. also D. M. Bose and P. K. Raha, *ibid.*, **127**, 520 (1931).

† Phil. Mag., **8**, 250 (1929). Cf. also Brunetti, Rend. Ac. Linc., **9**, 754 (1929).

between it and the boundary curve (11) has been shaded in Fig. 136. The observed magneton numbers are to lie in this region, according to the amount of interaction, and they will lie nearer to (13) than to (11) because in general we expect great perturbation in the iron group. Fig. 136 shows that this is actually the case. It is clear that for the middle and for both ends of the group the equations (11*a*) and (13) must coincide because an S-term is always present here, so that then $L = 0$ in any case.

The curve (13) is approximately straight because the 2 may be neglected in (13*a*) for the greater values of z and z'. This accounts for the integral relation, previously observed by the author, between the magneton numbers of the ions of different degrees.* The content of eqn. (13) may also be expressed thus: in the case of strong interaction with the neighbourhood the magneton numbers behave as if the state were always given by an S-term.

Papers by D. M. Bose † arrive at the same result as Stoner, and are made physically intelligible by Stoner's hypothesis of a strong interaction at temperatures that are not too high. Bose succeeds in representing the facts of observation tolerably well by means of the formulæ (13), (13*a*).

One might be led to expect the same conditions as in the iron group, also in the palladium and the platinum group. This is, however, not so. The magneton numbers of the latter groups are, so far as they are known at present, considerably smaller than in the iron group, as they lie between one and two Bohr magnetons. The reason is probably as follows: in the vertical columns of the periodic system the ionic volume increases towards the bottom, and hence the ionogenic character decreases (cf. the last paragraph of p. 149). The electrostatic fields are the stronger the smaller the ionic size: the fluorine ion behaves more strongly negative than the chlorine ion, and so forth, the lithium ion more strongly positive than the sodium ion. Accordingly, in the solutions of salts of the Pd and Pt group we expect the ionic character to be less marked than in those of the Fe group. But then we may also not expect the paramagnetic regularities in the magneton numbers of the former, since our theory of magneton numbers rests entirely on the existence of pronounced ions.

Hitherto we have spoken only of the paramagnetism of atoms or of their ions. The classical example for the theory of paramagnetism and for Curie's law is given by the *molecular* gas O_2 and (as it at first appeared) also NO. As we shall not describe the theory of molecular spectra till the next chapter, and do not wish to anticipate it, we must

* Phys. Zeits., *loc. cit.*; Ann. d. Phys., **70**, 32 (1923). *E.g.*, Cr^{+++} has 3, Cr^{++} has 4, and Cr 6 Bohr magnetons; in the same way, S. Freed, Journ. Amer. Chem. Soc., **49**, 2456 (1927), finds 1 Bohr magneton in V^{++++}, 2 in V^{+++}, and appropriately 3 in V^{++}.

† Zeits. f. Physik, **43**, 864 (1927); Como Congress, 1927.

be satisfied here with only a few brief remarks. The ground-state of the O_2-molecule is a triplet S-term (called $^3\Sigma$). If we apply to it eqn. (11a) with S = 1, L = 0, we obtain

$$\frac{p}{4\cdot97} = 2\sqrt{2}, \quad p = 14\cdot0,$$

which agrees with the experimental results. We shall not explain here why the atomic formula (11a) may be applied to this case. Curie's law holds rigorously for O_2 (except at extremely low temperatures) without the otherwise necessary corrections (see below).

In NO the ground-state is a doublet P-term ($^2\Pi$), whose two levels are relatively widely separated ($\Delta\nu = 121$ cm.$^{-1}$). At very low temperatures, $kT \ll hc\Delta\nu$, only the lowest doublet-level comes into question on account of the Boltzmann factor; at high temperatures, $kT \gg hc\Delta\nu$, both levels according to their weights. The atomic formula may not be used in this case to calculate the paramagnetism. According to van Vleck, we obtain the magneton number $p = 0$ for the lower doublet-level and for the combined action of both

$$\frac{p}{4\cdot97} = 2.$$

Thus NO does not obey Curie's law in its original form; its magneton number p increases, rather, from zero at T = 0 to $\sim$ 10 at T = ∞. In the intermediate region a transition formula applies, which was derived by van Vleck and which is analogous to our equation (10); it has been confirmed by measurements made by Bitter * as well as by Aharoni and Scherrer.†

This is not the place to discuss the experimental data on which Figs. 135 and 136 are based. We remark only that they are not derived directly from the measurements, but are deduced indirectly from them after certain corrections have been applied. Such corrections are: "extrapolation to the concentration zero" in the case of solutions, taking into account the diamagnetism of the anion and the kation, and, above all, replacing Curie's law $\chi T = C$ by Weiss's law $\chi(T - \Theta) = C$, where Θ denotes an empirical auxiliary quantity which cannot be predicted by theory. It is found in many cases graphically that the $(1/\chi, T)$-diagram gives a straight line which does not pass through the origin as in Curie's law, but cuts the T-axis in a point $T = \Theta$, which may lie either on the positive side of the T-axis (as in the Curie point of ferro-magnetic substances) or on the negative side.

Obviously, by introducing this Θ we take into account to a first approximation the influence of the neighbourhood (solvent and anions, or crystal structure) on the paramagnetism of the kations. It is in

* Nat. Ac. Proc., **15**, 638 (1929). † Zeits. f. Physik, **58**, 749 (1929).

agreement with this view that in paramagnetic gases where this influence is absent Θ also becomes equal to zero, either because as in O_2 Curie's law holds directly or as in NO a derived form of Curie's law, arising from the double character of the ground-level, holds, which does not, however, contain an empirical parameter Θ.

It has not yet been found possible to derive Weiss's law theoretically from statistical considerations. It is also necessary to build up on a statistical foundation the proof (not given by us) for Stoner's assumption in the iron group which was to take into account the influence of the neighbourhood. Van Vleck has sketched how this is to be done on a wave-mechanical basis (cf. his book on electric and magnetic susceptibility which is about to appear).

(c) The Magneto-mechanical or Gyro-magnetic Experiments

We now deal with two mutually independent methods which may be briefly described as *magnetisation by rotation* and *rotation by magnetisation* · the former is associated with the name of S. J. Barnett, the latter chiefly with Einstein and de Haas. Two predecessors of Barnett who had no success in finding the effect were Maxwell * (1861) and Perry † (1890). Barnett's ‡ first successful experiments date from 1914. The experiments by Einstein and de Haas were published in 1915.‖ O. W. Richardson ¶ looked for the effect without success in 1908.

1. **Magnetisation by Rotation.**—A rod of ferro-magnetic material (Fe, Co, Ni or alloys), which is initially at rest, is made to rotate with angular velocity ω. The resulting magnetisation is observed (or the difference in the magnetisations when the rotation is reversed). The same rod is then placed at rest in a magnetic field H, which leads to the same magnetisation as was previously produced by the rotation (or, if the field is reversed, the same difference of the magnetisations when the rotation is reversed) ; for this purpose the rod has a conducting wire wound round over its whole length. The magnetic field H and the angular velocity ω are equivalent to one another, by Larmor's theorem (p. 325). The atomic electrons (or the free electrons) of the rod cannot distinguish whether they are situated in the field H or in a system of reference rotating with angular velocity ω. By equation (2) on p. 324 we expect the following relationship between H and ω :

$$H = s\omega, \quad s = 2m/e, \quad . \quad . \quad . \quad . \quad (14)$$

where e/m denotes the specific electron charge in the usual electromagnetic units ($e/m = 1{\cdot}76 \,.\, 10^7$). It is this ratio s which interests us

* Electricity and Magnetism, § 575.
† Cf. his book, *Spinning Tops*, p. 112.
‡ Phys. Rev., **6**, 239 (1915), given in a lecture in 1914.
‖ Verhandl. d. Deutsch. Phys. Ges., **17**, 152 (1915).
¶ Phys. Rev., **26**, 248 (1908).

here and in the sequel. According to (14) it is known when H and ω have been measured. The magnetic properties of the material (permeability or magnetisation) fortunately do not enter into the measurement. The material must be ferro-magnetic only in order that an appreciable magnetisation may be produced at all by rotation, and may be reproduced by applying the field H. The measurement of H makes the greatest possible demands on accuracy; this is evident from the fact that a frequency of revolution of 100/sec. corresponds by (14) to a field H which is less than $\frac{1}{1000}$ of the earth's field. Barnett therefore succeeded only after many years of arduous research in attaining a satisfactory accurary (of several per cent.). He obtained, as a result, in the mean

$$s = 1{\cdot}06 \, . \, m/e. \quad . \quad . \quad . \quad . \quad (15)$$

without a difference in the materials used showing itself. In comparison with equation (14) this result denotes the following: it is not the *revolving electrons* which produce the magnetisation of the rod, but the *spin moments of momemtum* of the electrons. Actually, by equation (2) on p. 331, the value of s out of (14) is equal to the ratio: mechanical moment to magnetic moment of the revolving electron, whereas the value of s that occurs in equation (15) and that is only half as great points according to equation (3) on p. 332 to the corresponding ratio for the electron spin. This state of affairs is in harmony with the view of ferro-magnetism which is likewise built up on the spin moment of momentum of more or less free electrons. The deviation from the one on the right-hand side of (15), which is real according to Barnett, however, remains unexplained.

A feature of particular interest in these experiments is their analogy with the *earth's magnetism*. It is difficult to avoid assuming that the magnetic moment of the earth and its rotation about almost the same axis are causally related. Barnett's experiments show how such a relationship is possible, but the order of magnitude is quite different. According to (14) and taking $\omega = 4\pi$/day we obtain for the earth's field a value that is more than 10^{11} times too small.

2. **Rotation by Magnetisation.**—The original object of Einstein's arrangement was to demonstrate the mechanical moments of momentum of the Ampère molecular currents, that is, to demonstrate the revolving motions of the electrons which were supposed to occur without constraint in Bohr's model of the atom. A magnetically saturated ferro-magnetic needle suspended by a vertical torsion thread is periodically demagnetised, the period is chosen so that it is in resonance with the torsion system. The moment of momentum of the recoil is measured by the magnitude of the torsional vibration. The experiments which were carried out in collaboration with W. J. de Haas first appeared to confirm the classical value $2m/e$ for the ratio $M_{mech}/$

M_{magn}. A repetition of the experiments by de Haas,* Stewart,† Beck,‡ Arvidson,‖ Sucksmith and Bates ¶ led with an increasing degree of accuracy ** to half this value, that is, here too to the action of the electron-spin.

The factor $\frac{1}{2}$ that occurs here is of course nothing else than the reciprocal of the g-factor 2 for S-terms (L = 0, the revolutions of the electrons do not contribute). Actually we have for the two total moments of the needle

$$M_{magn} = N\,\overline{\cos\theta\mu}\,.\,M_B, \quad M_{mech} = N\,\overline{\cos\theta J}\,.\,\frac{h}{2\pi}, \qquad . \quad (16)$$

where N denotes the number of atoms in the needle, θ the angle between the field and the magnetic axis of the atom, μ the magnetic moment of the atom expressed in units of $M_B = \frac{e}{m}\frac{h}{4\pi}$ and J the mechanical moment of momentum of the atom in units of $h/2\pi$; the horizontal bar over cos θ denotes that the mean is to be taken over all the N atoms. But in view of the result of the observations $\frac{M_{mech}}{M_{magn}} \sim \frac{m}{e}$ it then follows from (16) that

$$\mu = 2J, \quad \frac{\mu}{J} = g = 2. \qquad . \quad . \quad . \quad (17)$$

The fact that in the gyro-magnetic experiments we are actually dealing with the magnetic anomaly, that is, with the g-value 2, is firmly established by the result of more recent experiments by Sucksmith †† on Dy_2O_3. If we wish to do without ferro-magnetic material and seek to perform the gyro-magnetic experiment with para-magnetic material, we shall in the first place have to make use of the extremely para-magnetic substances dysprosium or holmium, whose magneton numbers lie near 50 Weiss units (cf. Fig. 135). We have for Dy^{+++} in the notation of equations (8) and (8a) on p. 511,

$$z' = 5, \quad J = J_{max} = \tfrac{15}{2}, \quad g = \tfrac{4}{3}.$$

By increasing the sensitivity as far as possible Sucksmith has succeeded in observing the recoil effect in demagnetising a rod of Dy_2O_3. From this he finds the corresponding value of g to be, not 2 as in the case of ferro-magnetic substances, but $1{\cdot}28 \pm 0{\cdot}07$, which is in agreement

* Proc. Amsterd. Acad., **18**, 1281 (1916).
† J. Q. Stewart, Phys. Rev., **11**, 100 (1918).
‡ Ann. d. Phys., **60**, 109 (1919). ‖ Physical Zeits., **21**, 88 (1920).
¶ Proc. Roy. Soc., **104**, 499 (1923).
** Whereas Sucksmith and Bates give the factor 1 in m/e with 1 per cent. accuracy, Barnett arrives in a somewhat modified repetition of their experiments, exactly as in his rotation experiments, at a factor > 1, namely, according to his provisional communication, at 1·04.
†† Proc. Roy. Soc., **128**, 276 (1930); **133**, 179 (1931).

with the theoretical value $\frac{4}{3}$. This shows that *in general not only the spin moment of momentum but also the orbital moment of momentum of the electrons contributes to the gyro-magnetic effect.*

§ 9. Intensity of Spectral Lines

Whereas the older spectroscopic data concerning the *intensity* of spectral lines had at best a qualitative significance, the workers in the Physical Institute of the University of Utrecht (under the direction of L. S. Ornstein) have worked out a method which makes it possible to determine the relative intensities of the line-configuration of a complex structure quantitatively.*

The only trustworthy result of the older measurements of intensity concerns the D-lines of sodium. The ratio of the intensities of D_2 to D_1 is equal to 2 : 1, as had been established by many different observers. This result was extended to the doublets (SP) and (PS) of the other alkaline metals (cf. I). This in itself leads us to conclude that this ratio does not depend on the principal quantum number n, which changes step by step in the series of alkali metals. An exception occurs in the case of the doublet of the blue cæsium line $\lambda = 4555$ and 4593, second term of the principal series, namely 1S — 3P in the conventional notation ; the intensity ratio is greater here, namely 3·5 : 1.† The reason has been found wave-mechanically by E. Fermi ; ‡ it has its origin in a perturbation due to the widely separated ground-doublet 1S — 2P. The same holds to a lesser degree for the second term of the principal series of rubidium.

The next result concerns the triplets (^{3}P ^{3}S) of the alkaline earths and the elements Zn, Cd. To about the same degree of accuracy the ratios 5 : 3 : 1 were obtained for the three triplet-components $^3P_2{}^3S$, $^3P_1{}^3S$, $^3P_0{}^3S$.

We may write down the results so far quoted in such a form that they may be generalised for the combinations (PS) or (SP) of the higher term systems :

* Dorgelo, Zeits. f. Physik, **22**, 276 (1924) ; Burger and Dorgelo, *ibid.*, **23**, 258 (1924) ; which are quoted in the text below as I. and II. Cf. also the comprehensive dissertation by Dorgelo, Utrecht, 1924, and his report in Physikal. Zeits., **26**, 756 (1925). Directions about the experimental arrangement and the working out of the measurements are given in Dorgelo, Zeits. f. Physik, **13**, 206 (1923), and in the booklet by L. S. Ornstein, *Photographische Photometrie* (Vieweg & Sohn, Braunschweig).

† Füchtbauer (" Absorption Measurements at High Pressures," Ann. d. Physik, **43**, 96 (1914)), and Roschdestwensky (" Dispersion Method," Optical Institute in Petersburg, Nr. 13, Berlin, 1921) ; H. Kohn and H. Jakob, Physikal. Zeits., **27**, 819 (1926) ; H. Jakob, Ann. d. Phys., **86**, 449 (1928) (" Emission in Flames,") ; W. Schütz (" Absorption Measurements at Low Pressures and Magneto-rotation "). Zeits. f. Physik, **64**, 682 (1930) ; R. Minkowski and W. Mühlenbruch (" Magneto-rotation "), *ibid.*, **63**, 198 (1930).

‡ Zeits. f. Physik, **59**, 680 (1930).

Doublet system	4 : 2 : 0
Triplet ,,	5 : 3 : 1
Quartet ,,	6 : 4 : 2
Quintet ,,	7 : 5 : 3
Sextet ,,	8 : 6 : 4
Septet ,,	9 : 7 : 5
Octet ,,	10 : 8 : 6

This generalisation was tested by Dorgelo for the Mn-triplets (SP), cf. I :

Sextet system . . . λ = 6021, 6016, 6013
Octet ,, . . . λ = 4823, 4783, 4754

We have already considered the second of these triplets in Figs. 127 *a*, *b*, *c* on p. 482 ; the first is the ground-triplet of the Mn-spectrum. We exhibit these results as well as those for the Cr-triplet in the quintet system λ = 5208, 5206, 5204 (cf. II) in the following table :

TABLE 54

	Measured	Expected
Cr, Quintet System . .	100 : 72 : 45	100 : 71·4 : 42·9
Mn, Sextet System . .	100 : 77 : 53 100 : 77 : 55	100 : 75 : 50
Mn, Octet System . .	100 : 81 : 61 100 : 79 : 62	100 : 80 : 60

The confirmation is the more convincing because in the triplet system the corresponding ratios deviate far from these values, for expressed in a similar way they amount to 100 : 60 : 20.

The theoretical basis of the arithmetic rule which has here been discovered empirically is as follows. We saw that the number of magnetic resolutions of a term is given without exception by the number

$$2J + 1.$$

It tells us in how many ways the originally degenerate state in question may be resolved magnetically. By regarding each of these resolutions as equally probable, as has already been done on p. 509 in averaging over $\cos^2\theta$, we call $2J + 1$ the *weight* of the state (statistical weight, *a priori* probability). We now see that *the relative intensity of the (SP)-combinations measures directly the statistical weight of the P-terms.* For example, for the three triplet P-terms we have successively

$$J = 2, 1, 0 ; \quad 2J + 1 = 5, 3, 1.$$

For the two doublet P-terms we had

$$J = \tfrac{3}{2}, \tfrac{1}{2} ; \quad 2J + 1 = 4, 2.$$

We consider as the next generalisation the case of (DF)-combinations, in which the F-term is no longer separated. In the triplet system the three D-terms have the inner quantum numbers J = 3, 2, 1, that is, the weights 7, 5, 3. We here expect the intensity ratios that are given by the last three numbers. Dorgelo actually obtains the following values (I) for Ca and Sr:

TABLE 55

	Measured	Expected
Ca, Triplet System λ = 4595, 4581, 4578	100 : 70 : 44·5 100 : 74 : 44·5	100 : 71·4 : 42·9
Sr, Triplet System λ = 4892, 4869, 4855	100 : 70 : 44 100 : 71 : 44	100 : 71·4 : 42·9

From this we conclude that *our weight rule holds for any arbitrary terms so long as they do not combine with a simple or appreciably simple term.*

But what happens when two multiple terms come into competition with one another, so to speak? A compromise must then be effected between the weights of the one and of the other term. The simplest case is that of the composite doublet (PD), two principal lines ($P_{\frac{3}{2}}D_{\frac{5}{2}}$) and ($P_{\frac{1}{2}}D_{\frac{3}{2}}$), and one satellite ($P_{\frac{3}{2}}D_{\frac{3}{2}}$). For this there is available one measurement (II) in the Cs group 2P—6D, λ = 6217, 6213, 6010:

Measurements

		²D 6	4	
²P	4	100	12	112
	2		60	60
		100	72	

Expected Values

		²D 3	2	
²P	2	9	1	10
	1		5	5
		9	6	

The measurements (left-hand scheme) are in the middle; to the left of and above them are the weights of the P- and the D-terms corresponding to the J-values $\frac{3}{2}$, $\frac{1}{2}$ and $\frac{5}{2}$, $\frac{3}{2}$. The numbers to the right and below denote the sums of the measured intensities in the horizontal and in the vertical direction. They are approximately in the ratio of the weights of the P- and the D-terms.

This indication combined with what we have already said about not separated or not appreciably separated terms leads to the following summation rule (II).

In multiple terms we suppose either the sub-divisions of the initial or of the final term to draw together; the sums of the intensities that then result are in the ratio of the weights of the terms that have not *contracted.*

The theoretical intensities (right-hand scheme) then come out according to this rule as follows:

Cancelling the common denominater 2 out of the weights, merely to simplify the calculation, we write on the left-hand side of and above our scheme the numbers 2, 1 and 3, 2, respectively. We have then to distribute the total weight $(2 + 1)(3 + 2)$. Of these the two vertical columns claim the parts $3(2 + 1)$ and $2(2 + 1)$, respectively, and the two horizontal rows $2(3 + 2)$ and $1(3 + 2)$, respectively. We write down these numbers below and in the right-hand side of our scheme. In this way we have already determined the two intensities 9 and 5 of the "principal lines," as they occur individually in a vertical or a horizontal row. The "satellite" then comes out from the prescribed sums in two ways as 1. The theoretical ratio 1 : 5 is in this case, for example, exactly equal to the measured 12 : 60.

The calculation may then be immediately applied to the combinations (DF), (FG) . . . and in general to the combinations of two doublet-terms having the azimuthal quantum numbers L and L + 1. The inner quanta of the former are, as we know, $J = L + \frac{1}{2}$ and $L - \frac{1}{2}$, and the weights, therefore, $2L + 2$ and $2L$; the ratio of the weights is thus $L + 1 : L$. The weights of the doublet term whose azimuthal quanta is L + 1 correspondingly bear the ratio $L + 2 : L + 1$ to one another. We write down those numbers on the left-hand side of and above our scheme, and form from them the sums for the vertical and horizontal rows, below and on the right-hand side. The principal lines

	L + 2	L + 1	
L + 1	$2L^2 + 5L + 2$	1	$(L + 1)(2L + 3)$
L		$2L^2 + 3L$	$L(2L + 3)$
	$(L + 2)(2L + 1)$	$(L + 1)(2L + 1)$	

are again determined directly, and again the relative intensity of the satellite comes out unambiguously as 1. As we see, the intensity of the satellite relative to that of the two principal lines becomes the smaller, the larger the value of L (II).

But it is only in the case of the ordinary doublet combinations that the summation rules determine the intensities *completely*. Even in doublet combinations of the character (PP'), (DD') . . . one intensity remains undetermined, since the four summation equations which are available in this case are not independent of each other. We exhibit this in the following scheme, which is set up in the manner of the previous schemes and satisfies the summation rules exactly:

		P′		
		2	1	
P	2	$6 - u$	u	6
	1	u	$3 - u$	3
		6	3	

We have denoted the intensity which remains undetermined here by u. In the triplet and the multiplet systems the degree of indefiniteness increases at each stage.

The ratio $K\alpha : K\alpha'$ has been measured by Siegbahn and Zacek for Fe, Cu, Zn with great accuracy,* and has been found to be equal to 2 : 1. On the other hand, the ratio $L\alpha : L\alpha'$ appears ocularly, and according to older measurements by Duane and Patterson, to be much greater, about 10 : 1. As we know, however, the lines $K\alpha$, $K\alpha'$ correspond to the optical doublet-lines $SP_{\frac{3}{2}}$ and $SP_{\frac{1}{2}}$. *Thus the ratio $K\alpha$ to $K\alpha'$ mirrors the ratio 2 : 1 of the D-lines.* But the lines $L\alpha$, $L\alpha'$, $L\beta$ are analogous to the composite doublet (PD) in the optical region.

According to the table on p. 524, they should show the following ratios :

$$L\alpha : L\alpha' : L\beta = 9 : 1 : 5,$$

which already explains what was found qualitatively about the intensity-ratio $L\alpha : L\alpha'$. Quantitative experiments involving the Geiger-point-counter have been carried out by A. Jönsson.† In the case of both W and Pt they gave

$$L\alpha : L\alpha' = 9 : 1{\cdot}0.$$

The problem of X-ray intensities is, however, still in a somewhat controversial state, and will not be pursued further here.‡

To complete the calculation of the intensities we must use the vector model and the correspondence principle as well as the summation rules. We base our remarks on Note 7 (e). There we find || that the intensities which correspond, according to the correspondence principle, to the three transitions

$$L \rightleftarrows L - 1 \begin{cases} J + 1 \rightleftarrows J \\ J \rightleftarrows J \\ J - 1 \rightleftarrows J \end{cases}$$

are in the following ratios :

$$(\cos\theta + 1)^2 : 2\sin^2\theta : (\cos\theta - 1)^2 \quad . \quad . \quad (1)$$

* Ann. d. Phys., **71**, 187 (1923).

† Zeits. f. Physik, **36**, 426 (1926) ; **41**, 221, 801 (1927) ; **46**, 381 (1928). The numbers given in the text represent energies and not numbers of light quanta (photons), which latter are given by the point-counter directly ; the former are derived from the latter by multiplication by the frequency ν of the line. The " correction for the same ν " given at the end of this section makes no difference in the case of the closely neighbouring lines $L\alpha$, $L\alpha'$, and $K\alpha$, $K\alpha'$.

‡ Cf. Allison and Armstrong, Phys. Rev., **26**, 714 (1925) ; Allison, *ibid.*, **30**, 245 (1927) ; **32**, 1 (1928) ; V. Hicks, *ibid.*, **36**, 1273 (1930).

|| Cf. also the original paper by Sommerfeld and Heisenberg, Zeits. f. Physik, **11**, 131 (1222).

Here θ denotes, in the case of normal coupling which we assume throughout for the present, the angle between J and L in the triangle J, L, S. Thus

$$\left.\begin{aligned} \cos\theta &= \frac{J^2 + L^2 - S^2}{2JL} \\ \cos^2\frac{\theta}{2} &= \frac{(J+L)^2 - S^2}{4JL}, \quad \sin^2\frac{\theta}{2} = \frac{S^2 - (J-L)^2}{4JL} \end{aligned}\right\} \quad . \quad (2)$$

From (1) we obtain in a somewhat more convenient method of notation :

$$I_p : I_i : I_a = \cos^4\frac{\theta}{2} : 2\sin^2\frac{\theta}{2}\cos^2\frac{\theta}{2} : \sin^4\frac{\theta}{2}. \quad . \quad . \quad (3)$$

Here the indices p, a and i denote " parallel," " anti-parallel " and " indifferent transition " between the two quantum numbers L and J relative to one another, the parallel transition being represented in the preceding scheme by the first row, the anti-parallel by the last, and the indifferent by the middle row, for both directions of the arrows in the scheme. If we substitute (2) in (3), we obtain

$$I_p : I_i : I_a = \frac{P \,.\, P}{4JL} : \frac{2PQ}{4JL} : \frac{Q \,.\, Q}{4JL}. \quad . \quad . \quad . \quad (4)$$

Here we have cancelled a factor 4JL in the denominator throughout, which is of course allowable in a proportion, and which will be found to be of importance for the sequel. In the numerator the expressions P and Q would denote by (2)

$$P = (J+L)^2 - S^2, \quad Q^2 = S^2 - (J-L)^2.$$

But we shall immediately replace it by its analogous wave-mechanical expression ($a(a+1)$ in place of a^2) :

$$\left.\begin{aligned} P(J) &= (J+L)(J+L+1) - S(S+1) \\ Q(J) &= S(S+1) - (J-L)(J-L+1) \end{aligned}\right\} \quad . \quad . \quad (5)$$

We make a similar change in our proportion (4), by writing

$$\left.\begin{aligned} I_p(J) &= \frac{P(J)P(J-1)}{4JL}, \quad I_a = \frac{Q(J)Q(J-1)}{4JL} \\ I_i(J) &= \left(\frac{1}{J} + \frac{1}{J+1}\right)\frac{P(J)Q(J)}{4L} \end{aligned}\right\} \quad . \quad . \quad (6)$$

The last of these expressions results from our dividing the factor 2/J in the middle term of the proportion (4) into

$$\frac{1}{J} + \frac{1}{J+1}$$

which agrees with 2/J for large values of J.

We assert that these formulæ (5) and (6) satisfy the summation rules, when taken for the horizontal rows and equally well for the

vertical columns so long as we agree that J is each time to denote the *greater* of the two numbers, between which the transition occurs in the multiplet-component in question.

Scheme I, Multiplet $L \to L - 1$

	0							
	0	0						
L+S−1	I_p	I_i	I_a					
L+S−2		I_p	I_i					
L−S−3			I_p					
L−S+1					I_p	I_i	I_a	
L−S						I_p	I_i	0
L−S−1							I_p	0 0
J	L+S	L+S−1	L+S−2		L−S+2	L−S+1	L−S	

To prove this we write down the general scheme of a multiplet of the structural type under discussion. For example, we choose the transition $L \to L - 1$ and assume $L > S$. In the initial state we then have $L+S \geqq J \geqq L-S$ and in the final state $L-1+S \geqq J \geqq L-1-S$. These J-values have been written down below and on the left-hand side of the scheme. Within the scheme the character of every possible transition is indicated by the symbols I_p, I_i and I_a. Every row and every column contains each of these symbols once except the two initial columns and the two final rows, where the I's that are missing are replaced by zeros. The I_p's lie in the principal diagonals of the scheme, the I_i's and I_a's then lie successively parallel to them.

We now form the intensity sums for any of the middle horizontal and vertical rows, namely

$$\left.\begin{matrix} I_p(J+1) + I_i(J) + I_a(J) \\ I_p(J) + I_i(J) + I_a(J+1) \end{matrix}\right\} \quad . \quad . \quad . \quad (7)$$

For if in the first of these equations J denotes the inner quantum number of the horizontal row in question, the transition I_p takes place between $J+1$ and J. In consequence of what we agreed about equations (5) and (6) we must therefore form I_p with the argument $J+1$; in the same way, in the second equation (7), where J denotes the inner quantum number of the vertical column under consideration and where the transition I_a takes place between J and $J+1$, we must form I_a with the argument $J+1$, and this must be done in both the

numerator and the denominator of the expressions (6). Dividing up the middle term of this proportion appropriately we first obtain in place of (7)

$$\left.\begin{aligned} P(J)\frac{P(J+1)+Q(J)}{4(J+1)L} + Q(J)\frac{P(J)+Q(J-1)}{4JL} \\ P(J)\frac{P(J-1)+Q(J)}{4JL} + Q(J)\frac{P(J)+Q(J+1)}{4(J+1)L} \end{aligned}\right\} \quad . \quad (7a)$$

In these fractions the denominators J and J + 1 cancel out. For by (5), as we may easily show by calculation,

$$\frac{P(J)+Q(J-1)}{4JL} = \frac{P(J+1)+Q(J)}{4(J+1)L} = \frac{2L+1}{2L},$$
$$\frac{P(J-1)+Q(J)}{4JL} = \frac{P(J)+Q(J+1)}{4(J+1)L} = \frac{2L-1}{2L}.$$

Instead of (7*a*) we may therefore write

$$\left.\begin{aligned} \frac{2L+1}{2L}(P(J)+Q(J)) \\ \frac{2L-1}{2L}(P(J)+Q(J)) \end{aligned}\right\} \quad . \quad . \quad . \quad (7b)$$

Further, by (5),

$$P(J) + Q(J) = 2L(2J+1).$$

Consequently (7*b*) becomes

$$(2L+1)(2J+1) \quad \text{and} \quad (2L-1)(2J+1) \quad . \quad . \quad (7c)$$

respectively. Both sums are therefore proportional to *the quantum weight* 2J + 1 *of the horizontal row and vertical column*. The factors 2L + 1 and 2L − 1 in (7*b*) are also in accord with the summation rules. For the sum of the quantum weights for all vertical columns or, respectively, that for all horizontal rows, is by our scheme of p. 528,

$$(2S+1)(2L+1) \quad \text{and} \quad (2S+1)(2L-1).$$

The factors 2L + 1 and 2L − 1 in (7*b*) are thus proportional to these weight-sums ; this corresponds exactly with our way of handling the summation rules, for example, in the doublet system, p. 525.

Our proof is, however, incomplete, inasmuch as we have not specially taken into account the initial columns and the final rows. We easily show that this was not necessary, because the I's in question vanish of themselves, as indicated in our scheme. Actually, for the left-hand upper corner,

$$J = L + S,\ Q(J) = 0,$$
$$J = L + S + 1,\ \ Q(J-1) = 0,$$

and hence, on account of (6), in the first case $I_i = I_a = 0$, and in the second $I_a = 0$. A corresponding result holds for the right-hand lower corner.

In the above we have assumed that $L > S$. But our formulæ also apply unchanged for $L < S$, in which case the full number of levels $2S + 1$ has not yet been attained and only a section of our scheme has a real significance. The reason for this is again the occurrence of zeros in certain fields adjoining this section.

Secondly, we consider that type of multiplet to which, for example, the PP′-combinations belong and which we characterise in general by

$$L \to L \begin{cases} J \to J & \ldots I_p \\ J \to J \pm 1 & \ldots I_a. \end{cases}$$

As indicated, the symbol I_p (parallel transition between J and L) is assigned to the transition in which J remains unaltered, whereas both transitions $J \to J \pm 1$ may be called anti-parallel. An argument along the lines of the Correspondence Principle leads us to expect in place of (3)

$$I_p : I_a = 2 \cos^2\theta : \sin^2\theta.$$

In view of (2) this denotes

$$I_p : I_a = \frac{(J^2 + L^2 - S^2)^2}{2J^2L^2} : \frac{((J + L)^2 - S^2)(S^2 - (J - L)^2)}{4J^2L^2}. \qquad (8)$$

The factors in the numerator of the second term are to be replaced, according to wave-mechanics, by P(J) . Q(J), equation (5). For the numerator of the first term we substitute

$$R(J) = J(J + 1) + L(L + 1) - S(S + 1). \qquad (8a)$$

Instead of (8) we first write, omitting the factor 2JL in the numerator,

$$I_p : I_a = \frac{R \,.\, R}{JL} : \frac{P \,.\, Q}{2JL}. \qquad (8b)$$

Finally we change this in a manner similar to that used in passing from (4) to (6) into

$$\left.\begin{aligned} I_a &= \frac{P(J)Q(J - 1)}{2JL} \\ I_p &= \frac{R(J)R(J - 1)}{2JL} + \frac{R(J + 1)R(J)}{2(J + 1)L} \end{aligned}\right\} \qquad (9)$$

We again assert that these expressions satisfy the summation rules if we take J to stand for the *greater* of the two numbers, between which the transition occurs each time.

To prove this we consider the general scheme of a multiplet of this type, again assuming $L > S$:

Scheme II, Multiplet L → L

L+S	I_p	I_a					
L+S−1	I_a	I_p	I_a				
L+S−2		I_a	I_p				
L−S+2					I_p	I_a	
L−S+1					I_a	I_p	I_a
L−S						I_a	I_p
J	L+S	L+S−1	L+S−2		L−S+2	L−S+1	L−S

The J-values now run both in the horizontal rows and in the vertical columns from $J_{max} = L + S$ to $J_{min} = L - S$. The I_p's lie in the principal diagonal, the I_a's to the right and left of it.

The intensity sums for one of the middle horizontal rows or middle vertical columns of the quantum number J assume the common form

$$I_a(J + 1) + I_p(J) + I_a(J). \quad . \quad . \quad . \quad (10)$$

Substituting in (9) we obtain

$$\frac{P(J)Q(J-1) + R(J)R(J-1)}{2JL} + \ldots,$$

where the . . . denote that the same expression is to be added once again with J + 1 in place of J. Calculation shows that all terms which contain S(S + 1) destroy each other and that the denominator 2JL cancels out. In this way we obtain for the above fraction 2(L+1)J and for the fraction denoted by . . . 2(L + 1)(J + 1), that is, all in all,

$$2(L + 1)(2J + 1).$$

That is to say, we get *proportionality with the quantum weight in every horizontal row and vertical column.* This also remains valid for the ends of the scheme and for L < S, thanks to the automatic appearance of the zeros.

The above treatment of the intensity problem of multiplet lines appeared simultaneously from three quarters.*

* R. de L. Kronig, Zeits. f. Physik, **31**, 885 (1925); A. Sommerfeld and H. Hönl, Sitzungsber. d. Preuss. Akad., 1925, p. 141; H. N. Russell, Nature, **115**, 835 (1925); Proc. Nat. Acad., **11**, 314 (1925). The most important application of these formulæ was given by Russell, who determined the percentages with which the elements occurred in the sun from the intensity of their multiplets; cf. Astrophys. Journ., **70**, 11 (1929).

A first consequence of the equations (9) concerns the special case $L = S$. Then $J_{min} = 0$ and the last field of the diagonal in Scheme II corresponds to the *transition* $J = 0 \to J = 0$ which, as we know (cf. p. 424) *is forbidden*. Actually, by equation (8*a*), $R = 0$ for $L = S$ and $J = 0$; consequently, by (9) we also have $I_p = 0$ [we must note that the factor J cancels out in the denominator in this process, since it occurs in R(J − 1) as well as in R(J)].

A second consequence concerns the combination of two S-terms, that is, the transition $L = 0 \to L = 0$. *We shall show that this is also forbidden*. For then $J_{min} = J_{max} = S$ and the Scheme II reduces to a single field I_p. This I_p becomes

$$I_p = \frac{R(S)}{2L}\left(\frac{R(S-1)}{S} + \frac{R(S+1)}{S+1}\right).$$

To work this out we first set $J = S$, which makes the L of the denominator in the first factor cancel out, and then set $L = 0$, which makes the first factor equal to $\frac{1}{2}$ and the second equal to 0.

To give the simplest possible example of the formulae (9) we consider the combination PP′ in the doublet system, in which the indefiniteness u remained on p. 525. Here $S = \frac{1}{2}$, $L = 1$, $J = \frac{3}{2}$ in the first and $J = \frac{1}{2}$ in the second horizontal row (but the transition I_a must also be calculated here with the greater $J = \frac{3}{2}$. From (9) we find that

$$\text{First row}: \quad I_p = \tfrac{10}{3}, \quad I_a = \tfrac{8}{3}.$$
$$\text{Second row}: \quad I_p = \tfrac{16}{3}, \quad I_a = \tfrac{8}{3}.$$

Hence if we omit the common factor $\frac{8}{3}$ the scheme runs

$$\begin{vmatrix} 5 & 1 \\ 1 & 2 \end{vmatrix}.$$

The u that occurred earlier has thus come out with the value 1.

In this example and in all those that follow we recognise the contrast between parallel and anti-parallel on the one hand and indifferent transitions on the other hand. The relative weakness of the latter confirms quantitatively our *qualitative intensity rule* which has so often been used; cf. for example, pp. 245 and 422.

As a second example we consider the group DD′ in the triplet system, for which measurements of Ca lines have been made by Dorgelot The scheme in this case is as follows, expressed in per cent. of the strongest line:

	$^3D'_3$	$^3D'_2$	$^3D'_1$	
$^3D_3$	100 (100)	12·5 (13·6)		(113·6)
$^3D_2$	12·5 (13·6)	56 (56)	12·0 (13·6)	(83·2)
$^3D_1$		12·0 (13·6)	36·2 (37)	(50·6)
	(113·6)	(83·2)	(50·6)	

The bracketed numbers are Dorgelo's experimental values. They agree excellently with the theoretical values which are written above them. The observed intensity-sums are given along the edges of the scheme.

A Cr-multiplet $^5D\,^5D'$ measured by Frerichs * agrees equally well with theory. Since $J_{min} = 2 - 2 = 0$ here, the *last* field shows in the principal diagonal the intensity zero (which agrees with the decree forbidding $J = 0 \rightarrow J = 0$); the field *before the last* then shows a very weak intensity, weaker than the neighbours on the right and on the left, which thus constitutes an exception to our qualitative intensity rule.

But it may also happen that the intensity in this field becomes directly equal to zero. We read off the condition for this from (9): I_p vanishes if $R(J) = 0$; in the field before the last $J = J_{min} + 1$. We need only consider the case $S > L$, $J_{min} = S - L$. (We would find no solutions for $J_{min} = L - S$.) Then $J_{min} + 1 = S - L + 1$. By (8*a*) we therefore require that

$$0 = (S - L + 1)(S - L + 2) + L(L + 1) - S(S + 1).$$

This gives

$$\begin{aligned} \text{for } L = 2 \;\ldots\; S &= 3 \\ L = 3 \;\ldots\; S &= \tfrac{7}{2}, \end{aligned}$$

i.e. ^7D- and ^8F-terms. (Other values of L give no possible solutions.) A combination of two such terms leads to the intensity in the diagonal decreasing to zero but increasing again at the last point. Experiment confirms this; cf. the Fe-multiplet $^7D\,^7D$ given on p. 465.

For multiplets of the type $L \rightarrow L - 1$, equation (6), it will suffice if we write down the simple example PD in the triplet system. We see that the intensities in the diagonal (parallel transitions) decrease uniformly from the left above to the right below; the intensities that follow on the left (indifferent transitions) are weaker, and the weakest is the anti-parallel transition (satellite of the second order, on the left below):

	$^3P_2$	$^3P_1$	$^3P_0$	
$^3D_3$	63			63
$^3D_2$	$\frac{45}{4}$	$\frac{135}{4}$		45
$^3D_1$	$\frac{3}{4}$	$\frac{45}{4}$	15	27
	75	45	15	

We next proceed to discuss the problem of the *intensities of the Zeeman components*, first in a *weak field*. Here all the J-levels are split up into $(2J + 1)$ individual levels. The statistical weight of

* Zeits. f. Physik, **31**, 305 (1925).

any such level numbered by its magnetic quantum number M is to be set equal to one. We shall then have to formulate the summation rules in such a way that the sum of the intensities of the transitions that start out from a fixed M is proportional to one, that is, is independent of M. We must not overlook here that the word intensity here stands for the intensity actually *emitted* as contrasted with the intensity which is *observed* in a definite direction of the field (cf. below). For observation perpendicular to the field we obtain, by refining * the *assertions* derived from the Correspondence Principle, the following formulæ which are also confirmed by wave-mechanics (A = observed intensity):

$$\left.\begin{array}{lll} \text{Transition} & \mathrm{J} \to \mathrm{J},\ \mathrm{M} \to \mathrm{M} : \mathrm{A} \sim \mathrm{M}^2 & \\ & \mathrm{M} \to \mathrm{M} \pm 1 : \mathrm{A} \sim \tfrac{1}{4}(\mathrm{J} \pm \mathrm{M} + 1)(\mathrm{J} \mp \mathrm{M}); & \\ & \mathrm{J} \to \mathrm{J} + 1,\ \mathrm{M} \to \mathrm{M} : \mathrm{A} \sim (\mathrm{J} + \mathrm{M} + 1)(\mathrm{J} - \mathrm{M} + 1) & \\ & \mathrm{M} \to \mathrm{M} \pm 1 : \mathrm{A} \sim \tfrac{1}{4}(\mathrm{J} \pm \mathrm{M} + 1)(\mathrm{J} \pm \mathrm{M} + 2); & \\ & \mathrm{J} \to \mathrm{J} - 1,\ \mathrm{M} \to \mathrm{M} : \mathrm{A} \sim (\mathrm{J} + \mathrm{M})(\mathrm{J} - \mathrm{M}) & \\ & \mathrm{M} \to \mathrm{M} \pm 1 : \mathrm{A} \sim \tfrac{1}{4}(\mathrm{J} \mp \mathrm{M} - 1)(\mathrm{J} \mp \mathrm{M}). & \end{array}\right\} (11)$$

The way in which these formulæ are derived (cf. Note 7 (*f*)) shows that they hold for any arbitrary coupling in a weak field.

We shall now verify the summation rule, say, for the last case: $\mathrm{J} \to \mathrm{J} - 1$. In doing so we must note that $\mathrm{M} \to \mathrm{M}$ gives a linear vibration parallel to the direction of the field, which is seen completely when transversely observed, but that if $\mathrm{M} \to \mathrm{M} \pm 1$ we have a left circularly and a right circularly polarised vibration perpendicular to the field. We see only a half of the intensity really emitted in the case of each of the latter vibrations when transversely observed; for every circular vibration may be regarded as consisting of the superposition of two independent mutually perpendicular linear vibrations of equal amplitude. One of these linear vibrations may be taken to lie in the direction of observation—so that it is not seen at all—whereas the other is then perpendicular to the direction of observation and is seen completely. Hence in the formulæ (11) which refer to the *observed* intensity A we must *double* the transitions $\mathrm{M} \to \mathrm{M} \pm 1$, to obtain the intensity J that is *actually emitted*.

The sum of the three possible transitions $\mathrm{M} \to \mathrm{M}$, $\mathrm{M} \pm 1$ that start from a fixed M is

$$\begin{aligned} \Sigma \mathrm{I} \sim \tfrac{1}{2}(\mathrm{J} - \mathrm{M})(\mathrm{J} + \mathrm{M} + \mathrm{J} - \mathrm{M} - 1) + \tfrac{1}{2}(\mathrm{J} + \mathrm{M})(\mathrm{J} - \mathrm{M} + \mathrm{J} + \mathrm{M} - 1) \\ = \mathrm{J}(2\mathrm{J} - 1), \end{aligned}$$

a value which is in fact independent of M.

To compare these results with those obtained experimentally †

* H. Hönl, Zeits. f. Physik, **31**, 340 (1925). The formulæ obtained according to the Correspondence Principle are given in Note 7 (*f*).

† W. C. van Geel, Zeits. f. Physik, **33**, 836 (1925), according to a photograph taken by Dorgelo.

we consider the lines $^3P_{2,1,0} - {}^3S$ of Mg (wave-lengths 5167, 5172, 5183 Å.) as an example. In the following schemes we see the intensities calculated according to (11): it must be noted that these equations give only the intensity ratio of the Zeeman components of any one J-combination among themselves. If we wish to compare Zeeman components of *different* J-combinations with each other—as is done in the measurements here under consideration—we must work out the total intensity of each J-line and bring these total intensities of the "field-free" lines into relationship by means of the rules derived for them. In our case we have $^3P_2{}^3S_1 : {}^3P_1{}^3S_1 : {}^3P_0{}^3S_1 = 5 : 3 : 1$. Hence in the following schemes we have therefore immediately to multiply the intensity calculated from (11) by such factors that the ratio just mentioned comes out for the *total* intensity. The experimental intensity is given in round brackets.

TABLE 56

λ 5167, $^3P_0 - {}^3S_1$

	J = 1		
M =	1	0	−1
J = 0, M = 0	2 (23)	4 (46)	2 (23)

λ 5172, $^3P_1 - {}^3S_1$

	J = 1		
M =	1	0	−1
1	6 (75)	3 (38)	
0	3 (38)	0 (0)	3 (33)
−1		3 (34)	6 (71)

λ 5183, $^3P_2 - {}^3S_1$

	J = 1		
M =	1	0	−1
2	6 (76)		
1	6 (75)	3 (37)	
0	1 (?)	8 (100)	1 (?)
−1		3 (37)	6 (72)
−2			6 (76)

The lines accompanied by a note of interrogation were not found. The agreement between theory and experiment is very good. In λ 5172 there is a weak asymmetry in the experimental intensities, which is due to the incipient Paschen-Back transformation.

The Correspondence Principle enables us to understand why the summation-rules are valid. If we assume pure Russell-Saunders coupling the spin-frequencies do not appear appreciably in the Fourier expression for the electric atomic-moments (for the smallness of the

mutual action (LS) see also Note 7 (*e*)), but only the frequencies corresponding to the l_i, . . . L. If we consider a definite multiplet the quantum transition in the l_i's and L's is the same for all lines of the multiplet, or, expressed in terms of the correspondence principle: the lines all belong to the same frequency in the Fourier expansion of the electronic motion, that is, to the same Fourier coefficient. According to the Correspondence Principle this determines the probability of transition for quanta and is therefore independent of the level of the initial term from which we start out. Hence all that enters into the question of the intensity is the number of atoms "in transition." Now we may set the number of atoms that are in a definite state proportional to the statistical weight of the state, if there is thermodynamic equilibrium (cf. also what is said below about the Boltzmann factor). If we consider the magnetically resolved levels the weight of each of these levels is equal to one, but for the J-levels, which are not influenced by the magnetic field, the weight is equal to $(2J + 1)$. The number of transitions from a definite initial state and hence the intensity of the quantum transitions in question is proportional to the number of atoms that happen to be in the state of the initial level. Thus the intensity of all the lines that come from one initial level is proportional to the weight of this level; but this states nothing else than what is asserted by the summation rules. What holds for the initial level also holds, in the case of thermodynamic equilibrium, for the final level. We also see from this line of reasoning that, as on p. 534, it is the intensity actually *emitted* that counts in the summation rules and not the intensity observed in a particular direction.

From this discussion, based on the Correspondence Principle, it follows that the summation rules of the "field-free" lines in the form above given is linked up with normal coupling. Inter-combination lines are then forbidden theoretically (cf. Note 7 (*e*)). If they actually occur with appreciable intensity in the spectrum the summation rules must be stated more broadly. For this purpose we imagine a definite electron configuration to be given and assume the mutual action between the quantum-vectors to be so small that all terms of this configuration form a group which is separated by an appreciable distance from other configurations. We may then, as an approximation, disregard the mutual actions in the Fourier expression. If we now consider a combination of all levels of the first configuration n with a second m we again obtain as before one and the same Fourier coefficient for all transitions between the two configurations, but now we have in general several levels, say r_J, with the same J-value in one configuration. The total number of atoms in all levels having a fixed J is, by an argument analogous to that used above, proportional to $r_J(2J + 1)$ and the total intensity of all the lines that start out from a fixed J is likewise proportional to $r_J(2J + 1)$.

A simple example is given by the two-electron system in the transition $(sd) \rightarrow (sp)$; with approximately normal coupling (sp) gives the terms $^3P_{2,1,0}$, $^1P_1$; (sd) gives $^3D_{3,2,1}$, $^1D_2$. Table 57 shows the possible lines and the intensity sums at the right-hand side and at the lower edge. In calculating the latter the weights of the middle rows had to be doubled; the absolute value was chosen in such a way that the intensity of the strongest line $^3P_2{}^3D_3$ has the same value as in the table on p. 533.

TABLE 57

	$^3P_2$	$^3P_1 + {}^1P_1$		$^3P_0$	
$^3D_3$	$^3P_2{}^3D_3$				63
$^3D_2 + {}^1D_2$	$^3P_2{}^3D_2$	$^3P_1{}^3D_2$	$^1P_1{}^3D_2$		90
	$^3P_2{}^1D_2$	$^3P_1{}^1D_2$,	$^1P_1{}^1D_2$		
$^3D_1$	$^3P_2{}^3D_1$	$^3P_1{}^3D_1$,	$^1P_1{}^3D_1$	$^3P_0{}^3D_1$	27
	75	90		15	

Hence in general in the case of spectra of the second vertical column we must take into consideration not only the triplet lines but also the inter-combinations and the singlet lines. An interesting inference may be drawn from the above scheme if we allow the intensities of the inter-combinations to decrease again to zero, as occurs approximately for the lighter elements of this vertical column. Then there only remains, besides the combination $^3P\,{}^3D$, whose intensity we know for this case from our earlier discussion, the singlet line $^1P\,{}^1D$. Comparison with the table on p. 533 shows that for this line the intensity 45 results (in our arbitrary measure relatively to the intensities of the triplet lines). In a similar way we may also compare the ratio of the intensities of various multiplicities with each other for other configurations, if the inter-combinations are weak.

