THE BOOK WAS DRENCHED

THEORY OF GROUPS

AND

ITS APPLICATION TO PHYSICAL PROBLEMS

BY

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PREFACE TO FIRST EDITION

Application of the theory of groups to the solution of physical problems is known to have been quite fruitful. This subject has acquired considerable importance in recent years and some literature has grown around it. The authors have felt that physicists will stand to gain by making an extensive use of this powerful tool of investigation in their efforts and have accordingly undertaken the writing of this book, prompted by the feeling that there is no connected account in the English language dealing with the important applications of group theory. This book is intended as an introductory study of the theory of groups to a person who has no easy access to an orthodox mathematical treatise on the subject for the purpose of making him understand the method of applying the same to various problems and appreciate the advantages thereof. There are, of course, many standard works dealing with the mathematical theory of groups but only a few articles have been written which deal with the physical aspect and that too scattered in different journals.

Wigner, *Gruppentheorie und ihre Anwendung auf die Quantenmechanike der Atome*; Weyl, *The Theory of Groups and Quantum Mechanics*; Van der Waerden, *Die Gruppentheoreitsche Methode in Der Quantenmechanik*; *Moderne Algebra*; Littlewood, *The Theory of Group Characters and Matrix Representations*; Speiser, *Die Theorie der Gruppen Von Endlicher Ordnung*; Burnside, *The Theory of Groups*; Hilton, *Mathematical Crystallography and The Theory of Groups of Movements* are amongst the books consulted by the authors. Eckart, "Application of Group Theory to the Quantum Dynamics of Monatomic Systems," *Rev. Mod. Phys.*, Vol. 2, p. 305 (1930); Rosenthal and Murphy, "Group Theory and the Vibrations of Polyatomic Molecules," *Rev. Mod. Phys.*, Vol. 8, p. 317 (1936); Sponer and Teller, "Electronic Spectra of Polyatomic Molecules," *Rev.*

Mod. Phys., Vol. 13, p. 75 (1941); Wigner, "Uber die Elastischen Eigenschwingungen Symmetrischer Systeme," *Gott. Nach.*, p. 133 (1930); Tisza, "Zur Deutung der Spektren Mehratomiger Moleküle," *Zeit. Phys.*, Vol. 82, p. 48 (1933) are some of the more recent journal articles dealing with the physical applications of group theory. The authors would like to acknowledge their indebtedness to these sources of information.

It is earnestly hoped that this account of the theory of groups in its application to physical problems will serve a real need for physicists interested in the subject.

Department of Physics,
Andhra University,
Waltair (India),
15*th May* 1948.

S. BHAGAVANTAM.
T. VENKATARAYUDU.

PREFACE TO SECOND EDITION

First Edition of this book was received well in several quarters and the increasing demand for the same has necessitated the preparation of a Second Edition. A few alterations and additions have been made.

S. BHAGAVANTAM.
T. VENKATARAYUDU.

15*th April* 1951.

PREFACE TO THIRD EDITION

With a view to meet the increasing demand for the book, we have prepared a Third Edition. Some alterations and additions have been made.

S. BHAGAVANTAM.
T. VENKATARAYUDU.

15*th May* 1962.

FOREWORD

Professor Bhagavantam is the author of a treatise entitled "*Scattering of Light and the Raman Effect*" which was published a few years ago and which met with a gratifying reception. The investigations on which he has been engaged both before and since the publication of that book led him to interest himself deeply in the theory of groups and in its applications to various branches of Physics. Many valuable publications in this field have emerged from the Andhra University. The present book is in a sense the fruit of those activities. It represents a serious effort to present a branch of mathematics which is of great and growing importance to physicists generally in a manner which will appeal to and interest them. I believe that the book will be widely used and appreciated.

BANGALORE,
15*th May* 1948.

C. V. RAMAN.

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CHAPTER I

GROUPS

Group Postulates.—A group is a set of distinct elements $a, b, c, \ldots$ satisfying the postulates given below. By means of a composition rule R, there arises from any two elements a and b of the set, a unique element aRb which is usually written as ab and called the product ab. If a and b represent the same element, the product ab will be written as a^2 and called the square of that element. The product element ab may be further combined by the same composition rule R with another element c and the result of such a combination will be represented by $(ab)\,c$. If on the other hand, the product bc is first formed and the combination of a with bc is then obtained, the result will be represented by $a\,(bc)$. With this interpretation, if the two results $(ab)\,c$ and $a\,(bc)$ are identical, the three elements a, b, c are said to obey the associative law. The composition rule R itself may be of a very general kind. For example, it may be ordinary multiplication or addition or it may stand for any other specified process. Irrespective of the process which it connotes, R is generally referred to as multiplication. There is also no restriction on the nature of the elements that constitute a group. The postulates are:

1. The product of any two elements and the square of each element of the set are also elements in the set.
2. The associative law, namely $a\,(bc) = (ab)\,c$, holds for all elements in the set.
3. The set contains an element E called the identity element such that $aE = Ea = a$ for every element a in the set.
4. Each element a of the set has an inverse element, represented by the symbol a^{-1} belonging to the set and satisfying the relations $aa^{-1} = a^{-1}a = E$.

In postulates 3 and 4 it is sufficient to assume that either $aE = a$ and $aa^{-1} = E$ or $Ea = a$ and $a^{-1} a = E$. The other pair of relations will then follow. For, assuming the first set of relations namely $aE = a$ and $aa^{-1} = E$, we have $a^{-1} a = a^{-1} aE = a^{-1} a (a^{-1}) (a^{-1})^{-1} = a^{-1} E (a^{-1})^{-1} = a^{-1} (a^{-1})^{-1} = E$ and $Ea = aa^{-1} a = aE = a$. It may similarly be shown that the second pair of relations will lead to the first pair. As a consequence of postulate 1, it follows that the product of any three or more elements is also an element in the set. If the product consists of the same element repeated p times, the result is written as a^p. The composition rule R, sometimes referred to as the group operation, is not necessarily commutative. When it is not commutative, ab and ba are distinct elements. Ordinary multiplication and addition are examples of commutative operations when the elements in the set are ordinary numbers. These operations are also associative whereas ordinary subtraction is an example of an operation which is neither commutative nor associative. On the other hand, if a, b, c, ... are ordinary numbers and ab stands for the arithmetic mean of a and b, it may be noted that such an operation is commutative but not associative. If the operation is commutative for all pairs of elements, the group is called an Abelian group.

If the elements in a group are finite in number, the group is said to be finite and the number of elements in it is called the order of the group. If the elements are infinite in number, the group is said to be an infinite group. A group which consists of a single element a and its powers $a^2, \ldots a^p = E$, is called a cyclic group of order p, if p is the smallest positive integer for which $a^p = E$. p is then the order of the cyclic group and is also called the order of the element a. It is easily seen that a cyclic group is Abelian for $a^r a^s = a^s a^r$, because each is the product consisting of the same element repeated $r + s$ times. It may be noted that a set of elements constituting a group under one composition rule does not necessarily constitute a group under a different composition rule. For example, all positive and negative integers including zero form a group under ordinary addition but do not do so under ordinary multiplication.

It may be verified that the group postulates are satisfied in the simple example consisting of the set 1, i, $-i$, -1 where the composition rule R is ordinary multiplication. They thus form a group of order four. 1 is the identity element, 1 and -1 are inverses of themselves and i and $-i$ are inverses of each other in this group. It may further be noted that the group is cyclic because the different elements are powers of the single element i or $-i$.

Displacement of a Rigid Body.—If a point of a rigid body is held fixed, it is free to rotate about that point. If another point of the body is also kept fixed, the body is free to rotate about the line joining the two fixed points. The fixing of a third point of the body, not collinear with the other two, fixes the position of the body. Hence the position of a body in space is uniquely determined, if the positions of any three non-collinear points in it are known. The most general displacement of a rigid body is therefore one in which any three points A, B, C of the body are displaced to say A', B', C'. It may be proved* that this displacement can be effected by a translation of the body as a whole followed by a rotation about a suitable axis.

In the above displacement, the translation is not necessarily in the direction of the rotation axis, but it can be effected by a rotation of the body about a suitable parallel axis followed by a translation in the direction of the rotation axis itself. The latter operation is called a screw. A general displacement of a rigid body is thus a screw.

Symmetry Operations.—We shall define the movement of a body as an operation by which the distance between any pair of points is not altered. Simple examples of movements are bodily translations and rotations. A general displacement of a rigid body is also a movement as it is a

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* E. T. Whittaker, *Analytical Dynamics of Particles and Rigid Bodies.*

combination of these two simple movements. It is possible to perform certain other operations which may be classed as movements, because the condition that the distance between any pair of points in the body remains unaltered may be satisfied. Reflection in a plane is an operation of this kind. Since a general displacement of a rigid body is a screw, a general movement can be considered as a combination of the simple movements, namely, translations, rotations and reflections. That this in fact is the case follows from the result that a general movement which keeps the distance $x^2 + y^2 + z^2$ from a fixed origin invariant is either a rotation or a rotation-reflection (Appendix II).

If in the case of a rigid body or a geometrical figure, from amongst all the possible movements we pick out those that have the special property of bringing the body or the figure as the case may be into superposition with itself, we shall be picking out movements which may be called symmetry operations. These symmetry operations* give an indication of the shape possessed by the body. In the case of a finite body, because of the condition of superposition, all movements which involve a bodily translation either by itself or in combination with other movements cannot be counted as symmetry operations. From the definition of the symmetry operations, it follows that a complete set of them in respect of any particular body or figure will satisfy all the group postulates under the composition rule of consecutive application of the symmetry operations. Such a

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* It is more appropriate to call such operations geometrical symmetry operations, because we may conceive of other types of operations which merely bring the body or the geometrical figure into superposition with itself but are not movements as per the definition already given. For example, in a system of identical particles occupying the corners of a regular pentagon, the interchange of a pair of particles satisfies the condition of superposition but is not a movement because the condition that the relative distances between all pairs of points in the body should remain unaltered is not satisfied. In physical applications, the invariance of the energy expression is of primary importance. In several problems, the potential energy is assumed to be such that it is invariant under all transformations which correspond to movements. But this is not necessarily so in all cases.

set of operations will therefore form a group and this group is called a point group appropriate to the body or the figure.

Symmetry operations in finite bodies are of various kinds. Rotations about lines passing through a fixed point and reflections in specified planes containing the fixed point are typical ones. Combinations of rotations are again rotations and the combination of reflections in two planes is a rotation about the line of intersection of the two reflection planes, the angle of rotation being twice the angle between the reflection planes. Combinations of rotations and reflections are of two kinds. In the first, the plane of reflection contains the axis of rotation and this combination is equivalent to a reflection in a different plane. In the second, the plane of reflection is inclined to the axis of rotation, and this combination is equivalent to a rotation about a different axis followed by a reflection in a plane perpendicular to that axis. Such an element in which the reflection plane is perpendicular to the rotation axis is called a rotation-reflection. A simple reflection may, however, be considered as a special case of a rotation-reflection where the rotation is through 0 or 2π. A rotation by π about any axis followed by a reflection in a plane perpendicular to it is of special significance, because as a result of such an operation every point of the figure or the body gets inverted about the point of intersection of the reflection plane and the rotation axis. Such a point will be called a centre of inversion. Every symmetry operation in the case of a finite body can therefore be reduced to a simple rotation or a rotation-reflection. When the smallest angle of rotation which brings the body to superposition with itself is $2\pi/p$, then the corresponding axis is called a p-fold axis of rotation and the symmetry operation is usually designated by the symbol C_p. A plane of reflection is designated by the symbol σ. The plane of reflection may sometimes contain the symmetry axis of the body in which case the subscript v is used to describe it. The plane of reflection may sometimes be perpendicular to the symmetry axis and in this case the subscript h is used to describe it. When a body contains reflection planes of more than one type, they are described by different superscripts as σ'_v, σ''_v, etc. When it contains several symmetry elements of the same type, the number p of such symmetry elements is indicated by a coefficient as in pC_2, $p\sigma_v$, etc. Other elements such as rotation-reflections are described by the symbol S_p which stands for an operation in which a rotation of $2\pi/p$ about an axis is followed by reflection in a plane normal to the rotation axis. The special element of a centre of inversion which is an S_2 is designated by the symbol i. The symbols C_x, C_y, C_z are used for digonal rotations about the co-ordinate axes X, Y, Z respectively. Similarly the symbols σ_x, σ_y, σ_z are used for reflections in the co-ordinate planes YZ, ZX and XY respectively. Identity operation, which is the same as rotation through 0 or 2π about any axis, is a symmetry operation for all bodies and is designated by the symbol E, because this element takes the place of the identity element in the group.

Point Groups.—As an illustration of a simple point group, we enumerate the symmetry operations appropriate to an isosceles triangle. This figure can be brought to superposition with itself by a rotation of 2π about any axis (E), by a rotation of π about an axis in the plane of the triangle and bisecting the vertical angle of the triangle (C_2), by a reflection in the plane of the triangle (σ_h), by a reflection in a plane perpendicular to the plane of the triangle and containing the C_2 axis (σ_v). These symmetry elements constitute a point group of order four. The group is Abelian because all the elements taken in pairs are commutative. Also the result of combining any two of the three elements C_2, σ_h, and σ_v is the third one. It may be noted that every element is its own inverse in this group.

We shall next take the example of a regular tetrahed on and deal with its symmetry operations in some detail. A tetrahedron can be brought to superposition with itself by a rotation of 360° about any axis through its centre (E , by a rotation of 120° either way about the four tetrahedral axes formed by joining the centre to each one of the vertices ($8C_3$), by a rotation of 180° either way about the three mutually perpendicular lines obtained by joining the middle points of opposite edges of the tetrahedron ($3C_2$), by reflection in any one of the six planes formed by the centre with each one of the six edges (6σ) and by a rotation through 90° either way about the three mutually perpendicular lines cited above followed by reflections in planes passing through the centre and perpendicular to the rotation axis in each case ($6S_4$). The coefficients like 8 in $8C_3$, 3 in $3C_2$, etc., denote the number of symmetry operations of the particular type. It may be noted that in the case of C_3, the two rotations in opposite directions about the same axis are counted as distinct elements whereas in the case of C_2 they are counted as one element. This is a consequence of the fact that in the latter case, any given point of the body moves into the same position for both types of rotation which thus become indistinguishable from each other. In the former case, the point moves into different positions. The symmetry operations will be written as E, $8C_3$, $3C_2$, 6σ, $6S_4$. They constitute a point group of order 24 and thus become the group elements. That these elements satisfy all the group requirements may easily be verified.* The molecule of phosphorus (P_4) is an example of a structure possessing this type of symmetry.

The case of benzene (C_6H_6) molecule is instructive as it exhibits several of the typical symmetry operations appropriate to a finite body. This molecule is known to possess a plane regular hexagonal structure and the symmetry operations are just those of a regular hexagon. They are identity (E), a rotation of 60° either way about the symmetry axis normal to the hexagonal plane ($2C_6$), a rotation of 120° either way about the same axis ($2C_3$), a rotation of 180° either way about the same axis (C_2), a rotation of 180° either

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* A hollow geometrical model will greatly help in picturing the various symmetry operations and the results of their combination. Verification may also be done analytically.

way about the three lines joining the opposite vertices of the hexagon ($3C_2$), a rotation of 180° either way about the three lines joining the middle points of opposite edges ($3C_2'$), a centre of inversion at the centre of the hexagon (i), a rotation of 60° either way followed by a reflection in the plane of the molecule ($2S_6$), a rotation of 120° either way followed by a reflection in the same plane ($2S_3$), a reflection in the plane of the molecule (σ_h), a reflection in any one of the three planes perpendicular to the plane of the molecule and passing through opposite vertices ($3\sigma_v$), a reflection in any one of the three planes perpendicular to the plane of the molecule and passing through the middle points of opposite edges ($3\sigma'_v$). These operations constitute a point group of order 24.

In this manner, every geometrical body or molecular structure is characterized by a set of symmetry operations which, when completely enumerated, constitute a point group.