Our extended form of the summation rules holds, as its mode of derivation shows, for any arbitrary coupling; only the restriction concerning the mutual position of the configuration must not be lost sight of. The latter condition is well fulfilled in the lower terms of the neon spectrum. For the combination

$$2p^5 3p \rightarrow (2p^5 3s)$$

some measurements by Dorgelo * are available. We use Paschen's notation for the terms (cf. p. 472) and add the inner quantum number J in brackets. $(2p^5 3s)$ gives the Paschen s-terms $s_2(1)$, $s_3(0)$, $s_4(1)$, $s_5(2)$; $(2p^5 3p)$ gives the p-terms $p_1(0)$ to $p_{10}(1)$, cf. the following table. In the spaces of the table we have the observed intensities, at the lower edge and on the right we have first the observed intensity-sums of the vertical columns and the horizontal rows and then the sums

* H. B. Dorgelo, Physica, 5, 90 (1925).

calculated according to the extended summation rules, where we have taken as the basis for the calculation observations with the line $p_9(3) - s_5(2)$. For this reason its intensity has been bracketed in the case of the calculated values. Observation and theory agree well in their results.*

TABLE 58

	$p_1(0)$	$p_3(0)$	$p_2(1)$	$p_5(1)$	$p_7(1)$	$p_{10}(1)$	$p_4(2)$	$p_6(2)$	$p_8(2)$	$p_9(3)$	ΣI_{obs}	ΣI_{calc}
s_3 (0)			10·5	16	15	1					42·5	42·9
s_3 (1)	14	0·1	17	19·5	2	2	31·5	26	5		259·7	257·1
s_4 (1)	1	15	4	0·1	32·5	20	20·5	10	39·5			
s_5 (2)			9	3	10	20	17·5	34	34	100	227·5	214·3
ΣI_{obs}		30·1			181·6			218·0		100		
ΣI_{calc}		28·6			171·4			214·3		(100)		

Our assumptions contain the implication that the lines that are compared together do not lie far apart. If this is not the case the intensity ratios must be subjected to further corrections. In the first place, we may no longer set the number of the atoms in a quantum state proportional to the statistical weight of the state but we must in general, as on p. 513, take into account the difference in the Boltzmann factors, in accordance with the equation

$$\frac{N_i}{N} = \frac{p_i e^{-E_i/kT}}{\sum_i p_i e^{-E_i/kT}},$$

where N_i = the number of atoms in the i^{th} state, p_i its weight, E_i its energy, N the total number of atoms. If the energies E_i of the initial level are widely different this correction must obviously be considered; but it decreases with increasing temperature. On the other hand, the second correction is independent of the temperature. To find a basis for it we must go back a little way. Fourier analysis resolves the electronic motion into a superposition of independent individual vibrations, that is, of linear oscillators, whose amplitudes are given by the corresponding Fourier coefficients. If we wish to determine the intensity emitted by an individual vibration of this kind we must form, in accordance with equation (3) on p. 25,

$$\text{emitted energy} = \frac{2}{3}\frac{e^2}{c^3}\overline{\dot{v}^2} \quad . \quad . \quad . \quad (12)$$

* G. R. Harrison remarks in a paper to appear in Phys. Rev. that the Dorgelo values have not been reduced by means of the factor ν^4 (cf. p. 539). The reason that the above table nevertheless satisfies the summation rule must be that the reduction factors essentially compensate each other.

where the horizontal bar denotes the time mean. In the case of the oscillator the displacement x from the position of rest is given by, say,

$$x = a \sin \omega t.$$

Then equation (12) becomes

$$\text{emitted energy} = \frac{1}{3}\frac{e^2}{c^3}\omega^4 a^2. \quad . \quad . \quad . \quad (13)$$

In (13) we must imagine a to be replaced by the Fourier coefficients, and instead of the classical frequency $\omega = 2\pi\nu$ we must imagine the frequency $2\pi\nu_{quant}$ given by the quantum transition—a step which is confirmed by wave-mechanics. Hence it follows that the intensity of a line is proportional to the fourth power of its frequency. Formerly we set the probability of transition and hence the intensity directly proportional to the square of the Fourier coefficient and inferred that if the coefficients were equal the probability of transition was the same. We now see that this is permissible only if the frequencies of all lines of the combination in question are in sufficiently close agreement. In the general case we must " correct " for equal frequency by means of the factor ν^4.

We must mention that the problem of the intensity decrease of the lines within a series may be treated only by means of wave-mechanics, and likewise the problem of the intensity ratios of different series.

§ 10. Resolution of Multiplet Terms. Hyperfine Structure

From the discussion in Chapter VI, § 5, we see that the " natural " field-free resolutions of the multiplet terms in the case of *one* outer electron arise according to the model from the magnetic interaction (ls), cf. pp. 331 and 337. We must now use this idea to draw quantitative conclusions and we shall do so at once for the general case of any arbitrary number of outer electrons.

Let us consider, say, the mutual action between the l_i and the s_i of an individual electron.

This mutual action arises because the electron, being an electric charge, in its orbital motion generates a magnetic field $\mathbf{H}$, which we may symbolise by means of the quantum number l_i of the orbital motion. The field acts on the magnetic moment μ, which is assigned to the spin moment of momentum of the electron (quantum number $s_i = \frac{1}{2}$), and causes a precession of s_i about l_i.

By Chapter VI, § 5, μ has the value of one magneton. We obviously obtain as the contribution to the total energy

$$W(l_i s_i) = \overrightarrow{(\mathbf{H}\mu)}, \quad . \quad . \quad . \quad . \quad (1)$$

where the horizontal bar denotes that the time mean is to be taken. $\mathfrak{H}$ is in the direction of the quantum-vector $\vec{l}_i$ and may be set proportional to it, likewise $\vec{\mu}$ to the quantum-vector $\vec{s}_i$, so that we may write (1) in the form

$$W(l_i s_i) = a_i(\overrightarrow{l_i s_i}) = a_i \mid l_i \mid \mid s_i \mid \overline{\cos\,(\overrightarrow{l_i s_i})}. \quad . \quad . \quad (2)$$

The factor of proportionality a_i is calculated in Note 12 and comes out as

$$a_i = \frac{R\alpha^2 hc Z_{eff,i}^4}{n_i^3 l_i (l_i + \frac{1}{2})(l_i + 1)}, \quad . \quad . \quad . \quad (3)$$

where R denotes Rydberg's number (in cm^{-1}), α the fine-structure constant, $Z_{eff,i}$ the nuclear charge that acts on the i^{th} electron in its orbit, which is assumed to be hydrogen-like (for penetrating orbits a somewhat different expression applies, cf. Note 12), and n_i is the principal quantum number of the electron.

Besides the mutual actions (l_i, s_i) there are clearly others between the l_i of the i^{th} electron and the s_k of the k^{th} electron. In Note 12 we show that these mutual actions may in general be neglected (that is, if the nuclear charges are not too small).

Hence we obtain altogether as the total energy of interaction (l, s) of all the outer electrons (the closed shells make no contribution), by summing up over terms of the form (2):

$$W(l, s) = \Gamma = \sum_i a_i \mid l_i \mid \mid s_i \mid \overline{\cos\,(\overrightarrow{l_i s_i})}. \quad . \quad . \quad (4)$$

We have therefore now to calculate these time means. If we assume the coupling to be of the Russell-Saunders type the $\vec{l}_i$'s combine into $\vec{L}$ and the $\vec{s}_i$'s to $\vec{S}$. To calculate $\cos\,(\overrightarrow{l_i s_i})$ it is simplest to consider the spherical triangles that are cut out of the unit sphere by the quantum vectors $\vec{l}_i$, $\vec{L}$, $\vec{s}_i$, $\vec{S}$. We obtain successively:

$$\cos\,(\overrightarrow{l_i s_i}) = \cos\,(\overrightarrow{l_i L})\cos\,(\overrightarrow{s_i L}) + \sin\,(\overrightarrow{l_i L})\sin\,(\overrightarrow{s_i L})\cos\,\alpha;$$
$$\cos\,(\overrightarrow{s_i L}) = \cos\,(\overrightarrow{LS})\cos\,(\overrightarrow{s_i S}) + \sin\,(\overrightarrow{LS})\sin\,(\overrightarrow{s_i S})\cos\,\beta,$$

where α is the angle at L in the spherical triangle $l_i s_i L$, and β the angle at S in the triangle $s_i LS$.

In forming the time mean for the second equation the second term in the right-hand side drops out because the three factors fluctuate independently of one another and because $\overline{\cos\,\alpha} = 0$. In the same way in the first term we may replace the mean value of the product

by the product of the mean values. Hence we have left: $\overline{\cos \overrightarrow{l_i s_i}} = \overline{\cos \overrightarrow{l_i L}}\ \overline{\cos \overrightarrow{s_i L}}$.

With the help of the second equation we finally obtain

$$\overline{\cos (\overrightarrow{l_i s_i})} = \cos (\overrightarrow{l_i L})\ \overline{\cos (\overrightarrow{s_i S})}\ \overline{\cos (\overrightarrow{LS})}, \quad . \quad . \quad (5)$$

where we may omit the bar over $\cos (\overrightarrow{LS})$ because the vectors L and S perform a uniform precession about one another, in which the $\cos (\overrightarrow{LS})$ is constant in time. From the vector triangle L, S, J we obtain, if we take into account the "wave-mechanical correction," that is, replace J^2 by $J(J+1)$ and so forth:

$$\cos (\overrightarrow{LS}) = \frac{J(J+1) - L(L+1) - S(S+1)}{2 \mid L \mid \mid S \mid}. \quad . \quad . \quad (6)$$

From (4), (5) and (6) it finally follows that

$$\left.\begin{aligned} \Gamma &= \frac{J(J+1) - L(L+1) - S(S+1)}{2} \cdot \sum_i a_i \frac{\mid l_i \mid}{\mid L \mid} \frac{\mid s_i \mid}{\mid S \mid} \overline{(\cos \overrightarrow{l_i L})}\ \overline{(\cos \overrightarrow{s_i S})} \\ &= \frac{J(J+1) - L(L+1) - S(S+1)}{2} \cdot A \end{aligned}\right\} \quad (7)$$

where we have used the abbreviation

$$A = \sum_i a_i \frac{\mid l_i \mid}{\mid L \mid} \frac{\mid s_i \mid}{\mid S \mid} \overline{\cos (\overrightarrow{l_i L})}\ \overline{\cos (\overrightarrow{s_i S})}. \quad . \quad . \quad (8)$$

According to our view, then, the resolution of a multiplet term is given by (7) and (8) for normal coupling. For, by (4), Γ represents the energy of interaction (calculated from a zero-level) which would correspond to the total energy *without* taking into account the interaction energy (4). From equation (8) we see that the resolution factor A does not depend on the inner quantum number J. Further, it follows from (7) that the multiplet term L, S is *regular*, if $A > 0$. Γ is then positive and has its greatest value for the greatest J which equals L + S; but since Γ represents an *energy*, the greatest value of Γ represents the greatest atomic energy, that is, the level which lies highest above the ground-state of the atom; thus, the term is *regular*. Conversely $A < 0$ results in *inverse terms*.

We find the physical meaning of the "zero-levels" just mentioned as follows. We add J as a suffix to the Γ and multiply each Γ_J by the quantum weight $(2J+1)$ of the associated J-level (cf. the previous §, p. 523) and sum up over all J's of the term L, S:

$$\left.\begin{aligned} \sum_{J_{min}}^{J_{max}} (2J+1)\Gamma_J &= \frac{A}{2}\{\Sigma(2J+1)J(J+1) \\ &\quad - (L(L+1) + S(S+1))\Sigma(2J+1)\} = 0 \end{aligned}\right\} \quad . \quad . \quad (9)$$

as a simple calculation shows. The zero-level is thus the *centre of gravity of the term* (L, S), as was only to be expected.

We may deduce still another result from (7). For this purpose we form the difference of two T-values that belong to the quantum numbers J and J − 1, but to the same L and S:

$$T_J - T_{J-1} = \tfrac{1}{2}\{J(J+1) - (J-1)J\}A = J \,.\, A. \quad . \quad (10)$$

*The intervals between neighbouring term-levels are, in the case of normal coupling, in the ratio of the greater of the two inner quantum numbers which belong to the corresponding levels. This is Landé's Interval Rule.** According to our method of derivation it holds for regular terms equally well as for inverse terms. We shall, in fact, find both kinds of terms represented in the following examples.

From the enormous material available we first give some examples for odd multiplicities. In the first place, we must mention the triplets of the alkaline earths and of the Zn-Cd-Hg-series, in which the Interval Rule was first observed. Let us consider the Ca-terms which we used on p. 425 to illustrate the structure of multiplets. The p-term gives 105·8 : 52·3 = 2 : 1·02; by (10) we should expect theoretically 2 : 1. The p'-term gives 86·8 : 47·1 = 2 : 1·08; theoretically it should be 2 : 1 again.

In the D-terms d and d' we expect 3 : 2; empirically

$$21{\cdot}7 : 13{\cdot}9 = 3 : 1{\cdot}94 \text{ for } d,$$
$$40{\cdot}0 : 26{\cdot}7 = 3 : 2{\cdot}00 \text{ for } d'.$$

As other examples we give: a ^{3}G-term ($3d^7 4p$) of Fe, for which

$$\Delta\nu_{54} : \Delta\nu_{43} = 388{\cdot}4 : 311{\cdot}8 = 5 : 4{\cdot}01 \; ; \quad \text{theoretically } 5 : 4.$$

Then the term ^{5}D($3d^6 4s^2$) of Fe (ground-term of the spectrum):

$$\Delta\nu_{43} : \Delta\nu_{32} : \Delta\nu_{21} : \Delta\nu_{10} = 416{\cdot}0 : 288{\cdot}2 : 184{\cdot}2 : 90{\cdot}0$$
$$= 4 : 2{\cdot}77 : 1{\cdot}77 : 0{\cdot}86 \; ; \text{ theoretically } 4 : 3 : 2 : 1.$$

As exemplifying the septet system we may take the ^{7}F-term ($3d^4 4s4p$) of Cr:

$$\Delta\nu_{65}:\Delta\nu_{54}:\Delta\nu_{43}:\Delta\nu_{32}:\Delta\nu_{21}:\Delta\nu_{10} = 222{\cdot}9 : 189{\cdot}0 : 153{\cdot}6 : 116{\cdot}8 : 78{\cdot}5 : 39{\cdot}6$$
$$= 6 : 5{\cdot}08 : 4{\cdot}12 : 3{\cdot}14 : 2{\cdot}10 : 1{\cdot}06 \; ; \text{ theoretically } 6 : 5 : 4 : 3 : 2 : 1.$$

* A. Landé, Zeits. f. Physik, **19**, 112 (1923). W. Heisenberg took the first step towards formulating it generally. He generalised the empirical result that the intervals between the ^{3}P-terms often bear the ratio 2 : 1 to each other, by extending it to the other triplet-terms in the sense of the Interval Rule. Instead of the above mode of formulation: "they are in the ratio of the greater of the two inner quantum numbers" . . . we may say more comprehensively: "they are in the ratio of the arithmetic mean of the quantum weights that belong to the levels in question.

Of the even multiplicities we take

$^4G(3d^34s4p)$ of V : $\Delta\nu_{\frac{11}{2}\,\frac{9}{2}} : \Delta\nu_{\frac{9}{2}\,\frac{7}{2}} : \Delta\nu_{\frac{7}{2}\,\frac{5}{2}} = 192{\cdot}9 : 157{\cdot}7 : 122{\cdot}0$
$= 11 : 9{\cdot}00 : 6{\cdot}95$; theoretically $11 : 9 : 7$.

$^3P(3d^54s4p)$ of Mn : $\Delta\nu_{\frac{9}{2}\,\frac{7}{2}} : \Delta\nu_{\frac{7}{2}\,\frac{5}{2}} = 173{\cdot}71 : 129{\cdot}18 = 9 : 6{\cdot}70$;
theoretically $9 : 7$.

We have intentionally not always chosen the most favourable examples in order to show that the Interval Rule often holds only approximately. Like our qualitative intensity rule, however, on p. 422 it is in many cases a valuable guide for finding and interpreting multiplets, and, what is at least as important, it gives (in addition to the Zeeman effect, the intensity of the lines, and so forth, a criterion, particularly simple to apply, of the *validity of the Russell-Saunders coupling.*

In terms with very wide separations the Interval Rule is obeyed less and less, as we may see in the spectra on the right-hand edge of the periodic system (inert gases, Co, Ni and homologues) and in the lower horizontal rows of the periodic system. For example, the low ^3D-term ($3d^94s$) of the Ni-spectrum has instead of the theoretical ratio $3 : 2$ in reality $675{\cdot}00 : 833{\cdot}29 = 3 : 3{\cdot}70$ for $\Delta\nu_{32} : \Delta\nu_{21}$. In the lower horizontal rows Ba and Hg already show in many low terms systematic deviations from the Interval Rule and the discrepancies rapidly become greater as we pass towards the right in the periodic system in these series. In these cases the scheme of the normal coupling clearly becomes invalidated ; strictly speaking, there is no longer a physical meaning in assigning S- and L-values to the terms. We are then dealing with transition stages between Russell-Saunders and (jj)-coupling, for which it is indispensable to use wave-mechanics.* Furthermore, we must point out that the Interval Rule no longer holds for the *lightest elements.* The reason for this is different from before : on account of the small nuclear charge the interactions which we may symbolise by $(l_i s_k)$ also become appreciable here (cf. p. 540). The anomalous interval ratios of the triplets of He, Li^+ and perhaps also of Be may also be explained in this way, as Heisenberg has shown by wave-mechanical calculations with the help of the vector model.† He calculates the resolutions for the term $^3P(1s2p)$ of helium-like spectra and finds in He an inverse term (order of sequence from below upwards : $^3P_2$, $^3P_1$, $^3P_0$) with the theoretical interval ratio : $\Delta\nu_{21} : \Delta\nu_{10} = 2 : 19$, in Li^+ a partially inverted term (order of sequence $^3P_1$, $^3P_2$, $^3P_0$) with the interval ratio $\Delta\nu_{21} : \Delta\nu_{10} = 2 : 5$. Empirically it had been suggested for some time ‡ that the helium ^3P-term just

* Cf. W. V. Houston, Phys. Rev., **33**, 297 (1929) ; S. Goudsmit, *ibid.*, **35**, 1325 (1930).

† W. Heisenberg, Zeits. f. Physik, **39**, 499 (1926).

‡ Cf. p. 599 of the fourth German edition of the present book, and J. C. Slater, Proc. Nat. Acad., **11**, 732 (1925).

mentioned might be inverted with a far too small $\Delta\nu_{21}$-resolution; the exact measurement of the combination $2^3S - 2^3P$ by Houston,* which was carried out to test Heisenberg's calculation, has shown that this view is correct.

Hitherto we have used equation (7) only to obtain information about the ratios of the resolutions; but it also gives the *absolute magnitude of the resolutions*, if we know the factor A. We do this for the case of two electrons; † the general case has been treated by Goudsmit.‡ We give the essential parts of his treatment a little later.

We again assume normal coupling, so that equations (7) and (8) hold. The cosine that occurs in (8) is obtained from the triangle of the vectors l_1, l_2, L and s_1, s_2, S, respectively:

$$\cos(\vec{l_1}\vec{L}) = \frac{|l_1|^2 + |L|^2 - |l_2|^2}{2|l_1|\,|L|}; \quad \cos(\vec{s_1}\vec{S}) = \frac{|s_1|^2 + |S|^2 - |s_2|^2}{2|s_1|\,|S|} \tag{11}$$

Corresponding equations hold for $\cos(l_2L)$, $\cos(s_2S)$. Taken all together, we have || by (8) and (11):

$$\left.\begin{aligned} A = a_1 \frac{l_1(l_1+1)+L(L+1)-l_2(l_2+1)}{2L(L+1)} \cdot \frac{s_1(s_1+1)+S(S+1)-s_2(s_2+1)}{2S(S+1)} \\ + a_2 \frac{l_2(l_2+1)+L(L+1)-l_1(l_1+1)}{2L(L+1)} \cdot \frac{s_2(s_2+1)+S(S+1)-s_1(s_1+1)}{2S(S+1)} \end{aligned}\right\} \tag{12}$$

Since $s_1 = s_2 = \frac{1}{2}$ the second factors reduce in each case to $\frac{1}{2}$. Moreover, we may use equation (12) in a more general sense, as Goudsmit and Humphreys have shown (*loc. cit.*). For if we may regard the atom schematically as composed of a "core" and a "radiating electron," that is, if the additional electron does not change the coupling of the configuration that is already present and is known from the spark spectra, we may substitute for l_1, s_1 the values of the spark term on which the arc term with the quantum numbers L, S is built and for l_2, s_2 the values of the "radiating electron."

We use equation (12) in order to explain the symmetrical structure (mentioned on p. 424) of the pp'-groups of Mg and of its analogous spark spectra Al II to Cl VI. The p-term—in the systematic notation $(3s3p)^3$ P—has $l_1 = 0$. $l_2 = 1$, $s_1 = s_2 = \frac{1}{2}$, L = 1, S = 1 and gives $A = a_p \cdot \frac{1}{2}$, where a_p denotes the a-value of the $3p$-electron. For the p'-term, which is $(3p^2)^3$P, we have $l_1 = l_2 = 1$, the other quantum numbers being as before; further, we have $a_1 = a_2 = a_p$ by (3), since for equivalent electrons Z_{eff} is the same, as well as n_i, l_i. From (12) it again follows that $A = a_p \cdot \frac{1}{2}$. From (7) we see directly that on account of the equality of the A-values the Γ's become equal for

* W. V. Houston, Phys. Rev., **29**, 749 (1927).
† Cf. S. Goudsmit and C. J. Humphreys, *ibid.*, **31**, 960 (1928).
‡ S. Goudsmit, *ibid.*, **31**, 946 (1928).
|| Cf. S. Goudsmit and C. J. Humphreys, *loc. cit.*

both terms because in each case we are dealing with the same term-character, that is, because J, L, S all coincide in value ; consequently the two ^{3}P-terms have theoretically the same resolutions.* It has already been mentioned on p. 424 that this is also the case experimentally.

For the Γ's there is a similar Permanence and Summation Law as for the g-values (cf. pp. 486 and 499). To arrive at the Permanence Law first we imagine the atom to be subjected to a *weak magnetic field*—weak in the sense that it does not appreciably disturb the coupling between the vectors. The interaction of the l_i's and s_i's then remains unperturbed, and the magnetic field produces only a uniform precession of J and hence of the whole vector-frame about the axis of the field.

Thence it follows first that Γ retains the same value in the weak field as in the field-free case and hence, in particular, does not depend on the magnetic quantum number M, and, secondly, that the action of the magnetic field consists only in superposing on the unperturbed term resolution a small resolution which arises from the precession mentioned by correspondence considerations and is determined, as we already know, by the Landé g-formula in the case of normal coupling (see § 6). We have used both results implicitly in § 6. In the case of normal coupling Γ has the value (7), otherwise the value (4).

Henceforth we again assume *normal coupling* and pass on to the case of the *strong field*. The coupling (L, S) is then disturbed and the vectors L, S take up their positions in the magnetic field independently of one another. The $\cos\,(\overrightarrow{LS})$ in (5) is, however, no longer constant ; rather, we obtain, from considerations similar to those applied above, from the spherical triangle of vectors L, S, H,

$$\cos\,(\overrightarrow{LS}) = \cos\,(LH)\,\cos\,(SH) \quad . \quad . \quad . \quad (13)$$

On account of $\cos\,(LH) = \dfrac{M_L}{|L|}$ and $\cos\,(SH) = \dfrac{M_S}{|S|}$ it follows from (4), (5) and (13) that

$$\Gamma_{strong} = M_L M_S \,.\, A, \quad . \quad . \quad . \quad (14)$$

where A is defined by (8) as before.

The following *Permanence Law* † now holds for Γ: *the sum taken over all Γ's of a term (L, S) is independent of the field-strength for a fixed M.* In symbols

$$\sum_J \Gamma_{weak} = \sum_{M_S} \Gamma_{strong} \;(M \text{ fixed}) \quad . \quad . \quad . \quad (15)$$

* First proved by R. A. Sawyer and C. J. Humphreys, Phys. Rev., **32**, 582 (1928). Cf. also K. Bechert, Zeits. f. Physik, **69**, 735 (1931).

† A. Landé, *ibid.*, **19**, 112 (1923).

We may verify this law in a way similar to that used in dealing with the Permanence Law of the g-values in § 7 of the present chapter. But we shall here only explain the law (15) by means of the same example as was used on p. 504,* namely the triplet D-term.

In Table 59 we give in the upper half for convenience the Γ-values for the weak field divided by A, according to equation (7), arranged in order of M-values. They are all equal for a fixed J (cf. above).

TABLE 59. ^{3}D, L = 2, S = 1

M =	+3	+2	+1	0	−1	−2	−3	
J = 3	2	2	2	2	2	2	2	Weak field (normal coupling)
2		−1	−1	−1	−1	−1		
1			−3	−3	−3			
$\Sigma\Gamma$/A =	2	1	−2	−2	−2	1	2	
M_S = 1	2	1	0	−1	−2			Strong field (normal coupling)
0		0	0	0	0	0		
−1			−2	−1	0	1	2	

In the middle row of the table we have the sums of these Γ/A's, which belong to the same M. In the lower half of the table we have written down the values of Γ/A for a strong field, in accordance with (14), arranged horizontally in order of M and vertically in order of the M_S-values. We see that the sum of these Γ/A's taken over M_S agrees with the value of the middle row in the case of each M.

If we now apply the Permanence Law to fields of such strength that all couplings, even those between the l_i's and s_i's become disturbed,† then (see Note 12) by subsequently proceeding to the limiting case where the field is zero we may derive a *summation rule* that corresponds to the g-summation rule on p. 486. This rule states that *in a given electron configuration the sum over all Γ's that belong to a fixed value of J is independent of the coupling.*

As Goudsmit (*loc. cit.*) has shown, the *Permanence Law* also gives us a means of determining the individual Γ's at least for *equivalent electrons and pure Russell-Saunders coupling.* Here we shall give only his results. In the case of equivalent electrons all the a_i's are equal (cf. p. 544); we may therefore in this case express all Γ's by the a of a single electron of the shell in question. According to Goudsmit we obtain for the splitting-factors A and the total resolution of the terms for equivalent p- and d-electrons the values given in Table 60.

* The Γ-resolution that is now to be given for the strong field superimposes itself as a fine-structure in the Paschen-Back resolution there considered.

† The sum must then be taken over all Γ's that belong to a fixed M in a given electron configuration.

TABLE 60. Normal Coupling

Configuration	Terms (without Singlets and S-Terms)	Resolution Factor A	Total Resolution
p^1, — p^5	^2P	a	$\frac{3}{2}a$
p^2, — p^4	^3P	$\frac{1}{2}a$	$\frac{3}{2}a$
p^3	^2D, ^2P	0	0
d^1, — d^9	^2D	a	$\frac{5}{2}a$
d^2, — d^8	^3F	$\frac{1}{2}a$	$\frac{5}{2}a$
	^3P	$\frac{1}{3}a$	$\frac{1}{2}a$
d^3, — d^7	^4F	$\frac{1}{3}a$	$\frac{5}{2}a$
	^4P	$\frac{1}{3}a$	$\frac{1}{3}a$
	^2H	$\frac{1}{5}a$	$\frac{11}{10}a$
	^2G	$\frac{7}{10}a$	$\frac{27}{10}a$
	^2F	$-\frac{1}{6}a$	$-\frac{7}{12}a$
	$^2D + {}^2D$	$\frac{1}{5}a$	$\frac{5}{6}a$
	^2P	$\frac{2}{3}a$	a
d^4, — d^6	^5D	$\frac{1}{4}a$	$\frac{5}{2}a$
	^3H	$\frac{1}{10}a$	$\frac{11}{10}a$
	^3G	$\frac{7}{20}a$	$\frac{27}{10}a$
	$^3F + {}^3F$	$\frac{1}{12}a$	$\frac{7}{12}a$
	^3D	$-\frac{1}{15}a$	$-\frac{5}{12}a$
	$^3P + {}^3P$	$\frac{1}{3}a$	$\frac{3}{2}a$
d^5	sämtlich	0	0

If the same term occurs several times in one configuration, such as the ^2D-term in the case of d^3, we can specify only the sum of the A's and of the total resolutions: this is denoted by using the notation $^2D + {}^2D$ in the second column. The notation of the first column is intended to denote that, for example, the configuration d^7 gives the same A-values and total resolutions as d^3, but with the reverse sign. The table shows that *in general z electrons that are present in a shell having a fixed l give the same terms with the same resolutions as z electrons that are wanting in this shell except that the terms are inverted in the latter case, if they were regular in the former, and vice versa.* It is easy to see in a general way how this " gap law " comes about. This gives us a precise formulation of the rule given on p. 451, that the terms are regular in the first half of a period and inverted in the second half. Actually most of the A's in the first half of the periods are positive according to Table 60; but there are exceptions; * the terms $^2F(d^3)$ and $^3D(d^4)$ are, theoretically, inverted terms. This is confirmed experimentally by the Ti II-spectrum in the case of $^2F(d^3)$.

* The inverted terms of some alkali-spectra (such as Cs-F-terms, etc.), which were mentioned on p. 451, do not come among these exceptions. They may be explained, according to a communication received from E. Fermi, on wave-mechanical grounds. The partially inverted terms that occasionally occur in spectra (cf. the above-mentioned Li^+-term ^3P) occur in passing from the normal to the (*jj*)-coupling and in very light elements for the reasons mentioned on p. 543.

In the middle of the periods, where there are just as many missing electrons as there are electrons present, the calculation gives zero resolutions. At anyrate we should expect theoretically unusually small resolutions. Examples of this are also to be found in the spectra.

A no less surprising assertion of the table, which has also been confirmed experimentally in many cases, is that the resolutions of the various terms of one configuration bear simple ratios to each other. Thus the total resolutions of the terms d^2 should bear the ratio 7 : 3 to one another.

Hyperfine Structure

It has been experimentally established that many lines (and hence many terms) of a spectrum, after analysis into multiplets (i.e. the "fine" structure), still possess a narrow, and often complicated, "hyperfine" structure. As all three quantum numbers L, S, and J of the external electronic system of the atom have been used to explain the multiplet structure of the spectrum, it is necessary to enlist the aid of the nucleus to supply a new degree of freedom to account for this further resolution.

From the time of Bohr's theory of the hydrogen spectrum (see p. 92) it has been known that the mass of the nucleus is involved in the expression for Rydberg's constant, so that the isotopic constitution of the element was thought to be responsible for the hyperfine structure. Rydberg's constant, for an atom with nuclear mass M, is given by

$$R_M = R \Big/ \left(1 + \frac{\mu}{M}\right),$$

where μ denotes the rest mass of the electron. Hence as R_M occurs as a multiplier in all the series formulæ (cf. p. 89) it is obvious that, on this simple theory, all the spectral lines of an element with n isotopes should possess identical n-fold structures, in which the component due to the heaviest isotope lies on the side of highest frequency. Such a theory served to explain qualitatively the doublet structures of certain lines in the spectrum of neon * (isotopes 20 and 22). Later observations on the arc spectra of H (isotopes 1 and 2), Li (6 and 7), Cl (35 and 37) and K (39 and 41) can be similarly explained; the measured displacements, however, are usually greater than those obtained by calculation. It was obvious from the first that such a theory was totally unable to explain any of the other hyperfine structures, since, on the one hand, the effect should become immeasurably small for the heavier elements, and, on the other, the various lines of an element (e.g. Hg) are found to possess widely different structures, in regard to number, relative intensity and arrangement of components.

* H. Hansen, Naturwiss., **16**, 163 (1927).

Also if the different components of a line arose from different isotopes, the Zeeman effects of the components should be mutually independent, as has been found for Ne alone.

The first step in the unravelling of the problem was made by Pauli * who assigned a quantised nuclear spin, $I\frac{h}{2\pi}$, to the nucleus. This rotation, through the associated magnetic moment, $Ig(I)$, interacts with the total momentum, J, of the external electronic system and produces, except when $J = 0$, a further subdivision of the individual multiplet terms. If the magnetic moment of the nucleus be small compared with that of the electron, then the new subdivision of the terms will be small compared with that due to electron spin—the " fine " structure. Actually in a given spectrum the ratio (1 : 2000) of " hyperfine " to " fine " (i.e. multiplet) separation is of the same order as m_{elec} : $M_{nucleus}$.

In consequence of the magnetic coupling between the nuclear spin I and the total momentum J of the outer electrons, they will both precess uniformly about their resultant F, *the total momentum of the whole atom*. This interaction between J, I and F is identical with that between L, S and J, so we may take over the results (see pp. 539 *et seq.*) derived for the multiplet separations simply by replacing L, S and J, by J, I and F, respectively. The possible values of F are therefore

$$|\, I + J \,| \geqslant F \geqslant |\, I \sim J \,| \quad . \quad . \quad . \quad (16a)$$

There are therefore

$$\left.\begin{array}{l} (2J + 1) \text{ . . . when } J \leqslant I \\ \text{or} \quad (2I + 1) \text{ . . . when } J \geqslant I \end{array}\right\} \quad . \quad . \quad . \quad (16b)$$

hyperfine levels corresponding to the F-values allowed by (16*a*). The possible transitions giving rise to hyperfine structure components are subject to the selection rules:

$$\left.\begin{array}{c} \Delta F = \mp 1 \text{ or } 0 \\ \text{with } F = 0 \rightarrow F = 0 \text{ " forbidden "} \end{array}\right\} \quad . \quad . \quad (17)$$

By means of considerations similar to those on pp. 540, 541 it is possible to show from our vector model that the interaction energy, W(I, J), between the nucleus and the outer electrons is of the form

$$\begin{aligned} W(I, J) &= A(J) \,.\, |\, I \,| \,.\, |\, J \,| \,.\, \cos (I\, J) \\ &= \tfrac{1}{2}A(J)\{F(F + 1) - I(I + 1) - J(J + 1)\} \end{aligned} \quad . \quad . \quad (18)$$

The problem is now to relate A(J), which governs the magnitude of the hyperfine separations, to the various constants characteristic of the particular energy-level, to atomic constants and to the nuclear magnetic moment. In the general case, A(J) is the resultant of the

* W. Pauli, Naturwiss., **12**, 741 (1924).

action of a number of valency electrons—each independently coupled to the nuclear spin and thus contributing, in differing amounts, to the total hyperfine separation of the term—so we may write

$$A(J) = \Sigma a_n \cdot f(l_n, s_n, j_n) \quad . \quad . \quad . \quad (18a)$$

where $f(l, s, j)$ is a known * function of the various quantum numbers of the n^{th} electron. The summation (18*a*) implies a knowledge of the coupling involved in the multiplet structure of the spectrum. In the special case of two *s*-electrons,

$$A(J) = \tfrac{1}{2}a_1 + \tfrac{1}{2}a_2.$$

No exact calculation of the factors a_n (18*a*) has yet been made, but Goudsmit † gives formulæ, both for *s*- and "non *s*-" electrons, which he considers suitable to give "fair approximations for the nuclear magnetic moments." The formulæ, which are too complicated to reproduce here, would seem to be reasonably accurate for penetrating electrons, into which class the $p_{\frac{1}{2}}$-electron must be placed. The general result is that wider structures are to be expected for penetrating than for non-penetrating orbits.

The separation between two hyperfine levels, F and (F + 1), is given by the difference of two expressions (18), so

$$\delta\nu = [A(J)] \times [(F + 1)] \quad . \quad . \quad . \quad (18b)$$

The last equation shows that the Landé Interval Rule (p. 542) when expressed in terms of F instead of J, should hold for hyperfine separations. This has been very generally confirmed by experiment, and conversely the application of the rule in cases of unknown nuclear moment often leads to a trustworthy value. Similarly, if one again replaces L, S, and J by J, I and F respectively, the intensity formulæ of pp. 527 *et seq.* are applicable. In all reported structures the intensities of the various components are in good qualitative agreement with theory.

In order to show how analysis of the hyperfine structure of a spectrum leads to the value of the nuclear moment, we will briefly consider the example of the Bi-I spectrum. The term-analysis ‡ shows that a number of multiplet levels (defined by L, S and J) are still further subdivided. By the use of (16*b*), together with the fact that terms with J-values up to $\frac{5}{2}$ have a (2J + 1)-fold hyperfine structure, we see that $I \geqslant \frac{5}{2}$. The application of the interval rule (18*b*) to the term system so obtained shows that I must lie between 4 and 5. The Bi-I hyperfine structures are particularly suitable for Zeeman effect measurements ‖ which, in the light of the discussion in the next paragraph, point unambiguously to the value $I = \frac{9}{2}$.

* S. Goudsmit and R. F. Bacher, Phys. Rev., **34**, 1499 (1929).
† *Ibid.*, **43**, 636 (1933).
‡ S. Goudsmit and E. Back, Zs. f. Phys., **43**, 321 (1927).
‖ E. Back and S. Goudsmit, *ibid.*, **47**, 174 (1928).

On account of the small separation of the hyperfine structure components it is possible with practical field-strengths (up to 43,000 gauss) to obtain a more or less complete Paschen-Back effect; for the case of the complete transformation we can easily calculate the line pattern to be expected. The vectors I and J orient themselves, independently of one another, to the field H, with components M_I and M_J along the H-direction. (We now replace the M of the earlier discussion by M_J.) The total magnetic interaction, W, is then

$$W = \{M_I \cdot g(I) + M_J \cdot g(J)\}\nu_{norm} \cdot hc + A(J) \cdot |I| \cdot |J| \cos(I, J). \quad (19)$$

The expression in the square brackets arises from the interaction between the nucleus and the field, on the one hand, and between the outer electrons and the field, on the other. ν_{norm} is the normal Lorentz frequency $\frac{eh}{4\pi mc}$, H, where m is the electronic mass. We may, however, neglect the first term within the bracket compared with the second (as $g(I) : g(J) \simeq 1 : 2000$).

The last term in (19) corresponds to the interaction (expressed in (18)) between the nucleus and outer electrons, and, though small compared with that in $g(J)$, may not be neglected since it assumes different values corresponding to the various possible values of cos (IJ). By a method similar to that on p. 545, we obtain $A(J) \cdot M_I M_J$ for this term, and hence (19) becomes

$$W = M_J \cdot g(J)\, \nu_{norm} \cdot hc + A(J) \cdot M_I M_J \quad . \quad . \quad (20)$$

M_I may assume any of the $(2I + 1)$ values from $-I$ to $+I$, therefore each Zeeman level becomes subdivided into $(2I + 1)$ levels. The selection and polarisation rules are as before, except that M_L and M_S are replaced by M_J and M_I respectively, and in particular M_I may not change in the Paschen-Back effect. In consequence of (20) each Zeeman line splits up into $(2I + 1)$ components, i.e. *one can deduce the nuclear moment from the number of hyperfine components of the Zeeman lines.* In this manner Back and Goudsmit found the value $I = \frac{9}{2}$ for Bi, and at the same time *proved definitely the existence of a magnetically coupled nuclear moment.* Later Zeeman effect measurements have been made to confirm the values of the nuclear moments of Tl ($I = \frac{1}{2}$) and Re ($I = \frac{5}{2}$).

The above theory of nuclear moments explains completely the experimental results in the spectra of Bi, Pr, La, Mn, I, Br, Cs, Na, Re, Cu, Ga, As, V and Ta, and it is noteworthy that the nucleii of all these elements have odd mass-numbers. The theory fails, however, when applied to elements consisting of "odd" and "even" isotopes. As Schüler and Brück * first showed for Cd (isotopes: 110, 112, 113, 114, 115, 116) the hyperfine structures in such elements can

* H. Schüler and H. Brück, Zs. f. Phys., **56**, 291 (1929).

only be explained if the odd isotopes have nuclear moments, while the even isotopes have $I = 0$.* Hence the multiplet terms of the even isotopes are not further subdivided into hyperfine levels and so give rise to an intense unresolved component in the midst of the hyperfine pattern due to the odd isotopes. This naturally made a consistent analysis, along the lines developed above, impossible. When this "foreign" line, which falls in the optical "centre of gravity" of the hyperfine pattern of the odd isotopes, is neglected, it is found that the structure so obtained is in remarkable agreement with the requirements of the theory. A similar effect has been reported for Ba, and measurements of the Zeeman effect show that the even isotopes have no nuclear magnetic moments.

When an element possesses two (or more) odd isotopes it is usually found that the hyperfine patterns of both are identical and, in fact, the analysis proceeds just as if there were only one odd isotope present (e.g. Br, Re, Cu, Tl, Cd, Ba and Sn). This means that, in all these cases, the odd isotopes have the same nuclear spins and magnetic moments. In the lines of Ga, Rb, Sb and Xe, however, it is found that two complete hyperfine patterns, of different total breadths, exist independently, which shows that here the nuclei of the odd isotopes have nuclear magnetic moments of different absolute magnitudes. In Ga the two patterns differ only in scale, but in the other elements mentioned the arrangement of the components is not the same in both patterns, indicating that the nuclear spins may also differ. In all these cases the centres of gravity of the two hyperfine patterns fall together and also coincide with the unresolved line due to the even isotopes, if such be present.

In certain spectra (particularly those of the elements Hg, Tl and Pb) many of the line structures do not fit into the above scheme. The patterns due to the odd isotopes are still traceable to the action of nuclear moments, but the centres of gravity of the two patterns do not fall together. In addition, although due to the absence of nuclear moments, the lines arising from the even isotopes individually show no hyperfine structures, these unresolved lines no longer coincide as in the case of Cd, Ba, Sn, Sr, Kr and Xe, but are now recognisable as a number of equidistant lines in the midst of the hyperfine structure. The spacing of these lines is the same as the separation of the centres of gravity of the odd isotopes and their relative intensities are always in good agreement with Aston's results. The line structures which do not exhibit this "isotopic displacement effect" (and, in Hg and Pb, these form the majority) are much more simple and give the key to the analysis.†

* All that hyperfine structure measurements can show is that, for the even isotopes, the product $I \cdot g(I)$ is vanishingly small compared with the value for the odd isotopes. It is extremely probable, however, that $I = 0$.

† For a full discussion of the data see Kallmann and Schüler, "Ergebnisse der exakten Naturwiss.," **11**, 134-175 (1932).

TABLE 61

Atomic No. Z	Element	Mass Numbers	Nuclear Spin I	Nuclear Magnetic Moment
1	H	1	½ (B)	2·5
		2	1 (B)	
2	He	4	0 (B)	—
3	Li	6	0	0
		7		3·29
6	C	12	0 (B)	—
7	N	14	1 (B)	—
8	O	16	0 (B)	—
9	F	19	½	—
11	Na	23		2·0
13	Al	27	½	2·1
15	P	31	½ (B)	—
16	S	32	0 (B)	—
17	Cl	35	(B)	—
19	K	39	(B)	—
23	V	51	(?)	—
25	Mn	55		—
27	Co	59		—
29	Cu	63 and 65		2·5
30	Zn	66, 68, 70	0	—
		67		—
31	Ga	69		2·01
		71		2·55
33	As	75		0·9
35	Br	79, 81		
36	Kr	78, 80, 82, 84, 86	0	—
		83	7/2 or 9/2	—
37	Rb	85		1·3
		87		2·7
38	Sr	86, 88	0	0
		87		1·0
48	Cd	110, 112, 114, 116	0	0
		111, 113	½	0·6
49	In	115		5·4
50	Sn	116, 118, 120, 122, 124	0	0
		117, 119, 121	½	0·9
51	Sb	121		2·7
		123		2·0
53	I	127		—
54	Xe	124, 126, 128, 130, 132, 134, 136	0	
		129	½	
		131		
55	Cs	133		2·6
56	Ba	136, 138	0	0
		137	(?)	0·9
57	La	139		—
59	Pr	141		—
73	Ta	181		—
75	Re	187, 189		—
79	Au	197		1·8
80	Hg	198, 200, 202, 204	0	0
		199	½	0·55
		201		0·62
81	Tl	203, 205	½	1·8
82	Pb	204, 206, 208	0	0
		207	½	0·60
83	Bi	209		0·89

(B) indicates that the nuclear moment concerned has been determined solely from measurements in Band Spectra. The nuclear magnetic moments are given in terms of the "nuclear magneton," which is 1/1838th part of the Bohr magneton.

The above conclusions regarding the occurrence of isotopic shifts in the heavy elements receive convincing support from observations made by Kopfermann,* who compared the lines emitted by uranium lead (Pb_{206}) with those of ordinary lead (principally Pb_{206}, P_{207} and Pb_{208}). The lines of uranium lead are single and each was found to coincide with the component assigned to Pb_{206} in the hyperfine structure of the corresponding line emitted by ordinary lead.

The nuclear spins and magnetic moments that have been determined from hyperfine structure measurements are collected in Table 61, which also contains data obtained from the study of alternating intensities in Band Spectra. In conclusion it should be noted that the nuclear spins deduced from hyperfine structures are supported by recent observations on the polarisation of resonance radiation in the case of Cd and Hg.

* H. Kopfermann, Zs. f. Phys., **75**, 363 (1932).

CHAPTER IX

BAND SPECTRA *

§ 1. Historical Preliminaries. Uniform View of the Deslandres and the Balmer Term

THE first step towards ordering band spectra and representing them by formulæ was taken by Deslandres. The formulæ which he obtained by considering a great mass of empirical data became the model of all later developments, just as Balmer's formula became the archetype of all series expressions. Both formulæ were proposed in 1885. Schwarzschild provided the foundation on which the Deslandres formula could be built up from the quantum theory and the Bohr atom ; this foundation was contained in the same paper in which the Stark effect was first explained (cf. p. 300). Schwarzschild started from the idea proposed by N. Bjerrum † to account for the infra-red absorption spectra, according to which the various lines of the bands correspond to various rotational states of the absorbing gas molecules. We are indebted to Heurlinger ‡ for testing and elaborating Schwarzschild's theory by considering the empirical data. But his results received general notice only when Lenz || came to the same conclusions, partly going beyond Heurlinger, by taking a more comprehensive theoretical point of view. Detailed papers by Kratzer ¶ closed the first phase of the

* As in the previous edition Mr. Kratzer very kindly co-operated in the account here given, which is in no way intended to be exhaustive, as the material which has accumulated in the meantime would go far beyond the limits of this book. Rather, it does no more than sketch the most important features in the historical development of Band Theory from our present point of view. Detailed accounts are given in : *Atoms, Molecules and Quanta*, by Ruark and Urey (McGraw-Hill, New York, 1929), or in Vol. 21, *Handbuch der Physik*, by Mecke (Springer, 1929). Cf. also the Report by R. S. Mulliken in Review of Modern Physics, **2**, 60, 506 (1930) ; **3**, 89 (1931) ; also *Bandenspektren auf Experimenteller Grundlage*, by R. Ruedy (Fr. Vieweg & Son, Brunswick, 1930).

† Nernst Festschrift (1912), p. 90.

‡ T. Heurlinger, *Investigations into the Structure of Band Spectra, Dissertation*, Lund, 1918 ; also, Arkiv. för Matematik, Astron. och Fysik, **12** (1916) ; Phys. Zeits., **20**, 188 (1919) ; Zeits. f. wissenschaft. Photographie, **18**, 241 (1919).

|| W. Lenz, Verh. d. D. Phys. Ges., **21**, 632 (1919).

¶ Ann. d. Phys., **67**, 127 (1922) ; **71**, 72 (1923) ; Zeits. f. Phys., **3**, 289 (1920) ; **16**, 353 (1923) ; **23**, 298 (1924). Cf. also Enzykl. d. Math. Wiss., **5**, Part III, 822 (1925).

theory; these papers dealt with the terms of diatomic molecules and their combination.

In the more recent phase of development the problem of the dependence of band structure on the electron configuration has been successfully attacked. Mecke and, particularly, Mulliken, were able to apply the ideas of the multiplet theory of atoms to molecules. The electron spin of the total molecule determines the singlet-, doublet- . . . character of the band lines. We have an Alternation Law for molecules exactly as for atoms, according as the number of electrons in the molecule is even or odd. Besides the electron spin also the nuclear spin shows itself in the sequence of intensities of the band lines. Hund has set up general schemes for the coupling of the spin- and orbital moments of momentum with the line connecting the nuclei in the case of diatomic molecules (cf. § 7). We may associate ourselves with Mulliken in saying that the most important spectroscopic problems no longer lie at the present time in the realm of atomic spectra but in that of molecular spectra.

In view of the complexity of the data of observation it is not easy to get a provisional survey of the empirical facts. We must therefore restrict ourselves to a few remarks concerning the nomenclature chiefly and we shall reserve the outstanding experimental results for later when we deal with their theoretical interpretation.

Expressed generally, band spectra are characterised by the close sequence of their lines and by the accumulation of the latter at the so-called *edges* or *heads* of the bands. The name **band spectra** has its origin in the fact that when the dispersion of the resolving apparatus is small they give the impression of continuously tinted bands. Some of the bands are shaded off towards the red, some towards the violet end of the spectrum; that is, some have edges on the red side and some on the violet side (cf. the beginning of § 2 of Chapter II).

Band lines that seem to start out from the same edge are grouped together into a branch (*Zweig*). Deslandres used the word "series" instead of "branches" for band lines. Associated branches form one or more *partial bands* (or *single bands*). The fact that the partial bands overlap increases the difficulty of ordering and interpreting the band spectra. The edges of the bands recur in more or less regular sequence. Among the band edges we may distinguish, at least in the clearer cases, several *groups of bands*. So each group of bands unites a series of heads of bands to a higher single unit. Fig. 141 on page 572 exhibits a group of this kind consisting of five band heads and the partial bands that start out from them towards the violet and that overlap. The various groups of bands, too, follow in regular sequence and form a *system of bands*. The complete band configuration of a molecule consists not of one but in general of several systems of bands.

But the appearance of the bands, as here described, is in some circumstances distorted by the overlapping of the various groups;

this applies particularly to the so-called many lines spectra (cf. § 5). The bands that lie in the infra-red are distinguished by being particularly simple; in their case a single band is observed alone and the overlapping of groups of bands does not occur. We shall therefore first deal with these spectra in § 2.

Our first task is to obtain the ground factor of band emission, the Deslandres term, theoretically and to connect it with the ground factor of series emission, the Balmer term.

We start out from Bjerrum and Schwarzschild's idea of the rotator and do not concentrate, as on page 81, on the single point-mass that revolves at a fixed distance but more generally on a rigid body which rotates about a principal axis, which may serve us schematically as a molecule. Let its moment of inertia about the principal axis be called J and its angular velocity ω or $\dot{\phi}$. As we know, the moment of momentum and the kinetic energy are

$$\mathbf{M} = j\omega, \quad \mathrm{E}_{kin} = \frac{\mathrm{J}\omega^2}{2} = \frac{(\mathrm{J}\omega)^2}{2\mathrm{J}}.$$

Since the angle of rotation ϕ is a cyclic co-ordinate of the motion, the quantum condition for this rotator runs, analogously to equation (18) on page 82,

$$2\pi\mathbf{M} = mh \ (m \text{ integral}).$$

Hence it follows that

$$\mathrm{J}\omega = \frac{mh}{2\pi}, \quad \mathrm{E}_{kin} = \frac{h^2}{8\pi^2\mathrm{J}}m^2. \qquad . \quad . \quad . \quad (1)$$

We now distinguish between two cases.

I. The moment of inertia has a principal component J_0, which is independent of the rotation and is only inappreciably affected by the rotation (example: the earth and its flattening or a molecule that rotates about a principal axis).

II. The moment of inertia is produced by the rotation itself and vanishes when the rotation vanishes (example: a centrifugal governor or the Bohr model of the hydrogen atom).

In Case I we have for the m^{th} quantum state

$$\mathrm{J} = \mathrm{J}_0 + \Delta\mathrm{J}_m \ (\Delta\mathrm{J}_m \ll \mathrm{J}_0) \qquad . \quad . \quad . \quad (2)$$

In Case II we have in particular for the hydrogen model

$$\mathrm{J}_m = \mu a_m^2 = \mu a_1{}^2 m^4, \quad . \quad . \quad . \quad . \quad (3)$$

where μ denotes the electronic mass, a_m and a_1 the radius of the m^{th} or the first Bohr circle.

If we substitute the values (2) and (3) in (1) then in Case I an energy-value results which is essentially *proportional* to m^2 (that is, if we neglect $\Delta\mathrm{J}_m$):

$$\mathrm{E}_{kin} = \frac{h^2}{8\pi^2\mathrm{J}}m^2,$$

whereas in Case II the m^2 of the numerator cancels out with the denominator and we obtain an expression which is *inversely* proportional to m^2,

$$E_{kin} = \frac{h^2}{8\pi^2\mu a_1^2}\frac{1}{m^2}.$$

By dividing by h we pass from the energy to the "term." In this way we obtain in Case I the *Deslandres term :*

$$Bm^2, \quad B = \frac{h}{8\pi^2 J}, \quad . \quad . \quad . \quad . \quad (4)$$

and in Case II the *Balmer term :*

$$\frac{R}{m^2}, \quad R = \frac{h}{8\pi^2\mu a_1^2} = \frac{2\pi^2\mu e^4}{h^3} \quad . \quad . \quad . \quad (5)$$

The second form of the value R follows directly from the first by equation (7) on page 86.

Concerning the Balmer term we have yet to add that in the above calculation we have taken into account only the *kinetic* energy of the rotator ; if we now add the potential energy, only the sign of the term becomes changed (cf. Note 3).

In the case of the Deslandres term, however, a wave-mechanical correction has yet to be applied. As already remarked on page 82 wave-mechanics leads in the case of the rotator in space to half-integral and not integral quantising of the moment of momentum. Accordingly we set

$$m = j + \tfrac{1}{2}, \quad m^2 = j(j+1) + \tfrac{1}{4},$$

and write for the *Deslandres term*

$$B(j + \tfrac{1}{2})^2 \quad . \quad . \quad . \quad . \quad (6)$$

and

$$Bj(j+1) \quad . \quad . \quad . \quad . \quad (6a)$$

respectively. In each case we have

$$B = \frac{h}{8\pi^2 J}.$$

In (6*a*) we have omitted the constant term B/4, since if we assume J to be fixed this term would cancel out when we form the term differences. We have also to remark that the expression (6*a*) is in fact the primary form, precisely as in formulating the Zeeman effect in the preceding chapter, in so far as we are concerned with the pure rotator. If oscillations are taken into account at the same time (§ 2) the expression (6) is the natural one.

Hence we may regard the Deslandres term as just as fundamental as the Balmer term, the first applying to systems *with* an initial moment of inertia (molecules), the latter to systems *without* a moment of inertia originally (atoms).

§ 2. Infra-red Absorption Bands. Rotation and Rotation-Vibration Spectra

Let the system considered in the preceding section be a *diatomic molecule*, for example, H_2, HCl, N_2, and so forth. Let it consist of two point-like nuclei surrounded by electronic systems that are negligible as regards distribution of mass. The line which connects the nuclei is a principal axis of the system (*axis of the figure*) and so, indeed, is every axis perpendicular to the latter (*equatorial axis*). It was an axis of the latter type that we meant when we spoke in the previous section of rotations about a principal axis of the rigid system. The moment of inertia J refers to it. But the axis of the figure has a moment of inertia that is practically zero ; rotations about this axis do not come into consideration for purposes of quantising (cf. Note 3).

When we treated the system as rigid on page 557 this was only approximately correct. Although the nuclei have a position of equilibrium on the axis of the figure they may move away from it under the influence of their mutual repulsions and the attractions due to the electrons in the case of disturbances from the position of equilibrium, collisions, energy-absorption and so forth. They then execute vibrations about this position of equilibrium. We assume that the vibrations occur in *the direction of the axis of the figure*. In this sense every molecule represents not only a *rotator* but also an *oscillator*. If the vibrations are infinitely small, we have a *harmonic* oscillator ; let its frequency be ν_0. If the vibrations are regarded as finite, that is, if the nuclei move away from the immediate vicinity of their position of equilibrium to neighbouring parts of the field, then their mutual bond varies with the value of the amplitude. The oscillator is then *anharmonic* and, indeed, appreciably anharmonic because the quantised oscillation already has fairly considerable amplitudes.

We know from the specific heat of gases that the rotational degrees of freedom (and also the translational degrees of freedom) are in full action at normal temperatures but that the vibrational degrees of freedom do not make themselves observed in the case of the simpler gases such as N_2, O_2, HCl and so forth. From this we conclude that the rotational component of the motion is always present to a considerable degree but that the vibration component is often not excited into action, and occurs only when energy is absorbed.

For the present we assume our oscillator to be harmonic. Further, we make the general remark that the important feature for spectroscopic questions is not the actual presence of a vibration but rather the change in the state of rotation. In the theoretical treatment we adopt the standpoint of the *emission* process. The application of the argument to the *absorption* process is then immediately given.

Let j' be an arbitrary and j a fixed quantum number of rotation. Let j' characterise the initial state and j the final state of the rotation in the emissive process. Let us first consider exclusively the energy of rotation, that is, let us assume that any vibrations that happen to occur simultaneously do not change their state ; then we obtain from Bohr's hypothesis ($h\nu$ = difference of the energies) and from the formula for the Deslandres term, eqn. (6) or (6*a*) of the preceding section :

$$\nu = \mathrm{B}(j'(j'+1) - j(j+1)) \quad . \quad . \quad . \quad (1)$$

We call the wave-numbers ν given by this formula the pure *rotation spectrum*.

More generally we shall assume that the change of the rotational energy is associated with a change of configuration of the molecule, no matter whether it consists in a rearrangement of the electrons, as Schwarzschild had already assumed when dealing with visible spectra, or in a sudden change in the oscillatory state, as we must now assume for the infra-red spectra, or, finally, as we shall assume later, in the simultaneous occurrence of both processes.

Like the rotations the oscillations are divided into quanta, namely, as a first approximation into energy-elements $h\nu_0$ as in the case of the harmonic oscillator. After what has just been said about the thermodynamical behaviour of gases, only the smallest values 0 or 1 come into consideration for the oscillation quantum at normal temperatures, whereas any arbitrary values are available for the rotational quantum. Let v' be the quantum number * of the initial oscillation, v that of the final oscillation. The energy difference then amounts to

$$h(v' - v)\nu_0$$

and the contribution of this transition to the wave-number is

$$(v' - v)\nu_0.$$

By superposing this amount on the amount (1) of the rotation we obtain

$$\nu = (v' - v)\nu_0 + \mathrm{B}(j'(j'+1) - j(j+1)) \quad . \quad . \quad (2)$$

We call the possible waves given by this formula the *rotation-vibration spectrum*.

But the transition $j' \to j$ (quantum transition of several units) contradicts the selection principle (cf. Note 7), according to which the change in the rotation quantum number must equal ± 1 ; we shall take into account later the fact that in some circumstances the quantum change 0 is also permissible. For the oscillation quantum number we

* Following Mulliken we adopt the symbol v for the " vibration quantum."

shall also first consider only the quantum change ± 1, which corresponds to a rigorously harmonic oscillator. We therefore write

$$j' = j \pm 1 \quad \text{and} \quad v' = v \pm 1 \quad . \quad . \quad . \quad (3)$$

and obtain from (1) with $j' = j + 1$

$$\nu = 2B(j + 1) \quad . \quad . \quad . \quad . \quad (4)$$

and from (2) with $v' - v = 1$ and $j' = j + 1$ or $j' = j - 1$

$$\nu = \begin{cases} \nu_0 + 2B(j + 1), \text{ for } j' = j + 1 \\ \nu_0 - 2Bj, \text{ for } j' = j - 1 \end{cases} \quad . \quad . \quad (5)$$

The following remarks must be added. In the case of the rotation spectrum (4) the assumption $j' = j - 1$ would lead to negative wave-numbers; such wave-numbers belong to absorption processes and therefore drop out here where we are taking the standpoint of emission alone. Consequently we had only to take into account in (4) the possibility $j' = j + 1$ for the change in the rotation quantum number. In the same way in the case of the rotation-vibration spectrum (5) the assumption $v' - v = 1$ would yield negative wave-numbers. For in general the value of ν_0 predominates considerably over that of B.

The common content of equations (4) and (5) consists in the circumstance that they represent *equidistant sequences of lines* having the constant wave-number difference

$$|\Delta\nu| = 2B = \frac{h}{4\pi^2 J} \quad . \quad . \quad . \quad . \quad (6)$$

In the rotation spectra (4) we have *one* such system, in the rotation-vibration spectra we have *two* systems, one "positive" and one "negative branch."

The first line of the positive branch corresponds to the transition $1 \to 0$, that is, $j = 0$, and is therefore, on account of the first row of (5), given by $\nu = \nu_0 + 2B$; the first line of the negative branch belongs to the transition $0 \to 1$, and thus corresponds to $j = 1$ and hence, on account of the second row of (5), gives $\nu = \nu_0 - 2B$. The "zero line" $\nu = \nu_0$, that is, the central line between the first line of the positive branch and the first line of the negative branch is *not* represented.

We have examples of both kinds of bands in the infra-red absorption spectra (also observed as emission spectra by Paschen *). *Pure rotation spectra* have been observed in water-vapour by Rubens † and Eva v. Bahr.‡ The measurement of the HCl-bands under high dispersion by M. Czerny ‖ is particularly instructive. Rotation-vibration spectra, resolved into lines, have been investigated with

* Ann. d. Phys., **53**, 336 (1894). † Berliner Ber., 1913, p. 513.
‡ Verh. d. D. Phys. Ges., **15**, 731 and 1150 (1913).
‖ Zeits. f. Physik, **34**, 227 (1925).

great precision in the laboratory of Ann Arbor University by the methods devised by Randall. The first important results were obtained by Imes * for HF, HCl, HBr. The rotation spectra lie in the far infra-red at approximately 100 μ (the last measurements by Rubens go as far as 132 μ), the rotation-vibration spectra lie in the nearer infra-red (at several μ).

Between the rotation spectra and the rotation-vibration spectra of the same molecule there is a relationship which was anticipated by Bjerrum and proved to exist by Eucken : the vibration differences $\Delta\nu$ of successive lines are essentially equal in the two spectra. By equation (6) this denotes theoretically that the moments of inertia of the molecules do not markedly differ from one another in the two states.

Bjerrum's original interpretation of the infra-red bands, which preceded Bohr's theory, was of course different.

Bjerrum quantised not only the moment of momentum but also

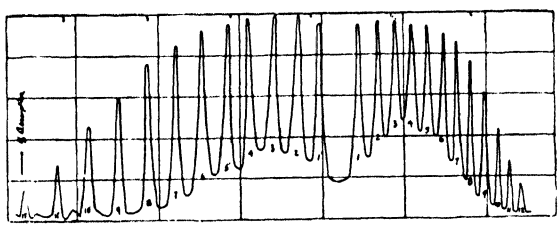


FIG. 137.—Rotation-vibration spectrum of HCl photographed by Imes with a reflection grating of high resolving power. The percentage absorption is plotted as ordinate, the angle of dispersion as abscissa. The middle of the band (the gap in the row of peaks) corresponds to $\lambda_0 = 3{\cdot}46$.

the energy of the rotating molecule ; furthermore, he assumed the absorption frequencies to be equal to the mechanical frequencies ; that is, he did not determine them from Bohr's frequency condition. In this way he obtained as the vibration difference of neighbouring rotation states

$$\Delta\nu = \frac{h}{2\pi^2 J}, \quad . \quad . \quad . \quad . \quad . \quad (7)$$

that is, twice our value (6) ; the same difference, involving the factor 2, is already familiar to us from page 82 where we compared the quantising of the rotator with that of the oscillator.

To pass on to the more detailed questions we consider Fig. 137, which is due to Imes (*loc. cit.*), and the diagram, Fig. 138, which goes with it. The gap in the succession of peaks in Fig. 137, the so-called

* Imes, Astrophys. Journ., **50**, 251 (1919). Further measurements with the same apparatus made by Colby and Meyer are recorded in Astrophys. Journ., **53**, 300 (1921), and by Colby, Meyer and Bronk, *ibid.*, **57**, 7 (1923).

zero-line, strikes the eye at once. Not only is there a peak missing here but the intensity of the continuous background and the size of the peaks are *clearly grouped around this gap*. This is to be understood as follows: the frequency of the different rotational states depends, in accordance with the Maxwell-Boltzmann distribution law, on the quantum number j, and the intensity of the absorption lines is proportional to the frequency of the initial state in question. Equal distances in the spectrum to the right and left of the zero line correspond to equal * values of j and hence exhibit absorption lines of approximately equal intensity. The change of intensity and the dependence of the intensity on the temperature (displacement of the two intensity maxima outwards being proportional to the square root of the absolute temperature, cf. Colby and Meyer, *loc. cit.*) correspond, apparently, perfectly with the Maxwell-Boltzmann law.

On account of the presence of the intensity minimum in the centre the rotation-vibration spectra were called "double bands," before they were successfully resolved, to distinguish them from the simple bands of rotation spectra, which exhibit no such gap.

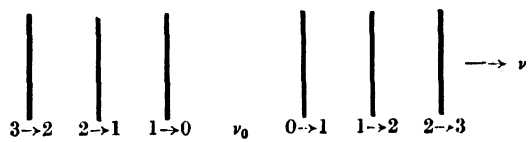


FIG. 138.—Relation of the lines to the transitions $j \to j \pm 1$ for absorption; for emission the transition arrows are to be reversed. The gap at ν_0 denotes that negative values of j are forbidden.

The explanation of the gap in Fig. 138 is given directly by the *wave-mechanical* expression for the Deslandres term (eqns. (6) and (6*a*) of the preceding section), but give rise to considerable difficulties from the point of view of the *older quantum theory* (eqn. (4) of the preceding section with an integral m). In the previous German edition of this book equation (4) was used with half-integral values of m, and this agrees with the transition to equation (6), as we see from the concluding remarks of § 1. Here, as everywhere else, the newer quantum theory leads without arbitrary assumptions to the hypothesis demanded by experimental results. The assumption (6) is confirmed most directly by the rotation bands of Czerny (see above), who could successfully represent the results of measurement only by a formula of the form of equation (4), with integral values for j (half-integral m, as Czerny remarks).

The equidistance between the successive band lines, which is

* More accurately, in absorption the n^{th} line of the positive branch denotes the transition $n - 1 \to n$, the n^{th} line of the negative branch denotes the transition $n \to n - 1$, cf. Fig. 138 and § 7B, where the above data are expressed more precisely.

expressed by equation (6), is only imperfect, as we see from Fig. 137 ; actually there is a *definite change*, namely a decrease of the distance $\Delta\nu$ in the direction of short waves. According to Kratzer,* the reason is as follows : whereas hitherto we simply superposed rotation and oscillation on one another they actually exert a mutual influence on one another. In consequence of the oscillation, the moment of inertia J of the molecule is no longer constant but variable. Its mean value is different from the original J when there is no oscillation. In consequence of the rotation, on the other hand, the position of equilibrium of the nuclei, and hence also—in the case of the *anharmonic* oscillator—the strength of the bond becomes changed.

Let W_{jv} denote the energy of the molecule which belongs to the rotation quantum j and the oscillation quantum v, and let W_{0v} correspondingly denote the energy of the rotationless molecule, the oscillation quantum being v. In the harmonic case we have (p. 80, eqn. (13*b*))

$$W_{0v} = (v + \tfrac{1}{2})h\nu_0.$$

In the anharmonic case we have, instead, an expansion of the form

$$W_{0v} = (v + \tfrac{1}{2})h\nu_0(1 - x(v + \tfrac{1}{2}) + \ldots) \quad . \quad . \quad (8)$$

which advances in powers of $x(v + \frac{1}{2})$. The small constant x depends on the law governing the anharmonic bond.

On the other hand, the formula for W_{jv} runs :

$$W_{jv} = W_{0v} - \alpha h(j + \tfrac{1}{2})^2(v + \tfrac{1}{2}) + \frac{h^2}{8\pi^2 J}((j + \tfrac{1}{2})^2 + \ldots) \quad . \quad (9)$$

The last term is the rotational energy, and corresponds to the Deslandres term. The dots in the bracket indicate that if we take into account centrifugal effects additional terms become added that apparently alter the moment of inertia J (cf. § 1, eqn. (2), where the corresponding change is indicated by ΔJ_m). The term immediately before the last expresses the interaction between rotation and oscillation. The coefficient α contains the moment of inertia J, and the vibration number ν_0. We must leave the derivation of (9) to Vol. II. In Note 13 we give the necessary preliminaries for the proof.

The explanation of the variation in the distances between the peaks of the absorption bands is now easy to give with the help of equation (9). We must note that by pp. 559 and 560 the initial value of v must be taken equal to zero in the absorption process. If we represent the same process as before as an emission process, we must set the final value of v in it equal to zero and the initial value equal to v. In the difference between the initial and the final state we obtain from (9),

* A. Kratzer, *loc. cit.*, Zeits. f. Physik (1920). We give Kratzer's result with the changes that result from the application of wave-mechanics.

if we write down only the terms that depend on j and use the earlier value of B, equation (4), p. 558 :

$$\left.\begin{aligned}\nu&=\frac{1}{h}(W_{j+1,v}-W_{j,0})=\ldots-\alpha[(j+\tfrac{3}{2})^2v+j+1]+2B[(j+1)+\ldots],\\ \nu&=\frac{1}{h}(W_{j-1,v}-W_{j,0})=\ldots-\alpha[(j-\tfrac{1}{2})^2v-j]-2B[j+\ldots]\end{aligned}\right\}\quad(10)$$

Hence we have for the distance between successive peaks :

$$\left.\begin{aligned}\Delta\nu &= 2B[1+\ldots]-\alpha[2(j+1)v+1],\text{ positive branch}\\ -\Delta\nu &= 2B[1+\ldots]+\alpha[2jv-1],\text{ negative branch}\end{aligned}\right\}\quad(10a)$$

The constant distance $|\Delta\nu|$ calculated in (6) is thus, on the one hand, as indicated by the brackets $[1+\ldots]$, slightly changed by the centrifugal actions of the rotation, and, on the other hand, and principally, is systematically *diminished* by the interaction between oscillation and rotation in the positive branch as j increases, but *increased* in the negative branch. It is just the latter that is shown in Fig. 137.

Whereas by equation (3) only changes of the oscillation quantum by 1 was possible for the harmonic oscillator, any arbitrary changes $\geqq 0$ are permissible for the *anharmonic oscillator* at present in question, corresponding to its overtone vibrations. Hence, it follows that in equation (5) the first term on the right-hand side is in general to be replaced by

$$\nu_0 v(1-(v+1)x+\ldots),\quad .\quad .\quad .\quad(11)$$

that is, for $v=1, 2, 3\ldots$ by

$$\nu_0(1-2x),\quad 2\nu_0(1-3x),\quad 3\nu_0(1-4x)\ldots$$

We infer this directly from equation (8) by assuming for the final state of the emission process (initial state of the absorption process) $v=0$ and for the initial state of the same process $v=1, 2, 3, \ldots$. From (11) we see two things : 1. Besides the "ground bands" hitherto considered, which also occur in the harmonic oscillator there are "overtone bands" of approximately twice, three times, . . . the wave-number of the centre of the band. 2. These wave-numbers are not exactly in the ratio $1:2:3\ldots$, but are out of tune according to the value of the quantity x.

Mandersloot (Dissertation, Amsterdam, 1914) appears to have been the first to look successfully for such overtone bands (in the case of CO). Next Brinsmade and Kemble * must be mentioned, who established the presence of an overtone band in measurements made by them with HCl. Hettner † has given a comprehensive tabulation of his own and other measurements of infra-red bands which have now in part been resolved into lines. We supplement them by results given by Clemens Schäfer and Max Thomas.‡ The following numbers denote

* J. B. Brinsmade and E. C. Kemble, Proc. Nat. Ac., **3**, 420 (1917).
† Zeits. f. Physik, **1**, 351 (1920). ‡ *Ibid.*, **12**, 330 (1923).

the observed wave-lengths of the " centres of the bands " (that is, essentially the zero-lines) expressed in terms of μ :

TABLE 62

	$\nu_0(1-2x)$	$2\nu_0(1-3x)$	$3\nu_0(1-4x)$
HF	2·52	1·27	
HCl	3·46	1·76	1·19
HBr	3·91	1·98	
CO	4·67	2·35	1·57

The band in HCl at $\lambda = 3{\cdot}46\ \mu$ which is here quoted, was exhibited in Fig. 137. The associated overtone band $\lambda = 1{\cdot}76\ \mu$, likewise first measured by Imes, is here given in a form that depends on the extraordinarily good measurements by Meyer and Lewin * (Fig. 139).

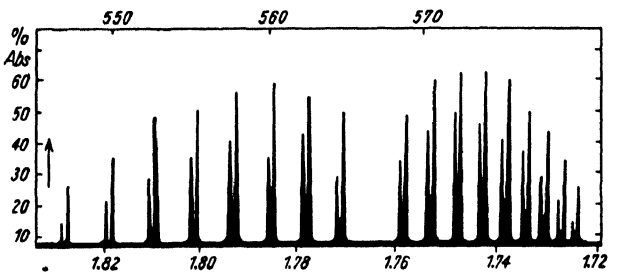


FIG. 139.—Overtone band of HCl at $\lambda_0 = 1{\cdot}76$ shown by the " silhouette-representation " of Meyer and Lewin. The height and breadth of the lines depend on quantitative measurements, but the background is levelled. The $\Delta\nu$-values on both sides of the gap are just as great as in Fig. 137, but the shift of $\Delta\nu$ is twice as great, both facts in accord with equation (10*a*) where $v = 1$ corresponds to Fig. 137 and $v = 2$ to Fig. 139.

Particular interest attaches here to the sharply separated *subsidiary maxima* (only just indicated in the original figure given by Imes). According to Loomis † and Kratzer ‡ they are explained by the isotopy of Cl_{35} and Cl_{37}! For, since the nuclear vibration ν_0 depends on the mutual binding, and the masses of the vibrating nuclei, and since the bindings are the same in the case of two isotopes, but the masses are different, we have two somewhat different values for ν_0, and hence two rotation-vibration bands that are somewhat displaced relatively to one another. The subsidiary maxima denote the band of Cl_{37} and are small compared with the principal maxima of the band

* Phys. Rev., **34**, 44 (1929). Cf. also for the theoretical evaluation W. Colby, *ibid.*, **34**, 53 (1929).

† F. W. Loomis, Astrophys. Journ., **52**, 248 (1920).

‡ A. Kratzer, Zeits. f. Physik, **3**, 460 (1920).

Cl_{35}, corresponding to the ratio 1 : 3 in which Cl_{37} and Cl_{35} occur quantitatively (cf. p. 141). Meyer and Lewin were also successful in proving the isotopic effect unambiguously in the ground-band at $\lambda = 3{\cdot}46\ \mu$, whereas it is not yet visible in Fig. 137, which was taken with a wider slit.

The difference between the two nuclear vibrations is obtained theoretically as follows. The formula for calculating the proper frequencies runs :

$$2\pi\nu_0 = \sqrt{\frac{f}{\mu}}.$$

Here f is the tightness of the binding, which is the same for both types of chlorine, and μ denotes, as in equation (3) on p. 91, the "resultant" mass of H and Cl, thus :

$$\frac{1}{\mu_{35}} = 1 + \frac{1}{35}, \quad \frac{1}{\mu_{37}} = 1 + \frac{1}{37}.$$

If we use $\delta\nu/\nu$ to denote the relative difference between the vibration frequencies of HCl_{35} and HCl_{37}, and $\delta\lambda/\lambda$ to denote correspondingly the relative wave-length difference, we obtain

$$\frac{\delta\nu}{\nu} = \frac{1}{2}\left(\frac{1}{35} - \frac{1}{37}\right) = \frac{1}{1295}.$$

Thus

$$\delta\lambda = -\frac{\delta\nu}{\nu}\lambda = -\frac{1{\cdot}76}{1295} \cdot 10^{-4}\ \text{cm.} = -13{\cdot}6\text{Å}. \qquad (12)$$

The negative sign denotes that the lines of Cl_{35} have the shorter wave-length, that is, that the peaks corresponding to Cl_{37} are superposed on them on the *longer wave* side ; this agrees with Fig. 139. The value of $\delta\lambda$ in (12) likewise agrees with the results of experiment in order of magnitude.* We have already referred on p. 142 to this beautiful spectroscopic confirmation of Aston's observations of isotopes.†

Whereas we have hitherto considered only $v = 0$, as the initial state in the absorption process, with rising temperature an increasing number of molecules will be in the state $v = 1$. Accordingly, an absorption band can then occur that corresponds to the transition $1 \rightarrow 2$ in the oscillation quantum number. One such band has actually been

* In Phys. Rev., **34**, 53 (1929), Colby gives an exact formula for the measurements of Meyer and Lewin. It is there shown that the isotope effect comes out not only in the oscillation term of the bands but also in the rotation term (on account of the different moments of inertia of the isotopes).

† R. S. Mulliken [Nature, **113**, 423, 489 (1924)] has described isotope effect in BO, SiN and the so-called Cu-bands, and has drawn inferences from them about the carriers of these bands. Cf. also the more recent papers by Birge, Mulliken and their pupils on isotopy in band spectra, in particular in O, N, C (Phys. Rev., 1929-31).

observed ; * it can be calculated beforehand from the absorption bands $0 \rightarrow 1$ and $0 \rightarrow 2$ by simple combination.

Lastly, we inquire in what other gases besides the halogen acids we may expect infra-red absorption bands that may be resolved into individual series by the means nowadays at our disposal. By equation (6) this is a question of the moment of inertia. Only if J is sufficiently small does $\Delta\nu$ become sufficiently great. In HCl the centre of gravity lies very close to the heavy atom Cl ; hence J becomes essentially equal to $m_H l^2$, where l denotes the distance between H and Cl. Hence we see immediately : in order that a sufficiently small J should occur *the molecule must contain only H-atoms besides the atoms that lie next to the axis.* This condition is fulfilled, for example, in CH_4 and NH_3. Actually, resolvable bands have been found in these two molecules that show themselves to be particularly simple ; in CH_4 they were found by Cooley † and in NH_3 by Schierkolk,‡ and Barker.‖ The simplicity is no doubt due to the fact that the H-atoms are arranged symmetrically about the heavy atom. The next molecule of this series, which would be the bridge to HF, is H_2O. But in H_2O the infra-red absorption bands are considerably confused. Hence we must infer that the two H-atoms do not lie diametrically with respect to the O-atom, as is also to be assumed from chemical data, so that we are here dealing with a triangular configuration which gives rise to three different moments of inertia.

§ 3. Visible Bands. Significance of the Head of the Band

To transfer our attention to the visible region we must add to the two transitions in the rotation and oscillation an electronic transition as a third factor, that is, we must add a change in the structure of the atoms or ions that constitute the molecule. The simultaneous occurrence of these three partial processes is demanded by the Correspondence Principle (cf. Note 7 (*g*)), at least for a non-polar molecule such as N_2.

Hence, in the initial and in the final state we are now dealing in a certain sense with different molecules, which differ by just the required change of configuration of their component parts. The result is that all constants that depend on the details of the molecular structure, in particular the moment of inertia J and fundamental frequency of the nuclear vibration ν_0, become different in the initial and the final state. We denote the values (analogously to j', j and v', v on p. 560) by J', J, ν'_0, ν_0, and so forth.

We first consider the rotation component, and proceed to obtain from it an understanding of the structure of a partial band in the

* Cf. Colby, Meyer and Bronk, *loc. cit.*, and also Colby, Astrophys. Journ., **58**, 303 (1923), who even at that time concluded that there must be " half-integral " values of j from the combination-relation.

† Phys. Rev., **21**, 376 (1923).

‡ Zeits. f. Physik, **29**, 277 (1924).

‖ Phys. Rev., **33**, 684 (1929).

visible region. Thus we form the difference of the Deslandres term, equation (6) in § 1, for the initial state (j', J') and the final state (j, J):

$$\frac{h(j'+\frac{1}{2})^2}{8\pi^2 J'} - \frac{h(j+\frac{1}{2})^2}{8\pi^2 J}. \quad . \quad . \quad . \quad (1)$$

and also add the contributions that result from the oscillation transition and the change of configuration in the electronic structure. Let ν_{el} be the contribution by the electronic transition, ν_{osc} the contribution by the oscillation transition, which we called $(v' - v)\nu_0$ under the simpler conditions at the beginning of the preceding section.

We distinguish the three cases (the nomenclature is that of Heurlinger):

$$\left.\begin{array}{ll} j' = j + 1 & \ldots \text{ R-branch,} \\ j' = j - 1 & \ldots \text{ P-branch,} \\ j' = j & \ldots \text{ Q-branch.} \end{array}\right\} \quad . \quad . \quad . \quad (1a)$$

In Note 7 (g) we prove that the third case must be added to the two first cases alone considered in the preceding section when an electronic transition occurs simultaneously. From (1) we obtain

$$\left.\begin{array}{ll} \text{R} & \nu = A + 2\bar{B}(j+1) + C(j+1)^2, \quad . \quad . \quad (2) \\ \text{P} & \nu = A - 2\bar{B}j + Cj^2, \quad . \quad . \quad . \quad . \quad . \quad (3) \\ \text{Q} & \nu = A + Cj + Cj^2. \quad . \quad . \quad . \quad . \quad . \quad (4) \end{array}\right.$$

The constants A, $\bar{B}$, C have the following significance:

$$A = \nu_{osc} + \nu_{el} + \tfrac{1}{4}C, \quad 2\bar{B} = \frac{h}{8\pi^2}\left(\frac{1}{J'} + \frac{1}{J}\right), \quad C = \frac{h}{8\pi^2}\left(\frac{1}{J'} - \frac{1}{J}\right). \quad (5)$$

For $J' = J$ (no electronic transition, case of the preceding section), C becomes equal to 0, $B' = B = h/8\pi^2 J$. The equations (2) and (3), as should be, then become transformed into the equations (5) of the preceding section, whereas equation (4) loses its meaning.

In Fig. 140 we have drawn the three parabolas (2), (3) (4); j is plotted on the axis of ordinates, ν on the axis of abscissæ. This kind of graphical representation appears to have been first used by Fortrat.* The parabolas are drawn continuously as far as the axis of abscissæ $j = 0$, and thence onwards partially dotted. The R-branch intersects the horizontal $j = -1$ at the point $\nu = A$; at the same point of axis of abscissæ the P-branch and the Q-branch intersect the horizontal line $j = 0$. We project the points of intersection of the parabola of the P-branch with the horizontals $j = 1, 2, \ldots$ on the axis of abscissæ. In this way we obtain in the lower strip of the figure the observable arrangement of the band lines ν of the P-branch. The lines that arise

* R. Fortrat, *Thèses* (Paris, 1914), p. 109. Cf. also G. Higgs, Proc. Roy. Soc. **54**, 200 (1893).

from the Q- and the R-branch and that would interpose themselves between the lines of the P-branch have been omitted for the sake of clearness.

In our figure it has been assumed that $C > 0$, that is, by equation (5) that $J' < J$. Hence in the P-branch a *band head* appears ; the band is " shaded off towards the red end." In the converse case $C < 0$, $J' > J$, the band head arises in the R-bands, because in the analytical representation of equations (2) to (4) in this case it is the R-band and

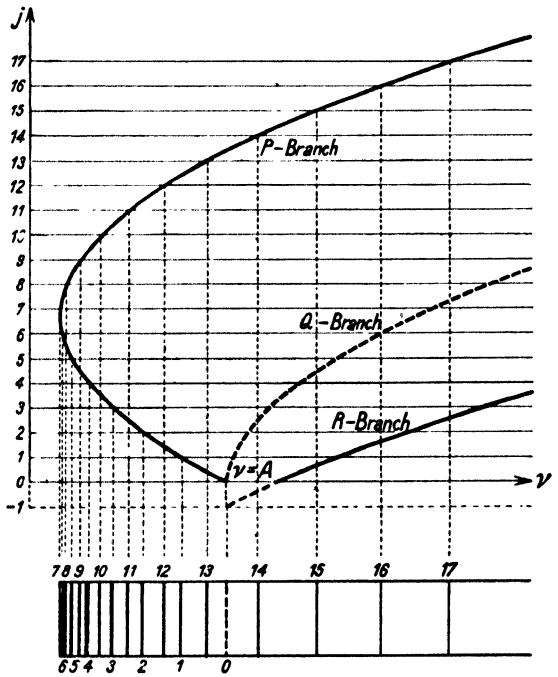


FIG. 140.—The parabolas (2), (3), (4) of the P-, Q- and R-branches for $C > 0$. The points of intersection of the P-branch parabola with the horizontal lines $j = 1, 2, 3 \ldots$ are projected on the ν-axis, and give directly the positions of the lines of the band. The lines of the Q- and R-branches could be obtained similarly.

not the P-band that exhibits a varying sign in the terms involving j. For small values of $j + 1$ the positive linear term first predominates and is compensated by the negative quadratic terms only when $j + 1$ has rather great values ; the corresponding parabola first runs towards greater ν's and later bends round to smaller ν's. In this case the band is shaded off " towards the violet." *

* H. Ludloff draws conclusions about the constitution of the associated molecule from this contradictory behaviour. Naturwiss., **14**, 981 (1926) ; **15**, 409 (1927).

We calculate the position of the band head by (2) or (4) (j being treated temporarily as a continuous variable) from the condition

$$\frac{1}{2}\frac{d\nu}{dj} = \begin{cases} -\mathrm{B} + \mathrm{C}j = 0 \ldots \mathrm{C} > 0 \\ \overline{\mathrm{B}} + \mathrm{C}(j+1) = 0 \ldots \mathrm{C} < 0 \end{cases} \quad (6)$$

$$\left.\begin{aligned} j &= \frac{\overline{\mathrm{B}}}{\mathrm{C}} \\ \text{or } j+1 &= -\frac{\overline{\mathrm{B}}}{\mathrm{C}} \end{aligned}\right\} \text{respectively} = \text{the nearest integer} \quad . \quad (7)$$

The band head is not, like the limit of the line-series, a natural point of accumulation, but in a certain sense an accidental point. The circumstance that the band lines run partly towards the band head and partly away from it apparently disturbs the regularity of the sequence of the lines. To J. N. Thiele goes the credit of having pointed out the view that the band head is an accumulation of lines that is conditioned *by the scale of the ν's and is rather accidental.*

To be able to draw inferences from the expressions (2) to (4) for the band about the properties of the emitting molecule it is essential to count the position number j of the band lines correctly. If we were to displace the zero-point of the counting we should change the significance of the constants A and $\overline{\mathrm{B}}$ in (5). The position number j must not be calculated from the band head, as was done by Deslandres; rather, it advances continuously as it approaches the band head and also subsequently when it moves away from it, since this corresponds to the circumstance that the band head denotes no real singularity of the band law.

To arrive at a natural way of counting j when a partial band is empirically given we revert to Fig. 137 of the infra-red bands. In this case the striking dip in the course of the intensity found the boundary between the positive and the negative branch, the R- and the P-branch in our present notation, and served as the starting-point for counting. We may show that even in the case of the visible bands there is a similar dip in the intensity distribution; it is likewise decisive for the numbering. The intensity of the line to be expected at this point is *zero;* on both sides of it the intensity first increases and then decreases, likewise agreement with Fig. 137 and the explanation there given according to the Maxwell-Boltzmann law. If we number the lines from the zero line the intensities of lines bearing the same number become equal in the R- and the P-branch. But in the scale of the ν's this symmetry becomes more or less unrecognisable. The thickness of the lines in the lower row of Fig. 140 indicates the increase and decrease of the intensity of the lines. As a result of the circumstance that in our diagram as well as in many real cases one of the two intensity maxima come to lie near the band head, we find that this often appears emphasised in the total spectrum as a strong "fluting"

(*kannelierung*). But this circumstance is accidental and, moreover, depends on the temperature.

The qualitative *intensity criterion* here developed for the numbering of the lines, that is, for counting j, is due to Heurlinger, *loc. cit.* He derives another criterion from a discovery of Fortrat (*loc cit.*): in the regular progression of band lines disturbances, anomalies of the vibration number, occur, and, indeed, in *pairs*. Heurlinger was then able to show that in his choice of the current number opposite current numbers must be allocated to the disturbed lines. Hence in addition to the intensity criterion we also have an equivalent *disturbance criterion* for the choice of the current number * Moreover, this criterion led of necessity to the half-integral numbering (in the older notation $m = j + \frac{1}{2}$) of the rotation quantum number even before wave mechanics.

The classical example of the theory of bands is given by the so-called cyanogen bands. Their lines consist of very close doublets that are separated only for the higher values of j. Their centres of gravity



Fig. 141. The cyanogen band λ 3884 of the carbon arc. At the edges the lines that are no longer resolved appear as continuous bands. Taken in the second order of a large concave grating.

obey the band laws (2) and (4) particularly well, and a simplifying circumstance is that here the Q-branch, eqn. (3), is not present at all. Heurlinger has subjected them to a new exact study and, in part, new measurement. In several of these bands there are approximately one hundred lines; for example, in one partial band of the group λ 4216 lines up to $j = +97$ have been measured by Heurlinger; the whole complex of lines is arranged in systematic order.

Runge and Grotrian † ascribed the cyanogen bands, in spite of their names, to the N_2-molecule. The majority of the other observers ‡ established that the presence of C-atoms is necessary to produce the

* In atomic spectra, too, there are similar disturbances at definite points of an otherwise regular series, in such a way that the resolutions of the series-terms suddenly increase anomalously and afterwards resume normal values again [cf. pp. 689 *et seq.* of the 4th German edition of this book, and E. Schrodinger, Ann. d. Physik, **77**, 43 (1925)]. The reason in both cases is probably to be found in a resonance with other quantum frequencies of the atom or molecule.

† Phys. Zeits., **15**, 545 (1914).

‡ Cf., for example, G. Holst and E. Osterhuis, Proc. Amsterdam Acad., **23**, 727 (1921); Mia Toussaint, Zeits. f. Physik, **19**, 276 (1923); R. T. Birge, Phys. Rev., **23**, 294 (1924).

cyanogen bands and that the carrier of the cyanogen bands condenses at a far higher temperature than N_2. We shall therefore regard the molecule CN as the carrier of the cyanogen bands.

Our Fig. 141 represents the group of five band heads already mentioned on p. 556. The one furthest on the long wave side has the wave-length $\lambda = 3884$. The second head lies at $\lambda = 3872$, the third at $\lambda = 3862$, and so forth. The partial band belonging to each head resolves itself into a P- and an R-branch. Heurlinger has determined the zero-lines belonging to the three band heads mentioned, and has calculated the constants $\bar{B}$ and C. The result is (if we use the more exact numerical values),

$$2\bar{B} = 3{\cdot}843 \text{ cm.}^{-1}, \quad C = 6{\cdot}73 \,.\, 10^{-2} \text{ cm.}^{-1}.$$

Thus C is essentially less than $\bar{B}$. This is to be expected by equation (5), since

$$\bar{B} \sim \frac{1}{J'} + \frac{1}{J}, \quad C \sim \frac{1}{J'} - \frac{1}{J},$$

that is, since C must be *small* compared with $\bar{B}$, as it is the difference between two quantities that presumably differ but little from one another.

A further test of the theory is given by the absolute value of $\bar{B}$. By assuming J and J′ as almost equal, we calculate from the given value $2\bar{B} = 3{\cdot}843$, and from equation (5) a mean value $\bar{J}$ (the factor c must be included on account of the transition from vibration-numbers per second to wave-numbers per second) :

$$\bar{J} = \frac{h}{8\pi^2 c\bar{B}} = \frac{6{\cdot}55 \,.\, 10^{-27}}{12\pi^2 \,.\, 3{\cdot}843 \,.\, 10^{10}} = 1{\cdot}44 \,.\, 10^{-39} \text{ gm. cm.}^2 \quad . \quad (8)$$

On the other hand, without introducing an appreciable error, we may write $J = 2 \,.\, 13 \,.\, m_H \,.\, l^2$, where l denotes half the distance between the two atoms C and N and $13m_H$, the mean of their masses. Hence we obtain

$$l^2 = \frac{1{\cdot}44 \,.\, 10^{-39}}{2 \,.\, 13 \,.\, 1{\cdot}65 \,.\, 10^{-24}} = 0{\cdot}34 \,.\, 10^{-16}, \quad 2l = 1{\cdot}16 \,.\, 10^{-8} \text{ cm.}$$

We thus arrive at the well-known order of magnitude of molecular quantities. The bands * of SiN, as is to be expected, show a complete analogy to the cyanogen bands CN.

A beautiful confirmation of the band theory was recognised by W. Lenz † in photographs of iodine fluorescence taken by R. W. Wood.‡ Wood illuminated iodine vapour at a low pressure by means of the Hg-line 5461 (fundamental term of the sharp subordinate series). The iodine molecule, by absorbing the energy-quantum $h\nu$ in question,

* R. S. Mulliken, Nature, **116**, 14 (1925).
† Phys. Zeits., **21**, 691 (1920). ‡ Phil. Mag., **35**, 236 (1918).

becomes transferred to an excited state. This belongs to a quite definite value of the rotation quantum j. The iodine molecule re-emits the absorbed energy, by passing from the excited state into one of less energy. But the selection principle * allows only the transition $j \to j-1$ and $j \to j+1$ (the oscillation quantum and the electron configuration being changed simultaneously). Hence the re-emission takes place as a *doublet* or, in consideration of the fact that in an unharmonic oscillator the oscillation quantum is capable of any arbitrary transitions, as a system of doublets that are scattered over the spectrum. Wood observed about twenty such doublets. As pointed out by Lenz, each of them proclaims in a very delightful way the ruling of the selection principle for the rotation quantum ; each shows us the way in which a partial band originates from two of its members. If, on the other hand, we make the iodine molecules collide with each other very frequently (at higher pressure) or with other atoms (by using an admixture of inert gases) in the interval between absorption and re-emission † then other values of the rotation quantum j are also produced. Every doublet then couples itself to a more extended partial band : in these circumstances, Wood's fluorescence photographs approach the ordinary band type.

§ 4. Law of Band Edges and Band Systems

Hitherto we have spoken only of the coefficients B and C of the band formula, which contain the influence of the rotations. To explain still further the general arrangement of the band systems, we must deal with the coefficient A, which contains the influence of the oscillation and the electronic transitions.

We are interested first of all with the oscillation contribution ν_{osc}, which we must analyse by equation (8) of § 2 ; let the electronic contribution be comprehended again in the symbol ν_{el} and remain unanalysed. Thus we assume that the oscillation quantum leaps from v' to v. In this transition the coefficients ν_0 and x of equation (8), § 2, change, say, from ν'_0, x' to ν_0, x. The application of Bohr's frequency condition to (8) then gives :

$$\left.\begin{aligned}\nu_{osc} &= (v'+\tfrac{1}{2})\,\nu'_0(1-x'(v'+\tfrac{1}{2})+\ldots)-(v+\tfrac{1}{2})\,\nu_0(1-x(v+\tfrac{1}{2})+\ldots)\\ &= (v'-v)\,\nu'_0+(v+\tfrac{1}{2})(\nu'_0-\nu_0)-\{(v'+\tfrac{1}{2})^2\nu'_0x'-(v+\tfrac{1}{2})^2\nu_0x\}+\ldots\end{aligned}\right\} \quad (1)$$

We must insert this value of ν_{osc} in the coefficient A, eqn. (5) of the preceding section. According to the values of v and v' we thus obtain a double manifold of A-values which define the zero lines of a *doubly infinite system of partial bands*, the so-called " band system."

We consider the second row of equation (1) more closely. Its

* The transition $j \to j$, which corresponds to the Q-branch, does not occur here either.

† In adopting this view of the process Lenz sees a possibility of estimating the " time of stay " (*Verweilzeit*) of the I_2-molecule in its excited state.

individual terms are arranged in order of magnitude. The first term is the principal one. It depends only on the *quantum transition* $v' - v$. The second term is small compared with the first, since the change $\nu'_0 - \nu_0$ is a small quantity and depends on the absolute value of the quantum number v. The third term is in general still smaller, since the coefficients x and x' are individually small (cf. p. 564, and Note 13).

The principal term has different values for the quantum transition 0 or the quantum transition 1 (" fundamental vibration ") or 2 (" first harmonic "), and so forth. By keeping the principal term fixed (that is, the quantum transition) and varying the value of v, we obtain a *singly infinite sequence* of partial bands, and so forth, or zero lines, which belong more closely together among themselves, and are neighbours within the band system; we call them a *band group*. The separate individuals of the band group are distinguished by the second and third terms of equation (1).

Fig. 142 is concerned with the system of cyanogen bands. It shows four groups, which, from left to right, correspond to the

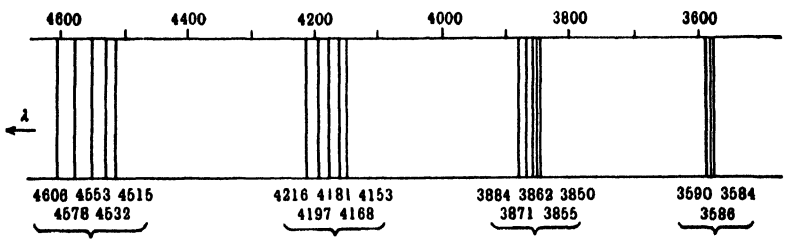


FIG. 142.—The band groups $\Delta v = -2$ to $\Delta v = +1$ of the cyanogen bands. The lines in the figure are the edges of the partial bands, which together constitute the individual band groups in question.

quantum transitions $v' - v = \Delta v = -2, -1, 0, +1$. The group $\Delta v = 0$ at $\lambda = 3884$ is already known to us from Fig. 141. It embraces five band heads, for which, from left to right, v is equal to 0, 1, 2, 3, 4. Thus these five band heads belong (on account of $\Delta v = 0$) successively to the " quantum transitions "

$$0 \to 0, \quad 1 \to 1, \quad 2 \to 2, \quad 3 \to 3, \quad 4 \to 4.$$

The zero line $\nu = \nu_n$ corresponds (cf. Fig. 140) to the value

$$\nu_n = A = \nu_{osc} + \nu_{el} + C/4,$$

and hence arises from the first line of (1) if we add on both sides $\nu_{el} + C/4$,

$$\left.\begin{aligned} \nu_n = \nu_{el} + C/4 &+ (v' + \tfrac{1}{2})\nu'_0(1 - x'(v' + \tfrac{1}{2}) + \dots) \\ &- (v + \tfrac{1}{2})\nu_0(1 - x(v + \tfrac{1}{2}) + \dots) \end{aligned}\right\} . \quad (2)$$

In this equation we have already essentially derived **Deslandres' "Law of Band Edges,"** which is a quadratic law in v and v'. Concerning its name, we must mention that the law accurately represents

not the position of the band edges or of the band heads, but of the corresponding zero lines, whose importance in the scheme of bands had escaped Deslandres' attention.

Table 63 * shows how accurately equation (2) represents the position of the zero lines in the " cyanogen bands." The horizontal rows in it denote the same initial quantum v', the vertical rows the same final quantum v. Hence the diagonal row corresponds to the quantum transition $v' \to v$, and represents the group $\Delta v = 0$ of Fig. 142 ; the parallels to the diagonal towards the right upwards correspond to the groups $\Delta v = -1, \Delta v = -2$, and towards the left below, to $\Delta v = +1$. The five available constants of the law (2), namely $\nu_{el} + C/4$, ν_0, ν'_0, x, x' have been chosen in such a way that, in particular in the first horizontal row of the table, where the empirical data are most exact, the agreement with the measured zero lines is perfect. The deviations in the other rows remain very small.

TABLE 63

	$v = 0$	1	2	3
$v' = 0$	(3884)	(4216)	(4606)	
	25,797·83	23,755·44	21,739·54	—
	25,797·83	23,755·44	21,739·55	
1	(3590)	(3872)	(4197)	(4578)
	27,921·3	25,879·0	23,863·0	21,873·4
	27,921·38	25,878·99	23,863·10	21,873·71
2		(3586)	(3862)	(4181)
	—	27,962·7	25,945·5	23,956·5
		27,962·04	25,946·15	23,956·76

1st line : Wave-length of the edge.
2nd ,, Wave-length of the empirical zero line.
3rd ,, Wave-length of the calculated zero line.

The values of ν_n shown in Table 63 at the same time give the values of the coefficient A for the cyanogen band system. In addition, we show in Table 64 the values $\bar{B}$ and C of the same system. The method of arrangement is the same as in the preceding table. Thus numbers that belong to the same group are in an oblique row sloping towards the left or towards the right : corresponding to the group $\Delta v = 0$ of Fig. 142, for example, we have the numbers

$$2\bar{B} = 3{\cdot}843 ; \ 3{\cdot}804 ; \ 3{\cdot}764 ;$$
$$100C = 6{\cdot}73 ; \ 6{\cdot}35 ; \ 5{\cdot}99.$$

What was said on page 573 about the ratio $\bar{B} : C$ applies to all terms of this and the remaining groups. But still more : the value of $\bar{B}$ is appreciably the same in the whole system, that of C varies

* A. Kratzer, Ann. d. Phys., **67**, 127 (1922).

TABLE 64

	$v = 0$		1		2		3	
	2 $\bar{B}$.	100 C.	2 $\bar{B}$.	100 C.	2 B.	100 C.	2 $\bar{B}$.	100 C.
v' 0	3·843	6·73	3·825	8·53	3·807	10·33	—	—
1	3·822	4·55	3·804	6·35	3·786	8·15	3·768	9·90
2	—	—	3·782	4·19	3·764	5·99	3·746	7·74

much more. This, too, may be understood from equation (5) on page 569. C, being the *difference* of the reciprocal moments of inertia J′ and J with respect to changes of form of the molecule in passing from the initial to the final state, is much more susceptible than $\bar{B}$.

We now need only to connect the law (2) for the zero lines with the law for the individual partial band (eqns. (2), (3), (4) of the preceding section), in order to arrive at the *complete law governing the lines of the whole band system*. In accordance with equation (5) in § 3 we divide the value of $2\bar{B}$ into the amount of the initial and the final term, which we call B′ and B; in B′ and B we at the same time take into account the interaction between the initial and the final term, which is represented by the coefficient α in equation (9) of page 564, so that B′ and B become dependent on v' and v, so that we find it better to write $B(v')$ and $B(v)$ instead of B′ and B; C is now equal to $B(v') - B(v)$. By collecting together the terms in $B(v)$ and $B(v')$ we then get

$$\left.\begin{array}{ll} \text{R} & \nu = A(v, v') - B(v)j(j+1) + B(v')(j+1)(j+2) + \ldots \\ \text{P} & \nu = A(v, v') - B(v)j(j+1) + B(v')j(j-1) + \ldots \\ \text{Q} & \nu = A(v, v') - B(v)j(j+1) + B(v')j(j+1) + \ldots \end{array}\right\} \quad (3)$$

Here

$$\left.\begin{aligned} B(v) = \frac{h}{8\pi^2 J} - \alpha(v+\tfrac{1}{2}), \quad B(v') = \frac{h}{8\pi^2 J'} - \alpha'(v'+\tfrac{1}{2}), \\ A(v, v') = \nu_{el} + \tfrac{1}{4}C + (v'+\tfrac{1}{2})\nu'_0(1 - x'(v'+\tfrac{1}{2}) + \ldots) \\ - (v+\tfrac{1}{2})\nu_0(1 - x(v+\tfrac{1}{2}) + \ldots \end{aligned}\right\} \quad (4)$$

Our law (3) thus contains three quantum numbers j, v, v' and nine disposable constants:

$$\nu_{el},\ \nu_0,\ \nu'_0,\ x,\ x',\ J,\ J',\ \alpha,\ \alpha',$$

of which the quantity ν_{el} may yet be resolved into its term-difference, that is, into the amount of the initial and the final state. With the help of these formulæ and constants we may represent over 1000 lines in the system of cyanogen bands, for example. In the case of greater values of j we must, however, also take into account the higher powers of j denoted by . . . in (3) if we wish to achieve numerical

agreement; these powers in the first place take account of the change in the moment of inertia (cf. p. 564).

But we have not yet finished with setting up the law (3) for the general system. One and the same molecule may have several band systems, since its electronic frequency ν_{el} may assume several different values; these band systems may lie in quite separate spectral regions, like the violet and the red cyanogen bands. We are led to surmise that the different values of ν_{el} may arrange themselves similarly to the manner in which the different electronic transitions arrange themselves in the line series of the atoms, although we are here dealing not with atoms but with the more complicated electronic systems of molecules. The band systems that are arranged together into series in this way may be called "system series." We shall become acquainted with some examples of them in the next section.

§ 5. Many-Lines Spectra

We have already mentioned on page 76 the band spectrum of hydrogen, the so-called many-lines spectrum. It is only the great number of these lines and not their arrangement that recalls the band character. The band heads are absent altogether. The Fulcher * bands have been known longest of all, one in the red and one in the green, both having only a few lines; four bands discovered by Croze have about 12 lines each.† The sequence of lines in the partial bands is so widely separated that the lines no longer appear at first sight to belong together. Merton ‡ has tested these lines as regards their behaviour with varying pressure, temperature, admixture of helium and so forth.

We shall show that this general character follows naturally from the small value of the moment of inertia of the hydrogen molecule and fits as a limiting case into the general theory of band spectra.

In equation (6), § 2, we saw that the distance of neighbouring band lines is

$$\Delta\nu = 2\mathrm{B} = \frac{h}{4\pi^2 \mathrm{J}} \quad . \quad . \quad . \quad . \quad (1)$$

In the case of the cyanogen bands (cf. Table 64) $2\overline{\mathrm{B}} = \Delta\nu = 3{\cdot}8$ cm.$^{-1}$, corresponding to a value $\Delta\lambda = 0{\cdot}6$ Å. In the ultra-violet absorption bands of H_2 analysed by Hopfield ‖ the distance between the lines

* The Fulcher bands have been extended by E. Gehrcke and E. Lau, Berliner Sitzungsber, 1922, p. 453, and 1923, p. 242; a third band consisting of six members was added in the blue region. Concerning the grouping of these bands, cf. G. H. Dieke, Amsterd. Akad., **33**, 390 (1924).

† The two Fulcher series have been recognised as associated P- and R-branches and have been supplemented by a Q-branch. Proc. of the Physico-Mathem. Soc. of Japan, **5**, 9 (1922).

‡ Proc. Roy. Soc., 1922, p. 388. Cf. also the similarly directed investigation by Kimura and Nakamura, Japanese Journ. of Phys., **1**, 85 (1922).

‖ G. H. Dieke and J. J. Hopfield, Proc. Nat. Ac. Wash., **30**, 400 (1927).

corresponds to the value $\Delta\nu \cong 100$ cm.$^{-1}$. The distance $\Delta\nu$ between the lines is thus twenty-five times as great here as in the case of cyanogen bands. By equation (1) it would follow from this (more exact data are given later) that the moment of inertia of hydrogen would be twenty-five times as small as in the case of the carrier of the cyanogen bands.

The value of the moment of inertia of the hydrogen molecule obtained in this way need not be the only one. Rather, we must picture to ourselves that the H_2-molecule is capable of very many different states and may thus also have different moments of inertia.* The estimate given above corresponds to the ground-state of the molecule (absorption bands !).

The small value of J explains immediately why there are only a few lines of observable intensity in each partial band.

Let us recall the fact, first discovered by Eucken, that at low temperatures (below 200° absolute) the rotation of the H_2-molecule dies down more and more and that the hydrogen approaches more and more closely to the monatomic gases in its thermal behaviour. The reason is, generally speaking, to be found in the Boltzmann factor (cf. p. 563). If we insert for the kinetic energy of the rotator its value from equation (1) or (6*a*), § 1, we obtain, except for a weight factor,

$$e^{-\frac{h^2}{8\pi^2 \mathfrak{J}} \frac{j(j+1)}{JT}} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The product JT is the decisive factor. The smaller JT, the less the probability for a definite rotation-quantum j. At very low temperatures all values of j except the smallest, namely $j = 0$, become suppressed statistically ; this is what Nernst predicted theoretically and what Eucken proved experimentally. But even at moderate and higher temperatures the product JT for hydrogen is, on account of its small value for J, much smaller than in the case of other gases. For this reason in the case of hydrogen greater values of j are statistically suppressed even at higher temperatures.