Space Groups.—It has been pointed out that in the case of finite bodies, while enumerating the symmetry operations, all movements which involve a bodily translation either by itself or in combination with other movements cannot be counted. If, however, we are considering an infinitely extending body or an idefinitely repeated pattern, we can conceive of a pure translatory motion which brings the body or the pattern as the case may be into superposition with itself. The introduction of a translatory motion automatically introduces new elements of symmetry which are in the nature of combinations of a translation with the symmetry elements appropriate to a point group. Screw axis which is a rotation followed by a translation along the axis and a glide plane which is a reflection followed by a translation along a direction lying in the plane of reflection are typical examples of such new elements. The translations τ in these two cases may be called fractional translations. Twice τ in the case of glides, because reflections are of order two, and $p\tau$ where p is the order of the rotation part in a screw will always be pure translations. It may be noted that a reflection in a plane followed by a translation along any direction can be reduced to that of a glide plane of reflection. In fact, if we take the reflection plane as the XY plane and the components of the translation as a, b and c, it is easily seen that the combination is equivalent to a reflection in a parallel plane at a distance of $c/2$ followed by a translation in the plane with the components a, b, 0. The simpler elements such as an axis of rotation or a plane of reflection may be regarded as particular cases of a screw axis and a glide plane respectively in which the translation is zero. Superscripts s and g are used along with C and σ to denote that the corresponding elements of symmetry are screw axes and glide planes. T is used to denote a pure translation. A suffix to this letter indicates the direction in which the translation is performed. The presence of symmetry operations involving translations either as such or in combination with the elements characteristic of a point group implies the presence of repetitive symmetry in space. Pattern decorations are common examples of such a symmetry. All symmetry operations characteristic of a given body or pattern, because of the condition of superposition, constitute a group which is called a space group. Space groups can be built up from point groups by considering all the possible ways in which translatory movements in space can be combined with the various symmetry operations characteristic of the point group under consideration. Examples of space groups will be furnished in the following Chapters.

CHAPTER II

ONE-DIMENSIONAL LATTICE

Symmetry of the Lattice.—Pattern decorations of different types furnish good examples for illustrating groups of symmetry operations. Strip decorations are the simplest and are obtained by using a one-dimensional lattice as the framework. A set of points all of which can be reached by starting from any one of them and by performing a basic or primitive translation T or an integral (positive or negative) multiple thereof, the translation being always confined to one direction is said to constitute such a lattice. It follows that all such points lie on a straight line which may be taken as the X axis. Such a single straight chain of equally spaced points will possess an infinite set of symmetry elements, because the axis itself is of infinite-fold rotational symmetry. At each of the lattice points, a sphere or a circular disc with its plane perpendicular to the X axis may be located such that the resulting pattern will still possess the infinite-fold rotational axis of symmetry. On the other hand, if a plane regular polygon of n sides is located at each one of the lattice points with its plane perpendicular to the X axis, what has been an infinite-fold rotational symmetry axis in the lattice becomes only an n-fold rotational symmetry axis in the pattern. There are obviously several alternative ways of building up symmetry patterns using such a unidimensional lattice. In order that we may confine ourselves to what may be called strip decoration, we shall impose the restriction of making the X axis digonal. With this restriction and confining ourselves to a finite portion of the lattice extending equally on either side of the origin along the X axis, the lattice will possess the following symmetry operations:

E	$X \to X$	$Y \to Y$	$Z \to Z$
C_x	$X \to X$	$Y \to -Y$	$Z \to -Z$
C_y	$X \to -X$	$Y \to Y$	$Z \to -Z$
C_z	$X \to -X$	$Y \to -Y$	$Z \to Z$
i	$X \to -X$	$Y \to -Y$	$Z \to -Z$
σ_x	$X \to -X$	$Y \to Y$	$Z \to Z$
σ_y	$X \to X$	$Y \to -Y$	$Z \to Z$
σ_z	$X \to X$	$Y \to Y$	$Z \to -Z$

All the elements except E are of order 2. The transformations of the co-ordinates are given against each symmetry operation. It may be noted that C_z, σ_x, σ_y, σ_z are the products C_xC_y, C_xi, C_yi, C_zi respectively. C_x, C_y and i constitute a set of generating elements of the above group, *i.e.*, every element of the group can be obtained as a combination of these three elements. Such a set of generating elements may be chosen in various ways. For example, σ_y, σ_z and C_z form an alternative set.

The set of lattice points need not, however, be finite as it is possible to repeat the primitive translation idefinitely. In such a case, the lattice will become an infinite one and operations of the type T_x, T_x^2, ... will be also symmetry elements of the lattice. A complete set of symmetry operations of an infinite strip will consist of the elements $E C_x C_y C_z i \sigma_x \sigma_y \sigma_z$ and their combinations with the translations $E T_x T_x^2$, etc. In this case, however, the symbols $E C_x C_y C_z i \sigma_x \sigma_y \sigma_z$ will still be used with the understanding that each symbol S stands for a class of symmetry operations obtained by combining S with all the translations $ET_xT_x^2$, etc.

One-Dimensional Motives.—If we now put a motive at every lattice point, we obtain a pattern of decoration. The motive may be quite general. However, by putting at each lattice point a motive which has no extension either in the Y direction or in the Z direction, we will be dealing with the very simple case of a chain-like pattern. The symmetry operations C_x, σ_y, σ_z then become indistinguishable from E as any given point of the pattern goes to its own or an equivalent position as a result of all these operations. Similarly the symmetry operations C_y, C_z, σ_x become indistinguishable from i as any given point of the pattern moves into an equivalent position by all these operations. In this way, by locating only a one-dimensional motive on the lattice, we get one of the two possible alternative patterns according as the motive possesses the symmetry elements E and i or E alone. The lattice is unique and one-dimensional.

Two-Dimensional Motives.—In the particular case when the motive has no extension in the Z direction but has an extension in the X and Y directions, the symmetry elements C_x, C_y, i, σ_z cannot be distinguished from σ_x, σ_y, C_z, E respectively. The group of symmetry operations then reduces to one of order 4 and consists of the following elements:

E	..	$X \rightarrow X$	$Y \rightarrow Y$
C_z	..	$X \rightarrow -X$	$Y \rightarrow -Y$
σ_x	..	$X \rightarrow -X$	$Y \rightarrow Y$
σ_y	..	$X \rightarrow X$	$Y \rightarrow -Y$

We can locate at every lattice point, a motive possessing all the above symmetry operations and obtain a pattern whose symmetry is the same as that given above. On the other hand, by locating a motive whose symmetry operations constitute a subgroup* of the above group, we will be obtaining patterns of that lower degree of symmetry. The subgroups of the above group are E; $E\,C_z$; $E\sigma_x$; $E\ \sigma_y$; and each one of these four can be used as the symmetry group of the motive for the pattern besides the main group $E\,C_z\,\sigma_x\,\sigma_y$ itself.

If we further consider an infinite lattice, the possibility of having new symmetry elements such as screw axes of

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* In a group, a subset of elements which forms a group by itself under the same composition rule is said to constitute a subgroup of the original group.

rotation and glide planes of reflection has to be taken into account. It has already been pointed out that the direction of a glide should lie in the plane of reflection and the direction of a screw should lie along the axis of rotation. In the symmetry groups relating to one-dimensional patterns, the translation is along one direction only and therefore glide planes of the σ_y class alone are possible. Such a plane will be analytically represented as $X \to X + \tau$ and $Y \to -Y$, where the least value of τ is $T_x/2$, because the glide performed twice should result in a full unit of translation bringing every lattice point to its immediate neighbour. Since the glide σ_y is equal to the product $C_z\sigma_x$, C_z and σ_x cannot both be situated at the origin. As a consequence of this, a general description of the symmetry elements appropriate to an infinite flat strip will be

E	..	$X \to X$	$Y \to Y$
C_z	..	$X \to -X + b$	$Y \to -Y$
σ_x	..	$X \to -X + a$	$Y \to Y$
σ_y	..	$X \to X + a + b$	$Y \to -Y$

where a and b are parameters. It may be noted that $2a$ or $2b$ is equivalent to identity, and thus there is no distinction between a and $-a$ or b and $-b$. As explained previously, each one of the symbols E, C_z, σ_x, σ_y stands for a class of symmetry elements. For example, C_z stands for an axis of rotation at the point $b/2$, 0 and for a combination of this rotation with all translations. The plane σ_x cuts the X axis, at the point $a/2$, 0 and other elements of this class pass through corresponding points. If C_z is chosen as the Z axis itself, b becomes zero and we will be left with a single parameter a alone. As every operation done twice should give rise to either the identity element E or a full unit of translation T_x, the parameter a can take the values 0 or $T_x/2$. It is obvious that a space group will contain a glide plane only when $a = T_x/2$. Otherwise, σ_y is a simple reflection plane. The distinct symmetry patterns may then be described by the space groups $E\,C_z\,\sigma_x\,\sigma_y$ and $E\,C_z\,\sigma_x\,\sigma_y{}^g$. We can also have symmetry patterns having subgroups of either of the above space groups. Each of the groups E; $E\,C_z$;

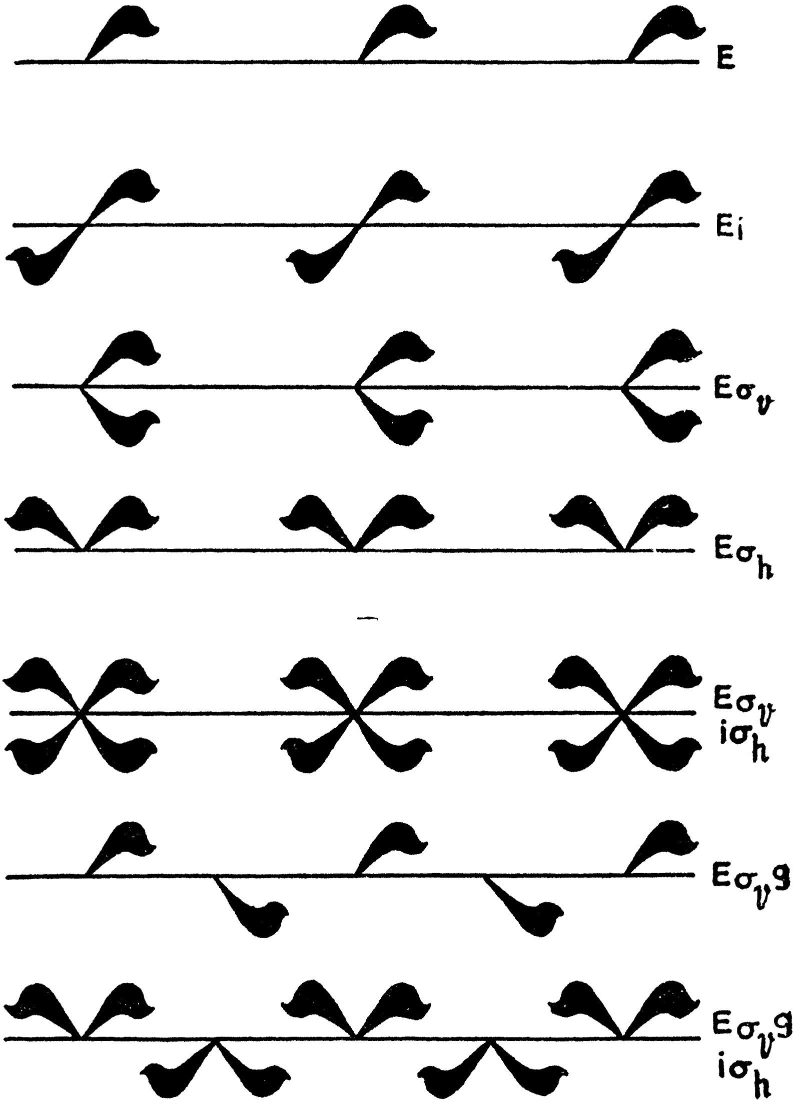
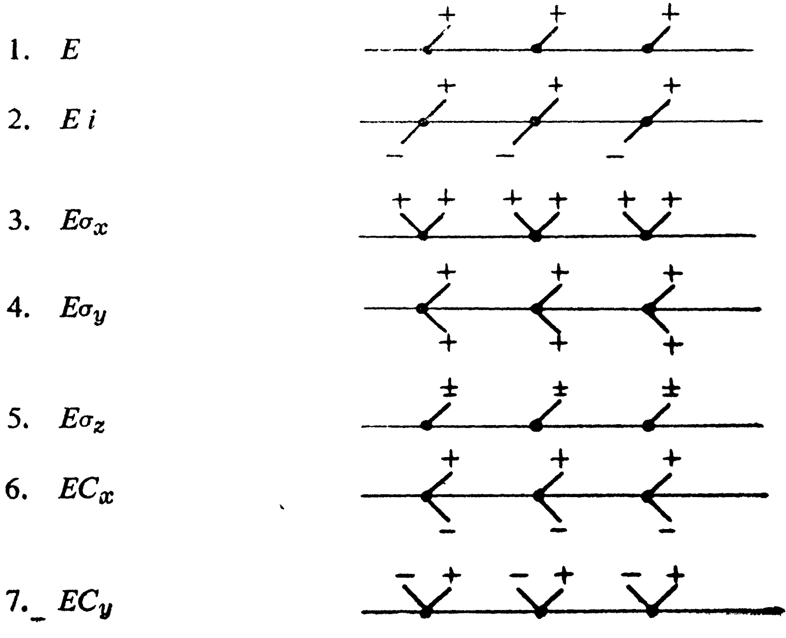


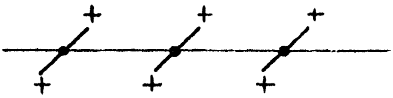
FIG. 1

$E\sigma_x$; $E\sigma_y$; $E\sigma_y^g$ is a subgroup of at least one of the above two space groups. Thus, when the lattice is an infinite one, two more symmetry patterns, namely, $E\,C_z\,\sigma_x\,\sigma_y^g$ and $E\,\sigma_y^g$ are possible in addition to the five that are present in the case of a finite lattice. The superscript *g* indicates, as has been already mentioned, that the symmetry element is a glide plane of reflection. We have thus been enabled to build seven space groups in the case under consideration, whereas, there are only five point groups. These seven alternatives are the well-known infinitely repeated strip decorations of the flat type and are diagrammatically represented in Fig. 1. The lattice is unique and one-dimensional.

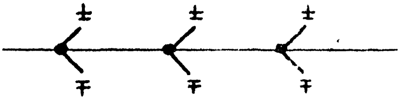
Three-Dimensional Motives.—In the above patterns, the motives used are only two-dimensional. If we do not impose the restriction of neglecting the *Z* axis but take it into account, *i.e.*, permit an extension of the motive in the *Z* direction also, the eight elements of symmetry of the flat strip already enumerated become distinct, and we can locate at every



8. EC$_z$

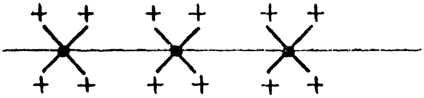


9. $EC_x\sigma_y\sigma_z$

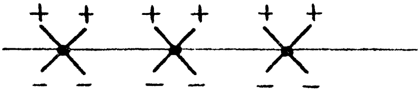


10. $EC_y\sigma_x\sigma_z$

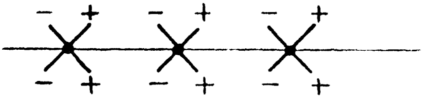
11. $EC_z\sigma_x\sigma_y$



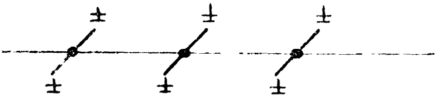
12. $EC_x\, i\sigma_x$



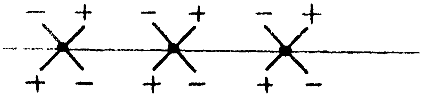
13. $EC_y\, i\sigma_y$



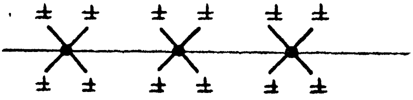
14. $EC_z\, i\sigma_z$



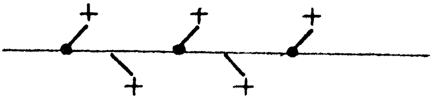
15. $EC_x\, C_y\, C_z$



16. $EC_xC_yC_z\, i\sigma_x\, \sigma_y\, \sigma_z$

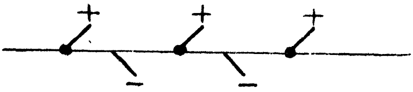


17. $E\sigma_y^g$ (*a*)



18. $E\sigma_z^g$ (*b*)

19. EC_x^s (*a* or *b*)



20. $EC_x^s\sigma_y^g\sigma_z$ (*a*)

21. $EC_x^s\sigma_y\sigma_z^g$ (*b*)

22. $EC_x\sigma_y^g\sigma_z^g$ (*a*, *b*)

23. $EC_y\sigma_x\sigma_z^g$ (*b*)

24. $EC_z\sigma_x\sigma_y^g$ (*a*)

25. $EC_yi\sigma_y^g$ (*a*)

26. $EC_x^si\sigma_x$ (*a* or *b*)

27. $EC_z\,i\sigma_z^g$ (*b*)

28. $EC_x^sC_yC_z$ (*a* or *b*)

29. $EC_x^sC_yC_zi\sigma_x\sigma_y\sigma_z^g$(*b*)

30. $EC_x^sC_yC_z$
$i\sigma_x\,\sigma_y^g\sigma_z$ (*a*)