Numerically we find that if J is twenty-five times smaller in H_2 than in CN we must also make $j(j + 1)$ twenty-five times smaller, to make the weakening due to the Boltzmann factor keep within the same limits as in CN. Whereas the cyanogen bands had partial bands of about 100 lines the partial bands in the many-lines spectrum of H_2 will consist roughly of only 20 lines.

This explains the general character of hydrogen bands : sequences of lines in small numbers with wide distances between the lines, in a certain sense, torsos of normally developed bands. In these circumstances there can be no question of the grouping together of these lines into band heads. If many such short sequences of lines overlap we

* R. T. Birge [Proc. Nat. Ac. Wash., **14**, 12 (1928)], and O. W. Richardson and K. Das [Proc. Roy. Soc., A, **122**, 688 (1929)] give numerical values for the moments of inertia and the other characteristic constants of the H_2-molecule in different states.

obtain the impression of the many-lines spectrum, a confused mass of lines without flutings and without apparent regularities.

As regards details the following results have been found. Lyman * and Werner † proved the existence of two band systems in the ultra-violet, having a different initial state but the same final state of the electronic configuration. This final state is at the same time the normal state of the hydrogen molecule. Until we introduce the systematic band notation, which must be postponed till § 7, we shall call it the 1 ^{1}S-state ; this is in harmony with the symbol given to the ground-state of He (H_2 is, like He, a two-electron system). Precisely as in He there are not only singlet but also triplet terms, the 1 ^{3}S-term, however, being absent ; this term would not lead to molecule formation. The initial state of the Lyman bands belongs to the singlet system ; let it be denoted by 2 ^{1}S. The initial state of the Werner bands is the 2 ^{1}P-term in the singlet system. The bands of the ordinary many-lines spectrum in the visible arise if we combine the more highly excited term steps with the terms 2 ^{1}S, 2 ^{1}P which are known from the ultra-violet bands. In addition there are combinations of higher triplet terms 3 ^{3}P, 4 ^{3}P, 5 ^{3}P and so forth with the lowest triplet term 2 ^{3}S. The electron transitions that then result follow the analogous electron transitions of the Balmer lines emitted by the atom and are denoted by the same letters α, β, γ, δ . . . . Cf. the scheme of levels in Fig. 143, which has been taken from a paper by Richardson.‡ Intensive work by various researchers, Witmer, Dieke and Hopfield (in the ultra-violet region), Mecke and Finkelnburg, Richardson and many of his pupils, Weizel and Füchtbauer (in the visible region), has made it possible to trace the majority of the strong lines back to definite electronic, oscillation and rotation states, and hence to divide up the apparently confused mass of lines definitely into short individual bands (P-, Q- and R-branches). Consequently we may now also determine the moment of inertia in the manner mentioned at the beginning (the correction term α being taken into account, cf. p. 564) and thence also the distance $2l$ between the nuclei. We obtain for the ground state ||

$$J = 4{\cdot}67 \cdot 10^{-41} \text{ gm. cm.}^2, \quad 2l = 0{\cdot}75 \cdot 10^{-8} \text{ cm.};$$

for the excited states we find greater values for J and $2l$, as is to be expected.

In finding the interpretation of the experiments on electronic collisions and in applying it to the H_2-molecule a point of view has become important which deals with the variable distance $2l$ between the two H-nuclei. The true explanation of the figure used in this

* Th. Lyman, Astrophys. Journ., **60**, 1 (1924).
† S. Werner, Proc. Roy. Soc., **113**, 107 (1926).
‡ *Ibid.*, **126**, 487 (1930).
|| T. Hori, Zeits. f. Physik, **44**, 834, 1927 ; cf. also E. C. Kemble and V. Guillemin, Proc. Nat. Acad., **14**, 782 (1928).

case cannot be given until we come to wave-mechanics ; it forms the essential content of an important paper by Heitler and London * on the constitution of the H_2-molecule.

The lowest curve in Fig. 144 represents the energy in the state $1\,{}^1S$ for a variable nuclear distance $2l$. Its lowest value corresponds to the stable ground-state with $2l = 0{\cdot}75 \cdot 10^{-8}$ cm. (cf. above). The higher curves denote excited states, for example, $2\,{}^1S$, $2\,{}^1P$, ...

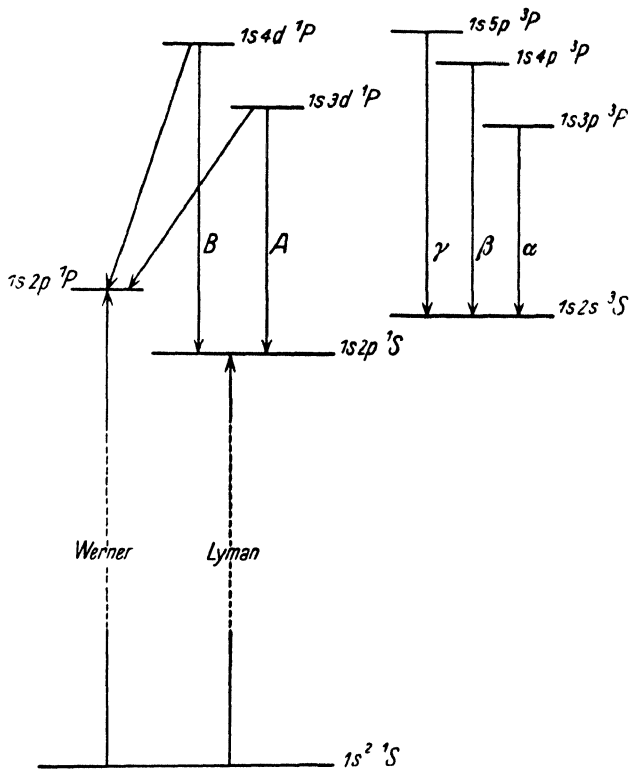


FIG. 143.—The most important terms of H_2 (according to Richardson). The letters A, B, α, β, γ refer to the old band notation. Inter-combinations between triplets and singlets are not known (cf. § 7, $\Delta\Sigma = 0$). The ground term lies far below the remaining terms, so that its distance from them could not be shown to scale.

The energy curve for the ground-state of the H_2-ion is also shown at the upper end of the figure. It is to be observed that the lowest points of the different energy steps lie at different values of the abscissæ. Hence it follows that if we excite the H_2-molecule in the ground-state, either by electronic collisions or by collisions with photons

* Zeits. f. Physik, **44**, 455 (1927) ; cf. also Y. Sugiura, *ibid.*, **45**, 484 (1927).

(that is, by the absorption of light), we do not arrive at a state of equilibrium but at a higher point of the energy curve, from which a vibration of the nuclear distance sets in about the lowest point of the energy curve in question, that is, about the equilibrium value of $2l$. We thus at the same time excite a higher electronic state simultaneously with an oscillation state. In the figure the quantised oscillation states are indicated by horizontal straight lines ; these indicate the region

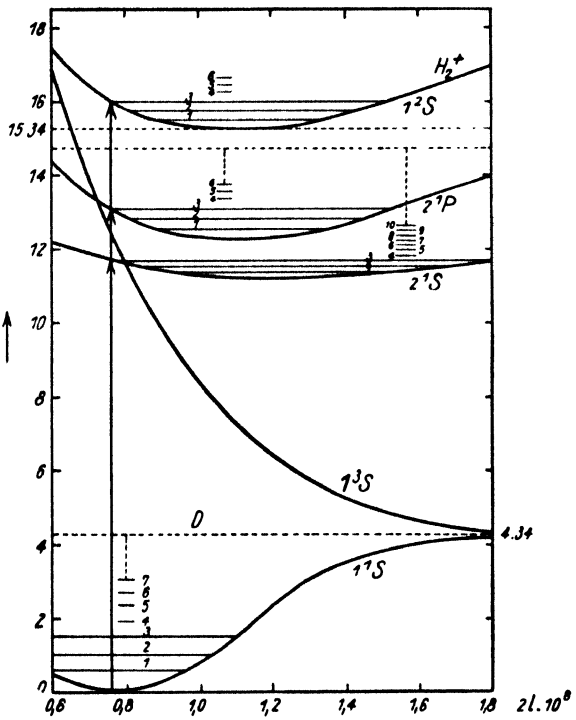


FIG. 144.—Potential curves of certain H_2 terms (from Ruark and Urey). The lowest curve $1\,^1S$ corresponds to the ground term $1s^2$; above the zero-level are shown oscillation-levels in the potential trough, just as with the higher stable terms. D = dissociation potential of two unexcited H atoms. $1\,^3S$ likewise belongs to the configuration $1s^2$ and provides the repulsion between the two H atoms. The curves $2\,^1S$ and $2\,^1P$ have the configuration $1s2p$ (cf. Fig. 143). At the very top the ground-state of H_2^+, $1\,^2S$ is shown.

within which the nuclear distance $2l$ varies. The fact that the region is delimited just by the energy curve is connected with the circumstance that each point where the oscillation reverses the potential energy has the same value.

In Fig. 144 we have drawn the excitation arrow in a direction exactly vertically upwards. This is based on the assumption that the gravitational system of the nuclei has no time in its collision

with the light electron or the still lighter photon, to alter its nuclear distance or its nuclear velocities. This explanation is due to J. Franck * and has been worked out further by E. U. Condon.†

The same conditions as in excitation also obtain in the case of ionisation. Here, too, we obtain, as shown in the figure, not the equilibrium state of the H_2^+-ion but a higher oscillation state. This confirms our remark on page 377 that "the electron collision experiments in the case of H_2 and of molecules generally give by no means such sharp and unambiguous results as in the case of atoms." The value of the ionisation potential, 15·34 volts, given in the same part of the text has now also been included in the figure and its precise meaning elucidated. Likewise the meaning of the dissociation-potential, D = 4·34 volts, is clear from the figure.

We have an instructive intermediate stage between the many-lines spectrum of hydrogen and the ordinary band spectra, namely the *many-lines spectrum of helium*. It was discovered by Goldstein ‡ and W. E. Curtis ‖ and measured for the first time by A. Fowler.¶ Several characteristic parts of it have been studied by Curtis,** Weizel †† and others. Whereas in the many-lines spectrum of hydrogen the band character was found to have disappeared entirely, in this helium spectrum it can still be recognised but by no means so strikingly as in the case of, say, the cyanogen bands. The sequences of lines are partly without a band head and partly with a band head. The maximum number of lines is 11, the distance between the lines in the neighbourhood of the zero line is of the order of magnitude $\Delta\nu = 30$. By (1) the moment of inertia that would result would then be

$$J = 1{\cdot}8 \cdot 10^{-40},$$

that is, about four times greater than for H_2. This number expresses the intermediate position of our spectrum with respect to the hydrogen many-lines spectrum and the true band spectra.

What are we to assume the "moment of inertia" of helium stands for? It can only refer to the moment of inertia of a transitory "He-molecule." For a molecule of this kind to arise at least one of the atoms must be excited. Wave-mechanical considerations taken in conjunction with the discussion of the band spectrum show that one of the two He-atoms is in the ground-state and the other in an excited state.

The excitation conditions for H and He are oppositely directed.

* Cf. Franck and Jordan, Anregung von Quantensprüngen durch Stösse, p. 252. Springer, Berlin, 1926.
† Phys. Rev., **28**, 1182 (1926).
‡ Verh. d. D. Phys. Ges., **15**, 402 (1913).
‖ Proc. Roy. Soc., **89**, 146 (1913).
¶ *Ibid.*, **91**, 208 (1915).
** *Ibid.*, 388 (1922); **103**, 315 (1923).
†† Zeits. f. Physik, **56**, 197 and 727 (1929).

In H the many-lines spectrum is produced more easily (at lower potentials) than the Balmer spectrum ; in the case of He, however, the many-lines spectrum requires higher excitation than the ordinary spectral series. This is quite compatible with the above view, according to which a preliminary condition for the production of the He_2-molecule is that one of the He-atoms be considerably " loosened."

Visually the structure of the He many-lines spectrum appears to be subdivided into fairly large units, groups and systems. Fowler succeeded in isolating within these larger units such series as satisfied a quantitative series formula in the manner of Rydberg, a formula in which the Rydberg number R occurs directly. This points to the " system series " of which we spoke at the end of the preceding section. We are thus concerned with energy steps of the electronic configuration in the He_2-molecule ; in our general system formulæ (3) and (4) of the preceding section they occur in the term ν_{el}.

§ 6. Gyroscopic Motion of Molecules

The assumption we have hitherto made that the molecule rotates about a fixed axis is very special and permissible only if the axis of rotation coincides with a principal axis of the mass distribution. The general motion of the molecule is not the rotation but the *gyroscopic (top) motion*. It is usual to distinguish the symmetrical and the unsymmetrical top, according as the ellipsoid of inertia of the mass distribution is an ellipsoid of rotation or a tri-axial ellipsoid. The diatomic molecule (H_2, HCl and so forth) represents a symmetrical top and one that has a very special mass distribution : the moment of inertia K about the line connecting the nuclei (axis of the figure, cf. the beginning of § 2) is vanishingly small compared with the moment of inertia J about the axes perpendicular to it (" equatorial axes "), namely, small in the ratio electron mass to nuclear mass. On the other hand, the tri- and multi-atomic molecules are as a rule (for example in the case of H_2O) represented schematically by an unsymmetrical top (unless, as in the case of CO_2, the three atoms lie in one straight line). Whereas the general motion of the symmetrical tops under no forces is a *regular precession*, the general motion of the unsymmetrical top is called a *Poinsot motion ;* the latter cannot be represented by elementary formulæ but only by elliptic integrals. In the case of the " spherical top " * the general motion under no forces merges into simple rotation.

We next consider a symmetrical top in which the moment of inertia K about the axis of the figure is not, indeed, vanishingly small but nevertheless small compared with the equatorial moment of inertia J.

* This case is presumably realised in the case of CH_4 in the ground-state (tetrahedral structure) ; this would explain the particularly simple infra-red spectrum mentioned on p. 568.

If we denote the momentum about the axis of the figure by N and the total moment of momentum by M, the component of the moment of momentum that is left for the equatorial plane is $\sqrt{|\mathrm{M}|^2 - \mathrm{N}^2}$, and the associated amounts of kinetic energy are

$$\frac{\mathrm{N}^2}{2\mathrm{K}} \quad . \quad . \quad (1) \qquad \text{and} \qquad \frac{|\mathrm{M}|^2 - \mathrm{N}^2}{2\mathrm{J}} \quad . \quad . \quad (2)$$

Let us make the quantum assumption *

$$\mathrm{N} = \frac{j_0 h}{2\pi} \quad . \quad . \quad (3) \qquad \text{and} \qquad |\mathrm{M}|^2 = j(j+1)\left(\frac{h}{2\pi}\right)^2, \quad (4)$$

where j_0 and j are the corresponding quantum numbers. To excite the rotation about the axis of the figure or the equatorial axis, respectively, we therefore require the amounts of energy :

$$\frac{j_0^2 h^2}{8\pi^2 \mathrm{K}} \quad . \quad . \quad (5) \qquad \text{and} \qquad \frac{(j(j+1) - j_0^2)h^2}{8\pi^2 \mathrm{J}} \quad . \quad (6)$$

On account of the ratio assumed for K/J the former amount is very much greater than the latter, if j_0 and j are of the same order of magnitude. Simultaneously with the energy also the angular velocity about the axis of the figure becomes very great. It is only when the excitation is very high, that is, at very high temperature, that a rotation about the axis of the figure should be able to take place, and even then only in comparatively small values of j_0. At moderate temperatures no rotation about the axis of the figure takes place. *The molecule does not then function as a top but as a simple rotator about an equatorial axis ;* there is no doubt that we are allowed to assume the diatomic molecules ($\mathrm{K} \to 0$) as such.

The method of deduction is precisely the same as in the preceding section for the hydrogen molecule. There it was the small value of J in the Boltzmann factor which made the rotations of the hydrogen molecule die away ; here it is the small value of K which in particular suppresses the rotations about the axis of the figure or restricts it to small values of j_0. What is essential in both cases is the discrete nature of the quantum number and the finite height of the first energy step ; if the possible states were continuously distributed, this deduction would not hold.

The total kinetic energy of the molecule of rotational symmetry is, by (5) and (6),

$$\mathrm{E}_{kin} = \frac{j(j+1)h^2}{8\pi^2 \mathrm{J}} + \frac{j_0^2 h^2}{8\pi^2}\left(\frac{1}{\mathrm{K}} - \frac{1}{\mathrm{J}}\right) \quad . \quad . \quad . \quad (7)$$

For $j_0 = 0$ it merges, of course, into the expression for a pure rotation (cf. eqn. (6*a*) of § 1). There is an important application of equation (7) in the beautiful researches by Victor Henri on the absorption spectrum

* The different treatment of N and M is justified by wave-mechanics, cf. Ch. VI, p. 333.

of formaldehyde,* H . COOH. Henri calls this molecule the Y-molecule, attributing to it the structure indicated in Fig. 145 which has been deduced from the band spectra. In this form the model is, strictly speaking, an " unsymmetrical top." One of the principal axes passes through OC, a second is perpendicular to the plane of the diagram, the third lies in the plane of the diagram parallel to the line connecting the H-atoms. But the mass of the two H-atoms is very small compared with the mass of the other two atoms. The mass distribution is only slightly changed if we allow the two H-atoms to rotate about the axis OC and distribute its mass uniformly over the circular orbit. In this way we replace Fig. 145 by the simplified model of a symmetrical top, and we shall use equation (7) in our calculations. Here the moment of inertia K about the axis of the figure OC, which arises only from the two H-atoms, is small compared with the moment of inertia J about the equatorial axes, which is essentially determined by the C- and the O-atom

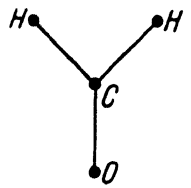


FIG. 145.—Scheme of the " Y-molecule " H_2CO. Dimensions in Ångström units: CO = 1·09, CH = 1·3, HH = 1·38.

$$K \ll J \quad . \quad . \quad . \quad . \quad . \quad (8)$$

From (7) it follows that if we allow j to change we obtain a band structure of ordinary dimensions, of the same order of magnitude as, for example, in the CN bands, such that $\Delta\nu$ becomes inversely proportional to the great moment of inertia J. If we allow j_0 to change we obtain a much wider structure, of the same order of magnitude as in the hydrogen many-lines spectrum, such that $\Delta\nu$ is inversely proportional to the small moment of inertia K. We thus expect a system of relatively widely separated band lines, corresponding to the quantum number j_0 of the proper moment of momentum (*Eigenimpuls*) about the axis of the figure, which has superposed on itself a much narrower line system, corresponding to the quantum number j of the total moment of momentum. Both sequences of lines consist not only of P- and R-branches ($j_0 \to j_0 \pm 1$, $j \to j \pm 1$), but also of Q-branches ($j_0 \to j_0$, $j \to j$), and the latter indicate, by pp. 568 and 569, and Note 7 (g), that the model is non-rigid (excited moments of inertia J′, K′ instead of the original J, K).

This whole line-structure now repeats itself more than ten times in the region between $\lambda = 3500$ and $\lambda = 2500$ Å. (corresponding to the various oscillation states of the model), every P-, Q- and R-branch again being developed as a triplet (P, P′, P″, and so forth, particularly in the more separated sequences of lines ; the narrow ones cannot be resolved). Henri particularly emphasises a fundamental change in

* Comprehensive account is contained in Zeits. f. Physik, **49**, 774 (1928), by Henri and Svend Aage Schou.

the appearance of the bands as the oscillation increases (increasing vibration number v) which expresses itself in a blurring of the band lines and is interpreted as "pre-dissociation." We have not space, however, to enter into this question any more than into the determination of the works of dissociation from band spectra by the method of J. Franck.

Since after their introduction into the equations (1) to (4) N and j_0 are respectively components of M or j, it follows that

$$j_0 \leqq j.$$

From this we conclude that in the case of a gyroscopic molecule with $j_0 > 0$ not only will the zero line be missing in the band numbered according to j, as in our Fig. 140, but that *on both sides of the zero line other adjacent lines must also be missing.* Lenz * was the first to enunciate this conclusion. Heurlinger pointed it out in his dissertation in the case of certain band spectra of rather complicated carriers, and Runge † showed that several band lines adjacent to the zero position were missing in certain O_2-bands.

§ 7. Multiplet Structure of Band Spectra

In the preceding sections of the present chapter we studied the influence of the rotation and the oscillation of the nuclei, but did not analyse the electron term in detail. It is to be expected that this will exhibit a finer subdivision that arises from the composition of the orbital and the spin moments of momentum. We shall now investigate this structure and shall restrict our attention to *diatomic molecules.*

A. The System of Quantum Numbers and Term Notation

We may imagine the molecule to be formed by allowing the two atomic nuclei to coincide in the first place ; we may then consider the field that acts on the radiating electron (*Leuchtelektron*) to be centrally symmetrical for diagrammatic purposes (cf. Ch. VIII, § 2). If we now allow the nuclei to move apart until they have reached their position of equilibrium, the effective field clearly becomes axially symmetrical about the line connecting the nuclei. We may imagine this resultant field as arising from the original central field (in the case of united nuclei), and of a superposed axially symmetrical electrical field. The latter must usually be assumed to be very strong if we are to be able to represent the true conditions in the molecule.‡

The electric field acts on the orbital motions of the electrons, that is, on the moment of momentum l, which we may ascribe to the electrons in the central field (without the superposed axial field). The

* In the paper quoted in § 1.

† Zeeman Jubilee Number, Physica, **1**, 254 (1921).

‡ F. Hund has estimated the field at 10^7 to 10^8 volts/cm. (Zeits. f. Physik, **36**, 661 (1926)).

result is that the resultant L of all the vectors l orientates itself with respect to the field ; * the projection of L on the axis of the field, that is, on the straight line connecting the nuclei, remains constant as a first approximation ; we call it M_L. It has the values $M_L = -L, -(L-1), \ldots +L$. All this is analogous to the behaviour of the atom in the magnetic field. The interaction between L and the total spin moment of momentum S is small compared with the interaction just considered (L, field). For (L, S) gives resolutions of the order of the distances between the multiplet lines in the atoms : the (L, field)-resolutions are in general much greater. (L, S) comes into consideration only in the next approximation. Here S will orientate itself with respect to the magnetic field ; but on account of the very rapid precession of L about the line connecting the nuclei, we find that for S only the component of L parallel to this line becomes appreciable, that is, S orientates itself with respect to the molecular axis, and in such a way that the projection M_S of S on this axis assumes the values $-S, -(S-1), \ldots +S$. Let the total projection of L and S on the molecular axis be M, where $M = M_L + M_S$.

The interaction (L, field) makes a contribution of the form $F(M_L)$ to the total energy of the molecule, the interaction (L, S), as in the strong magnetic field (cf. p. 545, eqn. (14)) makes a contribution AM_LM_S, or, in all,

$$W = F(M_L) + AM_LM_S \quad . \quad . \quad . \quad . \quad (1)$$

The function $F(M_L)$ is symmetrical in M_L, so that we have †

$$F(M_L) = F(-M_L).$$

Hence W remains unchanged if we reverse the signs of both M_L and M_S ; at the same time M becomes changed into $-M$.

In place of the quantum number M_L, we here introduce the usual symbol Λ, and we are to have $\Lambda = |M_L|$. To a first approximation, if A is neglected, W is determined by Λ alone. The terms with $\Lambda = 0$ are called Σ-terms, those with $\Lambda = 1, 2 \ldots$ are correspondingly called Π, Δ, . . . terms. To the next approximation, in which A is taken into account, M_S also becomes of importance. We write $M_S = \pm\Sigma$, where Σ is to be positive if M_L and M_S have the same sign, otherwise negative.

* The electric field is often stronger than the mutual action of the l's among themselves, so that there is no sense in speaking of a resultant L of the l's. The total projection of all the l's on the straight line connecting the nuclei, however, then always remains constant ($= M_L$).

† Proof : the field is axially symmetrical, so the planes through the axis of the field are planes of symmetry of the motion. If we describe a plane through the axis of the field and through the rotation vector L, the motion which corresponds to the position of the rotation vector L with the projection $+M_L$, becomes transformed when reflected at this plane into the motion which corresponds to the position of the rotation vector L with the projection $-M_L$. Thus the energy is of equal amount in both cases. Hence the term L resolves into only $L+1$ different energy-levels M_L through the action of the field if we disregard the term AM_LM_S in (1).

If, in particular, $\Lambda = 0$ the interaction (L, S) vanishes, and S has no means of taking up definite positions; the quantum numbers Σ and M then lose their meaning.

As an illustration, we give in Table 65 the quantum numbers for the case $L = 1$, $S = \frac{3}{2}$. In the last column we have the term-symbol, with the upper index $2S + 1$, which specifies the "multiplicity," and with the lower index $\Lambda + \Sigma$. It is clear that we here need different symbols only for terms which are different in energy. In the column before the last we have the number $\Omega = |\Lambda + \Sigma|$.

There is an "Exchange Law" for molecules precisely as for atoms. An even number of electrons (integral S) gives *odd* multiplicity; an odd number of electrons (half-integral S) is the condition for *even* multiplicity. That is why we have singlet and triplets in H_2 but doublets in CN.

TABLE 65. L = 1, S = $\frac{3}{2}$

M_L	M_S	M	Λ	Σ	$\Lambda + \Sigma$	Ω	Symbol
+ 1	$\frac{3}{2}$	$\frac{5}{2}$					
− 1	$-\frac{1}{2}$	$-\frac{3}{2}$	1	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$^4\Pi_{\frac{3}{2}}$
+ 1	$\frac{1}{2}$	$\frac{3}{2}$					
− 1	$-\frac{1}{2}$	$-\frac{1}{2}$	1	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$^4\Pi_{\frac{1}{2}}$
+ 1	$-\frac{1}{2}$	$\frac{1}{2}$					
− 1	$+\frac{1}{2}$	$-\frac{1}{2}$	1	$-\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	$^4\Pi_{\frac{1}{2}}$
+ 1	$-\frac{3}{2}$	$-\frac{1}{2}$					
− 1	$+\frac{3}{2}$	$\frac{1}{2}$	1	$-\frac{1}{2}$	$-\frac{1}{2}$	$\frac{1}{2}$	$^4\Pi_{-\frac{1}{2}}$
0	—	—	0	—	—	—	$^4\Sigma$

The resolution of "multiplet" terms is obtained from (1) if we keep Λ fixed, and allow Σ to vary. First we can put (1) without ambiguity of sign into the form

$$W = F(\Lambda) + A\Lambda\Sigma \quad . \quad . \quad . \quad . \quad (1a)$$

but since Σ changes by ± 1 in passing from one level to another (cf. also Table 65), we find that in the molecule terms *all resolutions between successive levels are equal* and of the same order of magnitude as the atomic resolutions, because A arises in both cases from the magnetic interaction (L, S).

The *total energy* of the molecule is composed now of the following components: * the greatest contribution is made by the energy of the electrons in their orbit (n, l). This is followed by the energy of the nuclear oscillation and then the fine resolution of the multiplet-terms just described. The contribution of the rotation requires closer attention.

* We give only the normal grading of the orders of magnitude; in many molecules the fine resolution is greater than the oscillation resolution. We do not enter into such details.

The vector of its moment of momentum which stands perpendicularly on the molecular axis and which we shall now call O will supplement itself by means of the moment of momentum Ω about the molecular axis to form a resultant of the total moment of momentum which we shall suppose to be denoted by its quantum number J. J is constant in magnitude and direction and has the values Ω, $\Omega + 1$, $\Omega + 2$, . . ., which are integral or half-integral according as S is integral or half-integral, that is, according as the number of electrons in the molecule is even or odd. From quantum-mechanical considerations we have for J : $|J|^2 = J(J + 1)$ (cf. p. 333). Following Hund * we call the case of the coupling of the vectors which has here been described and which occurs most commonly, the case *a* ; Hund was the first to

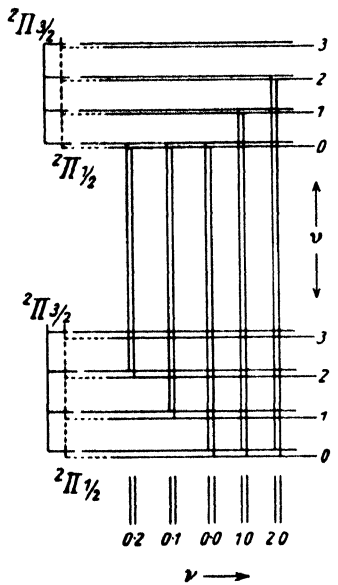


FIG. 146.—Multiplet structure in band spectra. Combination of two $^2\Pi$-terms differing somewhat in their configurations. Each of the two $^2\Pi$-terms is subdivided into oscillation levels ($v = 0$, 1, 2 . . .) and each oscillation level is double, corresponding to $\Omega = \frac{3}{2}$, $\frac{1}{2}$, in which the doublet nature of the terms manifests itself. In consequence of this, the oscillation bands (below) are also doubled. The relation to the transitions drawn above them is indicated diagrammatically by similar positions in the frequency scale. The division into rotation levels has been omitted. Each of the levels shown should again be split up into many discrete levels ($J \geq \Omega$).

investigate the various cases of coupling theoretically. The typical appearance of the band in this case is illustrated by the Fig. 146. It represents the combination of two $^2\Pi$-terms. For each of the two there is a series of oscillation levels (quantum number v), each of which further exhibits a fine resolution into two levels, corresponding to the character † of $^2\Pi$. Finally each of these two levels is to be imagined as again resolved into close levels that are to be numbered according to J.‡ This last structure has not been given in the Figure. At the

* F. Hund, Zeits. f. Physik, **36**, 657 (1926).

† By setting up a table similar to Table 65 it is easy to verify that $^2\Pi$-terms always consist of the two levels $^2\Pi_{\frac{3}{2}}$, $^2\Pi_{\frac{1}{2}}$, that is, $\Omega = \frac{3}{2}$ and $\frac{1}{2}$.

‡ The J of the molecules corresponds to the J of the atoms only in so far as it represents the total momentum. For the rest, the J of the atoms is represented by the Ω of the molecules.

lower edge we see represented diagrammatically the line spectrum that results from the combination of the two $^2\Pi$-terms. Here, too, the subdivision arising from J-transitions is not shown in the Figure.

If $S = 0$ and $\Lambda = 0$ ($^1\Sigma$-terms) J reduces to the moment of momentum of the nuclear rotation, which we called j earlier (§ 1 and the subsequent sections). The total energy then consists only of the contribution of the electronic motion (n, l) of the oscillation and of the rotation. A multiplet structure does not occur because $^1\Sigma$-terms are simple. This scheme of the molecule would correspond to the considerations of the preceding section. The case $\Lambda = 0$, $S > 0$ demands special consideration, which we shall, however, suppress here.

Lastly, the J-levels may also resolve into two components. In equation (1) we showed that the energies $+ M_L$ and $- M_L$ coincide (for a fixed Σ) ; every state with $\Lambda > 0$, v, Σ, J (cf. Fig. 146) consequently has the statistical weight 2. The rotation of the nuclei causes these states to be resolved into two levels, which are in general very close together. They form a so-called Λ-doublet. Only the terms $\Lambda = 0$ do not resolve, corresponding to the circumstance that here the states have only the weight 1 : M_L can only $= 0$.

Besides the case a other schemes of coupling are conceivable, according to the order of magnitude of the interactions in the molecule ; cf. the paper by Hund and the specialised literature quoted on page 555.

B. Intensities of Band Lines

The *selection rules* for our molecular model may be read off from the kinematical character of the vector motions. For M_L, M_S we have, as in the case of a strong magnetic field, that $\Delta M_L = 0, \pm 1$, $\Delta M_S = 0$, or, written in terms of Λ and Σ * : $\Delta\Lambda = 0, \pm 1$, $\Delta\Sigma = 0$. The selection rules of the atomic spectra for L and also those for l in the case of a very strong intra-molecular field are then no longer valid, analogously to the Stark effect for atoms (cf. Ch. VI, § 1, p. 299, and Ch. VII, § 2, p. 368). For the total moment of momentum J we have, of course, that $\Delta J = 0, \pm 1$. The transitions $J \to J$ form, in analogy with their earlier behaviour, the Q-branch, $J \to J + 1$ the P-branch, and $J \to J - 1$ the R-branch. Lastly, in the case of molecules there is an exact analogy with Laporte's rule for atomic spectra : the terms may be divided into two classes in such a way that only terms of the one class may combine with terms of the other class. The Λ-doublet levels before-mentioned have the property

* We may easily convince ourselves that these two formulations are equivalent. To make the selection rules more precise we must note that : (1) if $\Lambda = 0$ for one of the two combining states or for both, then Σ loses its meaning ; rather we have $\Delta\Lambda = 0, \pm 1$. (2) $\Delta\Sigma > 0$ occurs (as in atomic spectra $\Delta S > 0$) only for great (L, S)-resolutions, that is for heavy atoms in the molecule.

that one level always belongs to the one class and the other to the other class. That is why the combination of two Λ-doublets, J′, J″, leads always and only to two band lines.

As at the end of the preceding section the restriction $J \geqq \Omega$ (there written as $j \geqq j_0$) causes the absence of certain band lines around the "zero line" (*Nullinie*). Let us consider, say, the combination, ${}^1\Pi \rightarrow {}^1\Pi$. Here $\Lambda = 1$, $\Sigma = 0$, $\Omega = 1$ in both terms. Thus in both terms J has the possible values 1, 2, 3 . . . : $J = 0$ is missing. Consequently the first lines $0 \rightarrow 1$ and $1 \rightarrow 0$, respectively, are missing in the P-branch and the R-branch. In the combination ${}^1\Delta \rightarrow {}^1\Pi$ the first line would be missing in both the Q- and the R-branch; in the P-branch the first two lines would be missing.

For the *intensities* of the lines similar summation rules * hold as for the atoms. The sum of the intensities of all the lines that start out from a fixed initial level is proportional to the statistical weight of this level; the same applies *mutatis mutandis* for a fixed final level. The intensities of the individual band lines may be represented by formulæ which were first derived from correspondence consideration by Hönl and London.† We give them without proof. Let Ω', J′ be the quantum numbers of the initial state, Ω'', J″ those of the final state. In the formula we must always insert the greater of the two quantum numbers J′, J″ and Ω', Ω'' for J, Ω.

$$\left.\begin{aligned}
&(1)\ \Omega' \quad \Omega'', \quad J' \quad J'': \quad I \sim \frac{(2J+1)\Omega^2}{J(J+1)},\\
&\qquad\qquad J' \quad J'' \pm 1 : I \sim \frac{(J^2-\Omega^2)}{J};\\
&(2)\ \Omega' = \Omega'' \pm 1, J' = J'': \quad I \sim \frac{(2J+1)(J+\Omega)(J-\Omega+1)}{2J(J+1)}\\
&\qquad\qquad J' = J'' \pm 1 : I \sim \frac{(J+\Omega)(J+\Omega-1)}{2J},\\
&\qquad\qquad J' = J'' \mp 1 : I \sim \frac{(J-\Omega)(J-\Omega+1)}{2J}.
\end{aligned}\right\} (2)$$

The intensity sums in each case show proportionality with $2\bar{J}+1$, if $\bar{J}$ denotes the quantum number of the fixed level. Actually, the statistical weight of each J-level is given by the $2J+1$ possible positions of the total moment of momentum J in the magnetic field, precisely as in the case of the atom.‡ In the notation of page 527 the first row

* First applied to band spectra by R. H. Fowler, Phil. Mag., **49**, 1272 (1925), and G. H. Dieke, Zeits. f. Physik, **33**, 161 (1925).

† H. Hönl and F. London, Zeits. f. Physik, **33**, 803 (1925).

‡ Here we must note that in the case $\Lambda > 0$ every J-level (without a field) is resolved into two levels (cf. p. 591, Λ-doublet), so that the statistical weight amounts to $2(2J+1)$. Every band line then forms a Λ-doublet of lines which are of equal intensity; the intensity of each individual is to be calculated from the above formulæ.

in (1) and the second row in (2) denote "parallel transitions," the third in (2) "anti-parallel" transitions, the others "indifferent" transitions. This expresses itself in the magnitude of the intensities in question.

In the intensity of the band lines an important part is also played by the Boltzmann factor (cf. Ch. VIII, § 9, p. 538). Hence we must also multiply the values given above by the factor

$$e^{-E/kT}$$

to arrive at intensities that are comparable with those obtained by experiment. For E we must substitute the energy of the initial state in each case, that is, in the case of emission the higher of the two combining levels, in the case of absorption the lower. If we consider the lines of a rotation band, where we keep the electronic transition and the oscillation constant, E is given by the formula (6*a*) on page 558*:

$$E = \text{const.} + BJ(J+1) \quad . \quad . \quad . \quad (3)$$

For example, for $^1\Sigma \rightarrow {}^1\Sigma$-bands (no moment of momentum about the molecular axis, so that we may write $\Omega = 0$) we obtain in emission from (2) and (3), *

$$\left.\begin{array}{l} \text{P-branch } J \rightarrow J+1, \quad I \sim (J+1)e^{-BJ(J+1)/kT} \\ \text{R-branch } J \rightarrow J-1, \quad I \sim Je^{-BJ(J+1)/kT} \end{array}\right\} \quad . \quad (4)$$

Lines which, if counted from the zero line, have the same number in the P-branch and the R-branch (cf. Fig. 138, p. 563), have a J which is greater by unity in the R-branch than in the P-branch. It then follows from (4) that lines that correspond to one another in this way have the same intensity in both branches, if the Boltzmann factor makes no essential difference. This has already been mentioned on page 563. If the Boltzmann factor does exert an appreciable influence the lines of the P-branch are stronger in emission than the corresponding lines of the same number in the R-branch. In absorption this relationship would become inverted. These assertions are confirmed by experiment.

The question of the distribution of intensity for the transitions that arise from oscillation has been discussed by Condon.†

If the two nuclei of the diatomic molecule are exactly similar and if the nuclear spin vanishes, alternate lines drop out in the bands, as Heisenberg ‡ has shown from wave-mechanical considerations. The absence of these lines has been confirmed experimentally in the spectra of He_2, $(C_{12})_2$, $(O_{16})_2$, $(S_{32})_2$; *thus the atoms* He, C_{12}, O_{16}, S_{32} *have no spin*. If the nuclear spin is not equal to zero the lines exhibit a characteristic change of intensity, every alternate line being weaker than the normal line; from the experimental intensity-ratio of

* The Q-branch vanishes on account of $\Omega = 0$.
† E. U. Condon, Phys. Rev., **28**, 1182 (1926).
‡ W. Heisenberg, Zeits. f. Physik, **41**, 239 (1927).

neighbouring associated lines we may again draw conclusions about the magnitude of the nuclear spin. We made a brief allusion to this method of determining the nuclear moment of momentum on page 554. On the other hand, molecules that consist of *two isotopes* of the same element, such as $Cl_{35}\,Cl_{37}$, or $O_{16}\,O_{18}$, do not exhibit, either experimentally or theoretically, anomalies in intensity. For further details about the spectra of molecules consisting of similar atoms we refer to the literature quoted on page 555.

C. Zeeman Effect of Band Lines

Zeeman * himself looked unsuccessfully for a magnetic influence on band lines; likewise Becquerel and Deslandres.† It is only fairly recently that an effect could be shown to occur in the bands of C_2, CH and so forth. The resolutions in the neighbourhood of a zero line of a band were nearly of the order of magnitude of the normal Zeeman resolutions and decreased with increasing distance of the band lines from the zero line. Many bands were altogether insensitive to magnetic influences, and exhibited a quadratic effect only at greater magnetic intensities; very often only a diffuse widening was observable, and so forth.

For the case of the coupling *a* the theoretical Zeeman effect may easily be given in a manner analogous to that for atoms.‡

D. Electronic Configuration of Molecules

The problem of the allocation of molecular terms to certain electronic configurations may be treated similarly to that used for atoms. We suppose the interaction between the electrons to be small so that the electrons in the atom may be characterised by the quantum numbers n, l. In the molecule the numbering according to n and λ (= absolute value of the projection of l on the line connecting the nuclei, $= 0, 1, 2, \ldots l$) will have a physical meaning in the case where the nuclei lie close together. We distinguish between σ-, π-, δ- . . . electrons, according as $\lambda = 0, 1, 2, \ldots$. By p. 591 every state $\lambda = 0$ has the weight 1 and hence is not degenerate; the states $\lambda > 0$ are, however, singly degenerate and have the weight 2. The electron spin doubles each of the states for each electron. It follows from Pauli's Exclusion Principle (that each state may only be associated with one electron) that for a fixed n, l there are 2 σ-electrons, 4 π-electrons, 4 δ-electrons, and so forth. The arrangement of the electrons is then

* P. Zeeman, Astrophys. Journ., **5**, 332 (1897); Phil. Mag., **43**, 226 (1897).

† H. Becquerel and H. Deslandres, Comptes Rendus, **126**, 997, and **127**, 18 (1898).

‡ According to J. H. van Vleck, Phys. Rev., **28**, 980 (1926); D. M. Dennison, *ibid.*, **28**, 318 (1926). Experimentally investigated by E. C. Kemble, R. S. Mulliken and F. H. Crawford, *ibid.*, **30**, 438 (1927).

characterised, say, by $\{1s\sigma^2, 2s\sigma^2, 2p\sigma^2, 2p\pi^4, 3s\sigma\}$. The symbols $1s$, $2s$, . . . refer to the n, l-values of the electrons. Shells with σ^2, π^4, δ^4 and so forth are complete ; taken alone, they give $\Lambda = 0$ and a vanishing electron spin S. Our arrangement { } belongs to a molecule having 11 electrons, of which 10 have been domiciled in closed shells. In general we obtain the resultant terms most rapidly by adding quantum numbers vectorially exactly as in the case of the atom. The above example would give a $^2\Sigma$-term ; the inner shells with $1s$, $2s$, $2p$ contribute nothing to Λ and S ; the $3s$-electron gives $S = \frac{1}{2}$ and $\lambda = \Lambda = 0$. Using a method copied from Bohr's theory of the periodic system of the atoms Hund * made qualitative statements about the term-scheme of molecules.

* Cf. Ergebnisse der exakten Naturwiss., **8**, 166 *et seq.* Springer, 1929.

ADDENDUM

A BRIEF reference may be made to some recent advances which have been made in the interval between the appearance of the last German edition of the present book and the new English edition.

A great deal of effort has been expended in recent years to determine whether cosmic radiation is wholly undulatory or wholly corpuscular in character or whether it is composed of a mixture of both types of rays. A historical summary of the earliest work on cosmic rays has been given by Wigand † who describes the early balloon flights arranged by Gockel, Hess and Kolhörster between December, 1909 and 1913. It was Hess who first recognised that there was a hard type of radiation which was to be distinguished from the γ-radiation emitted by radioactive material in the earth's crust. Measurements at increasing heights from the ground showed that whereas the γ-radiation from the earth *decreased* in intensity during ascent the "cosmic" radiation *increased* in intensity. In recent years many measurements have been made at great heights in manned balloons (Piccard and Kipfer) and unmanned sounding balloons (sent up by Regener to a maximum height of 17 miles) to determine whether these highly penetrating ultra-γ-rays were produced in the stratosphere or in outer space. At the present time the evidence seems rather in favour of a cosmic origin for these rays. Measurements of the decrease of intensity of cosmic rays at various depths in snow-fed lakes (Millikan ; also by Regener in Lake Constance) have also been carried out in order to isolate the hardest components of the radiation and to determine their absorption coefficient (by applying the Klein-Nishina formula). The results suggest that a part of cosmic radiation is electromagnetic in character.‡ Regener's measurements indicate that the ionisation curve of cosmic rays approaches a maximum at the highest parts of the atmosphere hitherto explored.

The investigations into the nature of the rays are complicated by the secondary and probably also tertiary rays which are produced by the passage of the rays through the atmosphere. It seems to be definitely established that a considerable portion (perhaps 80 per cent.) of the cosmic rays that are detected at the earth's surface are corpuscular in character, although it is too early to state with certainty whether they are members of the primary stream of cosmic rays coming from outer space or whether they are secondary rays produced in the upper or lower air. The intensity of cosmic rays, whether

* Added by the translator.

† Phys. Zeits., **25**, 445 (1924). See also Hofmann, Phys. Zeits., **33**, 633-662 (1932), which contains 307 references.

‡ Regener, Nature, **132**, 698 (1933).

undulatory or corpuscular, is measured by their ionising power. Up to 1928 an ordinary ionisation chamber had alone been used to measure the intensity. A considerable improvement was effected when Geiger and Müller * invented their tubular counter for the express purpose of recording the arrival of individual corpuscles or photons. A third method, introduced by Skobelzyn, involved the use of the Wilson cloud chamber, in which the track of ions caused by the passage of a cosmic ray corpuscle, or, indirectly, by a cosmic ray photon, could be photographed. The appearance of the tracks enables conclusions to be drawn about the nature of the ionising agent. By applying magnetic fields up to 20,000 gauss to the ionising particles it is possible to determine their velocity and charge.† The interesting fact emerges from these experiments that some of the tracks are found to be due to electrons moving at a speed only a little less than that of light (corresponding to a volt-velocity of the order of 10^{10}) whereas other tracks that are equally curved in the opposite direction to that of the electrons had necessarily to be ascribed to particles having a mass of the same order as that of the electron but carrying an opposite charge. In other words, the long-sought-after positive electron (or *positron*, as it is now called) first disclosed its existence in experiments performed with cosmic rays. It suggested itself to various workers ‡ that positive electrons might also be produced by the interaction of radiations excited in beryllium (γ-rays and neutrons, see p. 598) and matter. Observations of the ionising power of the resultant radiation in the gas in the expansion chamber and loss of energy in an interposed metal plate were found to justify the assumption that the mass and magnitude of the charge of the positive particle emitted are the same as for the negative electron. Later experiments confirmed that γ-radiations from a thorium active deposit (the strongest component being a ray of $h\nu = 2{\cdot}62 \times 10^6$) can also produce positrons when they are made to impinge on a lead target. Curie and Joliot have shown that when positive and negative electrons are produced by the impact of γ-rays from different sources on various metals (Al, Cu, Pb, U), the ratio of the yield of positrons to that of electrons increases with the energy of the γ-quantum and with the atomic weight of the substance. In some cases an electron originates simultaneously with a positron, a fact which has led to the proposal that the two corpuscles were not originally present in the target but were created from the incident γ-radiation (energy of radiation corresponding to $\frac{1}{2}$ million electron-volts would be necessary to create an electron and the same amount to create a positron). This theory, however, has yet to be confirmed).‖

Further light has been shed on the nature of certain components of cosmic rays by the results of investigations into the possible variation

* Phys. Zeits., **29**, 839 (1928).

† Anderson, Phys. Rev., **41**, 405 (1932); Blackett and Occhialini, Proc. Roy. Soc., **139**, 699 (1933); Kunze, Zeits. f. Physik, **79**, 203 (1932).

‡ Chadwick, Blackett and Occhialini, Nature, **131**, 473 (1933); Meitner and Philip, Naturwiss., **21**, 286 and 468 (1933); Curie and Joliot, Comptes Rendus, **196**, 1105 (1933).

‖ For further details see Bothe, Das Neutron und das Positron, Naturwiss, **21**, 825-831 (1933).

of the intensity of cosmic rays with latitude.* In one group of experiments curves connecting the intensity with latitude at 69 representative places on the earth's surface were obtained. These not only show a rapid increase of intensity with altitude but also greater intensity at each altitude for higher latitudes than for those near the equator. The variation observed follows the geomagnetic latitude rather more closely than the geographic latitude. The variation over a range of 40° on either side of the equator amounts to 12 or 14 per cent. at sea-level. This " latitude effect " of cosmic rays indicates that a certain fraction of the primary cosmic rays consists of corpuscles which are deflected from equatorial regions by the extensive if weak magnetic field of the earth. This is analogous to the deflection of the streams of charged particles from the sun which were assumed by Birheland in order to account for the occurrence of the Northern Lights. The theory of the motion of such streams of charged particles in a heterogeneous magnetic field has been worked out by Stormer.†

Summaries of the present position regarding our knowledge of cosmic rays have been given by Blackett, Regener and Kolhörster.‡

In the realm of nuclear physics rapid and valuable progress is also to be recorded. In 1931 Bothe and Becker observed certain anomalies in γ-radiation which was emitted by light elements after bombardment by α-particles (cf. Rutherford's first disintegration experiment, p. 166). These anomalies were confirmed by Curie and Joliot as well as by Chadwick. It was Chadwick, however, who first recognised that a new type of neutral particle appeared when, say, beryllium was bombarded by α-particles thus :

$$Be_4^9 + He_2^4 \rightarrow C_6^{12} + n_0^1,$$

where the upper indices denote approximate atomic weights and the lower indices the atomic numbers (or net nuclear charges). This new particle called the " neutron " and denoted by n in our nuclear equation is regarded by Chadwick as consisting of a proton and electron in very close association ; its mass is approximately 1 and its atomic number zero. Neutrons are characterised by their great penetrating power. Dee has shown that the primary ionisation along the track of a neutron is less than 1 pair of ions per 3 metres length of path. Massey has calculated that it may be as low as 1 pair of ions per 10^5 km. Whereas the proton dissipates its energy almost entirely in collisions with electrons, the neutron loses its kinetic energy in collisions with nuclei. The actual yield of neutrons in the case of beryllium is about 30 neutrons for every million α-particles of polonium which fall on a thick layer of beryllium.

It has been suggested by Curie and Joliot that the proton, hitherto considered an elementary particle, is composed of a neutron and a positron held in close union. Although this assumption has the advantage of explaining difficulties that occur in certain nuclear

* See report by A. H. Compton, Phys. Rev., **43**, 387-403 (1933).

† *Handbuch der Kosmischer Physik*, Vol. I.

‡ Blackett, Journ. Royal Meteorological Soc., July, 1933 ; Regener, Nature, 696 (1933) ; Kolhörster, Phys. Zeits., **34**, 809 (1933).

reactions the general view is that the *neutron* is the composite element of structure and that the proton is a real unit.*

Another landmark in nuclear physics was reached in 1932 when Cockcroft and Walton † devised an apparatus capable of producing protons having energies of 700 kilovolts. With these protons they bombarded Li, B and F ; the process was accompanied in each instance by the ejection of an α-particle, for example,

$$Li_3^7 + H_1^1 \rightarrow 2He_2^4.$$

The neutrons themselves have been used in their turn to effect nuclear changes. Feather ‡ has shown that when nitrogen nuclei are bombarded by neutrons α-particles are ejected and nuclei of the boron isotope 11 are formed :

$$n_0^1 + N_7^{14} \rightarrow B_5^{11} + He_2^4.$$

This transformation is reversible, since it has been found that when nuclei of the boron isotope of atomic number 11 are bombarded by α-particles neutrons are produced together with nuclei of nitrogen. Transformations of this type allow the mass defect of the neutron to be calculated ; its value comes out as about ·0011, which corresponds to an energy of slightly more than a million electron-volts (about $1{\cdot}6 \cdot 10^{-6}$ erg). This binding energy is consistent with Chadwick's view that the neutron consists of the proton and electron as elementary constituents.

The discovery of the neutron has given rise to new theories concerning the composition of the nucleus. The most fruitful appears to be that suggested by Heisenberg,‖ according to which the nucleus is composed of protons and neutrons but no free electrons ; when two neutrons and two protons form a close bond we have the α-particle (sometimes called *helion*), which is a particularly stable configuration. The addition of one or more neutrons to a nucleus gives rise to one or more isotopes, certain conditions of stability determining the number of possible isotopes in any given case. The mass-defect gives information about the degree of stability of the nucleus. In the case of α-particles the packing fraction (= energy equivalent of the mass defect) amounts to $28 \cdot 10^6$ electron-volts, which is very considerable in comparison with the energy differences that ordinarily occur in nuclear processes. This tends to confirm the view that the α-particle is itself a sort of intermediate element of structure of nuclei. The stability of the α-particle exceeds that of the neutron, as may be seen by comparing their mass-defects. For further remarks on these questions the reader is referred to Beck (*loc. cit.*).

The last important advance to be recorded is the discovery of the heavy hydrogen isotope. With oxygen (isotope 16) as the standard the atomic weight of hydrogen, as deduced from Aston's results

* An admirable account of the properties of neutrons is given in Chadwick's Bakerian lecture, Proc. Roy. Soc., **142**, 1 (1933). Bothe's account (*loc. cit.*) is slightly more recent.

† Proc Roy. Soc., **136**, 619 (1932).

‡ *Ibid.*, **136**, 709 (1932). A list of 22 nuclear reactions, including many due to neutron bombardment, is given by Beck in Marx, *Handbuch der Radiologie*, Vol. VI, Part I, p. 386.

‖ Zeits. f. Phys., **87**, 1 (1932), and **78**, 156 (1932).

(obtained with a mass spectrograph) comes out at 1·00778. Chemical determinations lead to a slightly higher value. This fact led Birge and Menzel to suggest that the discrepancy was probably due to the existence of an isotope of hydrogen of mass 2 and nuclear charge 1. This conjecture was confirmed experimentally by Urey, Brickwedde, and Murphy.* They distilled six litres of liquid hydrogen in the neighbourhood of the triple point under a pressure of a few millimetres of mercury and obtained a small fraction (few cubic centimetres) which contained the heavy hydrogen isotope in the proportion of 1 : 500. The existence of this isotope was also confirmed by these authors in the first satellite which accompanied each of the spectral lines Hα, Hβ, Hγ, Hδ of the mixed hydrogen. These spectral results were accurately confirmed by Bleakney † and Bainbridge,‡ who used the mass spectrograph. Methods of preparing "heavy" water, that is, water composed of the heavy hydrogen isotope combined with oxygen, are briefly described in Nature (Oct., 1933, p. 536), where numerous references are given. Since there are two isotopes of hydrogen and three isotopes of oxygen there are six possible types of pure water; if we take nuclear spin into account, as expressed in the existence of para- and ortho-hydrogen molecules, this number becomes doubled. The name *deuton* (or deuteron) has been given by some writers to the ionised heavy hydrogen isotope, that is, to the nucleus of heavy hydrogen, which, according to Heisenberg's theory, consists of a neutron and a proton held in close union. Other terms (used chiefly in American publications) are: *protium* gas, namely hydrogen molecules consisting of nuclei composed of two protons; *protium-deuterium* gas, namely, hydrogen molecules consisting of one proton and one deuton; and lastly, *deuterium* gas, each molecule of which has a nucleus composed of two deutons. Apart from the interest attaching to the general physical and chemical properties of the new heavy hydrogen gas and its compounds (for example, "heavy water"), important information about nuclei in general may be gained by using the deuton as a new subatomic projectile. Thus Rutherford and Oliphant || have used nuclei of the heavy hydrogen isotope to bombard lithium, obtaining α-particles and neutrons as follows:

$$Li_3^7 + H_1^2 \rightarrow He_2^4 + He_2^4 + n_0^1.$$

In addition to investigating the constitution and stability of the various atomic nuclei, it is important to ascertain the various stationary states (α-ray energy-levels) of each nucleus. A study of the β-rays ejected photo-electrically under the action of primary γ-rays appears to promise the best results in this field, which is being actively explored by Ellis ¶ and his collaborators.

Not the least interesting feature of these fascinating researches is the way in which complementary and confirmatory results are obtained in the two extremes, the smallest regions of space (the interior of the atom) and the most distant parts of space where we suppose cosmic rays to be formed in regions of vast extent.

* Phys. Rev., **39**, 164, and **40**, 1 (1932). † *Ibid.*, **41**, 32 (1932).
‡ *Ibid.*, **40**, 130 and **42**, 1 (1932). || Proc. Roy. Soc., A, **141**, 722 (1933).
¶ See, for example, C. D. Ellis, "β-rays and γ-rays," Reale Academia Italia, x (1932).

MATHEMATICAL APPENDIX

1. Scattering by Bound Electrons

IF the electrons of the radiator are not assumed to be free but bound to the position of rest $x = 0$ by a restoring force $-fx$, we obtain instead of equation (5) on p. 30, if we take the x-axis as the direction of motion,

$$m\ddot{x} + fx = -e\mathbf{E}_p. \quad . \quad . \quad . \quad . \quad (1)$$

To integrate we must now resolve $\mathbf{E}_p$ and x spectrally. Let

$$\mathbf{E}_p = \int \mathrm{E} e^{i\omega t} d\omega,$$

$$x = \int \xi e^{i\omega t} d\omega$$

(continuous spectrum).

Also, let $\sqrt{\frac{f}{m}} = \omega_0$ be the proper frequency of the elastic connection. We assume that it lies, say, in the ultra-violet Schumann region. It then follows from (1) that

$$\left.\begin{aligned} \xi(\omega_0^2 - \omega^2) = -\frac{e}{m}\mathrm{E}, \quad x = -\frac{e}{m}\int \frac{1}{\omega_0^2 - \omega^2}\mathrm{E}e^{i\omega t} d\omega, \\ \dot{v} = \ddot{x} = \frac{e}{m}\int \frac{\omega^2}{\omega_0^2 - \omega^2}\mathrm{E}e^{i\omega t} d\omega \end{aligned}\right\} \quad . \quad (2)$$

as given in equation (5), p. 30.

. To arrive at a scattering formula which is also comparable with the results of experiment in the visible region it is best to proceed as follows. We restrict ourselves to monochromatic light of frequency $\omega = 2\pi c/\lambda$; the following relation then holds quite independently of the value of the frequency:

$$\dot{v} = -\omega^2 x = -\omega^2 \xi e^{i\omega t}. \quad . \quad . \quad . \quad (3)$$

Let the incident plane wave of direction OP in Fig. 147 be assumed to be unpolarised. We consider a definite direction PQ, starting from P, of the scattered radiation (P is the scattering particle, Q the point of observation, the length of PQ $= r$) and divide the incident wave into two components P1 and P2, the former being perpendicular to the plane OPQ, the other in this plane perpendicular to OP. The former P1 forms the angle $\theta = \pi/2$ with r, the other P2 the angle $\theta = \pi/2 + \phi$, where ϕ denotes the angle OPQ between the incident and the scattered ray.

If we substitute (3) in equation (2) on p. 24 and proceed to take the average value over the time, we obtain

$$\bar{\mathfrak{S}} = \frac{\omega^4}{4\pi c^3 r^2} \frac{\sin^2\theta}{2}(e\xi)^2.$$

For the component P1 we have $\theta = \pi/2$, $\sin\theta = 1$; for the component P2 we have $\theta = \pi/2 + \phi$, $\sin\theta = \cos\phi$. Hence we obtain as the sum for both components

$$\bar{\mathfrak{S}} = \frac{\omega^4}{4\pi c^3 r^2} \frac{1 + \cos^2\phi}{2}(e\xi)^2 \quad . \quad . \quad . \quad (4)$$

which represents the effect of a single scattering particle.

Under the ordinary conditions of optics the electrons that belong to the same molecule vibrate *coherently; hence it is not their radiant energy* $\mathfrak{S}$ *but their amplitude* ξ *that superposes itself.* Hence we have in (4) instead of $(e\xi)^2$ the term $(Se\xi)^2$, if we pass on to the whole molecule and take S to stand for the summation over all electrons of the individual molecule. On the other hand, the electrons that belong to different molecules vibrate *non-coherently*, so that in summing over different molecules we must superpose on one another not the amplitudes but the energies. In this way we obtain for the radiation scattered by unit volume

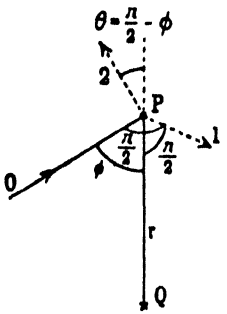


FIG. 147.

$$\bar{\mathfrak{S}}_1 = \frac{4\pi^3 c}{\lambda^4 r^2} \frac{1 + \cos^2\phi}{2} \sum (Se\xi)^2 \quad . \quad . \quad . \quad (5)$$

when we write $\omega = 2\pi c/\lambda$.

The symbol Σ denotes the summation over all molecules of the unit volume; $\Sigma Se\xi$ is thus the electric moment per unit volume, and by the definition of the index of refraction n in a sufficiently rarefied gas which is traversed by a light-wave of electrical amplitude E this is equal to $\frac{n^2 - 1}{4\pi}$E. (In a dense gas or a liquid of density $\frac{3(n^2 - 1)}{n^2 + 2}$ occurs in place of $n^2 - 1$.) From $\Sigma Se\xi = \frac{(n^2 - 1)}{4\pi}$E it follows that

$$Se\xi = \frac{n^2 - 1}{4\pi L}E, \quad \Sigma(Se\xi)^2 = \frac{(n^2 - 1)^2}{16\pi^2 L}E^2,$$

where L denotes Loschmidt's number for unit volume.

Hence from (5),

$$\bar{\mathfrak{S}}_1 = \frac{\pi c}{\lambda^4 r^2} E^2 \frac{1 + \cos^2\phi}{2} \frac{(n^2 - 1)^2}{4L}.$$

By equation (2) on p. 24 the time-mean of the incident energy is, if we calculate the sum for the two directions of polarisation,

$$\bar{\mathfrak{S}}_0 = \frac{c}{4\pi}E^2.$$

Hence

$$\frac{\bar{S}_1}{\bar{S}_0} = \frac{\pi^2}{\lambda^4 r^2} \cdot \frac{1 + \cos^2 \phi}{2} \frac{(n^2 - 1)^2}{L} \cdot \quad . \quad . \quad . \quad (6)$$

Equation (6) is identical with Rayleigh's formula for the intensity of the scattered light from the sky. The factor $1/\lambda^4$ explains the predominance of the short waves in the scattered light, that is, the blue colour of the sky, and the predominance of long wave-lengths in the transmitted light, that is, the red colour of the setting sun. The formula may serve to determine Loschmidt's number. Observations on Peak Teneriff * gave

$$L = 2{\cdot}89 \,.\, 10^{19}$$

whereas Planck obtains from the theory of radiation

$$L = 2{\cdot}76 \,.\, 10^{19}.$$

The above discussion, taken from optics, is appropriate for pointing out the limits within which the equations (4) to (10) on pp. 30 and 31 are alone valid. For optical purposes we were able to superpose in the case of the electrons of one molecule not its radiation (intensity) but rather its field (amplitude). The interest in the earlier calculation in the X-ray region consisted in the fact that it gave us the total number Z of the electrons of an atom ; this was possible because in that case the *intensity* of these Z electrons became superposed. In the optical case the wave-length is great compared with the inner molecular electrons and that is why these electrons vibrate coherently. In the X-ray region the wave-lengths must be small if we wish to calculate with the complete non-coherence of the waves, that is, with the superposition of the intensities. Hence our method of calculation applies only to *sufficiently hard* X-rays.

For softer rays there is a conically limited region in the neighbourhood of the primary ray, in which interferences, that is, superposition of the *amplitudes*, occur. Debye has investigated this theoretically and experimentally.†

In contrast with this our calculations of pp. 30 and 31 should hold for sufficiently hard rays, particularly those dealing with the mass-absorption coefficient s/ρ, according to which the value 0·2 (eqn. (12) on p. 31) should hold for all elements. It is found, however, strangely enough that it is just in the case of very short wave-lengths, those of γ-rays, that deviations from the classical value 0·2 occur.

For Kohlrausch ‡ found in the case of γ-radiation from a Radium preparation that the total weakening coefficient (true absorption coefficient + scattering coefficient) has a value less than 0·2. But according to Richtmyer ‖ there is no sign of a value less than that given by classical theory in the case of the hardest X-rays of λ about 0·1 Å. Hence the transition to smaller values occurs only at wave-lengths of the order of magnitude of the wave-length $\Lambda = 0{\cdot}024$ Å (cf. p. 47)

* Cf. Dember, Ann. d. Phys., **49**, 609 (1916).
† Ann. d. Phys., **43**, 49 (1914).
‡ K. W. F. Kohlrausch, Wien. Ber., **126**, 441, 683, 887 (1917).
‖ Phys. Rev., **18**, 13 (1921).

which is decisive in the Compton effect, and this is a manifestation of the double nature of light (light quantum and light wave) which expresses itself in the Compton effect. Hence the question may be treated quantitatively only by means of the methods of wave-mechanics* (with Dirac's elaboration of it).

2. Proof of the Invariance of Hamilton's Equations for Arbitrary Transformations of Co-ordinates. Contact Transformations

From Newton's foundations of mechanics we inferred on pp. 77 and 78 the validity of Hamilton's equations :

$$\frac{\partial q_k}{\partial t} = \frac{\partial H}{\partial p_k}, \qquad \frac{\partial p_k}{\partial t} = -\frac{\partial H}{\partial q_k}, \qquad p_k = \frac{\partial E_{kin}}{\partial \dot{q}_k}, \quad . \quad . \quad (1)$$

where we used rectangular co-ordinates $q_k = x, y, z$ for an individual point-mass and assumed that the potential energy depended only on the q_k's. But, as already remarked on p. 78, what holds for *one point-mass* also holds for a *system of point-masses* between which conservative forces act. The equations (1) hold for each of them if we take q_k to stand consecutively for the rectangular co-ordinates of each individual point of the system. We now show that the form of the equations (1) remain preserved also if we introduce by means of any arbitrary " point-transformation " (one that does not, however, contain the time) the new position coordinates

$$Q_k = f_k(q_1, q_2 \ldots) \quad . \quad . \quad . \quad . \quad (2)$$

instead of the rectangular co-ordinates.

To show this we consider the q_k's to be calculated from (2) as functions of the Q_k's. The $\dot{q}_k$'s derived in this way by differentiating with respect to t become linear functions of the $\dot{Q}_k$'s with coefficients that depend on the Q_k's. The kinetic energy expressed in the rectangular co-ordinates of velocity $\dot{q}_k$ is a homogeneous quadratic function of the $\dot{q}_k$'s. We called it E_{kin} in (1). If we now insert the values of the $\dot{q}_k$'s expressed in terms of the $\dot{Q}_k$'s and Q_k's, we obtain a homogeneous quadratic function of the $\dot{Q}_k$'s with coefficients that depend on the Q_k's. We call this $\bar{E}_{kin}(\dot{Q}_k, Q_k)$ and have by definition

$$\bar{E}_{kin}(\dot{Q}_k, Q_k) = E_{kin}(\dot{q}_k). \quad . \quad . \quad . \quad (3)$$

From the homogeneity of the expressions it follows that

$$E_{kin} = \tfrac{1}{2}\sum_k \frac{\partial E_{kin}}{\partial \dot{q}_k}\dot{q}_k, \qquad \bar{E}_{kin} = \tfrac{1}{2}\sum_k \frac{\partial \bar{E}_{kin}}{\partial \dot{Q}_k}\dot{Q}_k.$$

Precisely as in the equations (1) p_k was defined by differentiating E_{kin}, so we now define P_k by the convention (cf. also Chap. II, § 6, p. 99, eqn. (9)) :

$$P_k = \frac{\partial \bar{E}_{kin}}{\partial \dot{Q}_k}. \quad . \quad . \quad . \quad . \quad (4)$$

* O. Klein and Y. Nishina, Zeits. f. Physik, **52**, 853 (1928) ; Nature, **122**, 398 (1928).

We then have

$$E_{kin} = \tfrac{1}{2}\sum_k p_k\dot{q}_k, \quad \bar{E}_{kin} = \tfrac{1}{2}\sum_k P_k\dot{Q}_k \quad . \quad . \quad (5)$$

and conclude from (3)

$$\Sigma P_k\dot{Q}_k = \Sigma p_k\dot{q}_k. \quad . \quad . \quad . \quad . \quad (6)$$

This equation may serve to define the P_k's instead of (4). For by differentiating (2) with respect to t calculating $\dot{q}_k$ as a linear function of the $\dot{Q}_k$'s, substituting in (6) and comparing the coefficients of $\dot{Q}_k$ on both sides we obtain the P_k's as linear functions of the p_k's with coefficients that depend on the Q_k's.

If we reverse the last relationships and substitute the expressions for the p_k and the values of the q_k's obtained from (2) in the Hamiltonian function $H(p, q)$, we obtain the expression for Hamilton's function in the co-ordinates P, Q; we call it $\bar{H}(P, Q)$ and have by definition

$$\bar{H}(P_k, Q_k) = H(p_k, q_k). \quad . \quad . \quad . \quad . \quad (7)$$

Our assertion now implies that for the quantities P_k, Q_k, $\bar{H}(P, Q)$ so defined the Hamiltonian equations again hold:

$$\frac{dQ_k}{dt} = \frac{\partial\bar{H}}{\partial P_k}, \quad \frac{dP_k}{dt} = -\frac{\partial\bar{H}}{\partial Q_k}. \quad . \quad . \quad . \quad (8)$$

To make the proof capable of being generalised as far as possible we apply the method of the calculus of variations. Although we have nothing new to say about this calculus we shall epitomise the essential features here for the convenience of the reader. We first imagine the differential equations (1) of point mechanics to be compressed into the form of d'Alembert's principle:

$$\sum p_k\delta q_k\Big|_0^t = \int_0^t \delta L d\tau, \quad . \quad . \quad . \quad . \quad (9)$$

cf. Chap. II, § 6, p. 98, eqn. (4). But, as proved on pp. 98, 99, this equation holds for arbitrary co-ordinates and momenta and may therefore be written in the form

$$\sum P_k\delta Q_k\Big|_0^t = \int_0^t \delta\bar{L}d\tau, \quad \text{where } \bar{L} = \bar{L}(Q_k, \dot{Q}_k) = L(q_k, \dot{q}_k). \quad (10)$$

As shown in p. 98 we obtain Hamilton's Principle from this equation. This principle is commonly used to derive the general Lagrange equations, where L is then regarded as a function of the Q's and $\dot{Q}$'s. We shall use it here to arrive at the Hamiltonian equations for general co-ordinates Q_k and momenta P_k. From the definition of L and H

$$L = E_{kin} - E_{pot}, \quad H = E_{kin} + E_{pot}$$

it follows, in view of (5), that

$$\bar{L}(Q, \dot{Q}) = \Sigma P_k\dot{Q}_k - \bar{H}(P, Q). \quad . \quad . \quad . \quad (11)$$

We may therefore also write Hamilton's Principle in the form

$$\delta\int_0^t[\bar{H}(P, Q) - \Sigma P_k\dot{Q}_k]d\tau = 0 \quad . \quad . \quad . \quad (12)$$

and may further choose the Q_k's, P_k's as *those quantities with respect to which we perform variation.* From (12) we obtain

$$\sum_k\int_0^t\Big(\frac{\partial\bar{H}}{\partial P_k} - \dot{Q}_k\Big)\delta P_k d\tau + \sum_k\int_0^t\frac{\partial\bar{H}}{\partial Q_k}\delta Q_k\delta\tau - \sum_k\int_0^t P_k\delta\dot{Q}_k d\tau = 0.$$

If we integrate the last integral by parts, taking into account that at the limits we must have $\delta Q_k = 0$, we transform the last equation into

$$\sum_k\int\Big(\frac{\partial\bar{H}}{\partial P_k} - \dot{Q}_k\Big)\delta P_k d\tau + \sum_k\int\Big(\frac{\partial\bar{H}}{\partial Q_k} + \dot{P}_k\Big)\delta Q_k d\tau = 0. \quad . \quad (13)$$

We must now bear in mind that the δP's and the δQ's are not independent but are connected by the equation

$$P_k = \frac{\partial\bar{E}_{kin}}{\partial\dot{Q}_k} = \frac{\partial\bar{L}}{\partial\dot{Q}_k}. \quad . \quad . \quad . \quad (13a)$$

It is therefore not permissible to set the coefficients of δP_k and δQ_k in (13) individually equal to zero. But we may show that the factor of δP_k in (13) vanishes on account of (13*a*). For if we vary (11) with respect to one of the quantities P_k while keeping Q_k and the remaining P_k fixed, we obtain

$$\sum_i\frac{\partial\bar{L}}{\partial\dot{Q}_i}\frac{\partial\dot{Q}_i}{\partial P_k}\delta P_k = \dot{Q}_k\delta P_k + \sum_i P_i\frac{\partial\dot{Q}_i}{\partial P_k}\delta P_k - \frac{\partial\bar{H}}{\partial P_k}\delta P_k. \quad . \quad (14)$$

On account of (13*a*) the left-hand side cancels out with the middle term of the right-hand side. Hence we deduce from (14)

$$\dot{Q}_k = \frac{\partial\bar{H}}{\partial P_k}. \quad . \quad . \quad . \quad . \quad (14a)$$

If we now return to (13) we obtain, since the δQ_k's are independent of each other,

$$\dot{P}_k = -\frac{\partial\bar{H}}{\partial Q_k}. \quad . \quad . \quad . \quad . \quad (14b)$$

The invariance of Hamilton's equations with respect to arbitrary point transformations is thus a direct consequence of their derivation from the (modified) Hamiltonian Principle.

If we glance back over the above proof we see that we assumed far more than was necessary for deriving the desired result, namely, equation (8). In (6) and (7) we assumed that

$$\Sigma P_k\dot{Q}_k = \Sigma p_k\dot{q}_k \quad \text{and} \quad \bar{H} = H.$$

But to be able to write down Hamilton's Principle in the form (12) it is only necessary to postulate instead of this that

$$H - \Sigma p_k \dot{q}_k = \bar{H} - \Sigma P_k \dot{Q}_k - \dot{F}. \quad . \quad . \quad (15)$$

Here F denotes an arbitrary function, for example, of the arguments p, Q and t; $\dot{F}$ is its complete differential coefficient with respect to t. Actually the additional term that occurs on (12) on account of $\dot{F}$ drops out when we integrate with respect to τ since it reduces to the values of δF at the limits which for their part vanish, just like δq, δQ, δt. In our special point-transformation (2) we clearly had $F = 0$. But much more general transformations of the following form are compatible with the equation (15):

$$Q_k = f_k(q_i, p_i, t); \quad P_k = g_k(q_i, p_i, t), \quad F = F(q_i, Q_i, t). \quad (16)$$

This method of writing F expresses that, as already remarked, we may conveniently regard q, Q and t as variables of F (if, instead, we had chose q, p, t as our arguments as in the first equation (16), we should have been able to calculate p_i from the first equation (16) and to substitute it in F). The choice of q, Q, t as independent variables makes it easier to specify the conditions which are imposed on the transformations (16) through the presence of (15). This choice is, however, possible only if there is no analytical relationship between the q's, Q's and t; it becomes impossible if, as at the beginning of this section, equations of the form (2) hold.

We arrange equation (15) according to the differentials of the independent variables, call dt the differential of t and indicate by means of δ those differentiations with respect to q and Q in which t is not subjected to variation. Accordingly we set

$$\dot{F}dt = \frac{\partial F}{\partial t}dt + \delta F,$$

and write (15)

$$\left(\bar{H} - H - \frac{\partial F}{\partial t}\right)dt + \Sigma p_k \delta q_k - \Sigma P_k \delta Q_k - \delta F = 0. \quad . \quad (17)$$

To specify our transformation (16) we now demand that this condition shall be fulfilled for *all* virtual changes δq, δQ, dt. On account of the independence of the variables t, q, Q (17) may be separated into two groups of postulates, which the transformations (16) must satisfy:

$$\bar{H} = H + \frac{\partial F}{\partial t}, \quad . \quad . \quad . \quad . \quad (17a)$$

$$\Sigma p_k \delta q_k = \Sigma P_k \delta Q_k + \delta F. \quad . \quad . \quad . \quad (17b)$$

Equation (17b) shows directly, if we vary only one of the quantities q_k, Q_k, that

$$p_k = \frac{\partial F}{\partial q_k}, \quad P_k = -\frac{\partial F}{\partial Q_k} \quad . \quad . \quad . \quad (17c)$$

hold. In the particular case where the additional function F is chosen as independent of t the equation (17a) reduces to the earlier equation

(7). Equation (17*b*) is, however, more general also in this case than equation (6) since here the term δF is also present.

The equations (16) evidently do not represent a " point transformation," since as they no longer, like (2), connect the point- and position-co-ordinates, q, Q with each other but with the momentum co-ordinates p, P. Since, moreover, in such a general transformation the mechanical significance of the momentum co-ordinates becomes blurred it is better to call the pairs of variables q, p, on the one hand, and Q, P, on the other, *canonical variables*. P is *canonically conjugate* to Q, likewise p to q. The general transformation of canonical variables, which is thus restricted only by the existence of the condition (17), is called a *canonical transformation*. We shall discuss at the conclusion of this section to what extent the term *contact transformation* may be used synonymously with this term. In the most general case, namely when the function F depends on t, the canonical transformation connects together not only the quantities q, p with Q, P but rather the quantities q, p, H with Q, P, $\bar{H}$.

In certain circumstances it is convenient to use as our basis instead of q, Q, t the quantities q, P, t as independent variables, for example, in the case above excluded, where there is an analytical relationship between the q's, Q's and t. It is easy to rewrite equation (15) in such a form that it becomes adapted to this point of view. It is only necessary to add on the right-hand side $\Sigma Q_k P_k$ with a positive and a negative sign, and to consider instead of F the " modified " function

$$F^* = F + \Sigma P_k Q_k. \quad . \quad . \quad . \quad . \quad (18)$$

Equation (15) then assumes the form

$$H - \Sigma p_k \dot{q}_k = \bar{H} + \Sigma Q_k \dot{P}_k - \dot{F}^*. \quad . \quad . \quad (19)$$

From it we obtain as analgous expressions to the equations (17*a*, *b*), if we now treat t, q and P as independent variables :

$$\bar{H} = H + \frac{\partial F^*}{\partial t} \quad . \quad . \quad . \quad . \quad (19a)$$

$$\Sigma p_k \delta q_k + \Sigma Q_k \delta P_k = \delta F^*. \quad . \quad . \quad . \quad (19b)$$

From this point of view we obtain the quantities p, Q that are " canonically conjugate " to the independent variables q, P by means of the formulæ

$$p_k = \frac{\partial F^*}{\partial q_k}, \quad Q_k = \frac{\partial F^*}{\partial P_k} \quad . \quad . \quad . \quad (19c)$$

that are analogous to (17*c*).

The expression " modified function " F^* is intended to serve as a reminder of the process that is commonly used in dynamics and thermodynamics in changing the independent variable, a process which is in its abstract form due to *Legendre* and is called a *Legendre transformation*.

It now only remains to give a reason for the term " contact transformation."

Let us consider a " surface " $s = s\,(q_1, q_2, \ldots q_f)$ in $(f + 1)$-

dimensional space by interpreting $q_1, \ldots q_f$ as rectangular point co-ordinates in a "plane" and s perpendicular to it. The quantities

$$p_k = \frac{\partial s}{\partial q_k}$$

then determine the position of the tangential plane at the surface s and may therefore be called "plane-co-ordinates." The following "condition of unified position" (*Bedingung der vereinigten Lage*) holds between the point- and plane-co-ordinates:

$$ds = \sum_1^f p_k dq_k. \quad . \quad . \quad . \quad . \quad (20)$$

Let us introduce new co-ordinates Q_k, P_k by means of the equations (16), but to make possible a simple geometrical interpretation let us suppose that the functions f and g are independent of t. Expressing the q_k's in terms of Q_i and P_i by means of equations (16) we form $s(q) = S(P, Q)$ and demand that the new configuration S should also represent a surface, that is, that it should be touched by the planes given by P at the points determined by Q. As a consequence of (20) we must then have

$$dS = \Sigma P_k dQ_k, \quad . \quad . \quad . \quad . \quad (20a)$$

that is, if ρ denotes an arbitrary function of the q, p, s's or Q, P, S's,

$$dS - \Sigma P_k dQ_k = \rho(ds - \Sigma p_k dq_k). \quad . \quad . \quad (21)$$

This is the condition which must be fulfilled if we are to be able to call our transformation (16) a *contact transformation in the geometrical sense.*

Although the condition (21) looks different from (17)—in (17) the factor ρ is absent, and, on the other hand, the term in dt which is absent in (21), is present in (17)—both conditions are *mathematically equivalent.* The differences may be eliminated formally. We may regard the most general canonical transformation of a problem of f degrees of freedom as a contact transformation in space of $f + 1$ dimensions. In the same way we may regard the most general contact transformation in space of f dimensions as a canonical transformation of a problem of $f + 1$ degrees of freedom.

3. Concerning the Ratio of the Kinetic to the Potential Energy in the Coulomb Field

At the close of his first paper in Phil. Mag.,* Bohr makes the following statement:

"In every system of nuclei at rest and electrons that move in circles with velocities which are small compared with c the kinetic energy is, except in the sign, equal to half the potential energy."

We shall show that this theorem applies much more widely: it holds not only for circular orbits but also for arbitrary forms of motion, in which (for varying kinetic and potential energy) the time-mean values of both energies have to take the places of the energy values themselves

* Vol. 26, p. 24 (1913).

in the enunciation of the theorem. It also remains valid except for a small change if we allow any arbitrary central force to act in place of Coulomb's law of force.* It is not necessary nor even convenient in the sequel to assume the nuclei at rest.

We take as our basis rectilinear co-ordinates x, y, z which we distinguish by affixing numbers for the electrons and nuclei and denote by $q_1 \ldots q_f$. Let $p_1 \ldots p_f$ be the corresponding momenta. Then the kinetic energy of our system of nuclei and electrons can, by equation (5) of the preceding note, be put into the form

$$E_{kin} = \tfrac{1}{2}\sum_k p_k \dot{q}_k. \quad . \quad . \quad . \quad . \quad (1)$$

Let the potential energy be a homogeneous function of degree $n+1$, of the co-ordinates q_k. This is the case, for example, if central forces proportional to r^n act between the point-masses of the system, that is, between the i^{th} and j^{th} point-mass (no matter whether it be nucleus or electron), a force acts in the line connecting both, its amount being $C_{ij} r_{ij}^n$ (n is the same throughout but C may under certain circumstances change from point-pair to point-pair). Then we get (cf. eqn. (3) on p. 77)

$$E_{pot} = \frac{1}{n+1}\sum_k \frac{\partial E_{pot}}{\partial q_k} q_k = -\frac{1}{n+1}\sum_k \dot{p}_k q_k. \quad . \quad . \quad (2)$$

We next form

$$\frac{d}{dt}\sum p_k q_k = \sum p_k \dot{q}_k + \sum \dot{p}_k q_k \quad . \quad . \quad . \quad (3)$$

and take the mean value in time, which we denote by a horizontal bar. If the motion is periodic or at all stable in the sense that the position of the point-masses does not systematically deviate from its initial configuration to an extent that increases indefinitely with the time, the time-mean on the left-hand side of (3) becomes equal to zero. Thus

$$\overline{\sum p_k \dot{q}_k} = -\overline{\sum \dot{p}_k q_k} \quad . \quad . \quad . \quad . \quad (4)$$

must hold. By (1) and (2) this means that

$$\overline{E_{kin}} = \frac{n+1}{2}\overline{E_{pot}}. \quad . \quad . \quad . \quad . \quad (5)$$

If we finally set $n = -2$ (Coulomb force), then Bohr's assertion is valid in its extended form, namely,

$$\overline{E_{kin}} = -\tfrac{1}{2}\overline{E_{pot}}. \quad . \quad . \quad . \quad . \quad (6)$$

Our theorem does not hold in relativistic mechanics, because here equation (1) falls out of action.

* In what follows we continue from Burgers, Diss. Haarlem, 1918, p. 168, whose simple proof we extend to the case in which any central force, not merely Coulomb's, acts. This extension already occurs in Jacobi, Vorlesungen über Dynamik, p. 22.

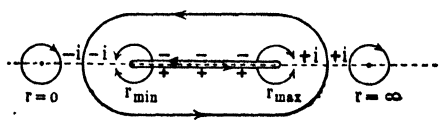
4. Integration with the Help of Complex Variables

It is well known that the method of complex variables has the advantage of enabling us to evaluate integrals over a closed path of integration without the use of special devices. As stated on p. 106 it is intimately connected with the problems of the quantum theory.

(*a*) The integral

$$J = \oint \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}}\,dr \quad . \quad . \quad . \quad (1)$$

constitutes the natural basis for the treatment of the radial quantum condition (see also pp. 111 and 256). The constants A, B and C have a somewhat different meaning in the relativistic and non-relativistic cases. In the diagram of Fig. 148 we take them so that the branch points of the integrand—we call r_{min} and r_{max} the perihelion and the aphelion distance on p. 111—have real positive values. The path of integration originally ran from r_{min} to r_{max} and back again to r_{min}, cf. p. 111, and, as shown in Fig. 148, it is drawn out into a closed curve in the complex r-plane. This is possible because there are certainly no singularities in the immediate neighbourhood of the initially real path of integration. The r-plane is to be imagined slit between r_{min} and r_{max} and represents the upper sheet of a two-sheeted Riemann surface. On account of the positive character of the phase-integrals the sign of the square root is to be taken as *positive* if dr is positive (lower edge of the slit), and *negative* if dr is negative (upper edge of the slit). Hence it follows immediately that the square root outside the slit on the real axis of the r-plane is imaginary, being *positive* and imaginary for $r > r_{max}$, and *negative* and imaginary for $0 < r < r_{min}$, as is likewise indicated in the figure. We see this if we start from the positive or negative side of the branching slit and make half a revolution around the branch-points $r = r_{max}$ or $r = r_{min}$.



r – plane

FIG. 148.

We continue the process of extending the path of integration and contract it around the poles * of the integrand. These are the points

$$r = 0 \text{ and } r = \infty.$$

At the point $r = 0$, J behaves like

$$\sqrt{C}\int \frac{dr}{r}\left(1 + \frac{B}{C}r + \ldots\right).$$

The integration is to be taken, as the figure shows, in the clockwise direction and the first member of the series therefore gives the value

* To investigate the behaviour of a function at infinity we must, as we know, project the point at infinity into finite regions. This is done by means of the transformation $s = 1/r$, in the notation used in the text.

$-2\pi i$; the subsequent terms, however, vanish in the process of integration. Hence the contribution of the point $r = 0$ is, all in all,

$$-2\pi i\sqrt{C}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The point at infinity is indicated in the figure in the finite region. We set

$$s = \frac{1}{r}, \quad dr = -\frac{ds}{s^2},$$

and obtain from (1)

$$J = -\int\sqrt{A + 2Bs + Cs^2}\frac{ds}{s^2}$$

$$= -\sqrt{A}\int\left(1 + \frac{B}{A}s + \ldots\right)\frac{ds}{s^2}.$$

The residue of this integral for the point $s = 0$ is determined solely by the term in s^{-1}; this term has the coefficient

$$-\frac{B}{\sqrt{A}}.$$

Hence the contribution of the point at infinity becomes (cf. the sense of traverse in the figure)

$$+2\pi i\frac{B}{\sqrt{A}}. \quad . \quad . \quad . \quad . \quad (2a)$$

From the sum of (2) and (2*a*) we obtain as the value of J

$$J = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}}\right). \quad . \quad . \quad . \quad (3)$$

We add a supplementary remark about the sign of $\sqrt{C}$. In (2) $\sqrt{C}$ was defined as the residue of the expression

$$\sqrt{A + \frac{2B}{r} + \frac{C}{r^2}}$$

for $r = 0$. This expression is, as has already been indicated in the figure, imaginary and negative in the neighbourhood of the zero-point when r is real and positive. For this reason $\sqrt{C}$ must also be reckoned as imaginary and negative in (3). We infer correspondingly that $\sqrt{A}$ is imaginary but positive.

(*b*) We add a correction term Dr under the root sign of the integral J. We call the resulting integral

$$K = \oint\sqrt{A + \frac{2B}{r} + \frac{C}{r^2} + Dr}\,dr. \quad . \quad . \quad . \quad (4)$$

The position of the branch-point is not essentially altered by the correction term. Hence we may take over Fig. 148 with its determinations of the sign and path of integration.

To be able to perform the integration we shall expand the root in

power series after the correction term. For this purpose it is necessary to deform the path of integration in given cases in such a way that the expansion is possible along its whole course. If D is sufficiently small this is always possible. Any new branch-points that may become added owing to the correction term must be circumvented by the deformed path of integration. If we now perform the integration term by term we may proceed with the path of integration for every term as in Fig. 148, since in the individual term only the branch section $r_{min} \to r_{max}$ and the poles $r = 0$ and $r = \infty$ occur.

The first term that results is the earlier integral J. We call the integral of the second term K_1

$$K = J + \frac{D}{2} K_1 \quad . \quad . \quad . \quad . \quad (5)$$

by setting

$$K_1 = \oint \frac{r dr}{\sqrt{A + \frac{2B}{r} + \frac{C}{r^2}}} = \oint \frac{r^2 dr}{\sqrt{C + 2Br + Ar^2}} . \quad . \quad (6)$$

Here we are concerned only with the point $r = \infty$ as now the integrand is regular at the point $r = 0$. We introduce the new variable of integration $s = 1/r$ and have

$$K_1 = -\oint \frac{ds}{s^3 \sqrt{A}} \left(1 + 2\frac{B}{A} s + \frac{C}{A} s^2\right)^{-\frac{1}{2}} .$$

By expanding in a power series as far as s^2 we obtain

$$K_1 = -\oint \frac{ds}{s^2 \sqrt{A}} \left[1 - \frac{B}{A} s + \left(\frac{3}{2}\frac{B^2}{A^2} - \frac{C}{2A}\right) s^2 + \ldots\right],$$

and by contracting the path of integration about $s = 0$,

$$K_1 = \frac{2\pi i}{\sqrt{A}} \left(\frac{3}{2}\frac{B^2}{A^2} - \frac{C}{2A}\right) . \quad . \quad . \quad . \quad (7)$$

Accordingly we obtain from (5), in view of (3),

$$K = -2\pi i \left\{\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{D}{4A^{\frac{3}{2}}} \left(\frac{3B^2}{A} - C\right)\right\} . \quad . \quad (8)$$

We shall apply this in the theory of the Stark effect.

(*c*) We shall also require (in the quadratic Stark effect) the second term in the expansion of the integral (4) in powers of D. This second term is

$$-\frac{D^2}{8} L, \quad L = \oint \frac{r^2 dr}{\left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{\frac{3}{2}}} . \quad . \quad . \quad (9)$$

As in (*b*) the zero-point makes no contribution. Hence we transform to infinity and obtain

$$L = -\frac{1}{A^{\frac{3}{2}}} \int \frac{ds}{s^4} \left(1 + 2\frac{B}{A} s + \frac{C}{A} s^2\right)^{-\frac{3}{2}} . \quad . \quad . \quad (10)$$

Expanding by means of the multinomial theorem we easily obtain as the factor of s^3 in the numerator (the second and third power of the multinomial expansion also contribute):

$$\frac{15}{2}\frac{BC}{A^2} - \frac{35}{2}\frac{B^3}{A^3} = \frac{5}{2}\frac{B}{A^2}\left(3C - 7\frac{B^2}{A}\right).$$

By forming the residue at the point $s = 0$ (factor $-2\pi i$) we therefore obtain for L

$$L = 2\pi i\frac{5}{2}\frac{B}{A^{\frac{7}{2}}}\left(3C - 7\frac{B^2}{A}\right), \quad . \quad . \quad . \quad (11)$$

and as the contribution of the term (9), which is quadratic in D, to the integral (4),

$$-2\pi i\frac{5}{16}\frac{BD^2}{A^{\frac{7}{2}}}\left(3C - 7\frac{B^2}{A}\right). \quad . \quad . \quad . \quad (12)$$

The formula (8) when corrected by the amount of this term therefore runs:

$$K = -2\pi i\left\{\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{D}{4A^{\frac{3}{2}}}\left(\frac{3B^2}{A} - C\right) - \frac{5}{16}\frac{D^2B}{A^{\frac{7}{2}}}\left(7\frac{B^2}{A} - 3C\right)\right\}. \quad (13)$$

(*d*) We next consider (for the purpose of the theory of spectra unlike that of hydrogen) the integral

$$J_1 = \oint\sqrt{A + \frac{2B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3}}dr. \quad . \quad . \quad (14)$$

We again expand according to the correction term. If we retain only the first power of D_1, the expansion runs:

$$\sqrt{A + \frac{2B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3}} = \sqrt{A + \frac{2B}{r} + \frac{C}{r^2}} + \left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-\frac{1}{2}} \cdot \frac{D_1}{2r^3}.$$

With the integration anticipated in (14) it gives

$$J_1 = J + \frac{D_1}{2}J_2, \quad J_2 = \oint\left(A + \frac{2B}{r} + \frac{C}{r^2}\right)^{-\frac{1}{2}}\frac{dr}{r^3}. \quad . \quad (15)$$

J_2 behaves regularly at the point $r = \infty$. For if we set $s = 1/r$ as above, we obtain

$$J_2 = -\int\frac{sds}{\sqrt{A + 2Bs + Cs^2}}.$$

At the point $r = 0$ we then have

$$\left.\begin{aligned} J_2 = \int\frac{dr}{r^2}(C + 2Br + Ar^2)^{-\frac{1}{2}} &= \frac{1}{\sqrt{C}}\int\frac{dr}{r^2}\left(1 - \frac{B}{C}\cdot r + \ldots\right) \\ &= +2\pi i\frac{B}{C\sqrt{C}}. \end{aligned}\right\} \quad (15a)$$

Hence in virtue of (3) we obtain from (15)

$$J_1 = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{BD_1}{2C\sqrt{C}}\right). \quad . \quad . \quad (16)$$

(*e*) In J_1 we add a second correction term having the small factor D_2, which is to be of the same order of magnitude as D_1^2, and consider

$$J_3 = \oint\sqrt{A + 2\frac{B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D_2}{r^4}}dr. \quad . \quad . \quad (17)$$

Fig. 148 again applies in respect of path of integration and sign.

We now expand, cancelling all powers that are higher than D_1, D_1^2 and D_2:

$$\sqrt{A + 2\frac{B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D_2}{r^4}} = \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2}} + \frac{1}{2}\left(A + 2\frac{B}{r} + \frac{C}{r^2}\right)^{-\frac{1}{2}}\left(\frac{D_1}{r^3} + \frac{D_2}{r^4}\right) - \frac{1}{8}\left(A + 2\frac{B}{r} + \frac{C}{r^2}\right)^{-\frac{3}{2}}\frac{D_1^2}{r^6},$$

and obtain

$$J_3 = J + \frac{D_1}{2}J_2 + \frac{D_2}{2}J_1 - \frac{D_1^2}{8}J_5, \quad . \quad . \quad (18)$$

$$J_4 = \oint\left(A + 2\frac{B}{r} + \frac{C}{r^2}\right)^{-\frac{1}{2}}\frac{dr}{r^4}, \quad . \quad . \quad . \quad (19)$$

$$J_5 = \oint\left(A + 2\frac{B}{r} + \frac{C}{r^2}\right)^{-\frac{3}{2}}\frac{dr}{r^6}. \quad . \quad . \quad . \quad (20)$$

In calculating J_4 and J_5 we need again consider only the point $r = 0$ since the point $r = \infty$ again behaves regularly here. Thence we find

$$J_4 = \frac{\pi i}{\sqrt{C}}\left(\frac{A}{C} - 3\frac{B^2}{C^2}\right),$$

and, further,

$$J_5 = \frac{3\pi i}{C\sqrt{C}}\left(\frac{A}{C} - 5\frac{B^2}{C^2}\right).$$

With the values of J and J_2 from (3) and (15*a*) this causes (18) to become

$$J_3 = -2\pi i\left\{\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{1}{2}\frac{B}{C\sqrt{C}}\left(D_1 - \frac{3}{2}\frac{D_2B}{C} + \frac{15}{8}\frac{D_1^2B}{C^2}\right) - \frac{1}{4}\frac{A}{C\sqrt{C}}\left(D_2 - \frac{3}{4}\frac{D_1^2}{C}\right)\right\}. \quad (21)$$

5. Further Remarks on Hamiltonian Mechanics, Angle Co-ordinates, Theory of Perturbations, Forces without a Potential

(*a*) **Angle Co-ordinates.**—To elaborate the conception of degeneracy used on p. 115 we shall follow Schwarzschild and introduce the *angle co-ordinates* that are ordinarily used in astronomy.

To arrive at a general definition of angle co-ordinates we must ask

whether it is not possible to describe the motion of a multiple periodic system by means of "cyclic co-ordinates" alone. A cyclic co-ordinate is one which does not occur in the energy-expression and whose corresponding momentum co-ordinate is therefore constant during the motion. Hence "cyclic co-ordinates" are also "force-free co-ordinates" and this is the characteristic which makes them peculiarly appropriate for describing the course of the motion. The simplest example of such a co-ordinate is given by the angle of rotation ϕ about an axis, with respect to which the moment of the force is zero. This example gave rise to the name "angle co-ordinate" although it is not really the angle (which increases irregularly with the time) but the surface described by the radius vector (which increases regularly in accordance with the law of sectorial areas) that plays the part of the angular co-ordinates in problems with axial symmetry. Actually, the angular co-ordinates are defined analytically by the *linear increase in time*. The constant factor which is disposable in the process is chosen in such a way that the angular co-ordinate is dimensionless and becomes of the *period* 1, that is, the position co-ordinates q_k are all to return to their initial values when the angle co-ordinates are changed by 1 or by any whole number.

We next show that we arrive at the desired angle co-ordinates in conformity with this requirement *if we introduce our phase-integrals* J_k *as momentum co-ordinates* * *and look for the position co-ordinates that are canonically conjugate to them.* To prove this we must take as our basis the scheme of the canonical transformations.

In a multiple periodic system the J_k's are pure functions of the constants α_k and W, cf. p. 106 (they are independent of the other constants that enter into the equation of the orbit and that we have denoted by β_k); thus we may express the α's in terms of the J's and substitute them in equation (21), p. 102. This equation then runs

$$S = S(q_1 \ldots q_f, J_1 \ldots J_f) \quad . \quad . \quad . \quad (1)$$

and gives

$$\delta S = \sum \frac{\partial S}{\partial q_k} \delta q_k + \sum \frac{\partial S}{\partial J_k} \delta J_k. \quad . \quad . \quad . \quad (2)$$

If we substitute p_k for $\frac{\partial S}{\partial q_k}$ by means of equation (18), p. 101, and introduce in place of $\frac{\partial S}{\partial J_k}$ the symbol

$$w_k = \frac{\partial S}{\partial J_k} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

which we regard for the present merely as an abbreviation, then (2) becomes

$$\delta S = \Sigma p_k \delta q_k + \Sigma w_k \delta J_k. \quad . \quad . \quad . \quad (4)$$

* We call the J_k's "action variables" (Schwarzschild) analogously to the "angle variables."

From (4) we see that the criterion of a canonical transformation, here in the form (19*b*) of p. 608 for the transition $p, q \to J, w$ is satisfied if we define w by means of (3). The new variables are denoted by P, Q in the earlier reference; one function of action S is there represented by the function F^*, and we deal with the special case where F^* is independent of t, that is, the equation (19*a*) on p. 608 assumes the form $\overline{H} = H$. Moreover, our present equation (3) now reveals itself as identical with the earlier equation (19*c*). According to Note 2 Hamilton's equations hold for the new variables w, J. Now, Hamilton's function $H = W$ (as also the remaining constants of integration α_k) is a pure function of the J's, that is, is independent of the w's and is constant during the motion. Hence we have

$$\frac{dJ_k}{dt} = -\frac{\partial H}{\partial w_k} = 0, \quad \frac{dw_k}{dt} = \frac{\partial H}{\partial J_k} = \text{const.} \quad . \quad . \quad (5)$$

The first equation states nothing new; it only confirms the constancy of the J_k's, which is identical with the fact that they can be calculated from the α_k's. But the second equation states that the w_k's *do in fact increase uniformly with the time*, as we demanded in defining the angle co-ordinates. If we denote the constant on the right-hand side by ν_k, we get

$$w_k = \nu_k t + \delta_k, \quad \nu_k = \frac{\partial W}{\partial J_k}. \quad . \quad . \quad . \quad (6)$$

The symbol ν_k is to indicate that ν_k plays the part of a constant *vibration number* for the cyclic co-ordinate w_k, which corresponds with the circumstance that w_k was to be dimensionless.

We now show that *every angle co-ordinate w_k increases by unity every time that the co-ordinate q_k moves once to and fro between its libration limits* (cf. p. 105).

If we make the co-ordinate q_k make a complete revolution within its domain of values while the other q_i's are kept fixed the action function S changes by the amount of its periodicity modulus J_k (cf. eqn. 22, p. 102). Hence we have that if we denote by 1 and 2 the initial and the final point of the closed revolution, that is, two points given by equal values for all the q's,

$$S_2 - S_1 = J_k. \quad . \quad . \quad . \quad . \quad (7)$$

If, as in equation (1), we imagine S to be a function of the q's and J's, we may differentiate (7) partially with respect to J_k, keeping the remaining J_i's and all q's constant and obtain in consequence (cf. (3)),

$$w_{k2} - w_{k1} = 1, \quad w_{i2} - w_{i1} = 0, \quad i \neq k. \quad . \quad . \quad (8)$$

Hence if the co-ordinate q_k returns to its initial value after a complete revolution, the values of the other q_i's remaining unchanged, the corresponding angle co-ordinate w_k increases by 1 while the values of the other angle co-ordinates remain preserved. And conversely: if one of the angle co-ordinates increases by 1 while all the other angle co-ordinates remain unchanged the co-ordinates q return to their initial values. *The q's are periodic functions of the angle co-ordinates of period* 1, as was demanded above.

Besides the q's also the "*modified action function*" S* has the same property of periodicity; we define this modified action function from the action function S as follows:

$$S^* = S - \Sigma w_k J_k. \quad . \quad . \quad . \quad (9)$$

For if we increase w_k by 1 in the sense of the equations (8) but make all the other w_i's return to their initial points, then $\Sigma w_k J_k$ changes by the amount J_k. Thus we see from equation (9) that in this change of the w's the simultaneous change of S* is equal to that of S diminished by J_k. Since by equation (7) the change of S was equal to J_k, the change of S* becomes equal to zero. *Whereas the action function S, being a function of the w's, has the additive periodicity moduli* J_k *the modified action function S* becomes a purely periodic function of the w's of period unity.*

It follows directly from the periodicity of the q's that, as functions of the w's, they may be expanded in an f-fold infinite Fourier series of the following form:

$$q_i = (\Sigma)^f C^i_{s_1 s_2 \ldots s_f} e^{2\pi i(s_1 w_1 + s_2 w_2 + \ldots + s_f w_f)}. \quad . \quad . \quad (10)$$

The C's are constant coefficients, that is, they depend only on the integration constants J_k, or, in quantum language, only on the integral quantum members n_k. The time occurs, namely linearly, only in the w_k's. The summations extend over the $s_1, s_2, \ldots s_f$ from $-\infty$ and $+\infty$. The corresponding expression holds, after what has been said, also, of course, for S*. If we substitute the expression (6) for the w's in (10), it follows that

$$q_i = (\Sigma)^f D^i_{s_1 s_2 \ldots s_f} e^{2\pi i(s_1 \nu_1 + s_2 \nu_2 + \ldots + s_f \nu_f)t} \quad . \quad . \quad (11)$$

with the following meaning for the coefficients D:

$$D^i_{s_1 s_2 \ldots s_f} = C^i_{s_1 s_2 \ldots s_f} e^{2\pi i(s_1 \delta_1 + s_2 \delta_2 + \ldots + s_f \delta_f)}. \quad . \quad (12)$$

The dependence of the q's on the time is, in contradistinction to that of the angle co-ordinates, *not periodic*, but corresponds rather to the *conditionally periodic character*. In general the orbital point never returns accurately to its initial point; nor does the individual co-ordinate q_k in general assume its initial value after equal periods of time. The individual factor

$$e^{2\pi i s_k \nu_k t}$$

appears to indicate the period $\tau_k = 1/\nu_k$; but the co-existence of f different factors of this kind and the irrationality of the ν_k's on the whole prevents any periodicity from coming about. Our example of the Lissajou motion, p. 105, was characterised by the circumstance that from the point of view of every co-ordinate taken individually there was perfect periodicity in time (thanks to the fact that here the infinite Fourier series in every co-ordinate reduced to a single term). But the character of the motion is on the whole also completely aperiodic in this case, as Fig. 25 shows, *unless some of the Lissajou frequencies* ν *become equal among themselves or commensurable to one another.*

We are now in a position to formulate rigorously Schwarzschild's definition of degenerate systems. The general case of non-degeneracy occurs when in the equations of definition (6) of the angle co-ordinates all the frequencies ν_k that occur in it are incommensurable with each other. The exceptional case of degeneracy occurs when one or several relationships of the form

$$s_1\nu_1 + s_2\nu_2 + \ldots = 0 \quad . \quad . \quad . \quad (13)$$

are obeyed for integral values of the coefficients s. The case where, in particular, two of the ν's become equal, is clearly included in equation (13). If r such relationships hold then the orbit does not, as in the general case, completely fill an f-fold continuum in the f-dimensional space of the $q_1 \ldots q_f$, but only an $(f - r)$-continuum. In this case we may speak of r-fold degeneracy. Complete degeneracy occurs in the case of a completely periodic orbit; then there must be $(f - 1)$ relationships of the form (13) or, in particular, when all the ν_k's are equal (Kepler ellipse without relativity).

(*b*) **Theory of Perturbations.**—Let us consider the fundamental astronomical problems of the theory of perturbations: given the unperturbed Kepler orbit, such as is described by a planet when under the influence of the sun's attraction alone, and let α_k, β_k (cf. Chap. II, § 6 *g*) be the elements of the orbit; and suppose the perturbing potential Φ to be superimposed, which is due, say, to the attraction of Jupiter. The method consists in describing the orbit at every moment as a Kepler orbit but with *variable* orbital elements, as a so-called osculating Kepler ellipse that approximates as closely as possible to the actually perturbed motion.

The following procedure corresponds generally with this method. We calculate the unperturbed motion with the help of the canonical elements α_k, β_k, W and introduce these as variables in the perturbation problem. For these and the co-ordinates p, q, by means of which we may describe both the perturbed motion and the unperturbed motion the equation (37) of p. 107 holds:

$$\delta S = \sum p_k \delta q_k + \beta_1 \delta W + \sum_2^f \beta_k \delta \alpha_k, \quad . \quad . \quad (14)$$

where S signifies the action function of the unperturbed motion. The α_k's, β_k's and W are thus canonical variables not only for the unperturbed but also for the perturbed problem and consequently satisfy Hamilton's equations. We write the Hamiltonian function of the perturbed problem in the form

$$H = H_0 + \Phi = W + \Phi. \quad . \quad . \quad . \quad (15)$$

H_0 is the Hamiltonian function of the unperturbed problem, that is, the W of the osculating orbit; Φ is given as a function * of the phase of motion p, q and is transformed by means of the orbital equations (43), p. 108, and the momentum equations (18) on p. 101 into a function of our co-ordinates β_k, α_k and W.