31. $EC_xC_yC_z$
$i\sigma_x\sigma_y^g\sigma_z^g$ (*a*, *b*)

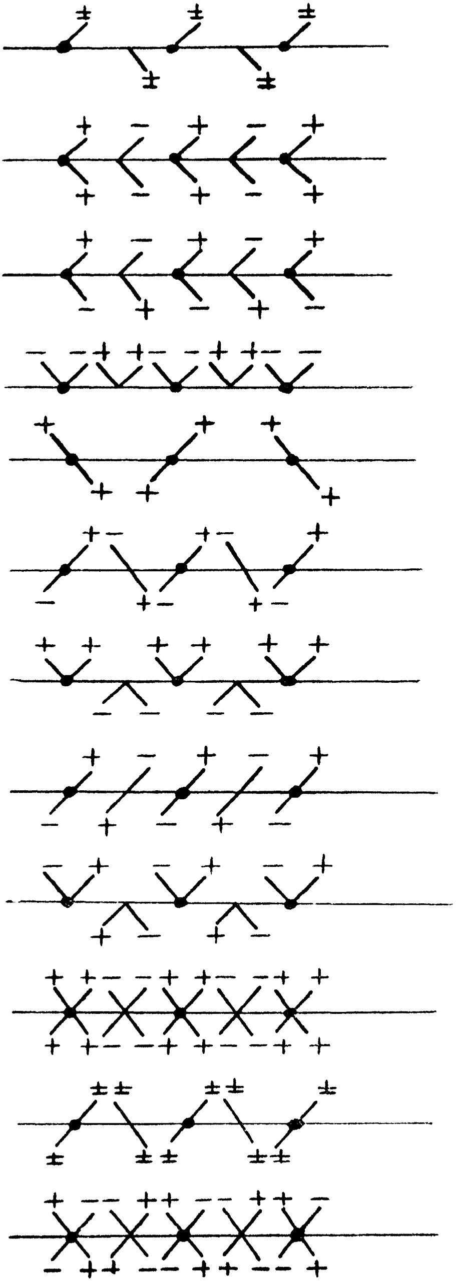


FIG. 2

lattice point, a point group possessing all or some of these elements of symmetry. Its subgroups are of order 1, 2 or 4. All the possible subgroups with their elements of symmetry are given above from 1 to 16 in Fig. 2. Translations, because they are confined to the X axis, will generate new elements in combination with C_x, σ_y, and σ_z only. By taking σ_y, σ_z and C_z as generating elements, a general description of the group may be given as follows:

E ..	$X \to X$	$Y \to Y$	$Z \to Z$
C_x ..	$X \to X + a + b$	$Y \to -Y$	$Z \to -Z$
C_y ..	$X \to -X + a + b$	$Y \to Y$	$Z \to -Z$
C_z ..	$X \to -X$	$Y \to -Y$	$Z \to Z$
i ..	$X \to -X + b$	$Y \to -Y$	$Z \to -Z$
σ_x ..	$X \to -X + a$	$Y \to Y$	$Z \to Z$
σ_y ..	$X \to X + a$	$Y \to -Y$	$Z \to Z$
σ_z ..	$X \to X + b$	$Y \to Y$	$Z \to -Z$

The parameters a and b can take the values 0 or $T_x/2$. There are four distinct ways of choosing the parameters. Accordingly, we get four groups of order 8, of which the one corresponding to $a = 0$, $b = 0$ has already been given on page 11. The other three along with their subgroups, repetitions not being counted, will give 15 new (space groups) symmetry patterns. The symmetry elements in each of these new groups together with the surviving parameters are given from 17 to 31 in Fig. 2. The values of the parameters, when mentioned, should always be taken as $T_x/2$. Against each one of the patterns 1 to 31 is shown the appropriate figure where a plus sign stands for a projection upwards and a minus sign stands for a projection downwards. The superscript s indicates that the symmetry element is a screw axis of rotation. We have thus been enabled to build 31 space groups utilizing only 16 point groups for the case under consideration. The lattice is unique and one-dimensional. The patterns may still be described as strip decorations but with elevations and depressions in the strip being permitted.

CHAPTER III

LATTICES IN TWO DIMENSIONS

Symmetry of the Lattices.—A set of points all of which can be reached by starting from any one of them and by performing basic or primitive translations T_x, T_y or integral (positive or negative) multiples thereof, the translations now being confined to two chosen directions X and Y, is said to constitute a two-dimensional lattice. Surface decorations are formed with such lattices as their framework.

From the definition it follows that the lattice points are at the intersections of two sets of equidistant parallel lines as in Fig. 3. Putting $OA = T_x$, $OB = T_y$, and $\angle AOB = \gamma$, we see that for a given γ two cases arise according as $T_x \neq T_y$ or $T_x = T_y$. The symbols T_x and T_y will be used for the respective operations as well as for the lengths of the corresponding vectors. In the former, except when $\gamma = 90°$, the lattice exhibits a rotation axis of order two only. This axis is perpendicular to the plane of the lattice. When $\gamma = 90°$, the lattice becomes rectangular and develops additional elements of symmetry. In the case $T_x = T_y$, two special values of γ, namely 120° and 90° have to be recognized, as they correspond respectively to trigonal and tetragonal symmetries.

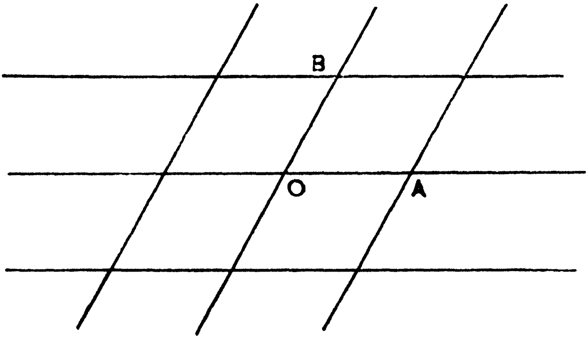


FIG. 3

Trigonal symmetry here is easily seen to imply hexagonal symmetry also. A fifth case is one where $T_x = T_y$ but $\gamma \neq 120°$ or $90°$. This exhausts all the possible types of symmetry as may be seen from the following argument. A symmetry axis lying in the plane of the lattice points should be digonal only, as otherwise, the plane will not come into superposition with itself as a result of such a rotation. For the same reason, a symmetry axis which is inclined to the lattice plane should be perpendicular to it. If this is a p-fold axis of symmetry, we will show that p can take values 1, 2, 3, 4 and 6 only. Taking OA in Fig. 2 as the X axis and a line perpendicular to it and passing through O as the Y axis, the co-ordinates of A and B may be taken as $(a, 0)$ and $(b \cos \gamma, b \sin \gamma)$. Here a and b are respectively the same as T_x and T_y which are the lengths of OA and OB. As a result of the symmetry operation C_p, the lattice point $(a, 0)$ goes over to the point $(a \cos 2\pi/p, -a \sin 2\pi/p)$ and this should coincide with a lattice point, a general form of which is $(ma + nb \cos \gamma, nb \sin \gamma)$, where m and n are positive or negative integers or may take the value zero also. Solving for m and n we obtain

$$m = \frac{\sin(\gamma + 2\pi/p)}{\sin \gamma} \text{ and } n = -\frac{a \sin 2\pi/p}{b \sin \gamma}.$$

Similarly taking the lattice point $(b \cos \gamma, b \sin \gamma)$ and putting the condition that it should go over to a lattice point as a result of the operation C_p, we obtain that

$$\sin(\gamma - 2\pi/p)/\sin \gamma \text{ and } (b \sin 2\pi/p)/a \sin \gamma$$

are integers. Combining this result with the previous one, we obtain that $2 \cos 2\pi/p$, $(a \sin 2\pi/p)/b \sin \gamma$ should be integers. p should therefore be either 1, 2, 3, 4 or 6.

The above result may also be proved in a slightly different way. Take any lattice point 0 as the origin of the co-ordinates and let A be a lattice point nearest to 0. Take OA as the X axis and a line perpendicular to it as the Y axis. Let the length of OA be a. We prepresent the point A by its co-ordinates in the form $(a, 0)$. By a rotation through ϕ, let

A be transformed into A' ($a \cos \phi$, $a \sin \phi$). Similarly, by a rotation through $-\phi$, let A be transformed into A'' ($a \cos \phi$, $-a \sin \phi$). We now have three vectors OA, OA' and OA''; A' and A'' being lattice points of rotation through ϕ is a symmetry operation. Three other lattice points may be formed by combining the vectors as $(OA' + OA)$, $(OA' - OA)$ and $(OA' + OA'')$. The three lattice points thus obtained are $(a \cos \phi + a,\ a \sin \phi)$, $(a \cos \phi - a,\ a \sin \phi)$ and $(2a \cos \phi, 0)$ and their distances from the origin should be either zero or $\geq a$, because a has been taken to be the distance from the origin to the nearest lattice point. It may easily be seen that $|2a \cos \phi/2|$, $|2a \sin \phi/2|$ and $|2a \cos \phi|$ are the distances of these three lattice points from the origin and these should be greater than or equal to a, in case they are different from zero. Consequently, ϕ can take the values 0, $\pm \pi/3$, $\pm \pi/2$, $\pm 2\pi/3$, or π only and if $\phi = 2\pi/p$, $p = 1, 2, 3, 4$ or 6.

The five lattices that are possible in the two-dimensional case are described below in terms of the parameters T_x, T_y, and γ. The names used are such that they lead to the conventional nomenclature of the three-dimensional lattices.

$$T_x \neq T_y \quad \begin{cases} \gamma \neq 90^\circ & \text{(Monoclinic)} \\ \gamma = 90^\circ & \text{(Orthorhombic)} \end{cases}$$

$$T_x = T_y \quad \begin{cases} \gamma = 120^\circ & \text{(Hexagonal)} \\ \gamma = 90^\circ & \text{(Tetragonal)} \\ \gamma \neq 120^\circ \text{ or } 90^\circ & \text{(Orthorhombic)} \end{cases}$$

It is important to note that the last of the five lattices ($T_x = T_y$; $\gamma \neq 120^\circ$ or 90°) can alternatively be referred to translations $T_x + T_y = T_x'$ and $T_x - T_y = T_y'$ which are unequal vectors along two mutually perpendicular directions. In fact, this description has the merit of bringing about the symmetry properties of the lattice explicitly by putting it under the orthorhombic class ($T_x' \neq T_y'$; $\gamma = 90^\circ$) but does not conform to the definition of a lattice because every lattice point cannot be covered by performing the new translations. It will be recognized that there are points at the centres of the various rectangles of the new system and the lattice may therefore be referred to as a cell-centred orthorhombic one or the derived orthorhombic one. In two dimensions, we have thus five lattices coming under four systems or types of symmetry.

The minimum symmetry possessed by a two-dimensional lattice is that of the monoclinic class ($T_x \neq T_y$; $\gamma \neq 90°$) characterized by the identity operation, a centre of inversion, a digonal axis normal to the lattice plane and a reflection plane coinciding with it. Lattices possessing higher symmetry are obtained as special cases of this simple type when the parameters T_x, T_y and γ take special values. The symmetry elements of four systems appropriate to the two-dimensional lattices are given below.

System	Symmetry Operations	Generating Elements
Monoclinic	$E\ C_z\ i\ \sigma_z$	$C_z\ i$
Orthorhombic	$E\ C_x C_y C_z\ i\ \sigma_x\ \sigma_y\ \sigma_z$	$C_x\ C_z\ i$
Tetragonal	$E\ 2C_4\ C_2\ 2C_2'\ 2C_2''$ $i\ 2S_4\ \sigma_h 2\sigma_v'\ 2\sigma_v''$	$C_4\ C_2'\ i$
Hexagonal	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''$ $i\ 2S_3\ 2S_6\ \sigma_h\ 3\sigma_v'\ 3\sigma_v''$	$C_6\ C_2'\ i$

Taking each one of the five lattices, we can locate at every lattice point a motive possessing all the symmetry operations of the lattice and obtain a pattern whose symmetry is called the holohedral symmetry of the lattice. Even if a motive of higher symmetry is located at each one of the lattice points, the pattern as a whole will not acquire that higher symmetry. By locating subgroups of the holohedral group at each lattice point, we obtain patterns of that lower symmetry. In fact, the point symmetry of the pattern, in a general case, has elements common to those of the lattice and the motive when the motive is appropriately oriented. It may be mentioned that we have not so far introduced symmetry elements involving fractional translations. If we take these also into account, the motives having the above symmetries may be split up to give rise to glide planes and screw axes in the place of the corresponding ordinary reflection planes and rotation axes. We should also note that under certain circumstances, different space groups may be built up by using the same lattice and the same motive but by adopting different orientations of the motive with respect to the lattice.

Two-Dimensional Motives.—Considering only motives which have no extension in the Z direction, the group of symmetry elements of the holohedral class of patterns in each lattice will reduce to one of order half that of the full group and the corresponding elements are given below. The rest of the symmetry elements in each case become indistinguishable from those given.

System	Symmetry Operations	Generating Elements
Monoclinic	$E\ C_z$	C_z
Orthorhombic	$E\ C_x\ C_y\ C_z$	$C_x\ C_z$
Tetragonal	$E\ 2C_4\ C_2\ 2C_2'\ 2C_2''$	$C_4\ C_2'$
Hexagonal	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''$	$C_6\ C_2'$

By locating one or other of the motives possessing symmetry elements $E\ C_z$ or E alone on the monoclinic lattice we get two patterns under this system. Patterns can, however, be built by putting either of these motives on the lattices of the remaining systems but they will not possess a symmetry higher than that of the monoclinic system.

To study the symmetry patterns that can be specially built by taking the orthorhombic system, we first consider a general description of the symmetry elements in this case.

$$\begin{array}{llll}
E & .. & X\rightarrow X & Y\rightarrow Y \\
C_x & .. & X\rightarrow X+a & Y\rightarrow -Y+b \\
C_y & .. & X\rightarrow -X+a & Y\rightarrow Y+b \\
C_z & .. & X\rightarrow -X & Y\rightarrow -Y
\end{array}$$

We here take the C_z axis as the Z axis itself and this involves no loss of generality. The various possibilities will give five new symmetry patterns which can be built by taking the simple orthorhombic lattice as the framework and they are:

$$\begin{array}{ll}
E\,C_x & \\
E\,C_xC_yC_z & \\
E\,C_x{}^s & (a) \\
E\,C_x{}^s\,C_y\,C_z & (a) \\
E\,C_x{}^s\,C_y{}^s\,C_z & (a, b)
\end{array}$$

It may be mentioned that $E\,C_z$ and $E\,C_y$ are also subgroups of this system but we do not count them as new patterns as the first one has been taken account of in the monoclinic system and the second one is indistinguishable with $E\,C_x$. Similarly, $EC_x{}^s\,C_y\,C_z\,(a)$ is indistinguishable from $EC_xC_y{}^s\,C_z$ (b). Since the derived orthorhombic lattice is a different one, we can locate motives possessing the above symmetries on that also. However, $EC_x{}^s$ on the derived lattice is equivalent to EC_x on the same, as can be seen from the equivalence of the expressions

$$\begin{array}{llll}
C_x{}^s & .. & X\rightarrow X+a & Y\rightarrow Y \\
C_x & .. & X\rightarrow X & Y\rightarrow Y+b
\end{array}$$

as $C_x{}^s$ is the combination of C_x and the primitive translation (a, b) in the derived lattice. Similarly, $E\,C_x{}^s\,C_y\,C_z$ and

$E\,C_x^s\,C_y^s\,C_z$ on the derived lattice are equivalent to $E\,C_x\,C_y\,C_z$ on the same. Thus, we obtain two new patterns by putting only the motives with symmetries $E\,C_x$ and $E\,C_x\,C_y\,C_z$ on the derived orthorhombic lattice.

A general description of the symmetry elements in respect of the tetragonal system is as follows:

E	..	$X \to X$	$Y \to Y$
$2C_4$	..	$X \to Y$	$Y \to -X$
		$X \to -Y$	$Y \to X$
C_2	..	$X \to -X$	$Y \to -Y$
$2C_2'$	..	$X \to X + a$	$Y \to -Y + a$
		$X \to -X + a$	$Y \to Y + a$
$2C_2''$	..	$X \to -Y + a$	$Y \to -X + a$
		$X \to Y + a$	$Y \to X + a.$

Omitting space groups that have been counted in the monoclinic and the orthorhombic systems, it is easily seen that the following space groups come under the tetragonal system.

$$E\,2C_4\,C_2$$

$$E\,2C_4\,C_2\,2C_2'\,2C_2''$$

$$E\,2C_4\,C_2\,2C_2'^{s}\,2C_2''.$$

Similarly we obtain the following space groups coming under the hexagonal system. In this system, taking X and Y axes along the basic directions, a general description of the generating elements may be given as

C_6	..	$X \to -Y$	$Y \to Y + X$
C_2'	..	$X \to Y + a$	$Y \to X + b$

In order that the squares of C_2', $C_6\,C_2'$ and $C_6^2\,C_2'$ may be lattice translations, the relation $a = b = 0$ should hold good. Thus we do not get any groups with translational type of symmetry elements in this case.

$E\,2C_3$

$E\,2C_3\,3C_2$

$E\,2C_3\,3C_2'$

$E\,2C_6\,2C_3\,C_2$

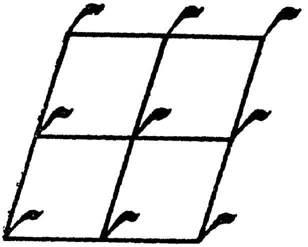
and $E\,2C_6\,2C_3\,C_2\,3C_2'\,3C_2''$.

It may be noted that the two space groups $E\,2C_3\,3C_2$ and $E\,2C_3\,3C_2'$ differ only in the orientation of the motive with respect to the lattice.

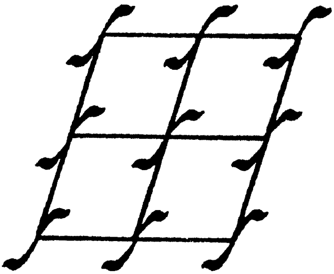
Thus altogether we have $2 + (5 + 2) + 3 + 5 = 17$ space groups in the two-dimensional case when we ignore the extension of the motives in the Z direction. These 17 types of infinitely repeated surface decoration are represented diagrammatically in Fig. 4. We have been enabled to build 17 space groups in two dimensions utilizing ten point groups and five space lattices coming under four systems of symmetry. The restriction that the Z axis is of no consequence has been imposed and this may be noted. Removal of this restriction will lead to further possibilities and they are dealt with in the following Section.

Space groups which do not involve screws or glides are called point space groups. Thus, only the patterns 1 to 13 below correspond to point space groups. The remaining four space groups are not point space groups as they contain screws.

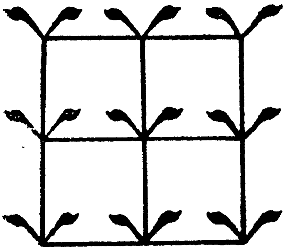
Three-Dimensional Motives.—If we permit an extension of the motive in the Z direction, all the elements of symmetry relating to each system as already enumerated will become distinct. We can then locate at every lattice point, a point group possessing all or some of these elements of symmetry. Taking the co-ordinate axes X and Y in the directions of the basic translations, a general description of a set of generating elements of the group of symmetry operations appropriate to each system is given below.



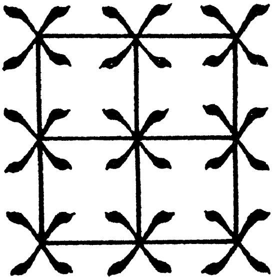
E



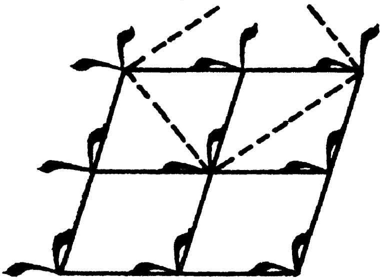
EC_z



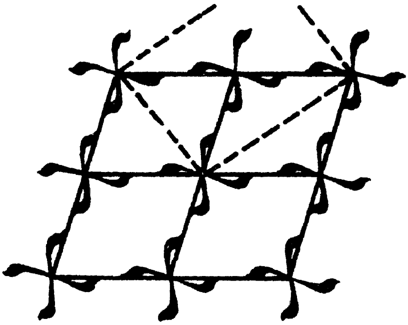
EC_x



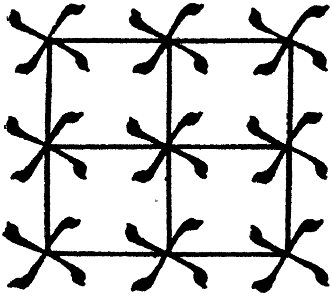
$EC_xC_yC_z$



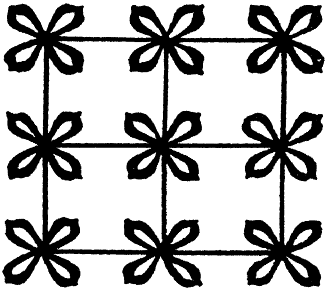
EC_x



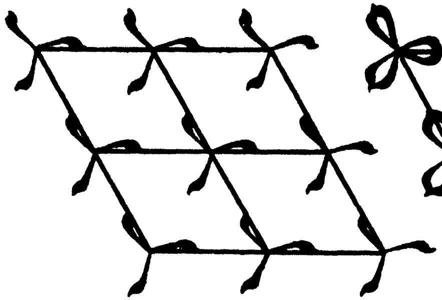
$EC_xC_yC_z$



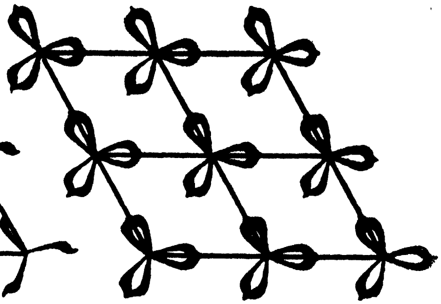
$E2C_4C_2$



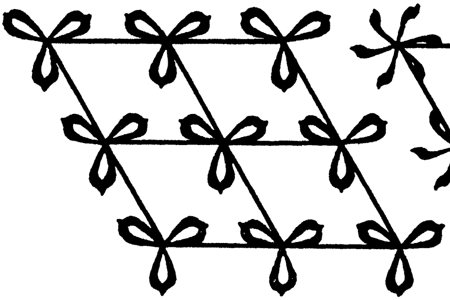
$E2C_4C_22C'_22C''_2$



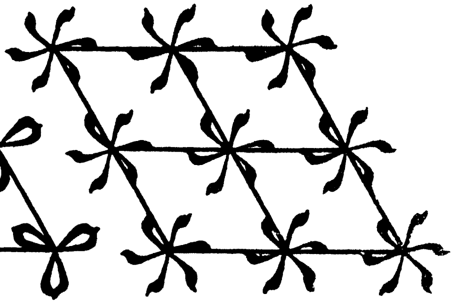
$E2C_3$



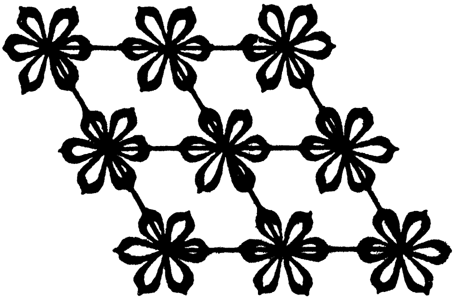
$E2C_3 3C_2$



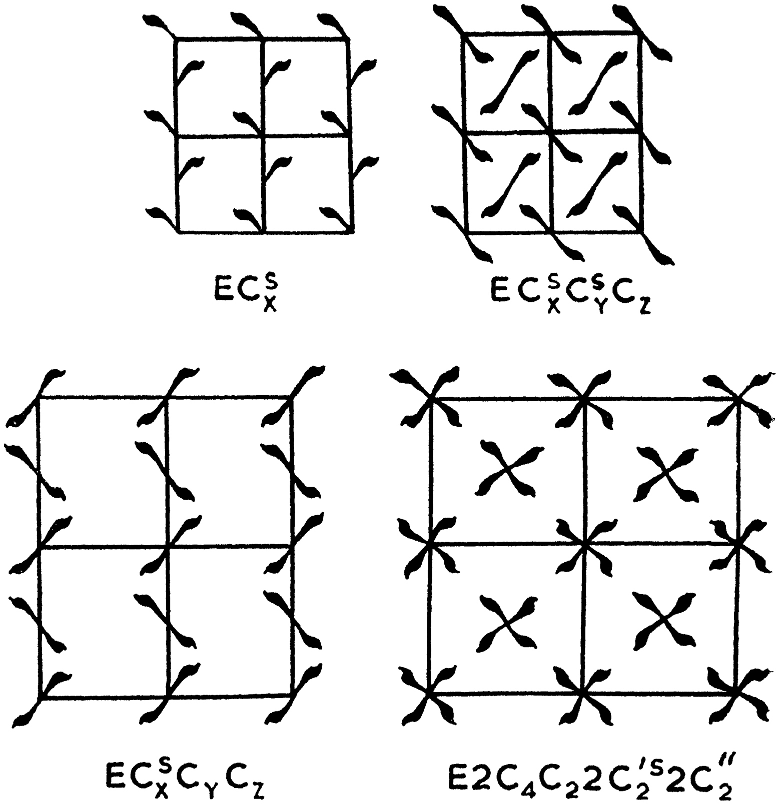
$E2C_3\,3C_2'$



$E2C_6\,2C_3C_2$



$E2C_6\,2C_3C_2\,3C_2'\,3C_2''$


EC_x^s $EC_x^sC_y^sC_z$

$EC_x^sC_yC_z$ $E2C_4C_22C_2'^s2C_2''$

FIG. 4

System	Generating Elements	Analytical Description		
Monoclinic ..	C_z	$X \rightarrow -X+a$	$Y \rightarrow -Y+b$	$Z \rightarrow Z$
	i	$X \rightarrow -X$	$Y \rightarrow -Y$	$Z \rightarrow -Z$
Orthorhombic	C_x	$X \rightarrow X+a$	$Y \rightarrow -Y+b$	$Z \rightarrow -Z$
	C_z	$X \rightarrow -X$	$Y \rightarrow -Y$	$Z \rightarrow Z$
	i	$X \rightarrow -X+c$	$Y \rightarrow -Y+d$	$Z \rightarrow -Z$
Tetragonal ..	C_4 or S_4	$X \rightarrow -Y$	$Y \rightarrow X$	$Z \rightarrow \pm Z$
	C_2'	$X \rightarrow X+a$	$Y \rightarrow -Y+a$	$Z \rightarrow -Z$
	i	$X \rightarrow -X+b$	$Y \rightarrow -Y+b$	$Z \rightarrow -Z$
Hexagonal ..	C_6	$X \rightarrow Y-X$	$Y \rightarrow -X$	$Z \rightarrow Z$
	C_2'	$X \rightarrow X$	$Y \rightarrow X-Y$	$Z \rightarrow -Z$
	i	$X \rightarrow -X$	$Y \rightarrow -Y$	$Z \rightarrow -Z$

A complete description of the two-dimensional space groups, which are 80 in number, together with the appropriate non-zero parameters in respect of the generating elements in each group is obtained by proceeding in the same manner as outlined in the previous Sections. The results are given below.

System	No.	Description	Parameters
Monoclinic ..	1	E	
	2	$E\,C_z$	
	3	$E\,i$	
	4	$E\sigma_z$	
	5	$E\,C_z i\,\sigma_z$	
	6	$E\,\sigma_z{}^g$	a or b or both
	7	$E\,C_z i\,\sigma_z{}^g$	a or b or both
Orthorhombic	8	$E\,C_x$	
	9	$E\,\sigma_x$	
	10	$E\,C_z\,\sigma_x\,\sigma_y$	
	11	$E\,C_x\,C_y\,C_z$	
	12	$E\,C_x\,i\,\sigma_x$	
	13	$E\,C_x\,\sigma_y\,\sigma_z$	
	14	$E\,C_x\;C_y\;C_z\;i\,\sigma_x\;\sigma_y\;\sigma_z$	
	15	$E\,C_x{}^s$	a
	16	$E\,\sigma_x{}^g$	b or d
	17	$E\,C_z\,\sigma_x{}^g\,\sigma_y$	b or d
	18	$E\,C_z\;\sigma_x{}^g\,\sigma_y{}^g$	a or c, b or d
	19	$E\,C_x{}^s\,C_y\,C_z$	a

System	No.	Description	Parameters
	20	$E\,C_x^s\,C_y^s\,C_z$	a, b
	21	$E\,C_x^s\,i\,\sigma_x$	a
	22	$E\,C_x\,i\,\sigma_x^g$	b or d
	23	$E\,C_x^s\,i\,\sigma_x^g$	a, b or d
	24	$E\,C_x^s\,\sigma_y^g\,\sigma_z$	a
	25	$E\,C_x\,\sigma_y\,\sigma_z^g$	d
	26	$E\,C_x^s\,\sigma_y^g\,\sigma_z^g$	a, d
	27	$E\,C_x\,\sigma_y^g\,\sigma_z$	c
	28	$E\,C_x\,\sigma_y^g\,\sigma_z^g$	c, d
	29	$E\,C_x^s\,\sigma_y\,\sigma_z^g$	a, c
	30	$E\,C_x^s\,\sigma_y\,\sigma_z^g$	a, c, d
	31	$E\,C_x\,C_y\,C_z\,i\,\sigma_x^g\,\sigma_y\,\sigma_z^g$	d
	32	$E\,C_x\,C_y\,C_z\,i\,\sigma_x^g\,\sigma_y^g\,\sigma_z^g$	c, d
	33	$E\,C_x^s\,C_y\,C_z\,i\,\sigma_x\,\sigma_y^g\,\sigma_z$	a
	34	$E\,C_x^s\,C_y\,C_z\,i\,\sigma_x\,\sigma_y\,\sigma_z^g$	a, c
	35	$E\,C_x^s\,C_y\,C_z\,i\,\sigma_x^g\,\sigma_y^g\,\sigma_z^g$	a, d
	36	$E\,C_x^s\,C_y\,C_z\,i\,\sigma_x^g\,\sigma_y\,\sigma_z^g$	a, c, d
	37	$E\,C_x^s\,C_y^s\,C_z\,i\,\sigma_x^g\,\sigma_y^g\,\sigma_z$	a, b
	38	$E\,C_x^s\,C_y^s\,C_z\,i\,\sigma_x\,\sigma_y^g\,\sigma_z^g$	a, b, d
	39	$E\,C_x^s\,C_y^s\,C_z\,i\,\sigma_x\,\sigma_y\,\sigma_z^g$	a, b, c, d
Orthorhombic derived	40	$E\,C_x$	
	41	$E\,\sigma_x$	
	42	$E\,C_z\,\sigma_x\,\sigma_y$	
	43	$E\,C_x\,C_y\,C_z$	
	44	$E\,C_x\,\sigma_y\,\sigma_z$	

System	No.	Description	Parameters
Orthorhombic derived	45	$E\,C_x\ i\ \sigma_x$	
	46	$E\,C_x\,C_y\,C_z\,i\ \sigma_x\ \sigma_y\ \sigma_z$	
	47	$E\,C_x{}^s\ \sigma_y\ \sigma_z{}^g$	a, c
	48	$E\,C_x\ C_y\ C_z\ i\,\sigma_x\ \sigma_y\ \sigma_z{}^g$	d
Tetragonal ..	49	$E\,C_4\,C_4\,C_2$	
	50	$E\,S_4\,S_4\,C_2$	
	51	$E\,2C_4\,C_2\,i\,2S_4\,\sigma_h$	
	52	$E\,2C_4\,C_2\,2\sigma_v{}'\,2\sigma_v{}''$	
	53	$E\,C_2\,2C_2{}'\,2S_4\,2\sigma_v{}'$	
	54	$E\,C_2\,2C_2{}''\,2S_4\,2\sigma_v{}''$	
	55	$E\,2C_4\,C_2\,2C_2{}'\,2C_2{}''$	
	56	$E\,2C_4\,C_2\,2C_2{}'\,2C_2{}''$ $i\,2S_4\,\sigma_h\,2\sigma_v{}'\,2\sigma_v{}''$	
	57	$E\,2C_4\,C_2\,i\,2S_4\,\sigma_h{}^g$	b
	58	$E\,2C_4\,C_2\,2\sigma_v{}'^g\ 2\sigma_v{}''$	a or b
	59	$E\,2C_4\,C_2\,2C_2{}'^s\ 2C_2{}''$	a
	60	$E\,C_2\,2C_2{}'^s\,2S_4\,2\sigma_v{}'$	a
	61	$E\,C_2\,2C_2{}''\,2S_4\,2\sigma_v{}''^g$	a
	62	$E\,2C_4\,C_2\,2C_2{}'^s\ 2C_2{}''$ $i\,2S_4\,\sigma_h\ 2\sigma_v{}'^g\ 2\sigma_v{}''$	a
	63	$E\,2C_4\,C_2\,2C_2{}'\,2C_2{}''$ $i\,2S_4\,\sigma_h{}^g\,2\sigma_v{}'^g\ 2\sigma_v{}''$	b
	64	$E\,2C_4\,C_2\,2C_2{}'^s\ 2C_2{}''$ $i\,2S_4\,\sigma_h{}^g\,2\sigma_v{}'\,2\sigma_v{}''$	a, b
Hexagonal ..	65	$E\,C_3\,C_3$	
	66	$E\,2C_3\,i\,2S_6$	