* In general Φ will also depend explicitly on t; but we may disregard this for our present purpose.

If we now form the Hamilton equations according to the model of (41*b*) on p. 107 with the expression (15) for H, we have

$$\frac{\partial H_0}{\partial \alpha_k} = \frac{\partial H_0}{\partial \beta_k} = 0,$$

and hence

$$\frac{d\alpha_k}{dt} = -\frac{\partial \Phi}{\partial \beta_k}, \quad \frac{d\beta_k}{dt} = \frac{\partial \Phi}{\partial \alpha_k}, \quad k = 2, \ldots f. \qquad (16)$$

These equations teach us how the orbital elements vary when the perturbation function is superimposed.

On the other hand, we obtain after the model of (41*a*), p. 107,

$$\frac{dW}{dt} = -\frac{\partial \Phi}{\partial \beta_1}, \quad \frac{\partial \beta_1}{\partial t} = 1 + \frac{\partial \Phi}{\partial W}. \qquad (17)$$

The second of these equations shows how the original *time-equation* (42) of p. 108 *becomes changed by the perturbation.* If Φ does not depend explicitly on t, the first equation, taken in conjunction with the other equations (16) and (17), contains the obvious assertion : H = const.

We shall now endeavour to get an insight into the numerical value of H in (15). Since H is constant in time we do not change the numerical value if we average over the time on the right-hand side. From Φ we then obtain $\bar{\Phi}$, the time mean of Φ, taken over the perturbed orbit or, if we assume Φ to be small to the first order of small quantities and neglect quantities of the second order, over the *unperturbed* orbit. We are now concerned with the numerical value of $H_0 = W$. This is likewise variable in time and its change is given by the first equation (17). We shall now express H_0 as a function of the J_k's and w_k's, H_0 becoming independent of the w_k's. The J_k's being orbital elements of the unperturbed motion are themselves, indeed, variable in time in the *perturbed* motion. Their change is obtained from the first of the equations (16) if we replace in it α_k by J_k, β_k by w_k. It is not the J_k's of the unperturbed motion that are constant in the perturbed motion but rather the phase-integrals—let us say J'_k's—that belong to the perturbed motion, and that differ from the J_k's by small periodic components.* In forming the time-mean of H_0 the latter cancel out, since we may expand in a Fourier series and neglect higher terms. If we now imagine the perturbation to be *adiabatic*, that is, to be effected by a sufficiently slow superposition of the perturbing field, then the numerical values of the J'_k's will be identical with those of the J_k's of the unperturbed motion, since both are equal to $n_k h$ (cf. Note 10 on adiabatic invariants). Thus the time-mean of H_0 is constant during the course of the adiabatic transformation and may be set equal to the W of the unperturbed motion. Hence our result is finally : *the numerical value of the Hamiltonian function H, that is, the energy of the perturbed motion, is, in the adiabatic transition, equal to the energy* W *of the unperturbed motion, increased by the time-mean of the perturbation function* Φ.

* Further details are given in Born and Pauli, Zeits. f. Physik, **10**, 137 (1922).

(*c*) **Forces without a Potential.**—It is easy to extend the Hamiltonian theory to the case where the time occurs explicitly, either in the potential energy (for example, perturbation of the planetary orbit through the motion of Jupiter), or, what comes to the same thing, in the equations of condition. We have then to take up t among the independent variables and to replace W in the Hamilton-Jacobi partial differential equation (20), p. 101, by $-\partial S/\partial t$.

The case is more difficult when the active forces have *no potential*. There is then no general method of linking the problem up with the Hamilton-Jacobi theory. The only general rule that can be given is this: bring the equations of motion into the form of a variation problem; the integral to be varied, regarded in the sense of p. 100, then becomes the function of action S and the function under the integral sign assumes the part of the Lagrange function L of p. 98.

This rule actually leads to the desired objective in the case which interests us here, if the effective force is *magnetic in origin* and hence has the form $e/c\,(\mathbf{vH})$. For Schwarzschild * has shown that the motion of an electron in any arbitrary electromagnetic field is represented by the variation principle

$$\delta\int_0^t \left\{\mathrm{E}_{kin} - \mathrm{E}_{pot} + \frac{e}{c}(\mathbf{vA})\right\}dt = 0. \qquad . \quad . \quad (18)$$

$\mathbf{A}$ is the vector potential of the field at any given point occupied by the electron and ϕ is taken up in the potential energy and contributes the amount $e\phi$ to it. In (18) the position and velocity is to be subjected to variation, and the electromagnetic field is to be regarded as given and is not varied. It is to be noted that the combination $-e\phi + e/c\,(\mathbf{vA})$ that occurs in (18) is a relativistic invariant, namely the four-dimensional scalar product of the "4-potential" ($\mathbf{A}_x$, $\mathbf{A}_y$, $\mathbf{A}_z$, $i\phi$) of the field and the "4-current" $e/c\,(\mathbf{v}_x, \mathbf{v}_y, \mathbf{v}_z, ic)$ of the electron.

As agreed above, we denote the quantity under the integral sign in (18) by L and transform the integral by means of the energy equation (the magnetic field does not enter into the energy balance):

$$\int_0^t L dt = \mathrm{S} - \mathrm{W}t, \quad \mathrm{S} = \int_0^t \left\{2\mathrm{E}_{kin} + \frac{e}{c}(\mathbf{vA})\right\}dt. \qquad . \quad (19)$$

If we first retain the definition of $p_k = \partial \mathrm{E}_{kin}/\partial \dot{q}_k$, we may write in place of (19)

$$\mathrm{S} = \int_{q_0}^{q} \sum \left(p_k + \frac{e}{c}\mathbf{A}_k\right)dq_k. \qquad . \quad . \quad . \quad (20)$$

Here $\mathbf{A}_k$ is the component of the vector potential that belongs to the co-ordinate q_k (which is not necessarily rectilinear); $\mathbf{A}_k$ is defined by the identity

$$(\mathbf{vA}) = \Sigma \mathbf{A}_k \dot{q}_k. \qquad . \quad . \quad . \quad . \quad (21)$$

The quantum conditions now result as moduli of periodicity of S and are, on account of (20),

$$\mathrm{J}_k = \oint \left(p_k + \frac{e}{c}\mathbf{A}_k\right)dq_k = n_k h, \qquad . \quad . \quad (22)$$

* Göttinger Nachr., Jahrg. 1903.

where the integration is to be taken over one complete libration of the co-ordinate q_k. This form of the quantum conditions has been discussed by W. Wilson * and O. W. Richardson.†

But we must emphasise that the p_k introduced here is not the momentum co-ordinate *canonically conjugate* to q_k. We shall distinguish the latter by calling it $\bar{p}_k$; it is to be defined by the equation

$$\bar{p}_k = \frac{\partial L}{\partial \dot{q}_k}.$$

As a result of the meaning of L and in view of equation (21) we obtain

$$\bar{p}_k = p_k + \frac{e}{c}\mathbf{A}_k, \quad J_k = \oint \bar{p}_k dq_k = n_k h. \quad . \quad . \quad (23)$$

Hence, *by using the canonical co-ordinate $\bar{p}$ the phase-integral retains the form familiar to us.* Our formulation of the quantum conditions on p. 83 holds in this sense also for systems without a force-potential. With regard to the choice of co-ordinates we must of course maintain the postulate of conditioned periodicity.

If, in particular, the magnetic field is homogeneous as in the Zeeman effect, $\mathbf{H} = \mathbf{H}_z = H$, we may write, since $\mathbf{H} = \text{curl } \mathbf{A}$,

$$\mathbf{A}_x = -\tfrac{1}{2}yH, \quad \mathbf{A}_y = \tfrac{1}{2}xH, \quad \mathbf{A}_z = 0.$$

If we use polar co-ordinates r, θ, χ in the " rest system " (the notation is the same as on p. 327) we have

$$(\mathbf{vA}) = \frac{H}{2}(x\dot{y} - y\dot{x}) = \frac{H}{2}r^2 \sin^2\theta\dot{\chi}.$$

From equation (21) it then follows that

$$\mathbf{A}_r = \mathbf{A}_\theta = 0, \quad \mathbf{A}_\chi = \frac{H}{2}r^2 \sin^2\theta.$$

Further, it is clear that

$$p_\chi = \mu r^2 \sin^2\theta\dot{\chi}.$$

Equation (23) then gives, if we consider the *negative* electron and replace e by $-e$,

$$\bar{p}_\chi = \mu r^2 \sin^2\theta\left(\dot{\chi} - \frac{e}{\mu}\frac{H}{2c}\right). \quad . \quad . \quad . \quad (24)$$

Here

$$\frac{e}{\mu}\frac{H}{2c} = o$$

is the Larmor precession; hence the brackets in equation (24) denote the angular velocity measured in the rotating system of reference, which we called ψ on p. 327. Accordingly our canonical $\bar{p}_\chi$ becomes identical with the moment of momentum p_φ in equation (16) on p. 327. The geometrical meaning of the canonical $\bar{p}_\chi = p_\varphi$ is simply that of the

* Proc. Roy. Soc., **102**, 478 (1922). † Phil. Mag., **46**, 911 (1923).

moment of momentum in the rotating system of reference. When we stated earlier that we had to apply the quantum conditions in the accompanying rotating system, this denoted directly the introduction of the canonical $\bar{p}_\chi$ in the sense of equation (23). Whereas earlier we based our procedure on the *adiabatic hypothesis* we have now linked it up directly with the general fundamental law of *Hamilton's theory*. It is evident that our present procedure has the advantage over the earlier procedure in that it may be applied analytically in general.

We must mention that the first quantum treatment of the Zeeman effect started out from this general analytical scheme, both in the paper by Debye, where the partial differential equation for S is set up directly and integrated, and in the simultaneous paper by the author* where the analytical and geometrical meaning of the canonically conjugate momentum is emphasised. We also refer to an exposition by Laue, in which the appearance of the vector potential in the equations of motion of the electron is discussed in general (also for the relativity theory).

6. Hamilton's Theory in Relativity Mechanics

In the theory of relativity the momentum co-ordinates are (cf. eqn. (1) on p. 251):

$$m\dot{x} = \frac{m_0}{\sqrt{1-\beta^2}}\dot{x}, \quad m\dot{y} = \frac{m_0}{\sqrt{1-\beta^2}}\dot{y}, \quad m\dot{z} = \frac{m_0}{\sqrt{1-\beta^2}}\dot{z}. \quad . \quad (1)$$

In ordinary mechanics they are represented as derivatives of the kinetic energy with respect to the corresponding velocity components. This is not feasible in the relativity theory. But we may confirm immediately that they are derivatives of the following quantity with respect to $\dot{x}$, $\dot{y}$, $\dot{z}$:

$$F = -m_0c^2\sqrt{1-\beta^2} + \text{const.}, \quad . \quad . \quad . \quad (2)$$

where it is convenient to choose the constant as follows:

$$\text{const.} = m_0c^2. \quad . \quad . \quad . \quad . \quad (2a)$$

We may follow Helmholtz and call F the "kinetic potential." If we number the momentum components by means of $p_1, p_2, \ldots p_k, \ldots$, more than one point-mass possibly being present, and if we call the corresponding rectangular co-ordinates $q_1, q_2, \ldots q_k, \ldots$, the corresponding velocity co-ordinates $\dot{q}_1, \dot{q}_2, \ldots \dot{q}_k, \ldots$ the relationship in question between F and the momentum co-ordinates is expressed as

$$\delta F = \Sigma p_k \delta \dot{q}_k. \quad . \quad . \quad . \quad . \quad (3)$$

On the other hand, by equation (2) on p. 251 the relativistic expression for the kinetic energy is, in particular, for a point-mass

$$E_{kin} = m_0c^2\left(\frac{1}{\sqrt{1-\beta^2}} - 1\right). \quad . \quad . \quad . \quad (4)$$

* Handb. d. Radiologie, **6**, Leipzig, 1924.

Since equation (1), when expressed in p's and q's, runs

$$p = \frac{m_0}{\sqrt{1-\beta^2}}\dot{q} \quad . \quad . \quad . \quad . \quad (4a)$$

it follows that

$$\Sigma p\dot{q} = \frac{m_0 c^2 \beta^2}{\sqrt{1-\beta^2}} \quad . \quad . \quad . \quad . \quad (5)$$

Hence we may confirm directly from this the relation

$$\Sigma p\dot{q} - \mathrm{E}_{kin} = \mathrm{F} \quad . \quad . \quad . \quad . \quad (6)$$

cf. (2) and (2a). Since in classical mechanics $\Sigma p\dot{q}$ is equal to twice E_{kin} (eqn. (5) on p. 605) but *not* in the mechanics of the relativity theory, we see that in the classical case F becomes identical with E_{kin}, but must differ from it in the case of relativity.

We now run through the developments on pp. 97 *et seq.*, which led to Hamilton's theory. D'Alembert's principle, expressed in the form (1) on p. 97, remains valid also for the relativity theory, and likewise the connected equation (3) if we replace E_{kin} in it by F. Consequently equation (4) also remains in force except that we must now take the " Lagrange function " as standing for

$$\mathrm{L} = \mathrm{F} - \mathrm{E}_{pot}, \quad . \quad . \quad . \quad . \quad (7)$$

and it is expedient to include in E_{pot} the " rest " energy $m_0 c^2$; for example, in the Kepler problem,

$$\mathrm{E}_{pot} = -\frac{Ze^2}{r} + m_0 c^2. \quad . \quad . \quad . \quad (7a)$$

This is the only change that must be applied to the earlier developments. From (6) and (7) it now follows that

$$\mathrm{L} = \Sigma p\dot{q} - \mathrm{E}, \quad . \quad . \quad . \quad . \quad (7b)$$

where $\mathrm{E} = \mathrm{E}_{kin} + \mathrm{E}_{pot}$ denotes the *total energy* (including the rest energy). The action function S is defined by this L by means of equation (13) on p. 99:

$$\int_0^t \mathrm{L}d\tau = \mathrm{S} - \mathrm{E}t, \quad \mathrm{S} = \int_0^t \Sigma p\dot{q}d\tau. \quad . \quad . \quad (8)$$

And now the following relationship holds not only for rectangular but also for any arbitrary co-ordinates $p_k q_k$:

$$p_k = \frac{\partial \mathrm{S}}{\partial q_k}. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

If we now set the left-hand side of the energy law

$$\mathrm{E}_{kin} + \mathrm{E}_{pot} = \mathrm{E}, \quad . \quad . \quad . \quad . \quad (10)$$

expressed as a function of the p_k's and q_k's, equal to H (" Hamilton's function "), the partial differential equation of relativity mechanics becomes, in formal agreement with equation (20) on p. 101,

$$\mathrm{H}\left(\frac{\partial \mathrm{S}}{\partial q_k}\,;\, q_k\right) = \mathrm{E}. \quad . \quad . \quad . \quad . \quad (11)$$

Hence all other conclusions, in particular those concerning the separation of variables, hold unchanged also in the relativity case.

It must be observed that our transposition from classical mechanics to relativity mechanics could be effected smoothly only because we wrote d'Alembert's principle from the outset in the rational form (1) of p. 97, where the changes of momentum $\dot{p}_k$ and not the products of the mass and the acceleration $m_k\ddot{q}_k$ occurred. Written in the latter form the inertial resistances cannot be generalised for relativity purposes. We must further note that in accordance with the meaning of H equation (7*b*) may also be written

$$L = \Sigma p\dot{q} - H. \quad . \quad . \quad . \quad . \quad (12)$$

This relationship which we have already encountered in classical mechanics in equation (11) on p. 605 is not bound by the circumstance that H is constant in the motion and is a complete quadratic function of the p's. It may serve to define Hamilton's function H and also to set up the canonical equations, if the problem is given originally in variation form, that is, if L is known initially. Conversely, if the problem is originally given by means of canonical equations, it may serve to calculate L and to transform the problem into the variation form.

We shall express the energy equation $H(p, q) = E$ in yet another form which will be of use in the next volume, which deals with wave-mechanics. By (4*a*) we have

$$p_x^2 + p_y^2 + p_z^2 = \frac{m_0^2}{1-\beta^2}\Sigma\dot{q}^2 = \frac{m_0^2\beta^2c^2}{1-\beta^2},$$

and hence

$$\sqrt{\frac{p_x^2 + p_y^2 + p_z^2}{m_0^2c^2} + 1} = \frac{1}{\sqrt{1-\beta^2}}.$$

Hence by (4) and (7*a*) we have for the case of the hydrogen electron :

$$E_{kin} + E_{pot} = m_0c^2\sqrt{\frac{p_x^2 + p_y^2 + p_z^2}{m_0^2c^2} + 1} - \frac{Ze^2}{r}.$$

This is the total energy expressed as a function of p, q, and hence is the Hamiltonian function H (p, q) of the problem. It is numerically equal to the energy-constant E, that is

$$c\sqrt{p_x^2 + p_y^2 + p_z^2 + m_0^2c^2} = E + \frac{Ze^2}{r}.$$

We square to remove the root sign and obtain

$$p_x^2 + p_y^2 + p_z^2 + m_0^2c^2 = \frac{1}{c^2}\left(E + \frac{Ze^2}{r}\right)^2. \quad . \quad . \quad . \quad (13)$$

The equation (6) on p. 253 of the text is identical with equation (13). If we introduce here the electromagnetic scalar potential ϕ in place of the special Coulombian potential, equation (13) runs (for the positive electron with the charge $+e$; for the negative electron $+e$ must be replaced by $-e$) :

$$p_x^2 + p_y^2 + p_z^2 + m_0^2c^2 = \frac{1}{c^2}(E - e\phi)^2. \quad . \quad . \quad (13a)$$

Our object is to generalise equation (13*a*) in such a way that it gives us the energy equation for the case of an arbitrary external electromagnetic field with the potential **A**, ϕ. We accomplish this most simply by means of a Lorentz transformation. For in reference to any other arbitrary Lorentz system equation (13*a*) runs :

$$\left(p_x - \frac{e}{c}\mathbf{A}_x\right)^2 + \left(p_y - \frac{e}{c}\mathbf{A}_y\right)^2 + \left(p_z - \frac{e}{c}\mathbf{A}_z\right)^2 - \frac{(\mathrm{E} - e\phi)^2}{c^2} = -m_0{}^2c^2. \quad (14)$$

Here **A**, ϕ now denote the potentials of the electromagnetic field, such as it appears to the observer from the new co-ordinate system, which is in motion relatively to the old system. By means of our arbitrary choice of the co-ordinate system we may clearly describe any arbitrary electromagnetic field with the help of (14) ; thus equation (14) is the required energy equation in the arbitrary external field.

We may here supplement our remarks on the motion of Mercury's perihelion referred to on p. 254. We use the expression (14), p. 254, for $\Delta\phi$ (ϕ now, of course, denotes the azimuth in the orbital plane) and take the value of γ from (13*a*, *b*) on p. 253 ; to a sufficient degree of approximation we have

$$\frac{1}{\gamma} = 1 + \frac{1}{2}\frac{\mathrm{Z}^2e^4}{p^2c^2}, \quad \Delta\phi = 2\pi\left(\frac{1}{\gamma} - 1\right) = \frac{\pi\mathrm{Z}^2e^4}{p^2c^2}, \quad p = \frac{n_\phi h}{2\pi}.$$

Supposing the Newtonian law to act instead of the Coulombian law we replace Ze^2 by $m\mathrm{M}$ and take m to stand for the mass of the planet and M for that of the sun. Further, we express the momentum constant p of the planet by the geometrical surface constant f :

$$p = 2mf, \quad f = \frac{\pi ab}{\tau} = \frac{\pi a^2\sqrt{1-\epsilon^2}}{\tau}$$

(τ is the period of revolution of the planet, πab the surface described in the time τ, ϵ the numerical value of the eccentricity). Thus

$$\Delta\phi = \frac{\pi m^2\mathrm{M}^2}{p^2c^2} = \frac{\mathrm{M}^2\tau^2}{4\pi a^4(1-\epsilon^2)c^2}. \quad . \quad . \quad . \quad (15)$$

Finally we give an expression of the sun's mass by means of Kepler's third law, equation (18) on p. 113, and obtain

$$\Delta\phi = \frac{4\pi^3a^2}{\tau^2(1-\epsilon^2)c^2}. \quad . \quad . \quad . \quad . \quad (16)$$

If the data for a, τ and ϵ in the case of Mercury are substituted in (16) we obtain the value $\Delta\phi = 7''$ per century mentioned on p. 255. The general theory of relativity leads to almost the same formula (16) but with the numerical factor 24 in place of 4. According to the latter theory then the value $\Delta\phi = 43''$, which is six times as great and which agrees perfectly with the value obtained by Newcomb, which was also mentioned on p. 254.

7. Bohr's Correspondence Principle

We have already given an account of the origin and significance of the Correspondence Principle in Chap. VI, § 1, in dealing with the

Balmer series. We proceed to generalise this account for multiple periodic systems.

(*a*) We consider the orbit of a multiple or conditionally periodic system with its f vibration numbers ν_k (see eqn. (11) on p. 618) or the associated periods of vibration $\tau_k = 1/\nu_k$. Here τ_k denotes the time in which the co-ordinate q_k moves to and fro between its libration limits. According to equation (6) on p. 617 we have

$$\nu_k = \frac{\partial W}{\partial J_k}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the energy W of the conditionally periodic system being supposed a function of the phase-integrals $J_1, J_2, \ldots J_f$.

According to the classical view the system built up of moving charges emits radiation in the periods of the motion: thus *the mechanical frequencies ν_k are at the same time optical frequencies;* in addition to the ν_k's themselves their multiples (harmonics) and linear combinations of the multiples (combination vibrations) also occur as mechanical and optical frequencies:

$$\nu = s_k\nu_k \quad \text{and} \quad \nu = \Sigma s_k\nu_k, \quad . \quad . \quad . \quad (2)$$

where s denotes integers, "order numbers" of the vibration process in question. On account of (1) we therefore obtain for the overtone vibrations and combination vibrations

$$\nu_{cl} = \frac{\partial W}{\partial J_k}s_k, \quad . \quad . \quad . \quad . \quad (2a)$$

and

$$\nu_{cl} = \Sigma\frac{\partial W}{\partial J_k}s_k, \quad . \quad . \quad . \quad . \quad (2b)$$

where *cl* indicates "according to classical theory."

The result is different if we adopt the quantum view. Here the system does not emit radiation in the stationary orbits; radiation is emitted only in the transition from one orbit to another. If ΔW is the energy difference between the initial orbit and the final orbit, Bohr's assumption holds:

$$\nu = \frac{\Delta W}{h}. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We shall first assume that in a transition only the one quantum number n_k changes by Δn_k. Since $J_k = n_k h$, that is, $\Delta J_k = \Delta n_k \cdot h$, we may write instead of (3):

$$\nu_{qu} = \frac{\Delta W}{\Delta J_k}\Delta n_k, \quad . \quad . \quad . \quad . \quad (4a)$$

where *qu* means "according to the quantum theory."

When $\Delta n_k = 1$ we have the analogous expression to equation (1), when $\Delta n_k = s_k$ the expression analogous to equation (2*a*). *The quantum transition unity is analogous to the fundamental vibration, the higher quantum transitions to the overtone vibrations of the classical radiation.* But there is also an analogy to the combination frequencies (2*b*) if

we take into consideration quantum transitions in which several quantum numbers change simultaneously. We resolve the total change of energy ΔW into steps (cascade-like) of partial changes ΔW_1, ΔW_2, . . . ΔW_f that are to correspond to the quantum transitions Δn_1, Δn_2, . . . Δn_f executed in succession. In the partial change of energy ΔW_1 all the n_2 . . . n_f have their initial values and only n_1 changes from its initial value by the amount Δn_1. In the case of ΔW_2 n_1 has its final value and n_3, . . . n_f their initial values, and n_2 changes by Δn_2, and so forth. Hence if we write instead of (3)

$$\nu = \frac{\Delta W}{h} = \frac{\Delta W_1}{h} + \frac{\Delta W_2}{h} + \ldots + \frac{\Delta W_f}{h},$$

or according to the model of (4*a*),

$$\nu_{qu} = \sum \frac{\Delta W}{\Delta J_k} \Delta n_k, \quad . \quad . \quad . \quad . \quad . \quad (4b)$$

then the quantities $\frac{\Delta W_k}{\Delta J_k}$ are true "partial differential quotients," defined individually by the change of the one phase-integral J_k and the invariability of the remainder, some of which retain their initial value and others their final value. Hence with $\Delta n_k = s_k$ the equation (4*b*) is exactly analogous to (2*b*). *The general quantum transition corresponds to the general combination vibration of classical radiation.* The characteristic feature in this analogy is that the greatest of differences is replaced by the differential coefficient; this has already been emphasised on p. 293. The equations (2*a*, *b*) and (4*a*, *b*) are the generalisations of equation (5) and equation (4) on p. 293.

(*b*) There are conditions under which the two sets of ideas and formulæ not only correspond but coincide. These conditions are

$$\Delta n_k \ll n_k, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

that is, *the change in each quantum number must be small compared with the quantum number itself. We then have asymptotically*

$$\frac{\Delta W}{\Delta J_k} \simeq \frac{\partial W}{\partial J_k}, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

that is, the difference between the quotient of the differentials and the differential coefficient becomes small compared with the absolute values of these quantities, so that the frequency calculated according to the quantum theory by equations (4*a*, *b*) merge into those calculated on the classical theory by equations (2*a*, *b*).

To illustrate this we recall the example of the rotator. We here have

$$W = \frac{1}{2}\frac{p^2}{\Theta} = \frac{J^2}{8\pi^2\Theta},$$

where p denotes the moment of momentum, Θ the moment of inertia of the system rotating about a fixed axis. $J = 2\pi p$ denotes the phase-integral for the rotator and is set equal to mh. Now, in the change of m by the amount Δm and of J by the amount ΔJ,

$$\Delta(J^2) = 2J\Delta J + (\Delta J)^2,$$

and so

$$\frac{\Delta W}{\Delta J} = \frac{J}{4\pi^2\Theta}\left(1 + \frac{1}{2}\frac{\Delta J}{J}\right) = \frac{J}{4\pi^2\Theta}\left(1 + \frac{1}{2}\frac{\Delta m}{m}\right).$$

But this quotient of differences differs by an arbitrarily small amount from the differential coefficient,

$$\frac{\partial W}{\partial J} = \frac{J}{4\pi^2\Theta},$$

only if the condition (5) is fulfilled.

Another example is given by the Balmer series considered in Chapter VI, § 1. We shall show by means of it how it is possible by transposing the classical into the quantum spectrum to deduce the *intensity* and the *polarisation* of the spectral lines. We must now perform this for general conditions.

(c) As a preliminary to this we show how the emission of a single partial vibration in an orbital revolution is found according to the classical theory. We must take our start from equation (1) on p. 24, in which the product of the charge and the acceleration $e\dot{\mathbf{v}}$ of the electron there considered occurs. By summing this product over all electrons (including the nucleus if it also vibrates) in the case of a composite atom we obtain a vector which is decisive for the emission,

$$\mathbf{Q} = \Sigma + e\dot{\mathbf{v}},$$

which we may resolve into its three rectangular components $\mathbf{Q}_x$, $\mathbf{Q}_y$, $\mathbf{Q}_z$. Instead of it we may rather more conveniently consider the vector $\mathbf{P}$ of the variable electric moment of the atom from which we obtain $\mathbf{Q}$ by two successive differentiations with respect to t :

$$\mathbf{P} = \Sigma + e\mathbf{r} \quad . \quad . \quad . \quad . \quad (7)$$

with its three components :

$$\mathbf{P}_x = \Sigma + ex, \quad \mathbf{P}_y = \Sigma + ey, \quad \mathbf{P}_z = \Sigma + ez. \quad . \quad (7a)$$

We must now resolve the whole complex of vibrations which is contained in the atomic orbit and is hence reproduced in $\mathbf{P}$ into its individual partial vibrations, because according to the Correspondence Principle, they have a physical meaning, namely that of the individual spectral lines. Hence the spectral resolution of the emitted light demands as its analytical counterpart the resolution of $\mathbf{P}$ (or $\mathbf{Q}$) into its periodic components. But we performed a resolution of this kind on an earlier occasion ; it is accomplished by the angle co-ordinates. In equation (10) of Note 5 we found for each separation variable q_f a Fourier expansion and from this we may pass on to a corresponding expression for every rectangular co-ordinate of the charges that participate in the structure of the atom since each such co-ordinate is for its part a definite function of the $q_1, \ldots q_f$. If we substitute these expressions in (7*a*) we may write generally :

$$\mathbf{P}_x = (\Sigma)' D^x_{s_1, s_2, \ldots s_f} e^{2\pi i(s_1\nu_1 + s_2\nu_2 + \ldots + s_f\nu_f)t}. \quad . \quad . \quad (8)$$

This is an f-fold summation which extends from $-\infty$ to $+\infty$. *Corresponding to each individual spectral line given by the quantum transition*

$\Delta n_1, \Delta n_2, \ldots \Delta n_f$ *we have that member of this series for which* $s_k = \Delta n_k$; it is the associated coefficient D, which is in general complex (cf. eqn. (11) on p. 618) that interests us here. If we pass from the vector **P** by means of two-fold differentiation with respect to t to the emission vector **Q** the coefficient D of our term becomes multiplied by the real factor:

$$-4\pi^2(s_1\nu_1 + s_2\nu_2 + \ldots + s_f\nu_f)^2.$$

Hence, when multiplied by this factor the complex coefficient D gives a measure for the classically calculated amplitude and phase of our partial vibration and, according to the Correspondence Principle, also a measure of the true quantum *amplitude and phase in the corresponding spectral line.* By determining the amplitude and the phase separately for the x-, y- and z-direction we obtain at the same time a measure of the *polarisation of the emitted radiation.*

(*d*) We take as the simplest example the Lissajou vibration figures. Thanks to the particular simplicity of the quasi-elastic binding the infinite Fourier expansion here reduces (cf. pp. 618 and 102) for every component of **P** to a single frequency:

$$\mathbf{P}_x = \mathrm{D}_1 e^{2\pi i\nu_1 t}, \quad \mathbf{P}_y = \mathrm{D}_2 e^{2\pi i\nu_2 t}, \quad \mathbf{P}_z = \mathrm{D}_3 e^{2\pi i\nu_3 t}, \quad . \quad . \quad (9)$$

where in each case we must suppose the conjugate imaginary term of the same frequency to be added. Compared with the general expression (8), then, of all the values s_1 between $-\infty$ and $+\infty$ only the one value $|s_1| = 1$ occurs for $\mathbf{P}_x$, whereas $s_2 = s_3 = 0$; a similar result holds for $\mathbf{P}_y$, $\mathbf{P}_z$. Hence we conclude in virtue of the Correspondence Principle: none of the three quantum transitions Δn_1, Δn_2, Δn_3 can combine with the other; if n_1 makes a transition, n_2 and n_3 remain unchanged, and conversely; moreover, n_1 (and likewise n_2, n_3) can change only by unity. The light emitted in the transition of n_1 is linearly polarised in the x-direction, that in the transition of n_2 is linearly polarised in the y-direction, and so forth (it is assumed that there is no degeneracy, that is ν_1, ν_2, ν_3 are all supposed different). According to this the whole spectrum of the quasi-elastically and anisotropically bound oscillator consists of only three separate lines polarised in the x-, y- and z-directions respectively. In this case we also have the peculiar feature that the quantum determined ν's come out as identical with the ν_1, ν_2, ν_3 given by classical theory (on account of the quantising of the energy of the oscillator $\mathrm{W} = \Sigma n_i . h\nu_i$), that is, that the correspondence becomes a coincidence here not only for great frequencies but also for small frequencies. Nor is there any arbitrariness in the application of the Correspondence Principle (cf. p. 296) since we have the same form of expression in all three co-ordinates for the initial and the final orbit.

Under the heading of Lissajou motions we must, of course, include Planck's linear harmonic oscillator. If there were a vibrating system of this simplicity in nature its spectrum would have to consist of a single line of the frequency given by the classical emission theory and it would have to be produced solely by the quantum transition ± 1. In the case of a linear anharmonic oscillator (for example, with a supple-

mentary quadratic term in the restoring force) the overtone vibrations would also occur. The formula then runs

$$\mathbf{P}_x = \sum_{-\infty}^{+\infty} \mathrm{D}_s e^{2\pi i s \nu_0 t}, \quad . \quad . \quad . \quad . \quad (9a)$$

where ν_0 is the fundamental frequency of the oscillation and the x-axis is the direction of the oscillation. Hence according to the Correspondence Principle we have arbitrary transitions $\Delta n = \pm s$ in the case of the anharmonic oscillator. We made use of this result in Chapter IX, §§ 2 and 4, and in dealing with band spectra.

(*e*) We now come to the case where one of the separation variables is cyclic. We call this cyclic variable ϕ and the others $q_2, q_3, \ldots q_f$. From the definition of cyclic variables (energy expression independent of ϕ, corresponding impulse $p = \dfrac{\partial \mathrm{S}}{\partial \phi} = \dfrac{\mathrm{J}_\phi}{2\pi}$ constant) we obtain as the expression for S

$$\mathrm{S} = \frac{1}{2\pi}\mathrm{J}_\phi \cdot \phi + s(q_2, \ldots q_f, \mathrm{J}), \quad . \quad . \quad (10)$$

where s is now independent of ϕ and depends only on $q_2 \ldots q_f$ and the phase-integrals J (including, in general, J_ϕ). According to the definition of the angle co-ordinates in Note 5, equation (3), we obtain by differentiating (10) with respect to J_k for $k = 2, 3, \ldots f$,

$$w_k = f_k(q_2, \ldots q_f, \mathrm{J}),$$

where we have set $f_k = \dfrac{\partial s}{\partial \mathrm{J}_k}$ and by converse expression, respectively,

$$q_k = \mathrm{F}_k(w_2, \ldots w_f, \mathrm{J}). \quad . \quad . \quad . \quad (11)$$

But for $k = 1$ we have by differentiating (10) with respect to J_ϕ,

$$w_\phi = \frac{\phi}{2\pi} + \psi(q_2, \ldots q_f, \mathrm{J}),$$

where ψ has been set equal to $\dfrac{\partial s}{\partial \mathrm{J}_\phi}$; in view of (11) we may also write

$$\phi = 2\pi w_\phi + \Psi(w_2, \ldots w_f, \mathrm{J}). \quad . \quad . \quad (11a)$$

The case of a cyclic variable also occurs in the case of a *force-free atom*. Here we shall find it convenient to refer the co-ordinates of its point-masses to the invariable plane described through its centre of gravity and to denote them by r_α, z_α, ϕ_α (z_α = distance of the α^{th} point-mass from the invariable plane, ϕ_α = the azimuth in this plane, and so forth). Then we may regard one of the ϕ_α's (for example, $\phi_1 = \phi$) as a cyclic co-ordinate and may express the relative azimuths $\phi_\alpha - \phi$, which are alone of importance for the inner forces, and also the r_α's and z_α's by the remaining separation variables q. If we consider the combination $x_\alpha + iy_\alpha$ for each of the point-masses we obtain

$$x_\alpha + iy_\alpha = e^{i\phi} \cdot r_\alpha e^{i(\phi_\alpha - \phi)} = e^{i\phi} f(q_2, \ldots q_f),$$

and hence also

$$\mathbf{P}_x + i\mathbf{P}_y = \Sigma \pm e(x_\alpha + iy_\alpha) = e^{i\phi} f_1(q_2, \ldots q_f),$$
$$\mathbf{P}_z = \Sigma \pm ez = f_2(q_2, \ldots q_f).$$

If we substitute from (11) and (11*a*) and set $w_\phi = \nu t + \delta$, $w_k = \nu_k t + \delta_k$ and write f_1 and f_2 in Fourier series by means of equation (8), we obtain

$$\mathbf{P}_x + i\mathbf{P}_y = e^{2\pi i \nu t}(\Sigma)^{f-1}\mathrm{D}_{s_2,\ldots s_f} e^{2\pi i(s_2\nu_2 + \ldots + s_f\nu_f)t}, \quad . \quad (12)$$

$$\mathbf{P}_z = (\Sigma)^{f-1}\mathrm{E}_{s_2,\ldots s_f} e^{2\pi i(s_2\nu_2 + \ldots + s_f\nu_f)t}. \quad . \quad . \quad (13)$$

Here we must note particularly that the summation letter (we shall call it s_1) corresponding to the cyclic azimuth occurs in (12) only with the value $s_1 = 1$ [and also with $s_1 = -1$, if we form the real part of (12) and hence add the conjugate imaginary part], but in (13) only with the value $s_1 = 0$. By the Correspondence Principle it therefore follows that if we denote the quantum number assigned to the cyclic coordinate by j then *the quantum transition in j is only able to have the values ± 1 or 0. Corresponding to the quantum transition ± 1 we have circular polarised vibrations parallel to the invariable plane, whereas for the quantum transition 0 there is a linearly polarised vibration perpendicular to the invariable plane.*

We have made no mention of electron spin. If we include it then we take J (as in Chap. VIII.) to stand for the quantum number that is assigned to the vector sum of the orbital moments of momentum l and spin moments of momentum s, that is, to the total moment of momentum of the atom. For this J (the so-called *inner quantum number*) the polarisation and selection rules derived just above apply equally well because they depend only on the existence of a cyclic angle. From the point of view of the vector model we actually have in the case of the Russell-Saunders coupling, for example, a uniform precession of the total moment of momentum L about the axis of J (cf. Chap. VI, § 5, and Chap. VIII, § 5, at the beginning). We lay down a first coordinate system ξ, η, ζ in such a way that the z-axis coincides with L, and a second system x, y, z so that the z-axis falls in the J-direction. If we disregard the precession for a moment we may make the η-axis coincide with the y-axis. Let the angle between z and ζ be θ. Then

$$x = \xi \cos\theta - \zeta \sin\theta,$$
$$y = \eta,$$
$$z = \xi \sin\theta + \zeta \cos\theta.$$

The uniform precession (radian frequency ω_J) changes these equations so that in place of $x + iy$ we now have $(x + iy)e^{i\omega_J t}$, while z remains unchanged. Thus we see that the frequency ω_J occurs in $x + iy$ with the factor ± 1, but not at all in z, and hence we may conclude that $\Delta J = \pm 1, 0$.

In a similar way we obtained the *selection principle* for l in Chap. VI, § 1, p. 299, by fixing our attention not on the whole atom but on an outer electron (valency or series electron). On the assumption that the action of the atomic core on the series electron may be described as a central field the orbit of the electron becomes plane and the azimuth of the revolution becomes cyclic. It follows from equation (9) on

p. 298, which is analogous to equation (12), that the azimuthal quantum number, which is assigned to the moment of momentum of this cyclic revolution, obeys the selection rule $\Delta l = \pm 1$; $\Delta l = 0$ is to be excluded in the case of a plane orbit. In the case of a non-planar orbit and hence particularly in the field of an external force $\Delta l = 0$ is permitted.* We do not enter into the question of the basis of Heisenberg's selection rule for double " transitions " (p. 444).

We obtain the *selection rule* for the L's and S's as follows : if we again assume (approximate) normal couplings then J is produced by vectorial addition of L and S. If the interaction (L, S) is very small, as is the case in the limit where the coupling is purely normal, the spin frequencies assigned to S will not occur appreciably in the expression for the electric moment of the electronic orbits, that is, then $\Delta S = 0$ will hold. *In the pure Russell-Saunders coupling there are no intercombination lines.* For the resultant L of all the orbital motions the same considerations now apply as in equations (12), (13), because L is directly equal to the j that occurs there. We have $\Delta L = 0, \pm 1$; corresponding to $\Delta L = 0$ we have linearly polarised vibrations along L, and to $\Delta L = \pm 1$ vibrations polarised circularly in the plane perpendicular to L.

To calculate the *intensities* † of such transitions we write down in full the moments of momentum corresponding to the x, y, z (normal coupling again being assumed) :

$$\left.\begin{aligned} \mathbf{P}_x + i\mathbf{P}_y &= (\mathbf{P}_\xi \cos\theta + i\mathbf{P}_\eta - \mathbf{P}_\zeta \sin\theta)e^{i\omega_J t}; \\ \mathbf{P}_z &= \mathbf{P}_\xi \sin\theta + \mathbf{P}_\zeta \cos\theta. \end{aligned}\right\} \quad . \quad (14)$$

The moments of momentum $\mathbf{P}_\xi$, $\mathbf{P}_\eta$, $\mathbf{P}_\zeta$, may be represented in a manner similar to that used in (12), (13) in the form

$$\left.\begin{aligned} \mathbf{P}_\xi + i\mathbf{P}_\eta &= e^{i\omega_L t}\Sigma\alpha_\varkappa e^{i\Sigma s_\varkappa \omega_\varkappa t} = e^{i\omega_L t}.(\Xi + i\mathrm{H}), \\ \mathbf{P}_\xi &= \Sigma_\varkappa b e^{i\Sigma s_\varkappa \omega_\varkappa t} = \mathrm{Z}. \end{aligned}\right\} \quad . \quad (15)$$

where Ξ, H, Z are self-explanatory abbreviations. If we substitute the values of $\mathbf{P}_\xi$, $\mathbf{P}_\eta$, $\mathbf{P}_\zeta$ to be calculated from (15) in (14) we obtain

$$\left.\begin{aligned} \mathbf{P}_x + i\mathbf{P}_y &= \Big((\Xi + i\mathrm{H})\frac{(\cos\theta + 1)}{2}e^{i\omega_L t} \\ &\qquad + (\Xi - i\mathrm{H})\frac{(\cos\theta - 1)}{2}e^{-i\omega_L t} - \mathrm{Z}\sin\theta\Big)e^{i\omega_J t}; \\ \mathbf{P}_z &= (\Xi + i\mathrm{H})\frac{\sin\theta}{2}e^{i\omega_L t} + (\Xi - i\mathrm{H})\frac{\sin\theta}{2}e^{-i\omega_L t} + \mathrm{Z}\cos\theta \end{aligned}\right\} . \quad (16)$$

* Here we assign l, as is demanded by the spin model of the electron and by wave-mechanics, to the orbital moment of momentum. This l plays exactly the part of n_ϕ in Chap. II, except that it is 1 less than n_ϕ [cf. eqn. (21), p. 115]. The orbits $n_\phi = 1$ have $l = 0$ according to this view and have a vanishingly small orbital moment of momentum. This leads to inconsistency with the strict orbital view, as we showed in Chap. II, and means that we must apply a correction in the sense of wave-mechanics and the spin-model, as has been emphasised repeatedly.

† Cf. A. Sommerfeld and W. Heisenberg, Zeits. f. Phys., **11**, 131 (1922).

We are interested in transitions in L and J; the transition in the other quantum numbers is fixed once and for all; it is represented by a definite set of numbers $s_\varkappa$ in the expansion (15). From them is composed the corresponding Fourier frequency $\Sigma s_\varkappa \omega_\varkappa$ which we shall call ω for short.

We first consider the case $\Delta L = 0$. We then have to take into account only those terms in (16) which do not involve ω_L, that is:

$$\mathbf{P}_x + i\mathbf{P}_y = \ldots - Z \sin\theta\, e^{i\omega_J t}, \quad \mathbf{P}_z = \ldots Z\cos\theta. \quad (16a)$$

We distinguish between the three subordinate cases:

$$(1)\ \Delta J = 0, \quad (2)\ \Delta J = +1, \quad (3)\ \Delta J = -1.$$

(1) By (16a) the Fourier term $Z\cos\theta$ belongs to $\Delta J = 0$, that is, by (15), the term $b\cos\theta$ $(e^{i\omega t} + e^{-i\omega t})$; actually the frequency $\omega + 0\cdot\omega_L + 0\cdot\omega_J$ occurs with a positive and a negative sign in $\mathbf{P}_z$ on account of the second of the equations (15); moreover, since Z is real in character we also have $b = b^*$, if the star denotes the conjugate complex value. For brevity we write b without an index, and likewise a, further below.

(2) For $\Delta J = +1$, $\mathbf{P}_x + i\mathbf{P}_y$ in (16a) gives the Fourier term $-Z\sin\theta$, namely, by (15), $-b\sin\theta e^{i(\omega+\omega_J)t}$. (The frequency $\omega + \omega_J$ occurs only once in $\mathbf{P}_x + i\mathbf{P}_y$.)

(3) For $\Delta J = -1$ we obtain from $\mathbf{P}_x - i\mathbf{P}_y$ by (16a) and (15) $-b\sin\theta e^{i(\omega-\omega_J)t}$.

From the Fourier coefficients we are now to calculate the intensity *observed* in any arbitrary direction. For the purpose we introduce a new frame of co-ordinate axes u, v, w and lay the w-axis, say, in the direction of observation. Then only the vibrations in the (u, v) direction contribute to the observed intensity (cf. Chap. I, p. 25). We resolve the vibrations in the (x, y) direction into their components in the (u, v) direction, which we shall call $\mathbf{P}_{xu}$, $\mathbf{P}_{xv}$ and $\mathbf{P}_{yu}$, $\mathbf{P}_{yv}$. The intensity then becomes $(\mathbf{P}_{xu} + \mathbf{P}_{yu})^2 + (\mathbf{P}_{xv} + \mathbf{P}_{yv})^2$. This intensity must now be averaged over all positions of the frame-work of axes, x, y, z with respect to u, v, w. To do this we introduce Euler's angles and finally obtain (denoting the mean by a horizontal bar)

$$\overline{(\mathbf{P}_{xu} + \mathbf{P}_{yu})^2 + (\mathbf{P}_{xv} + \mathbf{P}_{yv})^2} = \tfrac{2}{3}(\mathbf{P}_x^2 + \mathbf{P}_y^2) = \tfrac{2}{3}\,|\,\mathbf{P}_x \pm i\mathbf{P}_y\,|^2. \quad (17a)$$

In an analogous manner the z-vibration contributes

$$\overline{\mathbf{P}_{zu}^2 + \mathbf{P}_{zv}^2} = \tfrac{2}{3}\mathbf{P}_z^2. \quad (17b)$$

Hence for case (1) we should obtain according to (17b) the intensity $I = \frac{8}{3}b^2\cos^2\theta \cdot 4\cos^2\omega t$. But it is evident that we have yet to form the mean of this expression, so that we obtain finally

$$\Delta L = 0 \begin{cases} (1)\ \Delta J = 0 : I = \tfrac{4}{3}b^2\cos^2\theta \\ \quad \text{and analogous values for the other cases, by (17}a\text{):} \\ (2)\ \Delta J = +1 : I = \tfrac{2}{3}b^2\sin^2\theta, \\ (3)\ \Delta J = -1 : I = \tfrac{2}{3}b^2\sin^2\theta. \end{cases} \quad (18)$$

These formulæ have been applied in Chapter VIII, § 9, p. 530. We next consider the cases $\Delta L = +1$ and $\Delta L = -1$:

$$\Delta L=+1\begin{cases}(1)\,\Delta J=0.\ \text{Fourier coeff. of } \mathbf{P}_z: \frac{\sin\theta}{2}(ae^{i(\omega_L+\omega)t}+a^*e^{-i(\omega_L+\omega)t}),\\ (2)\,\Delta J=+1\ \ ,,\quad ,,\quad ,,\ \mathbf{P}_x+i\mathbf{P}_y: \frac{\cos\theta+1}{2}ae^{i(\omega_L+\omega_J+\omega)t},\\ (3)\,\Delta J=-1\ \ ,,\quad ,,\quad ,,\ \mathbf{P}_x-i\mathbf{P}_y: \frac{\cos\theta-1}{2}ae^{i(\omega_L-\omega_J+\omega)t}.\end{cases}$$

According to (17*a*, *b*) we obtain (it is again necessary to form the time-mean in the case of $\mathbf{P}_z$):

$$\Delta L=+1\begin{cases}(1)\ \Delta J=0: I=\tfrac{4}{3}|a|^2\frac{\sin^2\theta}{4},\\ (2)\ \Delta J=+1: I=\tfrac{2}{3}|a|^2\frac{(\cos\theta+1)^2}{4},\\ (3)\ \Delta J=-1: I=\tfrac{2}{3}|a|^2\frac{(\cos\theta-1)^2}{4}.\end{cases}\quad . \quad (19)$$

Analogously for $\Delta L = -1$:

$$\Delta L=-1\begin{cases}(1)\ \Delta J=0: I=\tfrac{4}{3}|a|^2\frac{\sin^2\theta}{4},\\ (2)\ \Delta J=+1: I=\tfrac{2}{3}|a|^2\frac{(\cos\theta-1)^2}{4},\\ (3)\ \Delta J=-1: I=\tfrac{2}{3}|a|^2\frac{(\cos\theta+1)^2}{4}.\end{cases}\quad . \quad (20)$$

(*f*) **The selection rule for the magnetic quantum number** M (cf. p. 299; for m we write M in order to keep the notation uniform) may also be deduced more rigorously now. Besides the axes x, y, z fixed in the atom we also use axes ξ', η', ζ' fixed in space, where ζ' = the direction of the magnetic lines of force, ξ', η' being perpendicular to ζ', and Θ being the angle between the ζ'- and the z-axis, that is, between the direction of the field and of the normal to the invariable plane of the atom, which is at the same time the axis of the moment of momentum $Jh/2\pi$.

Without loss of generality we may make the y- and the η'-axis coincide with the common perpendicular (" line of nodes ") to the axes ζ' and z for $t = 0$. For this moment of time the transformation formulæ between ξ', η', ζ' and xyz are:

$$\xi' = x\cos\Theta - z\sin\Theta, \quad \eta' = y, \quad \zeta' = x\sin\Theta + z\cos\Theta. \quad (21)$$

The whole atom is now turned out of its position at the time $t = 0$ about the direction ζ' of the lines of force with the uniform precessional velocity $\mathfrak{o}$ (for example, with the Larmor precession in the normal Zeeman effect). This denotes that $\xi' + i\eta'$ becomes multiplied by $e^{i\mathfrak{o}t}$, whereas ζ' is not changed by the precession. Hence for any arbitrary t we have in place of (21),

$$\xi' + i\eta' = e^{i\mathfrak{o}t}(x\cos\Theta + iy - z\sin\Theta), \zeta' = x\sin\Theta + z\cos\Theta. \quad (22)$$

The transformation formulæ for the electric moment in the two co-ordinate systems are then similar, according to (7*a*):

$$\left.\begin{aligned} \mathbf{P}_{\xi'} + i\mathbf{P}_{\eta'} &= e^{i\mathbf{o}t}(\mathbf{P}_x \cos\Theta + i\mathbf{P}_y - \mathbf{P}_z \sin\Theta), \\ \mathbf{P}_{\zeta'} &= \mathbf{P}_x \sin\Theta + \mathbf{P}_z \cos\Theta. \end{aligned}\right\} \quad . \quad (23)$$

The Fourier series $\mathbf{P}_x$, $\mathbf{P}_y$, $\mathbf{P}_z$ may, by (14), clearly be written in the form

$$\mathbf{P}_x + i\mathbf{P}_y = e^{i\omega_J t} \sum_\rho \mathrm{A}_\rho e^{i\omega_\rho t}, \quad \mathbf{P}_z = \sum_\rho \mathrm{B}_\rho e^{i\omega_\rho t}, \quad . \quad (24a)$$

or

$$\left.\begin{aligned} \mathbf{P}_x &= \tfrac{1}{2}[e^{i\omega_J t} \sum_\rho \mathrm{A}_\rho e^{i\omega_\rho t} + e^{-i\omega_J t} \sum_\rho \mathrm{A}_\rho^* e^{-i\omega_\rho t}], \\ i\mathbf{P}_y &= \tfrac{1}{2}[e^{i\omega_J t} \sum_\rho \mathrm{A}_\rho e^{i\omega_\rho t} - e^{-i\omega_J t} \sum_\rho \mathrm{A}_\rho^* e^{-i\omega_\rho t}], \\ \mathbf{P}_z &= \sum_\rho \mathrm{B}_\rho e^{i\omega_\rho t}. \end{aligned}\right\} \quad . \quad (24b)$$

The frequency **o** is to be assigned to the quantum number M. Hence equation (23) teaches us that *the quantum transition* $\Delta\mathrm{M}$ *is capable of having only the values* + 1 and 0. *Corresponding to the quantum transition* + 1 *we have circularly polarised vibrations perpendicular to the magnetic lines of force* (*σ-components*), *and to the quantum transition* 0 *linearly polarised vibrations parallel to the lines of force* (*π-components*). This is our selection rule of pp. 299 and 480.