System	No.	Description	Parameters
Hexagonal ..	67	$E\ 2C_3\ 3\sigma_v$	
	68	$E\ 2C_3\ 3C_2$	
	69	$E\ 2C_3\ 3C_2\ i\ 2S_6\ 3\sigma_v$	
	70	$E\ 2C_3\ \sigma_h\ 2S_3$	
	71	$E\ C_6\ C_6\ C_3\ C_3\ C_2$	
	72	$E\ 2C_6\ 2C_3\ C_2\ i\ 2S_6\ 2S_3\ \sigma_h$	
	73	$E\ 2C_3\ 3C_2\ \sigma_h\ 2S_3\ 3\sigma_v$	
	74	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''$	
	75	$E\ 2C_6\ 2C_3\ C_2\ 3\sigma_v\ 3\sigma_v'$	
	76	$E\ 2C_3\ 3C_2'$	
	77	$E\ 2C_3\ 3\sigma_v'$	
	78	$E\ 2C_3\ 3C_2'\ i\ 2S_6\ 3\sigma_v'$	
	79	$E\ 2C_3\ 3C_2'\ \sigma_h\ 2S_3\ 3\sigma_v'$	
	80	$E\ 2C_6\ 2C_3\ C_2\ 3C_2'\ 3C_2''$ $i\ 2S_6\ 2S_3\ \sigma_h\ 3\sigma_v'\ 3\sigma_v''$	

CHAPTER IV

SOME PROPERTIES OF GROUPS

Abstract Groups.—In Chapter I, a group has been defined in terms of abstract symbols. If the symbols represent any specified elements or operations as for example ordinary numbers or symmetry operations of a body, we will be dealing with groups of special type. But if the elements of a group are just symbols and have no specific interpretation attached to them, the group may be called an abstract group. For example, the elements $E\ a\ a^2\ b\ ab\ a^2b$ form an abstract group defined by the relations

$$a^3 = E, \quad b^2 = E \quad \text{and}\ a^2b = ba.$$

If A and B are any two elements of the above group, by taking A from the first column and B from the first row, the product AB can be read from the following multiplication Table:

	E	a	a^2	b	ab	a^2b
E	E	a	a^2	b	ab	a^2b
a	a	a^2	E	ab	a^2b	b
a^2	a^2	E	a	a^2b	b	ab
b	b	a^2b	ab	E	a^2	a
ab	ab	b	a^2b	a	E	a^2
a^2b	a^2b	ab	b	a^2	a	E

It may be noted that we do not get any new elements by taking b to the left of a, as it can be brought to its right by using the relation $a^2b = ba$.

Subgroups.—A sub-set of elements in a group forming a group by itself under the same composition rule is defined as a subgroup of the original group. For example, in the group defined by the relations $a^3 = E$, $b^2 = E$ and $a^2b = ba$

the sub-set of the elements $E\,b$ forms a subgroup of order 2. The sub-set of elements $E\,a\,a^2$ forms a subgroup of order 3 and so on. Identity forms a subgroup of order one in every group. It may be shown that the identity element E_0 in any subgroup H is the same as the identity element E in the original group G. For, if h is an element of H, $hE_0 = h = hE$ and if h^{-1} is the inverse of h in G we have $E_0 = EE_0 = h^{-1}hE_0 = h^{-1}h = E$.

In the case of finite groups, we prove that the order of a subgroup is a divisor of the order of the group. Let G be a group of order N and G a subgroup of order h. The N elements of G will be shown to be divided into a number of sets, each set containing h elements of G and no element of G being put into more than one set. Let $E\,(= s_1)$, s_2, s_3, ... s_r, ...s_g,...s_h be the h elements of H. If t_2 is an element of G not belonging to H, the h elements t_2s_1, t_2s_2, ... t_2s_h are all obviously distinct and also different from the elements of H, for if $t_2s_r = s_g$ then $t_2 = s_g\,s_r^{-1}$. This leads to the contradiction that t_2 is an element of H. We denote the h elements t_2s_1, t_2s_2, ... t_2s_h by the symbol t_2H. t_2H is called a coset in G with respect to H. If H and t_2H do not exhaust all the elements in G, let t_3 be an element in G not belonging to either H or t_2H. Then t_3 gives rise to a new coset t_3H of h elements. The elements t_3H can be shown as above to be distinct and different from the elements in the two sets H and t_2H. Since the group G is of finite order N, the above procedure when repeated a definite number of times should exhaust all the elements of G. The N elements of G thus fall into k sets H, t_2H, ... t_kH, every one of these sets containing h elements. Hence $N = hk$.

The order of an element in a group has been defined as the order of the cyclic group generated by the element. Since this cyclic group is a subgroup of the original group, it follows that the order of an element is also a divisor of the order of the group.

Classes of Conjugate Elements.—Let s and t be any two elements of a group. $t^{-1}st$ which may be denoted by u

will also be an element of the group. u is called the transform of s by the element t. It is easily seen that s is the transform of u by the element t^{-1}. Two such elements s and u which may be transformed into one another by one element or other of the group are called conjugate elements. If u happens to be the same as s, then $t^{-1}st = s$ or $st = ts$. In such a case, s and t are said to commute with each other. The complete set of distinct elements which are transforms of s with all the elements of a group G constitute a conjugate class of elements of G. The number of such elements in any class is defined as the order of the class. If s is the transform of a with t_1 and of b with t_2, then b is the transform of a with $t_1t_2^{-1}$. Thus if s is conjugate to a and b, it follows that a and b are conjugate to one another. Hence the elements of a conjugate class are conjugate to one another. Another property of the elements in a conjugate class is that all the elements in a conjugate class have the same order. For, if $u = t^{-1}st$, then $u^2 = t^{-1}st.\ t^{-1}st = t^{-1}s^2t, \ldots\ u^n = t^{-1}s^nt$ and $u^n = E$ when $s^n = E$ and *vice versa*.

We prove now that the order of a conjugate class in a group is a divisor of the order of the group. Let C_ρ be a conjugate class of order $h\rho$ in a group G of order N and $a, b, c, \ldots$ be the elements in $C\rho$. Let there be g elements $s_1, s_2, \ldots, s_g$ in G which commute with a. We proceed to show that the elements of G can be divided into $h\rho$ sets each set containing g elements and no element of G occurring in more than one set. Let K_1 denote the totality of the g elements which commute with a. Since b is the transform of a, there exists an element p of the group which transforms a into b. Then the elements $s_1p, s_2p, \ldots, s_gp$ all transform a into b for $(sp)^{-1}a(sp) = p^{-1}s^{-1}asp = p^{-1}ap = b$ where s stands for any one of the elements $s_1, s_2, \ldots, s_g$. The set of the g elements $s_1p, s_2p, \ldots, s_gp$ may be denoted by the symbol K_2. We can further show that any element which transforms a into b must belong to K_2. For, if there is an element q which transforms a into b then $(qp^{-1})^{-1}\ aqp^{-1} = pq^{-1}aqp^{-1} = pbp^{-1} = a$ so that qp^{-1} belongs to K_1 and therefore q to K_2. Proceeding in a similar manner we show that there are exactly g elements of G which transform a into c and so on. Thus the elements of G can be divided into $h\rho$ sets $K_1, K_2, \ldots, K_{h_\rho}$ which have no element in common and each of which contains g elements. Thus $N = h_\rho\, g$.

In every group, the identity element forms a class by itself. In the example of the abstract group already given, it may be verified that E constitutes one conjugate class, $a\ a^2$ constitute another and $b\ ab\ a^2b$ constitute the third.

Self-Conjugate Subgroups.—If H is a subgroup of G and if $t^{-1}\ at$ is an element of H for all elements a of H and t of G, H is called a self-conjugate subgroup of G. In the example of the abstract group given above, the sub-set of elements $E\,b$ may be seen to form a subgroup which is not self-conjugate whereas the set of elements $E\,a\,a^2$ forms a subgroup which is self-conjugate. It follows from the definition that a self-conjugate subgroup contains complete sets of conjugate classes of elements of the original group.

Factor Groups.—If H is a self-conjugate subgroup of a group G, the cosets of H in G may be taken as the elements of a group called the factor group G/H under a suitable operation. Let the cosets of H, in G be H, a_2H, a_3H, ... Now each coset consists of h elements where h is the order of H. Let the product $a_iH.a_j\,H$ denote the totality of the h^2 products formed by combining the h elements in a_iH with the h elements in a_jH by means of the group operation pertaining to G. $H.H$ consists of all the elements in H each repeated h times for if a is an element in H, the h elements $a.H$ are distinct and belong to H itself and this is true for every element a in H.

Let the symbol $\odot$ in $a_iH \odot a_jH$ represent the process of multiplying all the elements in a_iH with those of a_jH as above but taking only the distinct elements resulting from the process. The cosets of H in G form a group under the operation $\odot$. For, as H is a self-conjugate subgroup of G, $H\ a_j = a_j\,H$ and

$$a_iH \odot a_jH = a_ia_j\ H \odot H = a_ia_jH.$$

Now $a_i a_j H$ can be shown to be one of the cosets of H. $a_i a_j$ is an element in G and therefore belongs to one or other of the cosets of H say $a_k H$. Then $a_i a_j = a_k b$ where b is in H and $a_i a_j H = a_k(bH) = a_k H$. Thus the cosets of H combine among themselves under the operation $\odot$. H is the identity element in the factor group. The associative law for the elements in the factor group is a consequence of the associative law in G. The inverse of any coset aH in the factor group is the coset containing the element a^{-1}.

In the example of the abstract group given above, the subgroup $E\,a\,a^2$ has been shown to be a self-conjugate subgroup. The factor group G/H consists of the two elements H and bH and the multiplication Table of G/H is given below:

	H	bH
H	H	bH
bH	bH	H

An important example of a factor group is furnished by the group of symmetry operations of an infinite body or pattern. If we consider all the translational symmetry elements, they satisfy the group postulates and thus form a subgroup, say H, of the entire group of symmetry operations of the pattern. We will show that this group is a self-conjugate subgroup of G. If R stands for a rotation through ψ and T stands for a translation with components a, b, c along the co-ordinate axes, by taking the axis of rotation of R as the Z axis, the operation $R^{-1}TR$ changes x to $x + a\cos\psi - b\sin\psi$, y to $y + a\sin\psi + b\cos\psi$ and z to $z + c$ and is therefore equivalent to a translation $a\cos\psi - b\sin\psi$, $a\sin\psi + b\cos\psi$, c. If R and T are symmetry operations of the pattern, $R^{-1}TR$ is also a symmetry operation and therefore this translation belongs to H. Same result holds good even if R is a screw. Similarly if R stands for either a pure or a glide reflection plane, $R^{-1}TR$ is equivalent to a translation a, b, $-c$ and is an element belonging to H. Thus H is a self-conjugate subgroup of G. The elements of the factor group G/H will now consist of classes of elements which are obtained by taking any one typical element like R and multiplying that element by all the translations. Space groups are usually described in terms of the factor groups G/H.

Permutation Groups.—Let the integers 1 to 6 be regarded as symbols. These 6 symbols when written in the form $P = (143)\,(25)\,(6)$ imply that in the operation P each number in a bracket is to be replaced by the succeeding number in it, and the last number in the bracket is to be replaced by the first in that bracket. Thus the operation P changes the symbols 1, 2, 3, 4, 5 and 6 respectively into 4, 5, 1, 3, 2 and 6. Such an operation which involves a rearrangement of a set of chosen symbols is called a permutation. The unaltered symbols like 6 in P are sometimes omitted in writing the permutations. It follows from the definition that a permutation is not altered by changing the symbols in a bracket without affecting the cyclic order. The arrangement of the cycles in a permutation is also arbitrary. Thus P may be written as (25) (143) (6). If a permutation consists of only one cycle, it is called a cyclic permutation. If P and Q are two permutations, the product permutation PQ is defined as that which gives the same result as may be obtained by first performing the rearrangement as per the permutation P and then as per Q. If Q stands for (123) (46) (5), the product PQ where P stands for the permutation already chosen may be written as $(143)\,(25)\,(6) \times (123)\,(46)\,(5) = (164)\,(253)$. Denoting (164) (253) by S, the multiplication may easily be verified by taking any arbitrary arrangement of the six symbols 1 to 6 and operating upon it with the permutation S. The result will be identical with that obtained by operating first with P and then with Q which is the product permutation PQ. The process of writing down the product permutation PQ will also be clear from the above example. In the permutation P, 1 is followed by 4 and in the permutation Q, 4 is followed by 6. Therefore, 1 is to be followed by 6 in the product permutation S and similarly for 6 and the other symbols. The multiplication of permutations is not commutative. In the above example, whereas $PQ = (164)(253)$, $QP = (152)(346)$. If P, Q and R are three permutations on n symbols and if P changes the symbol α to β, Q changes β to γ and R changes γ to δ, it is easily seen that both the operations $(P.Q).R$ and $P.(Q.R)$ change α to δ. This is true for all the n symbols. Thus $(P.Q).R = P.(Q.R)$ which establishes the associative law for the multiplication of permutations. A set of permutations on n symbols, which forms a group under the combination rule explained above, is called a permutation group of degree n. The set of all possible permutations on n symbols forms a group of order $n!$ and is called the symmetric group of order $n!$ This may also be referred to as the symmetric group of degree n. It may easily be verified that the elements, E, (123) (456), (321) (654), (14) (26) (35), (15) (24) (36), (16) (25) (34) form a permutation group. If it is intended to write E explicitly, it is to be written as (1) (2) (3) (4) (5) (6). It may be noted that the permutation (321) (654) is the inverse of the permutation (123) (456). The inverse permutation is always obtained by writing down in the reverse order the symbols in each bracket of the original permutation.

If we take the digits 1, 2, 3 as our symbols and construct a group out of them taking all possible permutations, we obtain the symmetric group of order 3! and it consists of the following elements divided into three conjugate classes:

$$(1)(2)(3) \quad \ldots \quad \text{Class 1 } (E)$$

$$\left.\begin{array}{l}(12)(3)\\(13)(2)\\(23)(1)\end{array}\right\} \quad \ldots \quad \text{Class 2 } (C_1)$$

$$\left.\begin{array}{l}(123)\\(132)\end{array}\right\} \quad \ldots \quad \text{Class 3 } (C_2)$$

We shall use the word interchange to denote an operation in which two symbols are interchanged, the others remaining unaffected. A cyclic permutation (123 ... n) is equivalent to the product (12) (13) ... (1n). Any permutation is a product of cyclic permutations and is therefore expressible as a product of interchanges. The expression of a given permutation as a product of interchanges is not unique. It may be shown that the number of interchanges in various forms of the product is always odd or even according as it is odd or even in any one alternative. For, if we consider the effect of a permutation on the determinant

$$\begin{vmatrix} 1 & 1 \ldots\ldots\ldots\ldots & 1 \\ x_1 & x_2 \quad \ldots\ldots\ldots & x_n \\ x_1^2 & x_2^2 \quad \ldots\ldots\ldots & x_n^2 \\ \ldots\ldots & \ldots\ldots\ldots\ldots & \\ x_1^{n-1} & x_2^{n-1} \quad \ldots\ldots\ldots & x_n^{n-1} \end{vmatrix}$$

it should either keep it unaltered or should change its sign. Taking the first alternative, we find that when it is expressed as a product of interchanges, it should consist of an even number in whatever way we express it, because the effect of each is to interchange two columns and therefore to change the sign of the determinant. In the second alternative, similar argument shows that the product should consist of an odd number of interchanges only. Permutations can thus be divided into two types, namely odd and even, according as they can be expressed as products of an odd or an even number of interchanges. In the example cited earlier, the permutations (123) and (132) can be expressed as products of interchanges like (12) (13) and (13) (12). They may also be written as (12) (23) (13) (12) and (13) (23) (12) (13) and so on. Similarly permutations of the type (12) (3) may be written as (12) or (13) (12) (23), etc. Thus the permutations coming under the class C_1 are odd and those coming under the classes E and C_2 are even.

Isomorphous Groups.—If G_1 and G_2 are two groups of the same order, not necessarily with the same composition rule, and if each element of G_1 can be made to correspond uniquely to an element of G_2 in such a way that the product of two elements of G_1 corresponds to the product of the corresponding two elements of G_2 then, G_1 and G_2 are said to be simply isomorphous and the correspondence is called isomorphic mapping. The two groups $a^2 = E$, $b^2 = E$, $ab = ba$ and E, (12) (34), (13) (24), (14) (23) are easily seen to be simply isomorphous with the correspondence $E \rightarrow E$, $a \rightarrow (12)$ (34), $b \rightarrow (13)$ (24) and $ab \rightarrow (14)$ (23). The first group is the abstract form of the second group. In the following Chapters, we shall find it convenient to take permutation groups isomorphous with groups of symmetry operations. For example, it may be seen that the group of symmetry operations of a regular tetrahedron is isomorphous with the symmetric group of degree 4.