It is also easily possible to give intensity formulæ for the Zeeman effect, which correspond with the equations (18), (19) and (20). We see immediately that the equations (14) and (23) on the one hand, and the equations (15) and (24*a*) on the other are fully analogous. For the sequel it is important that in these equations x and ξ', ξ and x, and so forth, ω_J and **o** (for which we may now also write ω_M), ω_L and ω_J, a and A, b and B, θ and Θ correspond. In place of ω we now have one with the frequencies ω_ρ, which we shall denote briefly by Ω. Consequently we may immediately take over the expressions for the Fourier coefficients from the above expressions in *e*), if we make the specified substitutions and observe that L, J are replaced by the quantum numbers J, M. Let the direction of observation be perpendicular to the field; then our co-ordinate system u, v, w lies so that w is perpendicular to ζ'. The intensities $(\mathbf{P}_{\xi' u} + \mathbf{P}_{\eta' u})^2 + (\mathbf{P}_{\xi' v} + \mathbf{P}_{\eta' v})^2$ and $\mathbf{P}^2_{\xi' u} + \mathbf{P}^2_{\zeta' v}$ must again be averaged over all positions of ξ', η', ζ' with respect to u, v, w, the ζ'-direction (= direction of the field) now remaining fixed in space and always remaining perpendicular to w. We obtain

$$\overline{(\mathbf{P}_{\xi' u} + \mathbf{P}_{\eta' u})^2 + (\mathbf{P}_{\xi' v} + \mathbf{P}_{\eta' v})^2} = \tfrac{1}{2}\,|\,\mathbf{P}_{\xi'} \pm i\mathbf{P}_{\eta'}\,|^2,$$

$$\overline{(\mathbf{P}^2_{\zeta' u} + \mathbf{P}^2_{\zeta' v})^2} = \mathbf{P}^2_{\zeta'}.$$

For the (observed) intensities we thus obtain

$$\Delta\mathrm{J} = 0 \left\{\begin{aligned} &(1)\ \Delta\mathrm{M} = 0 : \mathrm{I} = 2\mathrm{B}^2 \cos^2\Theta, \\ &(2)\ \Delta\mathrm{M} = +1 : \mathrm{I} = \tfrac{1}{2}\mathrm{B}^2 \sin^2\Theta, \\ &(3)\ \Delta\mathrm{M} = -1 : \mathrm{I} = \tfrac{1}{2}\mathrm{B}^2 \sin^2\Theta. \end{aligned}\right\} \quad . \quad . \quad (25)$$

$$\Delta J = +1 \left\{ \begin{array}{l} (1)\ \Delta M = 0 : I = 2\,|\,A\,|^2 \dfrac{\sin^2\Theta}{4}, \\ (2)\ \Delta M = +1 : I = \tfrac{1}{2}\,|\,A^2\,| \dfrac{(\cos\Theta + 1)^2}{4}, \\ (3)\ \Delta M = -1 : I = \tfrac{1}{2}\,|\,A\,|^2 \dfrac{(\cos\Theta - 1)^2}{4}. \end{array} \right\} \quad (26)$$

$$\Delta J = -1 \left\{ \begin{array}{l} (1)\ \Delta M = 0 : I = 2\,|\,A\,|^2 \dfrac{\sin^2\Theta}{4}, \\ (2)\ \Delta M = +1 : I = \tfrac{1}{2}\,|\,A\,|^2 \dfrac{(\cos\Theta - 1)^2}{4}, \\ (3)\ \Delta M = -1 : I = \tfrac{1}{2}\,|\,A\,|^2 \dfrac{(\cos\Theta + 1)^2}{4}. \end{array} \right\} \quad (27)$$

The additional exclusion rule on p. 480, namely $0 \to 0$ *forbidden for* M *if* $\Delta J = 0$, may easily be deduced from (25). Here $I \sim \cos^2\Theta$ and $\cos\Theta \sim M$, since M denotes the projection of J on the direction of the lines of force and Θ the angle between this direction and the J-axis. Thus in our case $\cos\Theta$ is zero for the initial and the final state. By the first equation (25) we deduce from this that $I = 0$. This makes the exclusion rule in question comprehensible from the point of view of the Correspondence Principle.*

It is evident that the selection and polarisation rules for M are independent of whether we use a model without spin or one with spin, because J executes a precession about the direction of the field in both models, and it is this precession which lies at the base of our argument. But we must note that the M of the spin model is of course assigned to the J of the same model. Thus if the spin of the electrons exactly compensates itself ($S = 0$, $L = J$), then M denotes the "projection" of L on the field-axis and not, say, the projection of n_ϕ, as we might expect from the idea of orbits. Our treatment of the normal Zeeman effect in Chapter VI, § 4, still retains the old view-point of orbits, whereas the discussion of the next section on the anomalous Zeeman effect is based on the modern point of view.

The selection and polarisation rules for M become narrowed down in the Paschen-Back effect to the form given in the text on p. 494 : $\Delta M_L = \pm 1,\ 0$, $\Delta M_S = 0$; $\Delta M_L = \pm 1$ gives circular polarisation perpendicular to H, $\Delta M_L = 0$ gives linear polarisation parallel to H. The proof runs exactly as in Chapter VI, § 5, p. 338 : L and S are uncoupled, so that S has no influence on the precessional motion of L about H. Hence the Fourier expansion of the orbital motion does not contain the frequencies ω_{M_S}, which correspond to the precession of S about H, but only the frequencies ω_{M_L}. Consequently we have $\Delta M_S = 0$. From the kinematical character of the precession ω_{M_L}, which corresponds exactly with the precession $\mathfrak{o} = \omega^M$ in (22) and (23), we may deduce the given rules for M_L in a manner similar to that above given for M.

* We may of course also read it out of formulæ (11) on p. 534. There the observed intensity is denoted by A instead of by I as here.

Finally we remark that it is easy to predict from the model when the selection rules suffer exceptions. Thus besides $\Delta L = 0, \pm 1$ greater transitions will also occur as soon as the (LS)-interaction becomes appreciable. For the rule $\Delta L = 0, \pm 1$ depended on assuming a cyclic angle about the L-axis, that is, on a uniform precession about L; cf. the analogous calculations in the case of (12). If the motion about L becomes disturbed the precession becomes irregular and higher frequencies in ω_L occur. In the case of S, too, we have besides $\Delta S = 0$ also the transitions $\Delta S = \pm 1$, which present themselves when the interaction (LS) and hence the term resolution increases.

In spectra there are transitions as far as $|\Delta L| = 3$ and $|\Delta S| = 2$, but of course in these cases, which occur only when the resolution is very great, the allocation of L and S values becomes questionable from the physical point of view, cf. p. 469.

For the l's the most general selection rule would be: $\Sigma_i \Delta l_i =$ odd number (cf. p. 444). In spectra we find Heisenberg's rule for "double transitions" ((5) on p. 444) to be adequate in almost all cases.

If no field is present there are theoretically and experimentally no exceptions to $\Delta J = 0, \pm 1$. For the angle belonging to ω_J and counted around J is always cyclic, because the law of areas about J always holds in the force-free atom. For an analogous reason the selection rule for M in the magnetic field may never be transgressed.

(*g*) We pass on to *band spectra*, dealing first with the oscillation component. We must not lose sight of the fact that the Correspondence Principle is concerned with the emission from electric charges and that **P** in (7) is expressly defined as the moment, variable in time, of such charges. In the application to band spectra we thus fix our attention on an *oscillator with variable electric moment*. Corresponding to this we have a polar dipole such as $H^+ Cl^-$ or more complicated configurations such as $H^+ H^+ O^{- -}$; in apparent opposition to such dipoles we have non-polar molecules such as O_2, N_2, H_2, Cl_2. The latter have no electric moment and no emission according to classical theory when their equally charged constituents vibrate with respect to one another; hence also according to quantum theory they should not radiate. But non-polar molecules that consist of unlike atoms have a variable electric moment because then the centre of mass does not in general coincide with the electrical centre of gravity.

Nevertheless a non-polar configuration, such as O_2, N_2 . . . may also acquire an electric moment as soon as one of its components is electrically excited by disturbing the electron orbits. The oscillations (and also the rotations) of the molecule then become effective, *but only in conjunction with electron transitions*, which yield an electric moment.

We now give a formula which represents the simultaneous action of the oscillation and the rotation. Let the axis of the rotation be the z-axis, and its angular velocity ω; let the oscillation (which will in general be anharmonic) take place in the xy-plane, and let its fundamental vibration be denoted by ν_0 as in equation (9*a*). By multiplying equation (9*a*) by $e^{i\omega t}$ we obtain

$$\mathbf{P}_x + i\mathbf{P}_y = e^{i\omega t} \sum_{-\alpha}^{+\infty} \mathbf{D}_s e^{2\pi i s \nu_0 t}; \quad \mathbf{P}_z = 0. \quad . \quad . \quad (28)$$

If we allocate the quantum numbers v to the oscillations and the quantum numbers j to the rotations, we read off from equation (28) the quantum transitions $\Delta v = \pm s$ are arbitrary and are always connected with the quantum transitions $\Delta j = \pm 1$. *This contains the selection principle for the rotation and the oscillation quanta of the band spectra.* Since no term occurs that does not contain the factor $e^{i\omega t}$, $\Delta j = 0$ is forbidden. *A zero branch does not occur under the conditions here envisaged.* These assumptions correspond to infra-red spectra, for example, of HCl. .

But we deduce that a zero branch is possible under one of the following conditions :—

1. The oscillation does not occur perpendicularly to the axis of rotation. We then have, if we again regard the axis of rotation as the z-axis, a component $\mathbf{P}_z$ which differs from zero and which indicates the possibility of transitions $\Delta j = 0$. The case occurs in the infra-red spectra of polyatomic molecules, for example, of CH_4.

2. The electronic motion becomes added to the oscillation and the rotation. This may entail a $\mathbf{P}_z$ which differs from zero, no matter how the axes of oscillation and rotation are situated with respect to one another. This is the general case of bands in the visible spectrum. It occurs even in H_2 and He_2.

3. The general precessional motion of Chapter IX, § 6, takes the place of the simple rotation. If we place the z-axis through the axis of the total moment of momentum, the projection of the electric moment $\mathbf{P}$ on the z-axis or on the xy-plane is equal to $|\mathbf{P}| \cos\theta$ and $|\mathbf{P}| \sin\theta$ (θ denotes the angle between the axis of precession and the "figure axis" of the "top," which is assumed to be symmetrical or nearly symmetrical), and we obtain, if ω now denotes the precessional velocity of the top, in place of (28),

$$\mathbf{P}_x + i\mathbf{P}_y = e^{i\omega t} |\mathbf{P}| \sin\theta, \quad \mathbf{P}_z = |\mathbf{P}| \cos\theta. \qquad (29)$$

The second equation again denotes that the zero branch occurs. We have a case of this kind in the bands of formaldehyde (p. 586).

The above remarks will suffice to show the great fruitfulness of the Correspondence Principle.

8. Conservation of Moment of Momentum during Emission *

There are three elementary laws of conservation in mechanics : conservation of energy, of momentum (conservation of centre of mass), and of moment of momentum (law of areas). We shall apply them to the coupled system atom + ether (that is, surrounding field of radiation). The energy law demands that

$$h\nu = W_1 - W_2. \qquad (1)$$

On the left-hand side we have the energy emitted in the field, on the right the energy given up by the atom.

The conservation of momentum is fulfilled automatically if we

* A. Rubinowicz, Phys. Zeits., **19**, 441 and 465 (1918). Bohr also gives indications of this discussion at the end of the first part of his quantum theory of line spectra, loc. cit., p. 133, which appeared at the same time.

describe the radiation field as a centrally symmetrical spherical wave, that is, in the sense of the classical theory. The emission in one direction is then compensated by that in the opposite direction, and the resultant momentum of the radiation is zero. The law of conservation of the centre of mass holds for the stationary states of the atom both in the final state and in the initial state. Let us recall, for example, the hydrogen in the case where we take into account the relative motion of the nucleus. In the system of reference the total momentum of the atom is zero and no change occurs in it. The conservation of momentum thus leads to the equation $0 = 0$.

The position is different with the *moment of momentum*. We denote this, so far as it is due to the orbital motion of the electrons, by p; if we take into account the relative motion of the nucleus we must take p to stand for the total orbital moment of the electrons + the nucleus about the centre of gravity. This p is a whole multiple (L) of $h/2\pi$. In addition we must take into account the spin of the electrons. The total moment of momentum then becomes $Jh/2\pi$, where J is half-integral or integral (cf. Chap. VIII, § 2) according as the number of electrons is even or odd.

Thus every change ΔJ *in the quantum number* J *denotes a change in the total moment of momentum of amount*

$$\Delta J h/2\pi. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

This amount of moment of momentum must not get lost but must be transferred from the atom to the radiation if the atom is coupled during the emission process with the surrounding field. We also remark that ΔJ in (2) denotes the algebraic difference of the quantum numbers J only if the moment of momentum before and after the transition has the same axis; otherwise ΔJ is to be reckoned as a geometrical difference.

How are we to interpret the moment of momentum of the *radiation?* We must first define the individual momentum present in every direction of the rays. Calculated per unit volume this is equal to the energy-density of the radiation divided by c, cf. the law of the inertia of energy, p. 44. But the energy-density is, if calculated in appropriate (so-called rational) units,

$$W = \tfrac{1}{2}\mathbf{E}^2 + \tfrac{1}{2}\mathbf{H}^2.$$

In the field of radiation $\mathbf{E} = \mathbf{H}$ in magnitude, and in direction $\mathbf{E} \perp \mathbf{H}$ and both are perpendicular to the direction of the ray. Instead of W we may therefore also write

$$W = \mathbf{E}^2 = \mathbf{H}^2 = \mathbf{EH}.$$

Let the moment be called G, reckoned per unit volume. Then

$$G = \frac{W}{c} = \frac{\mathbf{EH}}{c}.$$

The direction of the momentum lies in the direction of propagation of the energy, that is, in the direction of the ray. We express this by writing

$$\mathbf{G} = \frac{[\mathbf{EH}]}{c} = \frac{\mathbf{S}}{c^2}. \quad . \quad . \quad . \quad . \quad (3)$$

Here $\mathbf{S} = c[\mathbf{EH}]$ is the ray vector.

The moment of momentum per unit volume of radiation is calculated as the vector product of the momentum $\mathfrak{G}$ and its perpendicular distance from the centre of the spherical wave

$$\mathfrak{M} = [\mathfrak{r}\mathfrak{G}], \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\mathfrak{r}$ denotes the radius vector from the centre to the unit volume in question. From the moment of momentum per unit volume we pass on to the moment of momentum emitted in the spherical wave in all directions, by forming

$$\mathfrak{N} = \int dt \int d\sigma \, \mathfrak{M}, \quad . \quad . \quad . \quad . \quad (5)$$

the first integral being taken over the whole duration of the emission, the second over the whole spherical surface of radius r.

It appears at first sight as if the momentum $\mathfrak{M}$ should vanish for every individual direction, and hence also the total momentum $\mathfrak{N}$. For if, as we said, $\mathfrak{G}$ is in the direction of the ray and if this is in the radial direction, the perpendicular from the centre of the sphere to $\mathfrak{G}$ would be equal to zero and hence $\mathfrak{M}$ would vanish. But it must be observed that this determination of the direction of ray and momentum is only asymptotic and does not hold exactly for finite values of $\mathfrak{r}$. Hence in the integral (5) $\mathfrak{M}$ is different from zero for finite values of $\mathfrak{r}$; for an $\mathfrak{r}$ that increases indefinitely $\mathfrak{M}$ does, indeed, decrease to zero, but at the same time the region of integration increase quadratically with an increasing spherical radius. This enables us to understand how both influences may compensate one another and that in the limit for infinitely increasing distances, as well as for finite distances, a finite amount may result for $\mathfrak{N}$. *The moment of momentum of the spherical wave is able to take up and keep the amount of moment of momentum given up by the atom.*

This brief discussion shows that the calculation of the moment of momentum of the radiation requires a more detailed method of proceeding to the limit. We shall furnish this at the end of the present note. Here we shall assume the result. We calculate the emitted moment of momentum $\mathfrak{N}$ from the emitted energy W and the frequency ν by means of the formulæ

$$\left.\begin{aligned} \mathfrak{N}_x &= \frac{W}{2\pi\nu} \frac{2bc \sin(\gamma - \beta)}{a^2 + b^2 + c^2}, \quad \mathfrak{N}_y = \frac{W}{2\pi\nu} \frac{2ca \sin(\alpha - \gamma)}{a^2 + b^2 + c^2}, \\ \mathfrak{N}_z &= \frac{W}{2\pi\nu} \frac{2ab \sin(\beta - \alpha)}{a^2 + b^2 + c^2}. \end{aligned}\right\} \quad . \quad (6)$$

Here xyz are three mutually perpendicular axes which we shall for the present fix arbitrarily through the point at which the emitting atom is situated, and we shall resolve the moment of momentum $\mathfrak{N}$ into components along these axes. We obtain the most general solution of Maxwell's equations corresponding to a spherical wave if we make three electrons vibrate along these three axes with the same frequency ν but with arbitrary amplitudes and phases, namely

$$ae^{i\alpha}, \quad be^{i\beta}, \quad ce^{i\gamma}. \quad . \quad . \quad . \quad . \quad (7)$$

According to the views of the classical electron theory these electrons would then give rise to a spherical field of radiation of the same frequency.

If the process of emission occurs in an external field of force (as in the Stark effect) the axes of the field are orientated according to the field. But if we are dealing with the emission from a force-free atom we may place the axes in such a way that one, say the third, of these vibration amplitudes (7) vanishes. The other two then define, in classical language, a "vibration ellipse" with a and b as principal axes and phase difference $\beta - \alpha$, which we shall call γ in future. On account of $s = 0$ the equations (6) reduce to

$$\mathbf{N} = \mathbf{N}_z = \frac{\mathrm{W}}{2\pi\nu} \frac{2ab \sin \gamma}{a^2 + b^2}, \quad \mathbf{N}_x = \mathbf{N}_y = 0. \quad . \quad . \quad (8)$$

The moment of momentum and with it the spherical wave in this way acquire a favoured axis and also a favoured plane, the plane of the vibration ellipse. Does this not contradict the concept of the spherical wave ? A spherical wave is usually taken to stand for an event which propagates itself symmetrically in all directions from the source of light. This concept corresponds with rough optical experience. According to Maxwell's equations (as well as the older ideas of an elastic medium) a spherical wave always has a favoured axis both for the distribution of intensity as well as for polarisation. Only the phase of the light is distributed with spherical symmetry and only the wave surfaces, that is, the surfaces of equal phase form a system of concentric spherical surfaces in the case of a spherical wave. On the other hand, the surfaces of equal intensity are by no means spherical surfaces. Consider, for example, the simplest case in which according to the mode of expression of the classical wave-theory an electron which vibrates linearly emits a spherical wave. On account of the general character of transversality of light vibrations no intensity is emitted in the direction of vibration. The intensity is a maximum perpendicular to this direction (cf. the innermost curve in Fig. 11, p. 33, which represents this case of emission). Hence the surfaces of equal intensity by no means have a spherical shape, rather the direction of vibration of the electron is at the same time a *favoured axis of the intensity distribution.* In a similar way in the case of our vibration ellipse with principal axes a, b the normal is a favoured axis for the intensity and polarisation.

From our present point of view we distinguish between the various cases of polarisation in the following way :

We have *linearly polarised light* when the moment of momentum $\mathbf{N}$ vanishes. According to (8) this occurs when either a or b or $\sin \gamma$ vanishes. The vibration ellipse then degenerates into a straight line which lies either in the direction of b (if $a = 0$) or of a (if $b = 0$), or in that of the one or other diagonal of the rectangle ab (when $\sin \gamma = 0$). This straight line is the *axis of symmetry* of the spherical wave. From its position we may determine, by means of the rules of the wave-theory, for every radius of the spherical wave the direction of the electric force and the observable plane of polarisation.

We have *circularly polarised light* when the moment of momentum $\mathbf{N}$ attains the maximum value of which it is capable for a given fixed intensity of the light (fixed given value of $a^2 + b^2$). This maximum occurs when $a = b$ and $\sin \gamma = \pm 1$ (phase-angle $\gamma = \pm \pi/2$) ; the

factor in (8) that depends on a, b, γ becomes equal to ± 1 in this case. The vibration ellipse changes into a vibration circle. In the direction of the axis of the moment of momentum we have circularly polarised light, and it is left or right circularly polarised light according as $\gamma = +\pi/2$ or $-\pi/2$. In all other directions the light is elliptically or in particular linearly polarised; in the latter case, perpendicularly to the axis of the moment of momentum.

In the general case when **N** neither vanishes nor attains a maximum we have *elliptically polarised light*, which degenerates into linearly polarised light only for special directions.

We now set the moment of momentum (8) of the radiation equal to the change (2) which the moment of momentum of the atom experiences in the transition in question. In this way we obtain, if we simultaneously replace W by $h\nu$ in (8) and cancel $h/2\pi$ on both sides,

$$\Delta J = \frac{2ab \sin \gamma}{a^2 + b^2}. \quad . \quad . \quad . \quad . \quad (9)$$

This equation holds both for magnitude and direction. If ΔJ is to be calculated as the *algebraic* difference between the initial and the final state (cf. the remark made with reference to equation (2)), which we shall assume for the present, then ΔJ is certainly *integral*.

But the right-hand side of equation (9) *is, taken absolutely, less than or at most equal to* 1. Actually we have, on account of $(a - b)^2 > 0$,

$$a^2 + b^2 > 2ab \quad . \quad . \quad . \quad . \quad (10)$$

and still more is

$$a^2 + b^2 > 2ab \sin \gamma. \quad . \quad . \quad . \quad (10a)$$

In place of this *inequality* we have the *equation*

$$a^2 + b^2 = \pm 2ab \sin \gamma, \quad . \quad . \quad . \quad (10b)$$

only in the case where $a = b$ and $\sin \gamma = \pm 1$, $\gamma = \pm \pi/2$. *In this particular case the right-hand side of* (9) *becomes equal to* ± 1. Hence the left-hand side of (9) is, taken absolutely, also *not greater* than 1.

There are, however, only three integers whose absolute values are not greater than 1, namely,

$$\Delta J = +1, \quad \Delta J = 0, \quad \Delta J = -1.$$

In the case $\Delta J = \pm 1$ equation (10*b*) holds. The corresponding values of a, b and γ are completely determined and have already been given in equation (10*b*). In the case $\Delta J = 0$ the numerator on the right-hand side must, according to equation (9), vanish. Hence it follows for a, b and γ that we must have either $a = 0$ or $b = 0$ or $\sin \gamma = 0$ ($\gamma = 0$ or π).

Hence we have the following three possibilities:

$$\Delta J = \begin{cases} +1 & a = b \text{ and } \gamma = +\pi/2, \\ 0 & a = 0 \text{ or } b = 0 \text{ or } \gamma = 0 \text{ or } \pi, \\ -1 & a = b \text{ and } \gamma = -\pi/2. \end{cases} \quad . \quad (11)$$

In the first and third cases the emitted light is left or right *circularly polarised* light, in the second case it is *linearly polarised.*

In this way, by means of a remarkably rigorous line of reasoning, that recalls the methods of the theory of numbers, we have arrived from the conservation of moment of momentum at a *selection principle* and a *polarisation rule.*

The *selection rule* states : *the quantum number of the moment of momentum can change by at most unity in changes of configuration of the atom. The polarisation rule demands that : if the quantum number changes by* ± 1 *the light is circularly polarised, but if it does not change it is linearly polarised. The general case of elliptic polarisation is suppressed by the laws of conservation.*

In the above we have assumed that the moment of momentum of the atom retains its axis in changes of configuration, that is, that ΔJ is to be calculated algebraically from J_1 and J_2. We shall now show that our conclusions are correct also in the contrary case.

Let Θ be the angle between the axes of the two moments of momentum before and after the transition ; let the corresponding quantum numbers be J_1 and J_2. Then we have for the geometrical difference of J_1 and J_2

$$\Delta J = \sqrt{J_1^2 + J_2^2 - 2J_1J_2 \cos \Theta} \quad . \quad . \quad (12)$$

and by a theorem of elementary geometry

$$\Delta J \geqq | J_1 - J_2 | \quad . \quad . \quad . \quad . \quad (13)$$

The equality sign here holds only if the triangle degenerates into a double straight line, so that $\Theta = 0$; which is the case already considered of similarly directed momentum axes.

According to equations (9) and (10) we now also have

$$\Delta J \leqq 1 \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and, in addition, from (13)

$$| J_1 - J_2 | \leqq 1. \quad . \quad . \quad . \quad . \quad (15)$$

But $J_1 - J_2$ is a whole number ; by (15) the whole number is again capable of only the three values :

$$J_1 - J_2 = +1, \quad J_1 - J_2 = 0, \quad J_1 - J_2 = -1.$$

Hence our *selection principle* also applies without change under the present more general assumption : *the quantum number of the moment of momentum can change by at most unity in changes of configuration of the atom.*

In the first and the third cases we also have $\Delta J = 1$ on account of the double equation which follows from (13) and (14) :

$$| J_1 - J_2 | \leqq \Delta J \leqq 1,$$

hence in these cases, as remarked in connection with (13), $\Theta = 0$. We then again have the conditions considered earlier and our *polarisation rule* also *applies unchanged. The light is circularly polarised ; the axis of the moment of momentum necessarily has the same direction before and after the transition.*

On the other hand, the second case $J_1 - J_2 = 0$ may be reduced to the earlier case $\Delta J = 0$ only with special assumptions ; we shall pass it by here.

We have now to add some remarks about the *emission in a field of force.*

We take the field of force to be electrical. On account of the order of magnitude of atomic dimensions it may certainly be treated as homogeneous. The moment of the force about the direction of the force obviously vanishes. According to mechanics the moment of the force determines the change in the moment of momentum, the latter being calculated as the geometric sum of the moments of momentum of all the mass parts of the atom. Its components in the direction of the force thus remains constant whereas the component in the plane perpendicular to it is permanently changed. Hence the law of areas holds in its special form, as the theorem of the conservation of areal velocity, only for the direction of the force itself. It is only for this direction that we may demand the conservation of the moment of momentum when the atom is coupled with the radiation.

This component of the moment of momentum, and not the whole moment of momentum, now becomes a multiple of $h/2\pi$. We call this multiple the *equatorial quantum number of the moment of momentum*, and in contrast with the earlier J we denote it by M. We take the direction of the lines of force as the z-axis and call the perpendicular xy-plane the *equatorial plane*. Let $\mathbf{N}_z$ be the component of the moment of momentum of the emitted spherical wave for the direction of the force. Its expression in terms of the amplitudes and phase-constants of the spherical wave has been given in equation (6). If we here substitute $W = h\nu$, it follows that

$$\mathbf{N}_z = \frac{h}{2\pi} \frac{2ab \sin(\beta - \alpha)}{a^2 + b^2 + c^2}. \quad . \quad . \quad . \quad (16)$$

It must be equal to the change in the corresponding component of moment of momentum of the atom, that is, equal to $\Delta M h/2\pi$. So we obtain

$$\Delta M = \frac{2ab \sin(\beta - \alpha)}{a^2 + b^2 + c^2}. \quad . \quad . \quad . \quad (17)$$

We may therefore conclude precisely as before.

The absolute value of the right-hand side of (17) is necessarily $\leqq 1$; namely, as in equation (10),

$$a^2 + b^2 > 2ab,$$

and hence still more,

$$a^2 + b^2 + c^2 > 2ab \sin(\beta - \alpha).$$

The right-hand side of (17) can accordingly become equal to ± 1 only if we have simultaneously

$$a = b, \quad c = 0, \quad \sin(\beta - \alpha) = \pm 1.$$

Accordingly the left-hand side of (17) must necessarily lie between the limits ± 1. Since it is integral, being the difference between two integers, it may assume only one of the three values:

$$\Delta M = +1, \quad 0, \quad -1.$$

For $\Delta M = \pm 1$ we have

$$a = b, \quad c = 0, \quad \sin(\beta - \alpha) = \pm 1.$$

We have a (*left or right*) *circularly polarised spherical wave. Its plane of vibration is the equatorial plane* (perpendicular to the direction of the force); *its favoured axis coincides with the direction of the force. The vibration component in the direction of the force, as measured by the amplitude c, vanishes. The vibration ellipse changes into a vibration circle lying perpendicularly to the direction of the force.*

For $\Delta M = 0$ we have, according to (17), either $a = 0$ or $b = 0$ or $\sin(\beta - \alpha) = 0$. But since all axes are of equal value in the direction perpendicular to the lines of force we cannot have $a = 0$ and $b \neq 0$ as otherwise the y-axis would be favoured as compared with the x-axis. If, on the other hand, we had $\sin(\beta - \alpha) = 0$, we should have a rectilinear vibration in the direction of the resultant of the two amplitude vectors a and b and then *this* direction would be favoured as compared with the other directions of the equatorial plane. The required equality of the equatorial directions is assured, however, if we assume $a = b = 0$. We are thus left with only the vibration amplitude c, which *is* favoured by being in the direction of the lines of force. *The resultant spherical wave is then linearly polarised and has its lines of force in the direction of the axis of symmetry of the linear polarisation.*

All in all, then, we may also confirm the *polarisation rule* and the *selection rule* when an external field is present, making only those changes which are due to the existence of a favoured field of force. *The selection principle* now refers only to the equatorial quantum number M of the moment of momentum, which is allocated to the component of the moment of momentum in the direction of the lines of force, just as the earlier quantum number J of the moment of momentum was assigned to the whole moment of momentum.

As already remarked on p. 300 the line of reasoning here followed, which we owe to Rubinowicz, has lately excited renewed interest owing to its relationship to the much-disputed problem of the electrodynamics of quanta. The question involved is: how is quantum mechanics (wave-mechanics) to be connected organically with the, possibly, modified electrodynamics? In the above discussion we used electrodynamics in Maxwell's form and the quantum theory in its form before the advent of wave-mechanics. The laws of conservation furnished the connection between the two. It is evident that these laws will also be essentially contained in quantum electrodynamics. They furnish necessary, even if not sufficient, conditions for the more intimate connection between the atom and the electromagnetic field which is required but is as yet unknown.

We conclude by adding the promised derivation of equation (6).

Extending Hertz's assumption we write the solution of Maxwell's equations which correspond to a spherical wave which starts out from $r = 0$ (a simple dipole) in the form

$$\left.\begin{aligned} &\mathbf{E} = \operatorname{curl}\operatorname{curl}\Pi = \operatorname{grad}\operatorname{div}\Pi - \Delta\Pi, \quad \mathbf{H} = \frac{1}{c}\operatorname{curl}\dot{\Pi} \\ &\Pi = \mathbf{P}\frac{e^{ikr}}{r}, \quad \mathbf{P} = \mathfrak{p}e^{-i\omega t}, \quad \mathfrak{p} = \begin{cases} \mathfrak{p}_x = ae^{i\alpha} \\ \mathfrak{p}_y = be^{i\beta} \\ \mathfrak{p}_z = ce^{i\gamma} \end{cases} \end{aligned}\right\} \quad (18)$$

Here $k = \frac{\omega}{c} = \frac{2\pi}{\lambda}$ is the wave-number for 2π units of length, $\omega = \frac{2\pi}{\tau}$ is the frequency for 2π units of time. The solution has six integration constants a, α, b, β, c, γ, which, together with the time of vibration $\tau = 2\pi/\omega$, just suffice to represent the most general process of monochromatic emission of the spherical type. Π satisfies the wave-equation

$$\frac{1}{c^2}\ddot{\Pi} = \Delta\Pi. \quad . \quad . \quad . \quad . \quad (19)$$

In the following calculation of the field we must make frequent use of well-known formulæ of vector analysis, which we give without explaining them in detail. The calculation of the moment of momentum is due to Abraham,* but our quantum view demands an expression that differs from his.

From equation (18) it follows that

$$\operatorname{div}\Pi = (\mathbf{Pr})\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}\right), \quad \operatorname{curl}\Pi = -[\mathbf{Pr}]\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}\right),$$

$$\operatorname{grad}\operatorname{div}\Pi = \mathbf{P}\cdot\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}\right) + (\mathbf{Pr})\frac{\mathbf{r}}{r}\frac{\partial}{\partial r}\left[\frac{1}{r}\frac{\partial}{\partial r}\left(\frac{e^{ikr}}{r}\right)\right].$$

The equations (18) then give, if we take (19) into account,

$$\left.\begin{aligned} \mathbf{E} &= \mathbf{P}\left(k^2 + \frac{1}{r}\frac{\partial}{\partial r}\right)\frac{e^{ikr}}{r} + (\mathbf{Pr})\frac{\mathbf{r}}{r}\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r}\frac{e^{ikr}}{r}, \\ (\mathbf{rE}) &= (\mathbf{rP})\left(k^2 + \frac{1}{r}\frac{\partial}{\partial r} + r\frac{\partial}{\partial r}\frac{1}{r}\frac{\partial}{\partial r}\right)\frac{e^{ikr}}{r}, \\ \mathbf{H} &= ik[\mathbf{Pr}]\frac{1}{r}\frac{\partial}{\partial r}\frac{e^{ikr}}{r}, \quad (\mathbf{rH}) = 0. \end{aligned}\right\} \quad . \quad (20)$$

Performing the differentiations and neglecting the higher powers of $\frac{1}{r}$ we obtain

$$\left.\begin{aligned} \mathbf{E} &= k^2\left\{\mathbf{P} - \frac{\mathbf{r}}{r^2}(\mathbf{Pr})\right\}\frac{e^{ikr}}{r}, \quad \mathbf{H} = -k^2[\mathbf{Pr}]\frac{e^{ikr}}{r^2}, \\ (\mathbf{rE}) &= -2ik(\mathbf{rP})\frac{e^{ikr}}{r^2}. \end{aligned}\right\} \quad . \quad (21)$$

The moment of momentum per unit volume at a distance r from the centre is, by equations (3) and (4) (concerning the factor 4π in the denominator cf. what was said about equation (2)),

$$\mathbf{M} = \frac{1}{4\pi c}[\mathbf{r}[\mathbf{EH}]] = \frac{1}{4\pi c}(\mathbf{E}(\mathbf{rH}) - \mathbf{H}(\mathbf{rE})),$$

or, in view of $(\mathbf{rH}) = 0$, equation (20),

$$\mathbf{M} = -\frac{1}{4\pi c}\mathbf{H}(\mathbf{rE}). \quad . \quad . \quad . \quad . \quad (22)$$

* "The Moment of Momentum of Light," Phys. Zeits., **15**, 914 (1914).

Let us multiply $\mathbf{M}$ by the element of volume in polar co-ordinates,

$$r^2\,dr\,d\Omega,$$

where $d\Omega$ denotes the conical aperture (solid angle) seen from the centre, and let us set $dr = cdt$ and integrate over all the $d\Omega$'s; we then obtain the moment of momentum contained in the spherical shell of radius r and of thickness dr or, otherwise expressed, the moment of momentum transported in the time $dt = dr/c$ through the sphere of radius r; we shall call this integrated moment of momentum $d\mathbf{N}$:

$$d\mathbf{N} = -\int \frac{d\Omega}{4\pi} r^2 \mathbf{H}(\mathbf{rE})dt. \quad . \quad . \quad . \quad (23)$$

The moment of momentum transported through this sphere during the whole duration of emission T was called $\mathbf{N}$ on p. 641:

$$\mathbf{N} = \int_0^T d\mathbf{N}. \quad . \quad . \quad . \quad . \quad (24)$$

Before performing the integration in (23) we must pass from our complex representation to its real part. We write, say,

$$\mathbf{Q} = \mathbf{Re}\{\mathbf{P}e^{ikr}\}, \quad \mathbf{Q}' = \mathbf{Re}\{-i\mathbf{P}e^{ikr}\} \quad . \quad . \quad (25)$$

$$\left.\begin{aligned} Q_x &= a\cos(kr-\omega t+\alpha), & Q_x' &= a\sin(kr-\omega t+\alpha),\\ Q_y &= b\cos(kr-\omega t+\beta), & Q_y' &= b\sin(kr-\omega t+\beta),\\ Q_z &= c\cos(kr-\omega t+\gamma), & Q_z' &= c\sin(kr-\omega t+\gamma). \end{aligned}\right\} \quad (25a)$$

By (23) and (21) we have

$$d\mathbf{N} = 2k^3\int \frac{d\Omega}{4\pi}\left(\frac{\mathbf{r}}{r}, \mathbf{Q}'\right)\left[\mathbf{Q}, \frac{\mathbf{r}}{r}\right]dt,$$

$$d\mathbf{N}_x = 2k^3\int \frac{d\Omega}{4\pi}\left(\frac{x}{r}\mathbf{Q}_x' + \frac{y}{r}\mathbf{Q}_y' + \frac{z}{r}\mathbf{Q}_z'\right)\left(\mathbf{Q}_y\frac{z}{r} - \mathbf{Q}_z\frac{y}{r}\right)dt.$$

Now,

$$\left.\begin{aligned} \int\frac{d\Omega}{4\pi}\frac{x^2}{r^2} &= \int\frac{d\Omega}{4\pi}\frac{y^2}{r^2} = \int\frac{d\Omega}{4\pi}\frac{z^2}{r^2} = \frac{1}{3},\\ \int\frac{d\Omega}{4\pi}\frac{xy}{r^2} &= \int\frac{d\Omega}{4\pi}\frac{yz}{r^2} = \int\frac{d\Omega}{4\pi}\frac{zx}{r^2} = 0. \end{aligned}\right\} \quad . \quad . \quad (26)$$

Consequently we obtain

$$d\mathbf{N}_x = \tfrac{2}{3}k^3(\mathbf{Q}_y\mathbf{Q}'_z - \mathbf{Q}_z\mathbf{Q}_y')dt = \tfrac{2}{3}k^3[\mathbf{QQ}']_x\,dt. \quad . \quad (27)$$

By equations (25a), however,

$$\left.\begin{aligned} [\mathbf{QQ}']_x &= bc\sin(\gamma-\beta),\\ [\mathbf{QQ}']_y &= ca\sin(\alpha-\gamma),\\ [\mathbf{QQ}']_z &= ab\sin(\beta-\alpha). \end{aligned}\right\} \quad . \quad . \quad . \quad (28)$$

Hence the moment of momentum emitted through the spherical surface r during the whole duration of emission has, by (24), (27) and (28), the components

$$\left.\begin{aligned} \mathbf{N}_x &= \tfrac{2}{3}k^3Tbc\,\sin(\gamma-\beta),\\ \mathbf{N}_y &= \tfrac{2}{3}k^3Tca\,\sin(\alpha-\gamma),\\ \mathbf{N}_z &= \tfrac{2}{3}k^3Tab\,\sin(\beta-\alpha). \end{aligned}\right\} \quad . \quad . \quad . \quad (29)$$

For comparison we also calculate the total energy emitted. In the time dt the following amount of energy is emitted through the angular element $d\Omega$:

$$dW = \mathfrak{S}_r r^2 d\Omega\, dt = \frac{1}{4\pi c}[\mathfrak{E}\mathfrak{H}]_r r^2 d\Omega\, dt. \quad . \quad . \quad (30)$$

From this we obtain, on account of equations (21) and (25a), for the emission taken over all directions during the time dt,

$$dW = -k^3\omega \int \frac{d\Omega}{4\pi}\left\{\left(\frac{\mathbf{r}}{r}\mathbf{Q}\right)^2 - \mathbf{Q}^2\right\}.$$

On account of (26) this is

$$dW = \tfrac{2}{3}k^3\omega\mathbf{Q}^2 = \tfrac{2}{3}k^3\omega(\mathbf{Q}_x^2 + \mathbf{Q}_y^2 + \mathbf{Q}_z^2). \quad . \quad . \quad (31)$$

We have now still to perform the integration with respect to t; on account of (25a) this gives, when $T \gg \tau$,

$$\int_0^T \mathbf{Q}_x^2 dt = \frac{T}{2}a^2, \quad \int_0^T \mathbf{Q}_y^2 dt = \frac{T}{2}b^2, \quad \int_0^T \mathbf{Q}_z^2 dt = \frac{T}{2}c^2. \quad . \quad (32)$$

Hence by (31) and (32) the total energy emitted is

$$W = \tfrac{1}{3}k^3\omega\, T(a^2 + b^2 + c^2). \quad . \quad . \quad . \quad (33)$$

By eliminating T we obtain from (29) and (33) the equation (6), that we set out to prove, if we replace ω by $2\pi\nu$:

$$\left.\begin{aligned} \mathbf{N}_x &= \frac{W}{2\pi\nu}\,\frac{2bc\,\sin(\gamma-\beta)}{a^2+b^2+c^2}, \\ \mathbf{N}_y &= \frac{W}{2\pi\nu}\,\frac{2ca\,\sin(\alpha-\gamma)}{a^2+b^2+c^2}, \\ \mathbf{N}_z &= \frac{W}{2\pi\nu}\,\frac{2ab\,\sin(\beta-\alpha)}{a^2+b^2+c^2}. \end{aligned}\right\} \quad . \quad . \quad . \quad (34)$$

9. Stark Effect of the Second Order

To calculate the stark effect of the second order we must carry the development of the quantum condition (24), on p. 308, a step further, that is, we must also consider terms in D^2.

By using equation (14) of Note 4 (under c) we obtain

$$-2\pi i\left\{\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{D}{4A^{\frac{3}{2}}}\left(3\frac{B^2}{A} - C\right) - \frac{5}{16}\frac{D^2B}{A^{\frac{7}{2}}}\left(7\frac{B^2}{A} - 3C\right)\right\} = 2nh,$$

or, in terms of B,

$$B = \sqrt{A}\left(\sqrt{C} - \frac{nhi}{\pi}\right) - \frac{D}{4A}\left(3\frac{B^2}{A} - C\right) - \frac{5}{16}\frac{D^2B}{A^3}\left(7\frac{B^2}{A} - 3C\right). \quad (1)$$

The meaning of A, B, C, D is the same as in (24a, b) on p. 308. D is thus proportional to F ; hence we may substitute in the latter term,

which is quadratic in F, the approximation of the first order, given in equation (26*a*) on p. 309. In this way we obtain

$$\frac{B}{\sqrt{A}}\Big(7\frac{B^2}{A}-3C\Big)=\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)\Big(4C-14\sqrt{C}\frac{nhi}{\pi}-7\frac{n^2h^2}{\pi^2}\Big). \quad (2)$$

The term before the last in (1) is of the first order in F. Hence we must here use the second approximation, which follows from equation (27) on p. 309 for B^2/A. Neglecting D^2, we easily calculate

$$\left.\begin{aligned}\frac{3B^2}{A}-C&=2C-\frac{6nhi}{\pi}\sqrt{C}-\frac{3n^2h^2}{\pi^2}\\ &+\frac{3}{2}\frac{D}{A^{\frac{1}{2}}}\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)\Big(\frac{3n^2h^2}{\pi^2}+\frac{6nhi}{\pi}\sqrt{C}-2C\Big).\end{aligned}\right\} \quad (3)$$

We insert the values (2) and (3) in (1) and collect in powers of D:

$$\begin{aligned}B=\sqrt{A}\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)&-\frac{D}{4A}\Big(2C-\frac{6nhi}{\pi}\sqrt{C}-\frac{3n^2h^2}{\pi^2}\Big)\\ &-\frac{3}{8}\frac{D^2}{A^{\frac{1}{2}}}\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)\Big(\frac{3n^2h^2}{\pi^2}+\frac{6nhi}{\pi}\sqrt{C}-2C\Big)\\ &-\frac{5}{16}\frac{A^2}{D^{\frac{1}{2}}}\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)\Big(4C-\frac{14nhi}{\pi}\sqrt{C}-\frac{7n^2h^2}{\pi^2}\Big),\end{aligned}$$

in which the last two terms may be collected together as follows:

$$\begin{aligned}&\frac{D^2}{A^{\frac{1}{2}}}\Big(\sqrt{C}-\frac{nhi}{\pi}\Big)\Big(\frac{17}{16}\frac{n^2h^2}{\pi^2}+\frac{17}{8}\frac{nhi}{\pi}\sqrt{C}-\frac{C}{2}\Big)\\ &\qquad=\frac{D^2}{2A^{\frac{1}{2}}}\Big(-C\sqrt{C}+\frac{21}{4}C\frac{nhi}{\pi}+\frac{51}{8}\sqrt{C}\frac{n^2h^2}{\pi^2}-\frac{17}{8}\frac{n^3h^3i}{\pi^3}\Big).\end{aligned}$$

Let us imagine this equation written down twice as on p. 309, once for $n=n_\xi$, $B=B_1$, $D=D_1$, and again for $n=n_\eta$, $B=B_2$, $D=D_2$ (the A and C have the same values both times) and form half their sum. The separation parameter on the left-hand side becomes eliminated in the process and we obtain

$$\begin{aligned}\mu e^2Z=\sqrt{A}\Big(\sqrt{C}-\frac{(n_\xi+n_\eta)hi}{2\pi}\Big)&+\frac{\mu eF}{4A}\Big(\frac{3(n_\eta-n_\xi)hi}{\pi}\sqrt{C}+\frac{3(n_\eta^2-n_\xi^2)h^3}{2\pi^2}\Big)\\ &+\frac{(\mu eF)^2}{2A^{\frac{3}{2}}}\Big(-C\sqrt{C}+\frac{21}{4}C(n_\xi+n_\eta)\frac{hi}{2\pi}+\frac{51}{8}\sqrt{C}(n_\xi^2+n_\eta^2)\frac{h^2}{2\pi^2}\\ &-\frac{17}{8}(n_\xi^3+n_\eta^3)\frac{h^3i}{2\pi^3}\Big).\end{aligned}$$

We here set (cf. p. 309)

$$\sqrt{C}=-\frac{n_\psi hi}{2\pi},\quad n=n_\xi+n_\eta+n_\psi,$$

and write, taking $\sqrt{A}$ over to the left-hand side

$$\left.\begin{aligned}\frac{\mu e^2 Z}{\sqrt{A}} &= -\frac{nhi}{2\pi} + \frac{3}{2}\frac{\mu eF}{A^{\frac{3}{2}}}(n_\eta - n_\xi)n\left(\frac{h}{2\pi}\right)^2 \\ &+ \frac{(\mu eF)^2}{2A^3}\left\{n_\psi^3 + \frac{21}{4}n_\psi^2(n_\xi + n_\eta) + \frac{51}{4}n_\psi(n_\xi^2 + n_\eta^2) + \frac{17}{2}(n_\xi^3 + n_\eta^3)\right\}\left(\frac{hi}{2\pi}\right)^3.\end{aligned}\right\} \quad (4)$$

The expression under the curly brackets may be divided by

$$n = n_\xi + n_\eta + n_\psi :$$

$$\left\{\quad\right\} = n\left(n_\psi^2 + \frac{17}{4}n_\psi(n_\xi + n_\eta) + \frac{17}{2}(n_\xi^2 + n_\eta^2 - n_\xi n_\eta)\right).$$

Hence we may take out the factor $-\frac{nhi}{2\pi}$ on the right-hand side (4) :

$$\left.\begin{aligned}\frac{\mu e^2 Z}{\sqrt{A}} &= -\frac{nhi}{2\pi}\left[1 + \frac{3}{2}\frac{\mu eF}{A^{\frac{3}{2}}}(n_\eta - n_\xi)\frac{hi}{2\pi}\right. \\ &\left. - \frac{(\mu eF)^2}{2A^3}\left(n_\psi^2 + \frac{17}{4}n_\psi(n_\xi + n_\eta) + \frac{17}{2}(n_\xi^2 + n_\eta^2 - n_\xi n_\eta)\right)\left(\frac{2\pi}{hi}\right)^2\right].\end{aligned}\right\} \quad (5)$$

Finally we must substitute the value of the first approximation, equation (29), p. 309, for A in the last term on the right-hand side, and in the term before the last we must insert the value of the second approximation, equation (29*a*), p. 309. We write the result thus :

$$\frac{\mu e^2 Z}{\sqrt{A}} = -\frac{nhi}{2\pi}\left\{1 - \frac{3h^4 F}{32\pi^4\mu^2 e^5 Z^3}n^3(n_\eta - n_\xi) + \left(\frac{h^4 F}{32\pi^4\mu^2 e^5 Z^3}\right)^2 n^6 N\right\}, \quad (6)$$

where we have used the abbreviation

$$N = 27(n_\eta - n_\xi)^2 - 2n_\psi^2 - \frac{17}{2}n_\psi(n_\xi + n_\eta) - 17(n_\xi^2 + n_\eta^2 - n_\xi n_\eta). \quad (7)$$

From (6) we obtain by squaring

$$\left.\begin{aligned}A = -\frac{4\pi^2\mu^2 e^4 Z^2}{n^2 h^2}&\left\{1 + \frac{3}{16}\frac{h^4 F}{\pi^4\mu^2 e^5 Z^3}n^3(n_\eta - n_\xi)\right. \\ &\left. + \left(\frac{h^4 F}{32\pi^4\mu^2 e^5 Z^3}\right)^2 n^6[-2N + 27(n_\eta - n_\xi)^2]\right\}.\end{aligned}\right\} \quad (8)$$

If, as in (30) on p. 310, we divide by $-2\mu h$ and arrive at the term $-W/h$, we find that the first two terms on the right-hand side are the same as on p. 310 ; the third term, which gives the *quadratic Stark effect*, becomes

$$\frac{h^5 F^2 n^4 Q}{8(2\pi e)^6\mu^3 Z^4}. \quad (9)$$

The factor Q here introduced is

$$\left.\begin{aligned}Q &= 27(n_\eta - n_\xi)^2 - 2N \\ &= -27(n_\eta - n_\xi)^2 + 4n_\psi^2 + 17n_\psi(n_\xi + n_\eta) + 34(n_\xi^2 + n_\eta^2 - n_\xi n_\eta) \\ &= \tfrac{1}{2}\{17n^2 - 3(n_\eta - n_\xi)^2 - 9n_\psi^2\}.\end{aligned}\right\} \quad (10)$$

As remarked on p. 320 the wave-mechanical calculation differs from this. Instead of (10) it gives

$$Q = \tfrac{1}{2}\{17n^2 - 3(n_\eta - n_\xi)^2 - 9m^2 + 19\}. \quad . \quad . \quad (11)$$

For the connection between m and n_φ see p. 310.

10. The Adiabatic Invariance of Phase-Integrals *

In the adiabatic changes of state we consider a parameter a, which enters somehow into the equations of motion of the system (as the length of a pendulum, charge of a point-mass, external field of force, and so forth). This parameter becomes changed in time, but by condition (1) on p. 342, it must be changed *infinitely slowly* (*reversibly*). For every value of a the equations of motion must remain valid in the form

$$\frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k}, \quad \frac{dq_k}{dt} = \frac{\partial H}{\partial p_k}, \quad . \quad . \quad . \quad (1)$$

where H is the same function of p, q and a as when a is kept fixed. We mean this when, in the conditions (2) on p. 342, we demand that the adiabatic action is not to attack *the co-ordinates of the system directly*. We shall revert to the condition (3) on p. 342 (*unsystematic change* of a) below.

Integrating the equations (1) by using a function of action S, keeping a constant, S becomes a function of a, and thus if we insert the time variation of a, it also becomes a function of t. From S we derive the phase-integrals J and the angle variables w as for a fixed a :

$$J_k = \oint p_k dq_k = \oint \frac{\partial S}{\partial q_k} dq_k, \quad w_k = \frac{\partial S}{dJ_k}. \quad . \quad . \quad (2)$$

The question is whether by using a *intermediately*, J *also becomes a function of* t. If the assertion of its adiabatic Hypothesis, that the quantum conditions $J_k = n_k h$ should remain adiabatically invariant, then J must be independent of t.

We answer this question by deriving the canonical equations for J and w as on p. 617. We are no longer dealing with the special case that $F^* = S$ is independent of t (cf. p. 617). Hence

$$\bar{H} = H$$

no longer holds for the transformed Hamiltonian function $\bar{H}$, but rather, by equation (17a) on p. 607,

$$\bar{H} = H + \frac{\partial F}{\partial t}. \quad . \quad . \quad . \quad . \quad (3)$$

By equation (18) on p. 608 the relationship between F and F^* is, with $P_k = J_k$, $Q_k = w_k$,

$$F = F^* - \Sigma J_k w_k.$$

* The first proof was given by J. M. Burgers, cf. Ann. d. Physik, **52**, 195 (1917), or Amst. Akad., 1917, p. 1055. We here follow a simple method also due to Burgers, cf. his Leyden dissertation, 1919, p. 242.

that is, on account of $F^* = S$,

$$F = S - \Sigma J_k w_k = S^* \quad . \quad . \quad . \quad . \quad (4)$$

(cf. equation (9) on p. 618).