Let G_1 and G_2 be two groups of different orders. If to each element of G_1, there corresponds one or more elements of G_2 and *vice versa* and also the product of any two elements of G_1 corresponds to the product of any two corresponding elements of G_2 and *vice versa*, the two groups G_1, G_2 are then said to be isomorphous. The relationship is called a general isomorphism or homomorphism (or homomorphic mapping) between them. An important example of a general isomorphism is afforded by the elements of a factor group G/H and the elements of the group G. Here every element of G/H corresponds to all the elements in G which form a coset of H in G. A more general isomorphism may easily be pictured by taking the factor groups G/H_1 and G/H_2 where H_1 and H_2 are self-conjugate subgroups of different orders in G.

Direct Product Groups.—If G_1 and G_2 are two groups with the same composition rule and if the elements of G_1 commute with the elements of G_2, there being no common element between G_1 and G_2 except the identity element, the totality of the elements t, where $t = s_1 s_2$, forms a group G

which is called the direct product of G_1 and G_2. Here s_1 is an element of G_1 and s_2 is an element of G_2. The direct product G may be symbolically written as $G_1 \times G_2$. The above definition may be extended to the direct product of any number of groups.

The direct product group may also be defined in either of the following two ways. G is called the direct product of G_1 and G_2 if G_1 and G_2 are self-conjugate subgroups of G, $g = g_1 g_2$ where g, g_1, g_2 are elements of G, G_1 and G_2 respectively and identity is the only common element between G_1 and G_2. Alternatively G may be called the direct product of G_1 and G_2 if as above $g = g_1 g_2$ and also equal to $g_2 g_1$ and g_1 and g_2 are uniquely determined for a given g. A more general definition of G may be given as the set of elements (g_1, g_2) in which multiplication is defined as

$$(g_1, g_2) \cdot (g_1', g_2') = (g_1 g_1', g_2 g_2').$$

As an example of a direct product group, it may be seen that the group G of symmetry operations of the benzene molecule which consists of E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$, i, $2S_3$, $2S_6$, σ_h, $3\sigma_v'$, $3\sigma_v''$ is the direct product of the group G_1 and G_2 where G_1 consists of the elements E, $2C_6$, $2C_3$, C_2, $3C_2'$, $3C_2''$ and G_2 of E and i. We may take the group of symmetry operations of the flat strip as an example of a direct product of three groups. It can be expressed as $G_1 \times G_2 \times G_3$ where G_1 consists of the elements $E\, C_x$, G_2 of $E\, C_y$ and G_3 of $E\, i$.

The elements of the group G defined by the relations $a^3 = E$, $b^2 = E$ and $a^2 b = ba$ can be written as products of elements of the group G_1 consisting of the elements $E\, a\, a^2$ and those of the group G_2 consisting of the elements $E\, b$. Nevertheless, G is not the direct product of G_1 and G_2 because the elements of G_1 do not commute with those of G_2.

CHAPTER V

MATRIX GROUPS

Matrices.—An array A $= | a_{pq} |$ of $m \times n$ elements a_{pq}, $(p = 1, 2, \ldots, m;\ q = 1, 2, \ldots, n)$ arranged in m rows and n columns in the following manner is called a matrix:

$$A = \begin{vmatrix} a_{11} & a_{12} & \ldots & a_{1n} \\ a_{21} & a_{22} & \ldots & a_{2n} \\ \ldots & \ldots & \ldots & \ldots \\ a_{m1} & a_{m2} & \ldots & a_{mn} \end{vmatrix}.$$

The matrix is called rectangular if $m \neq n$ and square if $m = n$. A rectangular matrix consisting of only one column is called a column matrix. Similarly, a rectangular matrix consisting of only one row is called a row matrix. In the case of a square matrix, n is called its degree. In general, the elements a_{pq} are complex numbers. If all the elements a_{pq} are zero, the matrix is called a zero matrix and is denoted by the symbol 0. Two matrices $A = | a_{pq} |$ and $B = | b_{pq} |$ are said to be equal, if $a_{pq} = b_{pq}$ for all indices p and q. A square matrix $A = | a_{pq}|$ in which $a_{pq} = 0$ if $p \neq q$ is called a diagonal matrix. If all the diagonal elements in a diagonal matrix are equal, it is called a scalar matrix. A scalar matrix whose diagonal elements are all unity is called the unit matrix and is denoted by I_n (or E_n or simply I or E). A matrix in which each row and each column consists of only one non-zero element, which is unity, is called a permutation matrix. The matrix obtained by changing rows into columns and columns into rows of a matrix A is called the transpose of A and is denoted by A^+ (or A'). The transposed conjugate matrix is usually written as A^*. A matrix $| a_{pq} |$ is called symmetric, anti-symmetric, Hermitian and anti-Hermitian according as $a_{pq} = a_{qp}$, $a_{pq} = - a_{qp}$, $a_{pq} = \bar{a}_{qp}$, $a_{pq} = - \bar{a}_{qp}$ respectively.

The sum of two matrices $A = | a_{pq} |$ and $B = | b_{pq} |$ is defined as the matrix $A + B = | a_{pq} + b_{pq} |$, that is, the matrix obtained by adding corresponding elements in the component matrices. If λ is a number (scalar) and A is a matrix (a_{pq}), we define λA as the matrix $| \lambda a_{pq} |$, that is the matrix obtained by multiplying every element in A by λ. This process is called scalar multiplication. It may be noted that matrix addition is both commutative and associative. The direct sum $A \dotplus B$ of two matrices A and B is defined as the matrix $\begin{vmatrix} A & 0 \\ 0 & B \end{vmatrix}$.

Linear Transformations.—Associated with every square matrix $| a_{pq} |$ of degree n, we can define a linear mapping of the complex space (called the carrier space) of n dimensions by the following equations:

$$\begin{aligned} x_1' &= a_{11}x_1 + \dots + a_{1n}\, x_n \\ x_2' &= a_{21}x_1 + \dots + a_{2n}\, x_n \\ &\dots\dots\dots\dots\dots\dots \\ x_n' &= a_{n1}x_1 + \dots + a_{nn}x_n \end{aligned}$$

or briefly

$$x_p' = \sum_q a_{pq}x_q. \qquad (p, q = 1, 2, \dots, n).$$

If the determinant $| a_{pq} |$ of the coefficients a_{pq} (called the determinant of the matrix $| a_{pq} |$) is not zero, $x_1, x_2, \dots, x_n$ may be solved in terms of $x_1', x_2', \dots, x_n'$ in the form

$$x_q = \sum_p a_{qp}'x_p'. \qquad (p, q, = 1, 2, \dots, n).$$

The matrix A, in this case, is called non-singular and the matrix $| a_{qp}' |$ is called the inverse of the matrix A and is written as A^{-1}. If the determinant of the matrix A is zero, A^{-1} does not exist and A is called a singular matrix.

If

$$x_p'' = \sum_q b_{pq}\, x_q'$$

is a second linear mapping defined by the matrix $B = | b_{pq} |$, the result of applying consecutively the two mappings

$$x_p' = \sum_q a_{pq} x_q$$

and

$$x_p'' = \sum_q b_{pq} x_q'$$

is the mapping

$$x_p'' = \sum_q c_{pq} x_q$$

where

$$c_{pq} = \sum_r b_{pr} a_{rq}.$$

This relation may be used for defining the product of the two matrices A and B as the matrix $C = BA$, whose elements c_{pq} are as given above. We may now define the product BA by the above rule even when the matrices A and B are rectangular. It is necessary that the number of columns in B must be equal to the number of rows in A. Two such matrices are called conformable. It may be noted that matrix multiplication is in general non-commutative but associative and also both sides distributive with respect to matrix addition, *i.e.*, $A\,(B + C) = AB + AC$ and $(B + C)\,A = BA + CA$.

A very important property of matrix multiplication, which we often use, is that two conformable matrices may be similarly partitioned into sub-matrices so that matrix multiplication can be applied in the same form as if the sub-matrices are elements of a matrix. For example, if $|A, P|$, $|B, Q|$, $|C, R|$, $|D, S|$ are pairs of conformable sub-matrices of two conformable matrices, we have

$$\begin{vmatrix} A & B \\ C & D \end{vmatrix} \; \begin{vmatrix} P & Q \\ R & S \end{vmatrix} = \begin{vmatrix} AP + BR & AQ + BS \\ CP + DR & CQ + DS \end{vmatrix}$$

The identity matrix corresponds to the identical mapping and it may be noted that for a non-singular matrix A, we have $AA^{-1} = A^{-1}A = E$. If x is a column matrix and if the quadratic form $x^*Ax \geqq 0$ and equal to 0 only when $x = 0$, A is called a positive definite matrix. Two matrices A and B are said to be equivalent if a relation of the form

$A = T^{-1}BT$ exists. The sum of the diagonal elements of a square matrix is called the spur of the matrix.

A square matrix $A = | a_{pq} |$ is said to be unitary, if the corresponding linear mapping keeps the quadratic form $\sum_{i=1}^{n} x_i\bar{x}_i$ invariant. The necessary and sufficient condition for A to be unitary is that $A^*A = AA^* = E$, *i.e.*,

$$\sum_r a_{rp}\bar{a}_{rq} = \delta_{pq}$$

or alternatively

$$\Sigma\, a_{pr}\, \bar{a}_{qr} = \delta_{pq}.$$

$\delta_{pq} = 1$ when $p = q$ and $\delta_{pq} = 0$ when $p \neq q$. A matrix A is called normal if $AA^* = A^*A$. Hermitian and unitary matrices are normal. A matrix A is said to be orthogonal, if the corresponding linear mapping keeps the form $\sum_{i=1}^{n} x_i^2$ invariant. The necessary and sufficient condition for a real matrix A to be orthogonal is $AA' = A'A = E$, *i.e.*,

$$\sum_r a_{rp}\, a_{rp} = \delta_{pq}$$

or alternatively

$$\sum_r a_{pr}\, \bar{a}_{qr} = \delta_{pq}.$$

From what has been said above, it is clear that we may find sets of matrices obeying all the group postulates. Any one such set defines a group of linear transformation. The following is an example of a group of linear transformation matrices:

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \qquad \begin{vmatrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix} \qquad \begin{vmatrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{vmatrix}$$

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{vmatrix} \qquad \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{vmatrix} \qquad \begin{vmatrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{vmatrix}$$

That this set of six matrices satisfies all the group postulates under the rule of matrix multiplication already explained may be verified.

Equivalent Matrices.—If $| a_{ik} |$ is a square matrix denoted by A and consisting of n rows and n columns and I is the unit matrix of the same order, the determinantal equation

$$\begin{vmatrix} a_{11}-\lambda & a_{12} & \cdots & a_{1n} \\ a_{21} & a_{22}-\lambda & \cdots & a_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ a_{n1} & a_{n2} & \cdots & a_{nn}-\lambda \end{vmatrix} = 0$$

which may concisely be written as $| A - \lambda I | = 0$, is called the characteristic equation of the matrix A. The n roots of this equation are called the characteristic roots of the matrix. The roots may all be distinct or some of them may be repeated. If B is a second matrix, the matrix $| B^{-1}AB - \lambda I |$ can be written as $| B^{-1}AB - \lambda B^{-1}IB |$ which is equal to the matrix product $| B |^{-1} | A - \lambda I.| \, | B |$. The determinant of the matrix $| B^{-1}AB - \lambda I |$ is therefore equal to the product of the determinants of the matrices $| B |^{-1}$, $| A - \lambda I |$, $| B |$ which is simply the determinant of the matrix $| A - \lambda I |$. Thus

$$| A - \lambda I | = | B^{-1}AB - \lambda I |$$

showing that equivalent matrices A and $B^{-1}AB$ have the same characteristic equation.

The sum of the elements in the leading diagonal of a matrix $| a_{ik} |$ has been designated the spur of the matrix. This is also the coefficient with its sign changed of λ^{n-1} in the characteristic equation of the matrix. Since equivalent matrices have the same characteristic equation, they have got the same spur.

Reducible and Irreducible Matrix Representations of Groups.—If G is a group consisting of the elements s_0, s_1, ..., etc., and H a group of matrices M_0, M_1, ..., etc., not necessarily of the same order as G, such that each element s_i corresponds to a matrix M_i and also the product of two s's corresponds to the product of the two corresponding M's, the group of matrices is said to define a representation Γ of the group G. The same matrix may correspond to several elements of the group but to each element of G there must correspond only one matrix in H. In other words, the groups G and H are isomorphous. If T is a fixed matrix and if the matrices TM_iT^{-1}, where M_i runs through all the matrices of H, take the form

$$\left|\begin{array}{c:c} A_i & B_i \\ \hdashline C_i & D_i \end{array}\right|$$

where A_i and D_i are square matrices not necessarily of the same dimension but each having a fixed number of rows and columns for all i and C_i is a zero matrix, Γ is said to be a reducible representation. An alternative definition of reducible and irreducible representations of a group will be given in Appendix I. If, in addition, B_i also is a zero matrix, Γ is said to be completely reducible. It will be shown later that such a situation arises when the variables x_1, x_2, . . ., etc., upon which the matrices may be assumed to operate can be combined into different linear combinations y_1, y_2, . . ., etc., which may be divided into two sets y_1, y_2, . . ., y_k; y_{k+1}, y_{k+2}, . . ., etc., such that $y_1, y_2, \ldots, y_k$ and y_{k+1}, y_{k+2}, . . ., etc., combine among themselves separately. The fixed matrix T referred to before will then be the matrix of transformation of the x's into the y's for, if $y = Tx$ and $x' = Mx$, we have $y' = Tx' = TMx = TMT^{-1}y$. When Γ is completely reducible, the matrices A_i and D_i separately define two representations Γ_1 and Γ_2 of G. When no such reduction is possible, we say that Γ is an irreducible representation of the group. If the matrices of H are all unitary, the representation is called unitary. In the simple case, where H consists of the identity matrix of dimension one, that is unity itself, the representation is called the identity (or the total symmetric) representation.

If for two non-singular matrix representations $\Gamma_i\,(M_0, M_1, \ldots,$ etc.) and $\Gamma_j\,(N_0, N_1, \ldots,$ etc.) of a group G, it is possible to find a fixed matrix T such that $N_r = T^{-1} M_r T$ for all r, the two representations Γ_i and Γ_j are said to be equivalent. Similarly, if S is a non-singular matrix, the set of matrices SMS^{-1} define another representation Γ_k of the group G, equivalent to Γ_i. It is easy to see that Γ_j and Γ_k are equivalent. The definition of equivalence thus satisfies the usual rules of equivalence, namely, (1) $\Gamma \sim \Gamma$, (2) if $\Gamma_1 \sim \Gamma_2$ then $\Gamma_2 \sim \Gamma_1$ and (3) if $\Gamma_1 \sim \Gamma_2$ and $\Gamma_2 \sim \Gamma_3$ then $\Gamma_3 \sim \Gamma_1$. The symbol $\sim$ denotes equivalence. The representations of a group can thus be divided into classes of equivalent representations and by representation we mean generally a class of equivalent representations.

As an example of a reducible representation of a group, we shall consider the isomorphism between the symmetric group of degree three and the group of matrices given below.

$$E \sim \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \qquad (23)\,(1) \sim \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix}$$

$$(12)\,(3) \sim \begin{vmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{vmatrix} \qquad (123) \sim \begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{vmatrix}$$

$$(13)\,(2) \sim \begin{vmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{vmatrix} \qquad (132) \sim \begin{vmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{vmatrix}$$

This isomorphism defines a reducible representation of the symmetric group because if we form $T^{-1}MT$ where M runs through all the above matrices; T being $\frac{1}{9}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 1 & -2 \\ 1 & -2 & 1 \end{vmatrix}$ and T^{-1} being $\frac{1}{3}\begin{vmatrix} 1 & 1 & 1 \\ 1 & 0 & -1 \\ 1 & -1 & 0 \end{vmatrix}$, we obtain respectively the matrices

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & -1 \\ 0 & 0 & -1 \end{vmatrix}, \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{vmatrix}, \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & -1 & 1 \end{vmatrix}, \begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & -1 \end{vmatrix}, \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 1 \\ 0 & -1 & 0 \end{vmatrix}$$

All these are of the form $\left|\begin{array}{c|c} A & B \\ \hline C & D \end{array}\right|$, where A and D are square matrices of dimensions one and two respectively and B and C are zero matrices. The matrices A and D respectively define irreducible representations of the symmetric group. Thus the original representation is reducible.

Kronecker Square and Symmetrized Kronecker Square Representations.—Consider the set of equations

$$x_1' = a_{11}x_1 + a_{12}x_2$$
$$x_2' = a_{21}x_1 + a_{22}x_2.$$

We have

$$(x_1')^2 = (a_{11}x_1 + a_{12}x_2)(a_{11}x_1 + a_{12}x_2)$$
$$= a_{11}^2x_1^2 + a_{11}a_{12}x_1x_2 + a_{12}a_{11}\,x_2x_1 + a_{12}^2x_2^2.$$

Similarly

$$x_1'x_2' = a_{11}a_{21}x_1^2 + a_{11}a_{22}x_1x_2 + a_{12}a_{21}x_2x_1 + a_{12}a_{22}x_2^2$$
$$x_2'x_1' = a_{21}a_{11}x_1^2 + a_{21}a_{12}x_1x_2 + a_{22}a_{11}\,x_2x_1 + a_{22}a_{12}x_2^2$$
$$(x_2')^2 = a_{21}^2x_1^2 + a_{21}a_{22}x_1x_2 + a_{22}a_{21}x_2x_1 + a_{22}^2x_2^2.$$

These equations may be written in the form

$$\left|\begin{array}{c} (x_1')^2 \\ x_1'x_2' \\ x_2'x_1' \\ (x_2')^2 \end{array}\right| \begin{array}{c} = \\ = \\ = \\ = \end{array} \left|\begin{array}{cccc} a_{11}a_{11} & a_{11}a_{12} & a_{12}a_{11} & a_{12}a_{12} \\ a_{11}a_{21} & a_{11}a_{22} & a_{12}a_{21} & a_{12}a_{22} \\ a_{21}a_{11} & a_{21}a_{12} & a_{22}a_{11} & a_{22}a_{12} \\ a_{21}a_{21} & a_{21}a_{22} & a_{22}a_{21} & a_{22}a_{22} \end{array}\right| \left|\begin{array}{c} x_1^2 \\ x_1x_2 \\ x_2x_1 \\ x_2^2 \end{array}\right| .$$

The matrix of transformation will be written as $A \times A$ or $| A |^2$ and is also equal to

$\left|\begin{array}{cc} a_{11}A & a_{12}A \\ a_{21}A & a_{22}A \end{array}\right|$, where A stands for the matrix $\left|\begin{array}{cc} a_{11} & a_{12} \\ a_{21} & a_{22} \end{array}\right|$

and is called the Kronecker square of the matrix A. It is easily verified that if a set of matrices define a representation of a group, the set consisting of the Kronecker squares of the corresponding matrices also defines a representation of the group.

If in the above set of equations we take x_1x_2 to be equal to x_2x_1, we obtain a matrix of three rows and three columns only as follows:

$$\left|\begin{array}{c} (x_1')^2 \\ x_1'x_2' \\ (x_2')^2 \end{array}\right| = \left|\begin{array}{ccc} a_{11}a_{11} & 2a_{11}a_{12} & a_{12}a_{12} \\ a_{11}a_{21} & a_{11}a_{22}+a_{12}a_{21} & a_{12}a_{22} \\ a_{21}a_{21} & 2a_{21}\,a_{22} & a_{22}a_{22} \end{array}\right| \left|\begin{array}{c} x_1^2 \\ x_1x_2 \\ x_2^2 \end{array}\right|$$

The transformation matrix may now be symbolically written as $| A |^{(2)}$ and is called the symmetrized Kronecker square of A. It may be noted that

$$\begin{aligned} \text{spur } | A |^2 &= (\text{spur } A)^2 = (a_{11} + a_{22})^2 \\ \text{spur } | A |^{(2)} &= \frac{(\text{spur } A^2) + (\text{spur } A^2)}{2} \\ &= \frac{(a_{11} + a_{22})^2 + a_{11}^2 + 2a_{12}a_{21} + a_{22}^2}{2} . \end{aligned}$$

If a set of matrices define a representation of a group, the symmetrized Kronecker squares also define a representation of the group. When the matrices A are only one-dimensional, there is no distinction between $| A |^2$ and $| A |^{(2)}$.

Kronecker Direct Product of Two Representations.—Consider the set of equations:

$$x_1' = a_{11}x_1 + a_{12}x_2$$
$$x_2' = a_{21}x_1 + a_{22}x_2$$

and

$$y_1' = b_{11}y_1 + b_{12}y_2$$
$$y_2' = b_{21}y_1 + b_{22}y_2.$$

The products $x_1'y_1'$, $x_1'y_2'$, $x_2'y_1'$, $x_2'y_2'$ will then transform as follows:

$$\begin{vmatrix} x_1'y_1' \\ x_1'y_2' \\ x_2'y_1' \\ x_2'y_2' \end{vmatrix} = \begin{vmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & a_{12}b_{21} & a_{12}b_{22} \\ a_{21}b_{11} & a_{21}b_{12} & a_{22}b_{11} & a_{22}b_{12} \\ a_{21}b_{21} & a_{21}b_{22} & a_{22}b_{21} & a_{22}b_{22} \end{vmatrix} \begin{vmatrix} x_1y_1 \\ x_1y_2 \\ x_2y_1 \\ x_2y_2 \end{vmatrix}.$$

This transformation matrix may be written as

$$\begin{vmatrix} a_{11}B & a_{12}B \\ a_{21}B & a_{22}B \end{vmatrix}, \text{ where } B \text{ stands for the matrix } \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix}.$$

The matrix is called the direct product matrix and is written as $A \times B$. The matrices A and B in the general case may be of any dimension and also need not operate on the same number of symbols. If A and B run through two sets of matrices each set defining a representation of a given group, the matrices $A \times B$ define also a representation of the group. The relation

$$\text{spur } A \times B = (\text{spur } A) \times (\text{spur } B)$$

easily follows. Kronecker powers and products involving more than two factors may be similarly defined. If $A = | a_{pq} |$ and $B = | b_{pq} |$ are two square matrices of degrees m and n respectively, the mn by mn matrix $A \times B$ defined by

$$A \times B = \begin{vmatrix} a_{11}\,B & a_{12}\,B & \dots & \dots \\ a_{21}\,B & a_{22}\,B & \dots & \dots \\ \dots & \dots & \dots & \dots \end{vmatrix}$$

is called the Kronecker or the direct product of the two matrices A and B. We may similarly define the product $B \times A$. If x and y are two vectors in the carrier spaces of A and B with components $x^1, x^2, \ldots, x^m$ and $y^1, y^2, \ldots, y^n$, the mn products $x^r y^s$ $(r = 1, 2, \ldots m, s = 1, 2, \ldots, n)$ may be regarded as components of a vector in the carrier space of $A \times B$. If the matrices are all equal, the Kronecker direct product of r factors is written as $| A |_r$. The dimension of $| A |_r$ is m^r.

The matrix $| A |_{(r)}$ called the symmetrized Kronecker rth power of A is the transformation induced on the distinct products $x^{j_1} x^{j_2}, \ldots, x^{j_r}$ by the trasformation $x \rightarrow Ax$. The dimension of $| A |_{(r)}$ is

$$\frac{(r + m - 1)!}{(m - 1)!\, r!}$$

CHAPTER VI

THE WAVE EQUATION AND ITS PROPERTIES

Vibrations of a String.—It is well known that the differential equation

$$\frac{\partial^2 Y}{\partial x^2} = \frac{1}{v^2}\frac{\partial^2 Y}{\partial t^2}$$

represents the propagation of a wave along the length of a string (x direction) with a velocity v. It is easily verified that $Y = A \sin(nt + mx)$ is a solution of this equation provided $v = \pm n/m$. If we further lay down the condition that at a given instant of time ($t = 0$), all the points of the string should be stationary, we will be ruling out advancing waves and restricting ourselves to the stationary ones. This means that dY/dt should be zero for all values of x when $t=0$. The solutions of the differential equation are then restricted to the form $Y = A \cos nt \sin mx$. They are continuous in their range because there is yet no restriction on the values that m can take and therefore on the values that n can take. Let us now confine ourselves to a finite length l of the string and introduce boundary conditions ($Y = 0$ at all values of t for $x = 0$ or l) resulting from the ends of the string being fixed. The solutions are discrete in such a case because they are subject to the condition $Y = A \cos nt \sin ml = 0$. This requires $ml = k\pi$ where $k = 1, 2, 3, \ldots$, etc. $k = 0$ is a trivial solution because it corresponds to a non-vibrating condition of the string. Moreover, Y is easily seen to repeat at intervals of $2\pi/m$ which may be called the wave-length and we get the relation $\lambda = 2l/k$. Integral values of k correspond to aliquot fractions of twice the length of the string. Boundary conditions thus impose very severe restrictions on the values of the parameter m and therefore on the wave-length λ which should be a sub-multiple of $2/k$.

We thus see that the problem in general has no solution except when the parameter k or the wave-length λ has one of a set of discrete values. These values for which alone the problem with boundary conditions has a solution, are called the eigenvalues (propervalues, characteristic values). The corresponding solutions are $Y = A \cos nt \sin mx = y \cos nt$. y stands for $A \sin mx$ and these functions with different permissible values of m are called the eigenfunctions (properfunctions, characteristic functions) of the problem. It may, however, be noted that the eigenvalues and eigenfunctions of the vibrating string could be obtained by removing the time factor from the differential equation in the beginning itself by assuming $Y = ye^{i\omega t}$.

The Wave Equation.—The propagation of a wave in three dimensions is represented by the differential equation

$$\frac{\partial^2 \Psi}{\partial x^2} + \frac{\partial^2 \Psi}{\partial y^2} + \frac{\partial^2 \Psi}{\partial z^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial t^2} \cdot$$

v is the velocity of wave propagation and Ψ is a quantity measuring the wave amplitude. We shall assume Ψ to be periodic in time and write

$$\Psi = \psi(x, y, z)\, e^{\pm 2\pi i \nu t}.$$

Substituting this value of Ψ in the differential equation, we have

$$\Delta\psi + \frac{4\pi^2\nu^2}{v^2}\psi = 0.$$

Assuming the De-Broglie relation $\lambda = h/p$ obtained by associating a wave of wave-length λ with every particle of momentum p, kinetic energy $p^2/2m$ and total energy $W = p^2/2m + V$ where V is the potential energy, we can write the above equation as

$$\Delta\psi + \frac{8\pi^2 m (W - V)}{h^2}\psi = 0.$$

This is the well-known Schrödinger amplitude equation and may be recast in the following form:

$$\left(-\frac{h^2}{8\pi^2 m}\Delta + V\right)\psi = W\psi.$$

If the expression occurring before ψ on the left-hand side of the equation is regarded as an operator H, it is empirically obtained in the usual manner by writing the operator $h/2\pi i\, \partial/\partial x$ for p_x, etc., and the operator $x\times$ (*i.e.*, multiplication by x) for x, etc., in the Hamiltonian form of the total energy. The relation may be represented symbolically as

$$H\psi = W\psi,$$

where H is now to be regarded as an operator. In case we are dealing with a system containing several particles of different masses, the operator H will then stand for

$$\sum_i\left(-\frac{h^2}{8\pi^2 m_i}\Delta_i + V\right)$$

and V and W are the potential and total energies of the whole system.

Eigenvalues and Eigenfunctions.—In the operational equation given above, ψ is a function of the various co-ordinates relating to the particles in the system. In the particular case we are dealing with, H is an energy operator and W a number independent of the co-ordinates. As ψ has ultimately to represent a physical quantity, we determine solutions of the above equation which satisfy the condition that it remains bounded, continuous and single valued throughout the whole range permitted for the co-ordinates. As in the case of the vibrating string, such solutions are called the characteristic solutions of the equation, and those values of W for which at least one such solution exists are called the characteristic energy values. It may be noted that while the boundary conditions in the case of the vibrating string resulted in the eigenvalues and eigenfunctions becoming a discrete set, in the wave mechanical problem, analogous quantization of the values of the parameter is obtained from the requirement that the ψ function shall be bounded, continuous and single valued in the permitted range. The values of the parameter thus quantized are called the eigenvalues and the corresponding solutions ψ are called the eigenfunctions. The eigenvalues may be discrete or continuous.

Linear Operators and Manifolds.—An operator H is said to be linear if $H(\psi_1 + \psi_2) = H\psi_1 + H\psi_2$ and $H(a\psi) = aH\psi$ where a is a constant. It is easily verified that the differential operator of the previous Section is linear in the above sense. If $\psi_1, \psi_2, \ldots$, etc., are the eigenfunctions associated with the operator H and a definite eigenvalues W, the linear character of the operator H results in every linear combination of the ψ's with constant coefficients becoming an eigenfunction for the same eigenvalue. If in any case, n independent eigenfunctions can be chosen such that any other eigenfunction can be expressed linearly in terms of the chosen ones, they are said to constitute the basis for an n-dimensional manifold corresponding to the given eigenvalue. The totality of the eigenfunctions constitutes the manifold.

The scalar product of two functions ψ_1 and ψ_2 is denoted by the symbol (ψ_1, ψ_2) and is defined as $\int \psi_1{}^*\psi_2 dV$, the integration extending over the whole range of the variables. If the scalar product of any two functions is equal to zero, the functions are said to be orthogonal. The scalar product of a function with itself is written as (ψ, ψ) and is equal to $\int \psi^* \psi dV$. If the functions are so chosen that this integral is equal to unity in each case, they are said to have been normalized. H is said to be a Hermitian operator, if the relation

$$(H\psi_1, \psi_2) = (\psi_1, H\psi_2)$$

holds good. Let us now consider two distinct eigenvalues W_1 and W_2 corresponding to two eigenfunctions ψ_1 and ψ_2 and confine ourselves to Hermitian operators. We have $H\psi_1 = W_1\psi_1$ and $H\psi_2 = W_2\psi_2$.

From the hypothesis

$$(H\psi_1, \psi_2) = (\psi_1, H\psi_2).$$

It then follows that

$$(W_1\psi_1, \psi_2) = (\psi_1, W_2\psi_2)$$

or $$W_1 \int \psi_1^* \psi_2 \, dV = W_2 \int \psi_1^* \psi_2 \, dV$$

or $$(W_1 - W_2)(\psi_1, \psi_2) = 0.$$

Since $$W_1 \neq W_2, (\psi_1, \psi_2) = 0.$$

Even if the eigenvalues are not distinct (*i.e.*) if there are a set of eigenfunctions $\psi_1 \ldots \psi_r$ corresponding to a single eigenvalue W, it is possible to choose them in such a way that they are mutually orthogonal. A proof by induction may be given in the following manner. If p of the above r functions are mutually orthogonal, we can construct a $p + 1$th orthogonal function given by

$$\psi_{p+1} = \phi - \psi_1 (\phi, \psi_1) - \psi_2 (\phi, \psi_2) \ldots - \psi_p (\phi, \psi_p),$$

where ϕ is such a member of the r-dimensional manifold that it is not expressible as a linear combination of $\psi_1 \ldots \psi_p$. It is now easy to verify that ψ_{p+1} is orthogonal to all functions ψ_1 to ψ_p. Normalization of eigenfunctions is easy to effect as it involves multiplication by suitable numerical factors only. Thus, in all problems where operators are confined to the Hermitian type, the basis eigenfunctions can always be taken as mutually orthogonal and may be normalized.

If out of an n-dimensional manifold, it is possible to pick out a set of eigenfunctions all of which can be represented as linear combinations of n_1 eigenfunctions where $n_1 < n$, the set will constitute a sub-manifold which is of n_1 dimensions. If a sub-manifold is of dimension n_1, it is often possible to find another sub-manifold of dimension n_2 such that $n_1 + n_2 = n$ and the members of the latter are orthogonal to those of the former.

Invariant Manifolds.—For every eigenfunction ψ belonging to a certain manifold, if $R\psi$ is also an eigenfunction in the same manifold where R is any operator operating on the ψ function, the manifold is said to be invariant under R. It may sometimes be possible to find a sub-manifold which is invariant under R or a set of such operators. In such a case, the manifold is said to be reducible with respect to the operators. If it is not possible to find an invariant sub-manifold, then the manifold itself is said to be irreducible. Generally every finite manifold can be reduced into two or more irreducible and mutually orthogonal sub-manifolds.

Physical Quantities as Operators.—While writing the wave equation in the form $H\psi = W\psi$, special emphasis was laid in the previous Sections of this Chapter to the case where H is the Hamiltonian function converted into an operator. In such form, the significance of the equation is that the eigenfunction ψ should be so chosen that the operator representing the energy, when acting on it, should result in a constant multiple of the function. The multiplying constant is then a possible energy value of the system. In addition, it has been possible to conceive of operators corresponding to various other physical quantities as well operating on such functions giving definite results. These operators are obtained by replacing the momenta and co-ordinates by the corresponding operators as in the case of the Hamiltonian function. If F is an operator of this type which when operating on one such eigenfunction ψ characteristic of the system results in the equation

$$F\psi = f\psi,$$

where f is a constant not depending on the co-ordinates defining ψ, f is an eigenvalue of the physical quantity F which the system can assume. If ψ simultaneously satisfies the equations

$$H\psi = W\psi \text{ and } F\psi = f\psi$$

then ψ is a simultaneous eigenfunction for the two operators H and F.