Instead of equation (5), p. 617, we therefore have on account of (3) and (4):

$$\frac{dJ_k}{dt} = -\frac{\partial \bar{H}}{\partial w_k} = -\frac{\partial H}{\partial w_k} - \frac{\partial}{\partial w_k}\frac{\partial S^*}{\partial t} \quad . \quad . \quad (5)$$

Here the term $\partial H/\partial w_k$ vanishes, because H, regarded as a function of the variables $J_1 \ldots J_k$, $w_1 \ldots w_k$, is independent of the w's. If we take into account further that S^* = like S depends on t only intermediately through a, we may write

$$\frac{\partial S^*}{\partial t} = \frac{\partial S^*}{\partial a}\dot{a} = \Phi\dot{a}, \quad . \quad . \quad . \quad . \quad (6)$$

with the abbreviation

$$\Phi = \frac{\partial S^*}{\partial a}. \quad . \quad . \quad . \quad . \quad (7)$$

From (5) and (6) it follows that

$$\frac{dJ_k}{dt} = -\dot{a}\frac{\partial \Phi}{\partial w_k}, \quad J_k\Big|_0^T = -\int_0^T \dot{a}\frac{\partial \Phi}{\partial w_k}dt. \quad . \quad . \quad (8)$$

We now also take into account that a by our condition (3) on p. 342 is to be changed *unsystematically**, that is, not in phase with the course of motion of the system. It is in accord with this if, for example, we keep $\dot{a}$ constant and write instead of (8),

$$J_k\Big|_0^T = -\dot{a}\int_0^T \frac{\partial \Phi}{\partial w_k}dt. \quad . \quad . \quad . \quad (9)$$

Like S^* (cf. p. 618) Φ is a periodic function of the w's, and may therefore be represented as a Fourier series in the w's. Hence $\partial\Phi/\partial w$ is a Fourier series without a constant term. Since the $w_k = \nu_k t + \delta_k$ (Eqn. (6) on p. 617) are linear functions of t, the integration with respect to t on the right-hand side of (9) may be performed in the Fourier terms and it leads to a value which remains below a finite value even when T increases indefinitely.

The circumstance that the frequencies ν_k themselves still depend on a, that is, also on t, makes no essential difference to these conclusions, but only has the effect of changing the value of the integral by terms of the order $\dot{a}T$. But $\dot{a}T$ denotes the total change in the parameter a in the interval of time T and as such is finite. Hence, on the right-hand side of (9) we have $\dot{a}$ multiplied by a quantity which is finite even for $T = \infty$. *In the limit* $\dot{a} \to 0$ and $T \to \infty$ *the right-hand side of* (9) *becomes equal to zero, that is,* J *is constant.*

* Cf. H. Kneser, Math. Ann., **91**, 156 (1924), where the condition is expressed as generally as possible.

On the other hand, this conclusion does not hold if the system passes through a degenerate state in the course of the adiabatic change. Then, on account of the relationship $\Sigma s_k \nu_k = 0$ (eqn. (13) on p. 619) constant terms will occur in the Fourier series and these will give quantities of the order of T when we integrate with respect to t. *The adiabatic invariance for all quantities J therefore applies only to general systems and not to degenerate systems.*

11. The Spectra of Atoms Unlike Hydrogen. Effect of the Supplementary Atomic Field in the case of Non-penetrating Orbits

In Chapter VII, §§ 2 and 4, we took as our scheme for the supplementary field of the electronic configuration that belongs to the atomic complex a *pure central field independent of time.* Let its potential energy for the outer "radiating electron" (*Aufelektron*) in a *non-penetrating orbit* be

$$V = -\frac{e^2}{r}\left[C_1\left(\frac{a}{r}\right) + C_2\left(\frac{a}{r}\right)^2 + \ldots\right]. \quad . \quad . \quad (1)$$

The sign of V is in conformity with the remarks on p. 388, according to which $V < 0$. The constants of the atomic field C_1, C_2 . . . are written here as pure numbers and are related to the constants c_1, c_2 . . . on p. 362 in the following manner:

$$c_1 = C_1 a, \quad c_2 = C_2 a^2, \quad c_3 = C_3 a^3, \ldots$$

where a denotes a comparison length which we find it convenient to choose as the radius of the first Bohr circle of hydrogen:

$$a = \frac{h^2}{4\pi^2 m e^2}. \quad . \quad . \quad . \quad . \quad (2)$$

Equation (1) denotes the special case of spherical symmetry of the general expansion of the potential in Bessel functions for the exterior of the attracting masses.

If we substitute the value (1) of V and the value $p = n_\phi \frac{h}{2\pi}$ in the radial quantum condition (2) of p. 387, we obtain

$$J_r = \oint \sqrt{A + 2\frac{B}{r} + \frac{C}{r^2} + \frac{D_1}{r^3} + \frac{D_2}{r^4} + \ldots}\, dr = n_r h, \quad . \quad (3)$$

with the abbreviations:

$$\left.\begin{aligned} A = 2mW, \quad B = mZe^2, \quad C = \frac{-n_\phi^2 h^2}{4\pi^2} + 2mC_1 e^2 a, \\ D_1 = 2mC_2 e^2 a^2, \quad D_2 = 2mC_3 e^2 a^3, \ldots \end{aligned}\right\} \quad . \quad . \quad (4)$$

The integration is to be taken along the complex route in the r-plane around the real branch points r_{min} and r_{max} of the integrand.

From (3) we determine the "quantum defect" Δ by means of equation (5) on p. 388.

To a first approximation ($C_1 = C_2 = \ldots = 0$) we have $\Delta = 0$. The term then has *Balmer's form.*

To a second approximation

$$(C_1 \neq 0, \quad C_2 = C_3 = \ldots = 0, \quad D_1 = D_2 = \ldots = 0),$$

(3) retains the same form as in the first approximation but with a new meaning for C. For, by (4), we have

$$\left.\begin{aligned}\sqrt{C} &= -in_\phi \frac{h}{2\pi}\sqrt{1 - \frac{8\pi^2 me^2 C_1 a}{h^2 n_\phi^2}} \\ &= -in_\phi \frac{h}{2\pi}\left(1 - \frac{C_1}{n_\phi^2} - \frac{1}{2}\frac{C_1^2}{n_\phi^4} - \frac{1}{2}\frac{C_1^3}{n_\phi^6} - \ldots\right)\end{aligned}\right\} \quad . \quad . \quad (5)$$

In the last transformation a is expressed by means of (2). In this approximation we shall retain only the first term with C_1, in the next approximation we shall retain only those in C_1 and C_1^2, and so forth, by supposing that C_1^2, C_1^3, . . . are of the same order of magnitude as the coefficients C_2, C_3 . . . in (1).

The evaluation of (3) in our second approximation is effected according to Note 4, equation (3):

$$J_r = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}}\right).$$

Let us pass on to the quantum defect Δ in equation (5) on p. 388; that is, we form the difference of two integrals of the above form J_r; one of the two integrals being hydrogen-like (all constants C_i, $D_i = 0$) and B and $\sqrt{A}$ having the same values, only $\sqrt{C}$ being different. It then follows on account of (5) that

$$\Delta = \frac{C_1}{n_\phi}, \text{ that is, independent of } n_r. \quad . \quad . \quad (6)$$

The corresponding term has Rydberg's form.

We arrive at the same form for the term if we retain besides C_1 also C_2, that is, if we set $D_1 \neq 0$, $D_2 = D_3 = \ldots = 0$. The integral (3) that is to be evaluated in this case is then, by Note 4, equation (16):

$$J_r = -2\pi i\left(\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{1}{2}\frac{B}{C}\frac{D_1}{\sqrt{C}}\right). \quad . \quad . \quad (7)$$

In the quantum defect Δ we again cancel out $B/\sqrt{A}$ and obtain on account of (5), (4) and (2),

$$\Delta = \frac{C_1}{n_\phi} + \frac{C_1^2}{2n_\phi^3} + \frac{(2\pi)^4 B D_1}{2n_\phi^3 h^4},$$

and, in view of the meaning of D_1,

$$\Delta = \frac{C_1}{n_\phi} + \frac{C_1^2}{2n_\phi^3} + \frac{C_2}{n_\phi^3}Z. \quad . \quad . \quad . \quad (8)$$

Since this quantity is also independent of n_r the term assumes, as was asserted, Rydberg's form.

For the third approximation we retain C_1, C_2 and C_3, so that now $D_1 \neq 0$ and $D_2 \neq 0$. By Note 4, equation (21), the integration gives

$$J_r = -2\pi i\left\{\sqrt{C} - \frac{B}{\sqrt{A}} - \frac{1}{2}\frac{B}{C\sqrt{C}}\left(D_1 - \frac{3}{2}D_2\frac{B}{C} + \frac{15}{8}D_1{}^2\frac{B}{C^2}\right) - \frac{1}{4}\frac{A}{C\sqrt{C}}\left(D_2 - \frac{3}{4}\frac{D_1{}^2}{C}\right)\right\}.$$

For Δ we obtain, by forming the difference indicated in equation (5), p. 388,

$$\Delta = \ldots + \frac{2\pi i A}{4C\sqrt{C}h}\left(D_2 - \frac{3}{4}\frac{D_1{}^2}{C}\right).$$

The terms denoted by . . . depend only on n_ϕ; we shall write the symbol $-q$ for them. We transform the last term by making substitutions from (4), (5) and (2). We get

$$\Delta = -q + \frac{W}{2Rn_\phi^3 h}\left(C_3 + \frac{3}{2}\frac{C_2{}^2}{n_\phi^2}\right). \quad . \quad . \quad . \quad (9)$$

Here the last term depends on n_ϕ but also on n_r, since $-W/h$ denotes the magnitude of the term. The factor with which W/h is multiplied is independent of n_r; we shall call it

$$\kappa = \frac{1}{2Rn_\phi^3}\left(C_3 + \frac{3}{2}\frac{C_2{}^2}{n_\phi^2}\right). \quad . \quad . \quad . \quad (10)$$

In this approximation we arrive precisely at Ritz's form of the term as expressed in equation (4*c*) on p. 363.

12. Resolutions of the Multiplet Terms

(1) Equation (3) on p. 540 may be derived as follows:

Among the interactions of the l's and s's we have those between the l_i's and s_i's of the same electron and those between the l_i's and s_k's of different electrons (i, k = index of the electrons). We first treat the interaction (l_i, s_i).

We may regard field **H** produced by the revolution of the electron (cf. p. 331) as produced in such a way that the electron is at rest while the nucleus moves round it. The motion of the nucleus then acts like a current $\vec{\mathbf{J}}$ of strength $Z_{eff}\mathbf{ev}$, where Z_{eff} is the nuclear charge that acts on the electron and **v** is the orbital velocity of the nucleus. According to Biot and Savart's law this current produces at the point where the electron is situated a magnetic field (measured in the electrical system of units):

$$\mathbf{H} = \frac{1}{cr^3}[\vec{\mathbf{J}}\mathbf{r}] = -\frac{Z_{eff}e}{cr^3}(\mathbf{rv}). \quad . \quad . \quad . \quad (1)$$

Here **r** is the radius vector drawn from the nucleus to the electron. On the other hand, the azimuthal quantum condition and the law of areas give

$$-m_0(\mathbf{rv}) = \vec{l}\frac{h}{2\pi}, \quad . \quad . \quad . \quad . \quad (2)$$

where m_0 = rest mass of the electron. The minus sign on the left-hand side of (2) is necessary because our $\mathbf{v}$ refers to the moving nucleus, whereas equation (2) applies to the moving electron, whose velocity must therefore be set equal to $-\mathbf{v}$. Writing $\vec{l}$ on the right-hand side of (1) in place of n_ϕ corresponds with the ideas of the vector model. It follows from (1) and (2) that

$$\mathbf{H} = \frac{Z_{eff}e}{m_0 c r^3}\frac{h}{2\pi}\vec{l}. \quad . \quad . \quad . \quad . \quad (3)$$

In this field the electron takes its position with its own moment of momentum $\vec{s}\cdot\frac{h}{2\pi}$. Its magnetic moment has the value of a Bohr magneton, $\mu = \frac{eh}{4\pi m_0 c} = \frac{e}{m_0 c}\cdot\frac{h}{2\pi}\cdot s$ (since $s = \frac{1}{2}$). The first factor e/m_0c corresponds to the "magnetic anomaly" of the spin (cf. also eqn. (3), p. 332). The direction of μ is opposite directly to that of the moment of momentum, because μ arises from the rotation of the *negative* charge of the electron. Consequently we obtain for the total energy of interaction l, s of an individual electron

$$W(l, s) = \overline{(\vec{\mathbf{H}}\mu)} = -\frac{Z_{eff}e^2}{m_0{}^2c^2}\cdot\frac{h^2}{4\pi^2}\cdot\overline{\frac{1}{r^3}}\cdot|l||s|\cos\overline{(\vec{l}, -\vec{s})}, \quad . \quad (4)$$

where the horizontal bar denotes the mean-time value. We take over the mean-time value of $1/r^3$ from wave-mechanics.* For a hydrogen-like "orbit" of nuclear charge Z_{eff} we obtain

$$\overline{\frac{1}{r^3}} = \frac{Z_{eff}^3}{a_0{}^3 n^3 l(l+\frac{1}{2})(l+1)}. \quad . \quad . \quad . \quad . \quad (5)$$

* The calculation according to the older theory given in this volume would be as follows. The energy (4) represents only a small part of the total energy of the electron in its orbit. Hence we may regard the interaction (l, s) as a slight perturbation and may use the result of Note 5, p. 620, for calculating it; according to this result the energy perturbation for the first approximation is equal to the mean-time value of the perturbation function averaged over the *unperturbed* orbit. Thus our $\overline{1/r^3}$ denotes averaging over the unperturbed electron orbit, which we assume to be hydrogen-like (τ = time of revolution of the electron in the unperturbed orbit):

$$\overline{\frac{1}{r^3}} = \frac{1}{\tau}\int_0^\tau \frac{1}{r^3}dt. \quad . \quad . \quad . \quad . \quad . \quad (a)$$

Here we may express dt by means of $d\phi$ by using the law of areas $m_0 r^2\frac{d\phi}{dt} = n_\phi\cdot\frac{h}{2\pi}$ (for the present we calculate here according to the older theory; hence n_ϕ). We obtain

$$\overline{\frac{1}{r^3}} = \frac{1}{\tau}\int_0^{2\pi}\frac{m_0}{r}\cdot\frac{2\pi}{hn_\phi}d\phi. \quad . \quad . \quad . \quad . \quad . \quad (b)$$

With the help of the orbital equation, cf. (12), p. 253, we may write $1/r$ in the form: $1/r = C + A\cos\phi$ (γ is here equal to 1; it is sufficient to calculate without taking

[*Continuation of note on next page.*

From (4) it then follows that

$$W(l, s) = 2\frac{R\alpha^2 hc \cdot Z_{eff}^4}{n^3 l(l+\frac{1}{2})(l+1)} |l| |s| \cos \overrightarrow{(l, s)}, \quad . \quad . \quad (6)$$

where $\left(R = \text{Rydberg's number} = \frac{2\pi^2 m_0 e^4}{ch^3}, \alpha = \text{fine-structure constant} = \frac{2\pi e^2}{hc}\right)$. But, as was first pointed out by Thomas,* an important correction must be applied here. The rigorous relativity treatment of the problem leads to an additional term for the interaction energy, which is half as great as (6) and has the reverse sign. We give a simplified derivation of this correction under (7) in the present Note. Taking this into consideration we finally obtain

$$W(l_i, s_i) = \frac{R\alpha^2 hc Z_{eff,i}^4}{n_i^3 l_i(l_i+\frac{1}{2})(l_i+1)} \cdot |l_i| |s_i| \cos \overrightarrow{(l_i, s_i)} = a_i |l_i| |s_i| \cos \overrightarrow{(l_i, s_i)} \quad (7)$$

where we have used the abbreviation †

$$\alpha_i = \frac{R\alpha^2 hc \cdot Z_{eff,i}^4}{n_i^3 l_i(l_i+\frac{1}{2})(l_i+1)} \quad . \quad . \quad . \quad (8)$$

and where the indices i have been added to indicate that the quantities in question refer to the i^{th} electron.

The second of the above-mentioned interactions, namely (l_i, s_k), may now be easily estimated. We have now to calculate the magnetic field that is produced by the motion of the k^{th} electron in place of the i^{th} electron. In (1) we then have simply e instead of $Z_{eff}e$; in other respects (1) remains unchanged at anyrate in order of magnitude. The same holds for the subsequent equations as far as (8). We also obtain an energy expression (due to the interaction (l_i, s_k)), which contains Z_{eff}^3 instead of Z_{eff}^4 as a factor but which is otherwise of the same order of magnitude as the expression (7). For sufficiently great values of Z we shall therefore have to cancel the terms (l_i, s_k) for a first approximation.

relativity into account). The integral (b) then gives directly

$$\overline{\frac{1}{r^3}} = \frac{m_0}{\tau}\frac{2\pi}{hn_\phi} \cdot 2\pi C. \quad . \quad . \quad . \quad . \quad . \quad (c)$$

If we substitute the values of C and τ from (10b), p. 253, (with $c \to \infty$) and (17), p. 113, ($a_0 = \frac{h^2}{4\pi^2 m_0 e^2}$ = radius of the first hydrogen orbit), this gives

$$\overline{\frac{1}{r^3}} = \frac{Z_{eff}^3}{a_0^3 n^3 n_\phi^3} = \frac{1}{b^3} \quad . \quad . \quad . \quad . \quad . \quad (d)$$

[b = semi-minor axis of the ellipse, cf. (16c) on p. 113]. We see that the expression differs in a characteristic manner from the wave-mechanical value given in the text.

* L. H. Thomas, Nature, **107**, 514 (1926).

† According to Landé, Zeits. f. Physik, **25**, 46 (1924), we may, in the case of penetrating orbits, use $Z_i^2 Z_a^2$ instead of Z_{eff}^4 in (8), where Z_i, Z_a, denote the mean nuclear charge on the inner and outer loop of the orbit.

Hence we retain only terms of the form (7) and obtain for the total energy arising from the interaction (l, s) precisely the formula (4) on p. 540 of the text, α_i having the meaning of (3) on p. 540.

(2) In the case of the pure Russell-Saunders coupling equation (14) on p. 545 gives that amount of energy in the Paschen-Back effect which is due to the $(l; s)$-interaction. By the discussion of § 7, Chap. VIII (cf. (5), p. 494), we must add to this the amount

$$(2M_S + M_L)\Delta\nu_{norm} \cdot hc$$

of the interaction between S or L, respectively, and the field H. All together then we have the amount

$$(2M_S + M_L)hc\Delta\nu_{norm} + M_L M_S A. \quad . \quad . \quad . \quad (9)$$

The first part easily predominates over the second, by the definition of the strong field. By p. 494 the first gives the normal Lorentz triplet; hence the second represents the fine-resolution of the energy level in the Paschen-Back effect produced by the interaction (l, s). For the case of the doublet $(S = \frac{1}{2})$ we easily obtain from (9) the results of p. 495, which were there deduced from Voigt's theory. In doing this * we must make use of the selection rules on p. 494 and take into account that the term-resolution (9) is calculated from the *centre of gravity* of the term (L, S) (cf. p. 542) and not from its centre, as in the case of Voigt's formula.

Equation (9) clearly enables us to deal with any arbitrary combinations for the case of strong fields. The fine-resolution is in each instance of the order of magnitude of the field-free term resolution (on account of the factor A in the second term). This places the qualitative reflections of p. 496 on a quantitative basis.

In addition to (9) we write down for the sake of completeness the corresponding formula for a weak field (by eqn. (7) on p. 541 and § 6, Chap. VIII):

$$\frac{J(J+1) - L(L+1) - S(S+1)}{2} \cdot A + Mg \cdot hc\Delta\nu_{norm}, \quad . \quad (10)$$

the sequence of the expression again being that of their order of magnitude.

(3) **Law of Permanence for Arbitrary Fields.**—Let the magnetic field be so strong that all couplings between the l_i's and s_i's are released. It then follows from the spherical triangle which the vectors l_i, s_i, H cut out of the unit sphere (cf. pp. 540, 541 and 545) that

$$\overrightarrow{\cos(l_i, s_i)} = \frac{m_{l_i}}{|l_i|} \cdot \frac{m_{s_i}}{|s_i|}. \quad . \quad . \quad . \quad (11)$$

In this way we obtain from equation (4) on p. 540

$$\Gamma_{very\ strong} = \sum_i \gamma_i\,; \quad \gamma_i = a_i m_{l_i} m_{s_i}. \quad . \quad . \quad . \quad (12)$$

* For $\Delta\nu_0$, the total resolution (in cm.$^{-1}$), we obtain for ^2P from equation (7), p. 541: $hc\Delta\nu_0 = \frac{3}{2} \cdot A$.

To obtain " permanent " sums we must clearly sum over the quantum numbers, which lose their meaning, namely L and S ; M retains its meaning and is defined by

$$M = \sum_i (m_{s_i} + m_{l_i}) \text{ (sum over all electrons of the configuration).} \quad (13)$$

The Law of Permanence * states : *for a given electron configuration the sum over all the Γ-values that belong to a fixed* M *is independent of the field-strength.* By our assumption this Γ-sum has the same value for *all couplings.*

(4) The last remark leads directly to the **Γ-sum rule.** In a weak field there is a series of J-values for a given configuration, and these J-values will in general occur several times. Let $J_{max} = J_1$ be present ν_1 times, and let $J_k = J_{max} - k + 1$ be present ν_k times. Thus all J-values together are represented by $J_1^{(1)} \ldots J_1^{(\nu_1)}$, $J_2^{(1)} \ldots J_2^{(\nu_2)}$, $J_{min}^{(1)} \ldots$. Now let us imagine the Γ_{weak}'s that belong to the individual J's be written down, say, as in the following table, arranged in order of M † (let M′ be the greatest of all the M-values that occur) :

TABLE 66

	M′	M′ − 1	M′ − 2	. . .	−(M′ − 2)	(−M′ − 1)	−M′
$J_1^{(1)}$	$\Gamma_{J_1}^{(1)}$	$\Gamma_{J_1}^{(1)}$	$\Gamma_{J_1}^{(1)}$	. . .	$\Gamma_{J_1}^{(1)}$	$\Gamma_{J_1}^{(1)}$	$\Gamma_{J_1}^{(1)}$
$J_1^{(2)}$	$\Gamma_{J_1}^{(2)}$	$\Gamma_{J_1}^{(2)}$	$\Gamma_{J_1}^{(2)}$	. . .	$\Gamma_{J_1}^{(2)}$	$\Gamma_{J_1}^{(2)}$	$\Gamma_{J_1}^{(2)}$
:	. . . . .						
$J_1^{(\nu_1)}$	$\Gamma_{J_1}^{(\nu_1)}$	$\Gamma_{J_2}^{(\nu_1)}$	$\Gamma_{J_1}^{(\nu_1)}$	. . .	$\Gamma_{J_1}^{(\nu_1)}$	$\Gamma_{J_1}^{(\nu_1)}$	$\Gamma_{J_1}^{(\nu_1)}$
$J_2^{(1)}$		$\Gamma_{J_2}^{(1)}$	$\Gamma_{J_2}^{(1)}$	. . .	$\Gamma_{J_2}^{(1)}$	$\Gamma_{J_2}^{(1)}$	
:		. . . . .					
$J_2^{(\nu_2)}$		$\Gamma_{J_2}^{(\nu_2)}$	$\Gamma_{J_2}^{(\nu_2)}$	. . .	$\Gamma_{J_2}^{(\nu_2)}$	$\Gamma_{J_1}^{(\nu_2)}$	
$J_3^{(1)}$			$\Gamma_{J_3}^{(1)}$	. . .	$\Gamma_{J_3}^{(1)}$		
:			. . . . .				
$\Sigma\Gamma$	c_1	c_2	c_3	. . .	c_3	c_2	c_1

The Γ-sums taken over each vertical column are denoted by c_k. They may be calculated from (12) by means of the Law of Permanence and are independent of the coupling. The equations that follow from the Table are

$$\sum_{\rho=1}^{\nu_1} \Gamma_{J_1}^{(\rho)} = c_1 \; ; \quad \sum_{\rho=1}^{\nu_1} \Gamma_{J_1}^{(\rho)} + \sum_{\rho=1}^{\nu_2} \Gamma_{J_2}^{\rho} = c_2 \; ; \quad \sum_{\rho=1}^{\nu_1} \Gamma_{J_1}^{(\rho)} + \sum_{\rho=1}^{\nu_2} \Gamma_{J_2}^{(\rho)} + \sum_{\rho=1}^{\nu_3} \Gamma_{J_3}^{(\rho)} = c_3 \; ; \ldots \quad (14)$$

* S. Goudsmit, Phys. Rev., **31,** 946 (1928). An analogous law holds for the g-values, W. Pauli, Zeits. f. Phys., **31,** 765 (1925).

† In a weak field the Γ's are equal for any coupling for all M-values (by p. 545).

or

$$\sum_{\rho=1}^{\nu_1} \Gamma_{J_1}^{(\rho)} = c_1 = c_{J_1}, \quad \sum_{\rho=1}^{\nu_2} \Gamma_{J_2}^{(\rho)} = c_2 - c_1 = c_{J_2}, \quad \sum_{\rho=1}^{\nu_3} \Gamma_{J_3}^{(\rho)} = c_3 - c_2 = c_{J_3},$$

and in general

$$\sum_{\rho=1}^{\nu_k} \Gamma_{J_k}^{(\rho)} = c_k - c_{k-1} = c_{J_k}. \quad . \quad . \quad . \quad (15)$$

The c_{J_k}'s are, of course, like the c_k's independent of the coupling. Hence the Γ-sum rule of p. 546 follows from (15): *in a weak field* (hence also for a field zero) *the sum over all Γ's that belong for a given configuration to the same J is independent of the coupling.* A Γ whose J appears only once is thus calculable even if alone, independently of the coupling.

(5) For the case of *one* electron we obtain from the equations (4), (3), (7) and (8) of pp. 540 and 541,

$$\Gamma = \frac{\mathrm{R}\alpha^2 \cdot hcZ_{eff}^4}{n^3 l(l+\frac{1}{2})(l+1)} \cdot \frac{j(j+1) - l(l+1) - s(s+1)}{2}, \quad (16)$$

since clearly $l_i = l$ is identical with L, and $s_i = s$ with S. Moreover, $j_{1,2} = l \pm \frac{1}{2}$, $s = \frac{1}{2}$. We obtain for the resolution of the term, since the numerator of the second factor of (16) assumes the value l for $j = l + \frac{1}{2}$ and the value $-l-1$ for $j = l - \frac{1}{2}$,

$$\Delta\nu = \frac{\Gamma_{j_1} - \Gamma_{j_2}}{hc} = \frac{\mathrm{R}\alpha^2 Z_{eff}^4}{n^3 l(l+1)}, \quad . \quad . \quad . \quad (17)$$

that is, the formula for the regular resolution of doublet terms (cf. (6), p. 418). This is the reason why we were able to apply these formulæ to optical spectra there.

In Chapter V we derived the fine-structure of the hydrogen terms from relativity considerations and by using the "old" quantum number n_ϕ. But here we adopt a totally different standpoint. If we wished to write down the energy of the H-atom here, it would look as follows. First we should have the energy of the central motion without spin and without relativity; this gives the Balmer formula. Secondly, we should have the relativity correction for a model with the wave-mechanical quantum-number l; it makes an addition to the energy which depends on l and not on j. Hence this correction is the same for two j-levels having the same terms l. As a third contribution we have the energy that arises from the interaction (l, s), that is, which is produced by the spin. This furnishes the additional energy (16) and hence is, by (17), also responsible for the occurrence of regular doublets. We may easily show wave-mechanically that the last two amounts of energy contract together in such a way that the correct hydrogen fine-structure results. In Vol. II we shall explain this in detail analytically and graphically. According to the view just outlined the regular doublets should be called "spin doublets," but the further development of wave-mechanics in Dirac's theory has shown that ultimately the electron spin owes its own origin to relativity.

This causes the fine-structure formula of the old theory to remain fully preserved ; only the view of the quantum numbers is modified and approaches the idea of spin. These remarks will suffice to establish the connexion with the earlier considerations.

From Table 60 on p. 547 we may now draw the important conclusion that the resolutions of the terms that arise from equivalent electrons are governed by the formula (17) of the regular doublets. Actually, we may use Table 60 to express the total resolution by means of the factor a of the electron, that is, also by means of the doublet formula (17), on account of

$$hc\frac{R\alpha^2 Z_{eff}^4}{n^3 l(l+1)} = (l+\tfrac{1}{2})a \quad . \quad . \quad . \quad (18)$$

(cf. (8)).

The doublet formula may also be used for two non-equivalent electrons, namely always when one is an s-electron. We easily find from equation (12), p. 544, and (7), p. 541, as well as from the preceding equations (18) and (17), that the total resolution of the triplet terms that may result from this configuration, is simply equal to the resolution (17) of the doublet terms, which is produced by the second electron (not an s-electron). If the quantum numbers of the latter are n, l and if Z_{eff} is the nuclear charge of its orbit, then we have *

$$\text{Total resolution of the triplet term} = \frac{R\alpha^2 Z_{eff}^4}{n^3 l(l+1)}.$$

This is the theoretical basis for the experimental observation mentioned on p. 418 that the doublet formula often holds also for triplets, if we inquire into the total resolution.

(6) The Gap Law for L-values, which was deduced from Table 60 for normal coupling, runs generally (we shall not give the proof) : *in a weak field and within one and the same configuration the sum of all Γ's that belong to the same J is, if there are z electrons present in an (n, l)-shell, equal and opposite to the Γ-sum for the case where there are z electrons missing in the same shell ; this holds for any coupling whatsoever.*

Special case : $z = 1$. Then there are only two J-values, $J = l \pm \frac{1}{2}$ for n, l and each occurs only once. Hence Γ_J for an electron that is present is equal to $-\Gamma_J$ for an electron that is missing, independently of the coupling. The latter case is realised in X-ray terms. For an electron that is present we obtain regular terms (cf. p. 541, $a > 0$), hence *all X-ray terms are inverted.* We also see that *for X-ray terms the same doublet formula* (17) *must hold as for the one-electron problem.* The doublet formula in Chapter V has been applied in precisely this sense.

(7) To derive the Thomas factor we note first that the electric force that acts from the nucleus on the electron is equal in magnitude, direction and sense to

$$-Z_{eff} \cdot e^2 \cdot \frac{\mathfrak{r}}{r_3} = m_0 \dot{\mathfrak{v}}.$$

* Since the first electron has $l = 0$, the L of the triplet terms is, of course, equal to the l of the second electron.

On the right-hand side $\dot{\mathbf{v}}$ denotes the acceleration of the electron in its motion around the nucleus. Instead of (1) we may therefore write, if we now take $\mathbf{v}$ to denote the velocity of the electron and not, as earlier, that of the nucleus,

$$\mathbf{H} = \frac{m_0}{ec}[\mathbf{v}\,\dot{\mathbf{v}}]. \quad . \quad . \quad . \quad . \quad (19)$$

This magnetic field acts on the magnetic moment μ of the electron and produces a precession of angular velocity :

$$\vec{\omega} = \frac{e}{m_0 c}\mathbf{H}. \quad . \quad . \quad . \quad . \quad (20)$$

As a proof of this we recall the analogous discussion in the case of the Barnett effect, p. 519. $\mathbf{H}$ and ω are "equivalent." The factor s given in equation (14) in p. 519 differs from our factor in (20) only in that we now suppose e is measured in electrostatic units and that we have taken into account the magnetic anomaly of the electron (cf., for example, equation (15) on p. 520), that is, we have used the true value of μ given under (1).

By combining (19) and (20) we have

$$\vec{\omega} = \frac{1}{c^2}[\mathbf{v}\,\dot{\mathbf{v}}]. \quad . \quad . \quad . \quad . \quad (21)$$

We must now specify more closely the system of reference in which this ω is measured. It is clear that ω refers to an "allowed" system that is attached to the electron, that is, that participates in its momentary velocity. "Allowed" here means "allowed in the sense of relativistic mechanics," since the value of ω (cf. the denominator c^2 in (21)) goes beyond the order of accuracy of classical mechanics.

Now, at the time t the electron has the velocity $\mathbf{v}$ relative to the nucleus, and at the time $t + dt$ the velocity $\mathbf{v} + \dot{\mathbf{v}}dt$. The systems of reference in question differ from one another and differ from the "rest" system of reference which is attached to the nucleus. Thus we distinguish between the systems

$$\mathrm{E}_1,\ \mathrm{E}_2,\ \mathrm{K},$$

which have the relative velocities

$$\begin{aligned} &\mathrm{E}_1 \text{ with respect to } \mathrm{K} = \mathbf{v} \\ &\mathrm{E}_2 \quad ,, \quad ,, \quad \mathrm{E}_1 = \dot{\mathbf{v}}dt. \end{aligned}$$

We call the ordinary Lorentz transformation (parallel displacement) a "rotationless" transition. We suppose the transitions $\mathrm{K} \to \mathrm{E}_1$ and $\mathrm{E}_1 \to \mathrm{E}_2$ to be performed without rotation and we assert then that the transition $\mathrm{K} \to \mathrm{E}_2$ is *not rotationless*. The proof may be performed analytically by compounding Lorentz transformations.* We prefer, however, to give a shorter geometrical proof.

As a preliminary we recall Einstein's addition theorem of two velocities v_1 and v_2 which are *in the same direction*. As we know, it assumes

* This was done in an unpublished lecture by P. Langevin in Zürich, 1926. I am indebted to W. Pauli for a reconstructed report of this lecture.

its simplest form if we introduce two imaginary angles ϕ_1 and ϕ_2:

$$\tan \phi_1 = i\frac{v_1}{c}, \quad \tan \phi_2 = i\frac{v_2}{c}, \quad . \quad . \quad . \quad (22)$$

and if we define the resulting velocity v_3 by

$$\tan \phi_3 = i\frac{v_3}{c}, \quad \phi_3 = \phi_1 + \phi_2. \quad . \quad . \quad . \quad (23)$$

Thus Einstein's addition theorm is shown to be identical with the addition theorem of tangent functions in *elementary plane trigonometry*, but applied to imaginary angles.

We shall next consider the composition of two velocities v_1 and v_2 *that are perpendicular to one another*. We have then to use the formulæ of spherical trigonometry,* likewise applied to imaginary angles. We illustrate this in Fig. 149, when ϕ_1 and ϕ_2 are defined as in (22), and we mark off ϕ_1 on a great circle (for example, the equator of the unit sphere) from the point K. ϕ_2 is then the end-point E_1 of ϕ_1 in the perpendicular great circle (meridian of longitude). The resulting spherical triangle KE_1E_2 has the side ϕ_3 as its hypotenuse. This side defined the resultant velocity v_3 for us, namely by means of the first of the equations (23). Instead of the second equation (23), however, the cosine law of spherical trigonometry now holds:

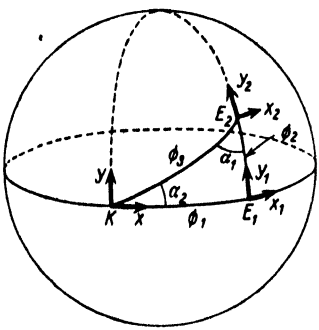


Fig. 149.

$$\cos \phi_3 = \cos \phi_1 \,.\, \cos \phi_2. \quad . \quad . \quad . \quad (24)$$

We shall also need the sine law for the angles α_1, α_2 of our right-angled triangle:

$$\sin \alpha_1 = \frac{\sin \phi_1}{\sin \phi_3}, \quad \sin \alpha_2 = \frac{\sin \phi_2}{\sin \phi_3}. \quad . \quad . \quad (25)$$

These sines (being quotients of two purely imaginary numbers) are real and < 1; thus the angles α_1 and α_2 also become real. Since ϕ_3 represents the resultant velocity v_3 (in magnitude *and* direction), and likewise ϕ_1, ϕ_2, the component velocities v_1, v_2, we see that α_1 gives the angle between v_3 and v_2 in E_2 and α_2 that between v_3 and v_1 in K.

We now follow out the rotationless transitions $K \to E_1$ and $E_1 \to E_2$. For this purpose we draw two mutually perpendicular axes of the systems of reference in question. We call then xy for K, x_1y_1 for E_1 and x_2y_2 for E_2, and we shall draw x in the direction of v_1 and hence y_1 in the direction of v_2. In the rotationless transition $K \to E_1$ x

* Cf. A. Sommerfeld, Phys. Zeits., **10**, 826 (1909). Spherical trigonometry with imaginary arcs means geometry on a sphere of radius i or, what amounts to the same thing, plane Lobatscheffsky trigonometry (negative curvative). We must picture the tangential plane of the sphere (or the Lobatscheffsky plane) to be perpendicular to both the z-axis and the imaginary time-axis *ict*.

points in the direction of the Equator, in the transition $E_1 \rightarrow E_2$ y points in the direction of the longitude. But if we wish to carry out the rotationless transition $K \rightarrow E_2$ we must pass along the great circle KE_2 in the direction of the resultant v_3, preserving the angle α_2. We then arrive in E_2 with *a position of the system of reference that differs from* x_2y_2; we shall call this new position x_3y_3.

We call the angle between x_2 and x_3 θ. As Fig. 150 shows, we have

$$\theta = \pi/2 - \alpha_1 - \alpha_2,$$
$$\sin\theta = \cos(\alpha_1 + \alpha_2).$$

In view of (25) we obtain

$$\sin\theta = \frac{\sqrt{\sin^2\phi_3 - \sin^2\phi_1}\,\sqrt{\sin^2\phi_3 - \sin^2\phi_2} - \sin\phi_1\sin\phi_2}{\sin^2\phi_3}. \qquad (26)$$

But according to (24) we have

$$\sqrt{\sin^2\phi_3 - \sin^2\phi_1} = \sqrt{1 - \cos^2\phi_1\cos^2\phi_2 - \sin^2\phi_1}$$
$$= \sqrt{\cos^2\phi_1(1 - \cos^2\phi_2)} = \cos\phi_1\sin\phi_2.$$

Likewise

$$\sqrt{\sin^2\phi_3 - \sin^2\phi_2} = \cos\phi_2\sin\phi_1.$$

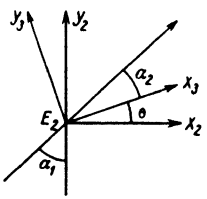


FIG. 150.

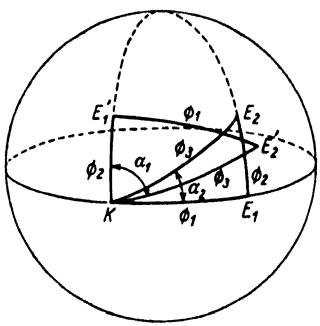


FIG. 151.

Hence by (26)

$$\sin\theta = \frac{\sin\phi_1\sin\phi_2(\cos\phi_1\cos\phi_2 - 1)}{\sin^2\phi_3}.$$

If we transform the denominator by means of (24) we may write

$$\sin\theta = -\frac{\sin\phi_1\sin\phi_2}{1 + \cos\phi_1\cos\phi_2}.$$

On account of (22) this becomes

$$\sin\theta = \frac{v_1v_2}{c^2}\,\frac{1}{1 + \sqrt{1 - \frac{v_1^2}{c^2}}\sqrt{1 - \frac{v_2^2}{c^2}}}. \qquad (27)$$

To be consistent we restrict ourselves to quadratic terms in c (equation (21) was also only of this order of accuracy) and obtain instead of (27),

$$\sin\theta = \frac{1}{2}\frac{v_1v_2}{c^2}. \qquad (28)$$

Before we apply this to our electron problem we must mention a deduction which has been particularly emphasised (*loc. cit.*). In the theory of relativity the succession of velocities in different directions does not allow of commutation; the result of compounding v_1 and v_2 is different from that of compounding v_2 and v_1 (cf. Fig. 151). By first drawing ϕ_1 and then ϕ_2 we obtain as before the point E_2, but if we first draw ϕ_2 and then ϕ_1 we obtain the arcs of circles KE_1' in the direction of the meridian of longitude through K and $E_1'E_2'$ in the direction of the great circle which runs perpendicularly to the meridian of longitude KE_1' in E_1'. The points E_2' and E_2 are different points, that is, *the velocities v_1 and v_2 may not be commutated*. And, indeed, the direction of the resultant velocity v_3 is different in both cases; the *magnitude* is the same since in both cases v_3 is given by the formula (24) which is symmetrical in ϕ_1, ϕ_2. We also see this from the fact that the two triangles KE_1E_2 and $KE_1'E_2'$ are congruent. At the same time we see that the angle between the two results is, except for the sign, exactly equal to our angle θ (cf. Fig. 151), namely, equal to $\alpha_1 + \alpha_2 - \pi/2$, where α_1 and α_2 have the same meaning as before.

This angle is nothing else than *the spherical excess* of the triangle KE_1E_2 (or $KE_1'E_2'$), and this emphasises its importance in the theory of surfaces. Actually the spherical excess of our right-angled triangle is defined by

$$\alpha_1 + \alpha_2 + \pi/2 - \pi = -\theta.$$

In our case (Lobatscheffsky's geometry) it is negative.

Reverting to our electron problem we first remark that the composition of two velocities in the *same* direction may not only be commutated but is also rotationless. Hence we need not trouble about the component of the additional velocity $\dot{\mathbf{v}}dt$ which is in the same direction as $\mathbf{v}$. Hence in our equation (28) we set v_2 equal to the component of $\dot{\mathbf{v}}\,dt$ which is perpendicular to $\mathbf{v}$; let v_1 be equal to $\mathbf{v}$. But this means that

$$v_1 v_2 = |\,[\mathbf{v}\,\dot{\mathbf{v}}]\,|\,dt. \quad . \quad . \quad . \quad . \quad (29)$$

Since θ becomes infinitesimal simultaneously with $v_2 = \dot{\mathbf{v}}dt$, we write $d\theta$ in place of sin θ in (28) and obtain, in view of (29),

$$\frac{d\theta}{dt} = \frac{1}{2}\frac{|\,[\mathbf{v}\,\dot{\mathbf{v}}]\,|}{c^2} = \frac{1}{2}\,|\,\vec{\omega}\,|. \quad . \quad . \quad . \quad . \quad (30)$$

Here $\vec{\omega}$ has the same meaning as in (21). If in Fig. 150 we now imagine the electron to be rotating or precessing about the z-axis (direction of the magnetic field $\mathbf{H}$, normal to the plane of the figure in three-dimensional space) with the angular velocity ω in the system of reference x_2y_2, then it rotates or precesses in the system of reference x_3y_3, that is, regarded from the nucleus, only with the angular velocity $\omega/2$, because this system accompanies the former in its rotation with the angular velocity $d\theta/dt = \frac{1}{2}\omega$. *In this way we have derived the Thomas factor in the simplest way.* As our method of derivation shows the first half of equation (30) has nothing to do with electron spin but is a direct consequence of the kinematics of relativity. It is only the relationship with

the electron precession ω in the second half of equation (30) that is connected with the spin anomaly of the electron.

The equivalence of ω and $\mathfrak{H}$ (see above) causes the same factor $\frac{1}{2}$ to occur in the interaction energy W (cf. eqn. (4)). Hence the factor 2 in (6) is to be cancelled and (6) must be replaced by (7). This justifies the calculations of this Note.

13. Quantising of the Rotating Anharmonic Oscillator *

Let us fix our attention on HCl, say, and let the two ions have the charges $+e$, $-e$ and the masses m_1, m_2. Their centre of gravity remains at rest and may serve as the origin of a polar co-ordinate system, r_1, ϕ_1 and r_2, ϕ_2 being the co-ordinates of m_1 and m_2. According to the theorem of the persistence of the centre of gravity we may introduce in their place the two new co-ordinates r, ϕ of the pair of masses by means of the equations

$$m_1 r_1 = m_2 r_2 = \mu r,$$
$$\phi_1 = \phi_2 + \pi = \phi.$$

As in p. 567 μ denotes the "reduced mass" of the two ions and r the distance between them:

$$\frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}, \quad r = r_1 + r_2.$$

The kinetic energy is easily expressed in the co-ordinates r, ϕ:

$$E_{kin} = \frac{m_1}{2}(\dot{r}_1^2 + r_1^2 \dot{\phi}_1^2) + \frac{m_2}{2}(\dot{r}_2^2 + r_2^2 \dot{\phi}_2^2) = \frac{\mu}{2}(\dot{r}^2 + r^2\dot{\phi}^2). \quad (1)$$

The potential energy is expressed electrostatically and depends only on $r = r_1 + r_2$:

$$E_{pot} = -\frac{e^2}{r}\left(1 + \frac{c_1}{r} + \frac{c_2}{r^2} + \frac{c_3}{r^3} + \ldots\right). \quad (2)$$

The coefficients c_i take into account the action of the electron systems that surround the ions and are to be regarded as arbitrary quantities between which the following condition of equilibrium holds:

$$\frac{d}{dr}E_{pot} = 0 \text{ for } r = r_0. \quad (3)$$

Here r_0 denotes the normal distance between the two ions when the molecule, in which the electrostatic attractions and repulsions between nuclei and electrons are in equilibrium, is at rest in space. We set

$$\rho = \frac{r}{r_0}, \quad \xi = \rho - 1. \quad (4)$$

Instead of (2) we write

$$E_{pot} = -a\left(\alpha + \frac{1}{\rho} - \frac{1}{2\rho^2} + b\xi^3 + c\xi^4 + \ldots\right). \quad (5)$$

* According to A. Kratzer, Zeits. f. Physik, 3, 289 (1920).

This assumption already satisfies the condition (3) and is just as general as (2); it has the advantage over (2) that the "correction terms" having the coefficients $b, c, \ldots$ are small in the neighbourhood of the position of equilibrium and that the "principal terms" which precede them may be taken into exact account when the quantising is effected later. We see that the expansion in ξ in equation (5) had to begin with the term ξ^3 and not with ξ^2 or ξ if we consider the mutual force that acts between the ions. This force is

$$\mathbf{K} = -\frac{d}{dr}\mathrm{E}_{pot} = -\frac{1}{r_0}\frac{d}{d\rho}\mathrm{E}_{pot}$$
$$= -\frac{a}{r_0}\left(\frac{1}{\rho^2} - \frac{1}{\rho^3} - 3b\xi^2 - 4c\xi^3 + \ldots\right),$$

or, on account of (4),

$$\mathbf{K} = -\frac{a}{r_0}\left(\frac{\xi}{\rho^3} - 3b\xi^2 - 4c\xi^3 + \ldots\right), \quad . \quad . \quad (6)$$

where we may set $\rho^3 = (1 + \xi)^3$ in the denominator. Since all the powers of ξ are represented here and are provided with arbitrary coefficients we have by adopting our assumption actually found the law of force of the most general anharmonic oscillator.

From the first term of the series (6) we may obtain the frequency ν_0 for an infinitesimal amplitude:

$$2\pi\nu_0 = \sqrt{\frac{a}{r_0^2\mu}}. \quad . \quad . \quad . \quad . \quad (7)$$

If we take as our definition of the moment of inertia of the molecule in the equilibrium state

$$\mathrm{J} = (m_1 r_1^2 + m_2 r_2^2)_0 = \mu r_0^2, \quad . \quad . \quad . \quad (8)$$

we may also write (7) in the form

$$2\pi\nu_0 = \sqrt{\frac{a}{\mathrm{J}}}, \quad a = 4\pi^2\nu_0^2\mathrm{J}. \quad . \quad . \quad . \quad (9)$$

On account of (4) and (8) (1) becomes

$$\mathrm{E}_{kin} = \frac{\mathrm{J}}{2}(\dot{\rho}^2 + \rho^2\dot{\phi}^2). \quad . \quad . \quad . \quad (10)$$

Hence it follows that

$$p_\rho = \frac{\partial \mathrm{E}_{kin}}{\partial\dot{\rho}} = \mathrm{J}\dot{\rho}, \quad p_\phi = p = \frac{\partial \mathrm{E}_{kin}}{\partial\dot{\phi}} = \mathrm{J}\rho^2\dot{\phi}.$$

Here p is constant and is equal to $mh/2\pi$ in consequence of the *azimuthal quantum condition* (in the other form, cf. p. 557). The energy equation runs

$$\frac{1}{\mathrm{J}2}\left(p_\rho^2 + \frac{p^2}{\rho^2}\right) + \mathrm{E}_{pot} = \mathrm{W}. \quad . \quad . \quad . \quad (11)$$

Hence it follows that

$$p_\rho = \sqrt{2\mathrm{JW} - 2\mathrm{JE}_{pot} - \frac{p^2}{\rho^2}}$$

and we have as the *radial quantum condition* (again in the older form, where n takes the place of v, cf. p. 560),

$$\oint p_\rho d\rho = \oint \sqrt{2J(W + a\alpha) + \frac{2Ja}{\rho} - \frac{1}{\rho^2}(aJ + p^2) + \ldots} d\rho = nh. \quad (12)$$

The terms of this equation so far as we have written them down have the form

$$\oint \sqrt{A + \frac{2B}{\rho} + \frac{C}{\rho^2}} d\rho = -2\pi i\left(\sqrt{c} - \frac{B}{\sqrt{A}}\right)$$

which is familiar to us from Note 4*a*, equations (1) and (3). And if we divide (12) by $\sqrt{aJ}$ the A, B, C have the meaning

$$A = 2\left(\alpha + \frac{W}{a}\right), B = 1, C = -\left(1 + \frac{p^2}{aJ}\right) = -\left(1 + \frac{m^2h^2}{4\pi^2 aJ}\right). \quad (13)$$

Consequently (12) becomes

$$\frac{nh}{\sqrt{aJ}} = -2\pi\left(\sqrt{1 + \frac{m^2h^2}{4\pi^2 aJ}} - \frac{i}{\sqrt{A}}\right) + Z. \quad . \quad . \quad (14)$$

Here Z contains the terms indicated in (12) by dots ; they arise from the expressions with b, c . . . in the expression assumed for the potential in (5). For the term $i/\sqrt{A}$ which, by (13), contains the energy W and hence is the unknown that interests us, we write y.

We obtain the successive approximations y_1, y_2 . . . for y :

$$y_1 = 1,$$

$$y_2 = 1 + nu,$$

$$y_3 = 1 + nu + u^2\left\{\frac{m^2}{2} - n^2\left(\frac{15}{2}b + \frac{3}{2}c + \frac{15}{4}b^2\right)\right\},$$

$$y_4 = 1 + nu + u^2\left\{\frac{m^2}{2} - n^2\left(\frac{15}{2}b + \frac{3}{2}c + \frac{15}{4}b^2\right)\right\} - 3u^3nm^2b.$$

Here u stands for the expression $\frac{h}{2\pi\sqrt{aJ}}$, which we may also write in the form $\frac{\Delta\nu}{\nu_0}$, where ν_0 is explained by (9) and $\Delta\nu = \frac{h}{4\pi^2 J}$ denotes the distance between neighbouring band lines (cf. (6), p. 561). Hence $u = \Delta\nu/\nu_0$ is at anyrate a small quantity with respect to which we may expand. This has already been done in the preceding formulæ.

The last approximation y_4 appears to be inconsistent inasmuch as here a term in u^3 has been taken into account whereas in the other approximations we went no further than the term in u^2. The reason is this : although u is a small quantity m may in given cases assume great values in fully developed bands, so that u^3m^2 may not be neglected. It is easy to show that even if we take into account higher powers the term written down is the only one in u^3 with the factor nm^2.

To arrive at the energy expression W we now form

$$\left.\begin{aligned} -\frac{1}{2}y_4^{-2} = \frac{1}{2}\mathrm{A} = \alpha + \frac{\mathrm{W}}{\alpha} = -\frac{1}{2} + nu \\ +u^2\left\{\frac{m^2}{2} - n^2\left(\frac{3}{2} + \frac{15}{2}b + \frac{3}{2}c + \frac{15}{4}b^2\right)\right\} - \frac{3}{2}u^3nm^2\,(1+2b) + \ldots \end{aligned}\right\} \quad (15)$$

By (9) we have

$$au = \frac{h}{2\pi}\sqrt{\frac{\bar{a}}{\mathrm{J}}} = h\nu_0, \quad au^2 = h\nu_0\, u = h\Delta\nu = \frac{h^2}{4\pi^2\mathrm{J}}.$$

Hence we obtain from (15), except for a constant quantity, that is, one that is independent of n and m,

$$\left.\begin{aligned} \mathrm{W} = nh\nu_0 + \frac{h^2}{8\pi^2\mathrm{J}}m^2 - h\nu_0 un^2\left(\frac{3}{2} + \frac{15}{2}b + \frac{3}{2}c + \frac{15}{4}b^2\right) \\ - \frac{3}{2}h\nu_0\, u^2nm^2(1+2b) + \ldots \end{aligned}\right\} \quad (16)$$

If we set $m = 0$ we obtain the pure *oscillation energy*, which was called W_{0v} in equation (8), p. 564, namely,

$$\mathrm{W}_{0v} = nh\nu_0(1 - xn + \ldots). \quad . \quad . \quad (17)$$

For the abbreviation x that we introduced earlier we now obtain from (16) the following meaning :

$$x = \left(\frac{3}{2} + \frac{15}{2}b + \frac{3}{2}c + \frac{15}{4}b^2\right)u. \quad . \quad . \quad . \quad (18)$$

The pure *rotational energy* is represented by the second term in the right-hand side of (16). It has the form of the Deslandres terms. Finally, the last term in (16) represents the *interaction term between the rotation and the oscillation*. If we write $-m^2n\alpha h$ for it α has the significance

$$\alpha = \frac{3}{2}\nu_0u^2\,(1 + 2b + \ldots). \quad . \quad . \quad . \quad (19)$$

The wave-mechanical formula for the total energy given on p. 564 of the text (in eqn. 9) differs from (16) in having $v + \frac{1}{2}$ in place of n and $j + \frac{1}{2}$ in place of m ; v and j are the true (wave-mechanical) quantum numbers, whose range of values includes all positive integers 0, 1, 2. . . . The wave-mechanical meaning of α and x is the same as in the preceding equations (18) and (19). We shall prove this in the volume on Wave Mechanics.

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