According to the postulates of quantum mechanics, the average value which a dynamical variable F can assume when the system is in a state described by a function ψ is given by the relation

$$\text{average}_\psi\ F = \frac{\int\psi^* F\psi dV}{\int\psi^*\psi dV} = \int \psi^* F\psi dV$$

if the ψ function is normalized. In the numerator, F is to be regarded as an operator. If ψ is such that $F\psi = f\psi$ and because f is a constant, we obtain average$_\psi$ $F = f$.

If the eigen ψ's of an operator F are assumed to be a complete set of orthogonal functions $\psi_1, \psi_2, \ldots,$ we can put any $\psi = \Sigma a_n \psi_n$ and write

$$f = \sum_m \sum_n a_m^* a_n F_{mn}, \text{ where } F_{mn} = \int\psi_m^* F\psi_n dV.$$

If $m = n$, F_{mn}'s are the several 'diagonal elements' of the matrix which may be associated with the quantity F and are to be interpreted as representing the average values which F can assume in the corresponding eigenstates of the system. If $m \neq n$, F_{mn}'s are the several 'non-diagonal elements' of the matrix associated with F and are to be interpreted as representing the transition probabilities connecting the state m with the state n.

Harmonic Oscillator.—The potential energy of a particle bound to a fixed point by a force $-kx$ will be $\frac{1}{2}kx^2$ when it is at a distance x. The wave equation can be written as

$$\frac{d^2\psi}{dx^2} + \frac{8\pi^2\mu}{h^2}(W - \tfrac{1}{2}kx^2)\psi = 0$$

We make the substitutions

$$x = aS; \quad a^2 = \frac{h\nu}{k}; \quad \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}; \quad \psi = U(S)\, e^{-\frac{1}{2}S^2}$$

and rewrite the equation as

$$\frac{d^2U}{dS^2} - 2S\frac{dU}{dS} + U\left(\frac{2W}{h\nu} - 1\right) = 0$$

Seeking for polynomial solutions of a finite degree, this differential equation can be solved by the power series method, if we express U as

$$U = a_0 + a_1 S + a_2 S^2 + \ldots\ldots\ldots$$

Substituting this series in the differential equation and obtaining the coefficient of S^n, we have

$$a_{n+2}(n+2)(n+1)+a_n\left(\frac{2W}{h\nu}-2n-1\right)=0.$$

If U is to be an nth degree polynomial it follows that $a_n \neq 0$ and $a_{n+1}=a_{n+2}=\ldots=0$. The above equation therefore requires that

$$W=(n+\tfrac{1}{2})\,h\nu \text{ for } n=0,1,2,\ldots,\text{etc.}$$

For each one of these energy values, the differential equation has, therefore, a solution which is a 0th, 1st, 2nd degree polynomial according as $n=0$, 1, 2, etc. These solutions are the Hermite polynomials. Some properties of these polynomials are given in Appendix V. The polynomials are even or odd functions of the parameter and therefore of the co-ordinate x as the degree n is even or odd. We give below the normalized eigenfunction corresponding to a polynomial solution of degree v. The oscillator in this state possesses energy equal to $(v+\frac{1}{2})\,h\nu$ and is ascribed a vibrational quantum number v.

$$\psi_v=\frac{1}{\sqrt{a}}\sqrt{\frac{1}{2^v\,v\,!\,\pi^{\frac{1}{2}}}}\,e^{-\frac{1}{2}\left(\frac{x}{a}\right)^2}H_v\left(\frac{x}{a}\right).$$

Eigenfunctions of Hydrogen-like Atoms.—The wave equation for a system consisting of a massive centre of charge Ze to which is bound an electron at a distance r, their mutual potential energy $V(r)$ being $-Ze^2/r$ when written in polar co-ordinates takes the form (Appenxid VI)

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)$$
$$+\frac{8\pi^2\mu}{h^2}[W-V(r)]\,\psi=0.$$

μ is the reduced mass of the centre and the bound electron. We seek for solutions of the form $\psi=S(r)\,T(\theta,\phi)$. Substituting this in the wave equation and dividing throughout by ST/r^2, we have

$$\frac{1}{S}\frac{\partial}{\partial r}\left(r^2\frac{\partial S}{\partial r}\right)+\frac{8\pi^2\mu r^2}{h^2}[W-V(r)]$$

$$=-\left[\frac{1}{T\sin^2\theta}\frac{\partial^2 T}{\partial\phi^2}+\frac{1}{T\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)\right].$$

Each of the above expressions can be equated to a constant λ, because the left-hand side is a function of r only while the right-hand side is a function of θ and ϕ only. We have

$$\frac{1}{\sin^2\theta}\frac{\partial^2 T}{\partial\phi^2}+\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial T}{\partial\theta}\right)+\lambda T=0$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial S}{\partial r}\right)+\frac{8\pi^2\mu S}{h^2}[W-V(r)]-\frac{\lambda S}{r^2}=0$$

Partial differentiation in the second equation is of no special significance. By making a further substitution

$$T(\theta,\phi)=P(\theta)\,Q(\phi),$$

in the first equation and proceeding in a similar manner, we can separate it into the following pair of equations:

$$\frac{d^2Q}{d\phi^2}+QC=0$$

$$\frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta\frac{dP}{d\theta}\right)+\lambda P-\frac{CP}{\sin^2\theta}=0$$

These three equations can be solved independently. Taking the equation in ϕ, we have the following solutions:

$Q = Ae^{im\phi}$ where $C = m^2$ and $m = 0, \pm 1, \pm 2$, etc.

The requirement that Q functions should be normal leads to the value $1/\sqrt{2\pi}$ for A.

Taking the equation in θ and substituting $x = \cos\theta$ and $C = m^2$, we have

$$(1-x^2)\frac{d^2P}{dx^2}-2x\frac{dP}{dx}+\left[\frac{m^2}{x^2-1}+\lambda\right]P=0.$$

Substituting $P = A(1 - x^2)^{\frac{m}{2}} v$, we have

$$(1 - x^2)\frac{d^2v}{dx^2} - 2(m + 1)x\frac{dv}{dx} + (\lambda - m - m^2)v = 0.$$

Writing v as a polynomial $\Sigma a_k x^k$ and substituting and picking out the coefficient of x^k and equating it to zero, we have $a_{k+2}(k + 2)(k + 1) - a_k[(k + m)(k + m + 1) - \lambda] = 0.$ If v is to be a polynomial of the kth degree, $a_{k+2} = 0$ and $a_k \neq 0$. The condition to be satisfied is, therefore,

$$(k + m)(k + m + 1) = \lambda.$$

Writing l for $k + m$, we have $\lambda = l(l + 1)$ with the condition that $l \geqslant m$. For a given l, m can be $0, 1, 2, \ldots, l$. Thus the P function for a particular l and m is given by

$$P_{lm} = A(1 - x^2)^{\frac{m}{2}} v_l^m(x).$$

The polynomial $v_l^m(x)$ can be expressed in the following manner:

$$v_l^m(x) = \frac{d^m}{dx^m}(P_l(x)].$$

P_l's are the Legendre polynomials. Using the properties of these polynomials, one can obtain the value of A so as to normalize the P functions (Appendix V). Substituting this value, we can write P_{lm} as

$$P_{lm} = \sqrt{\frac{2l + 1}{2} \cdot \frac{(l - m)!}{(l + m)!}} \sin^m\theta \, v_l^m(\cos\theta)$$

Taking the equation in S and substituting

$$R = rS; \quad W = \pm\frac{2\pi^2\mu e^4 z^2}{n^2h^2}; \quad r = \frac{nr_0}{2}x; \; r_0 = \frac{h^2}{4\pi^2\mu e^2 z};$$

we have

$$\frac{d^2R}{dx^2} + \left[\pm\tfrac{1}{4} + \frac{n}{x} - \frac{l(l + 1)}{x^2}\right]R = 0.$$

We consider the alternative with $-\frac{1}{4}$ as it gives the discrete set of eigenvalues. Putting $R = Ayx^{l+1}\, e^{-x/2}$, we get

$$x\frac{d^2y}{dx^2} + [2(l+1) - x]\frac{dy}{dx} + (n - l - 1)\,y = 0.$$

Expressing y as a polynomial and proceeding as in the previous case, we obtain the condition $n = J + l + 1$ if y is to be a polynomial of the Jth degree, n is obviously $\geqslant l + 1$ because $J = 0, 1, 2$, etc. We shall designate the polynomial y by $L_{n+l}^{2l+1}(x)$ and this represents the $2l + 1$th derivative of the Laguerre polynomial of degree $n + l$. y is a polynomial of degree $J = n - l - 1$. Obtaining the value of A from the known properties of the Laguerre polynomials (Appendix V) so as to normalize the eigenfunctions, we have

$$S_{nl} = \sqrt{\frac{1}{2n}\cdot\frac{(n-l-1)\,!}{[(n+l)\,!]^3}\cdot\left(\frac{2}{nr_0}\right)^3}$$

$$\times\left(\frac{2r}{nr_0}\right)^l e^{-\frac{r}{nr_0}}\, L_{n+l}^{2l+1}\left(\frac{2r}{nr_0}\right).$$

The full wave function ψ is $S_{nl}P_{lm}Q_m$.

The Rigid Rotator.—We have already shown in the previous section that for a rotator, the following equation holds good:

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial S}{\partial r}\right) + \frac{8\pi^2\mu S}{h^2}[W - V(r)] - \frac{\lambda S}{r^2} = 0.$$

In the case of a rigid rotator like a diatomic molecule with a fixed internuclear distance r, the first term vanishes and μr^2 is the moment of inertia I. Since $V(r)$ can be put equal to zero and $\lambda = l(l + 1)$, we have the following expression for W, the energy of the rotator:

$$W = \frac{h^2}{8\pi^2 I}\, l\,(l + 1).$$

l is called the angular momentum quantum number of the molecule.

CHAPTER VII

VIBRATIONS OF A DYNAMICAL SYSTEM

Kinetic and Potential Energies of a Dynamical System.—The configuration of a system of particles can be described in terms of a certain number of quantities $q_1, q_2, \ldots, q_n$ which may be called the co-ordinates of the system. We consider cases in which the number of co-ordinates required to specify the configuration is always finite. If x_i, y_i, z_i are the Cartesian rectangular co-ordinates of the ith particle in the system, x_i, y_i, z_i are functions* of $q_1, q_2, \ldots, q_n$. The kinetic energy T of the system is

$$\tfrac{1}{2}\Sigma m_i\,(x_i^2+\dot{y}_i^2+\dot{z}_i^2)$$

the summation extending over all the particles. The kinetic energy, when expressed in terms of the co-ordinates $q_1, q_2, \ldots, q_n$ and their time derivatives $\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n$, becomes a homogeneous quadratic function of $q_1, \dot{q}_2, \ldots, \dot{q}_n$. Since T is always positive, it follows that T is a positive definite quadratic form in $q_1, q_2, \ldots, \dot{q}_n$.

We choose the equilibrium configuration of the given system as a standard configuration. Suppose the system is displaced from such a configuration called the initial to another configuration called the final. If the forces acting on the system are such that the work done by these forces in a displacement is independent of the series of configurations through which the system moves but depends only on the initial and final configurations, the field of force is said to be a conservative field. For such a force field, the work done by the forces of the field in a displacement of the system from the configuration $q_1, q_2, \ldots, q_n$ to the standard con-

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* If the system contains moving constraints, x_i, y_i, z_i are functions, not only of $q_1, q_2, \ldots, q_n$ but time also. In what follows we assume that there are no moving constraints and that x_i, y_i, z_i do not involve time explicitly.

figuration is a function of $q_1, q_2, \ldots, q_n$ only. This function is called the potential energy of the system and is denoted by the symbol $V(q_1, q_2, \ldots, q_n)$.

Lagrangian Equations of Motion.—A dynamical system is said to be holonomic if a displacement represented by any arbitrary infinitesimal changes in the co-ordinates is possible. Otherwise it is said to be non-holonomic. We consider here only holonomic systems. Consider the displacement of the system in which the co-ordinate q_r is changed to $q_r + \delta q_r$ while the rest are unaltered. This displacement of the system is possible since the system is assumed to be holonomic. If we introduce a new function L defined by the relation $L = T - V$, the equations of motion may be written as*

$$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_r}\right) - \frac{\partial L}{\partial q_r} = 0.$$

These are called Lagrangian equations of motion and L is called the Lagrangian function.

Normal Modes of Oscillation.—A configuration in which a dynamical system can remain permanently at rest is defined as an equilibrium configuration of the system. The values of the co-ordinates $q_1, q_2, \ldots, q_n$ in the several possible equilibrium configurations can be obtained by solving the Lagrangian equations of motion in which $\ddot{q}_1, \ddot{q}_2, \ldots, \ddot{q}_n$; $\dot{q}_1, \dot{q}_2, \ldots, \dot{q}_n$ are all put equal to zero. This reduces to solving the equations $\partial L/\partial q_r = 0$. If we expand V in ascending powers of $q_1, q_2, \ldots, q_n$, the term independent of the co-ordinates can be omitted as it gets eliminated in the equations of motion. There cannot be terms which are linear in the co-ordinates on account of the equations $\partial V/\partial q_r = 0$. Thus, only the second and higher degree terms in the potential energy function enter into the Lagrangian equations of motion.

Suppose a system is initially placed near an equilibrium configuration. In some cases, the particles in the system remain always in the neighbourhood of their equilibrium

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* E. T. Whittaker, *Analytical Dynamics of Particles and Rigid Bodies.*

positions and never acquire large displacements. Motions of this type are called vibrations about an equilibrium configuration and the system is said to be stable. In some other cases, the particles in a system when placed near an equilibrium configuration tend to move further and further away from the equilibrium position assuming large values for the co-ordinates. Such configurations are unstable. We consider now the vibrations of a system about a configuration of stable equilibrium and confine ourselves to small amplitudes of motion. We have already shown that T is a homogeneous quadratic function of $q_1, q_2, \ldots, q_n$ with coefficients involving $q_1, q_2, \ldots, q_n$ if we consider the case where T does not involve time explicitly. We can, without loss of generality, assume that the equilibrium configuration corresponds to the zero values of the co-ordinates. Since $q_1, q_2, \ldots, q_n$ are very small in the problem under consideration, we may, in the expression for T_2 replace the coefficients of the squares and products of $\dot{q}_1, q_2, \ldots, \dot{q}_n$ by the constant values which they assume when $q_1, q_2, \ldots, q_n$ are put equal to zero. The kinetic energy is therefore a homogeneous quadratic function of $q_1, \dot{q}_2, \ldots, \dot{q}_n$ with constant coefficients. Neglecting the higher terms in the potential energy expression also for the same reason, V can be expressed as a homogeneous quadratic form in the co-ordinates q. The kinetic and potential energies of the system may thus be written as general quadratic forms:

$$T = \tfrac{1}{2} \Sigma\, a_{ij} \dot{q}_i \dot{q}_j ; \qquad i, j = 1, 2, \ldots, n$$

$$V = \tfrac{1}{2} \Sigma\, b_{ij} q_i q_j ; \qquad i, j = 1, 2, \ldots, n.$$

These two expressions can be simultaneously reduced to the canonical forms (Appendix II)

$$2T = \Sigma\, \dot{Q}_k{}^2; \quad 2V = \Sigma\, \lambda_k Q_k{}^2;$$

by suitable linear combinations Q's of the original co-ordinates q. The λ's in the latter expression can be shown to be the roots of the equation (Appendix II)

$$\begin{vmatrix} b_{11} - \lambda a_{11} & b_{12} - \lambda a_{12} & \dots & b_{1n} - \lambda a_{1n} \\ b_{21} - \lambda a_{21} & b_{22} - \lambda a_{22} & \dots & b_{2n} - \lambda a_{2n} \\ \dots & \dots & \dots & \dots \\ b_{n1} - \lambda a_{n1} & b_{n2} - \lambda a_{n2} & \dots & b_{nn} - \lambda a_{nn} \end{vmatrix} = 0.$$

Normal Frequencies.—When the kinetic and potential energies are put in the form

$$2T = \Sigma \dot{Q}_k^2; \quad 2V = \Sigma \lambda_k Q_k^2;$$

the Lagrangian equation of motion corresponding to any normal co-ordinate Q_r can be written as

$$\frac{d}{dt}\left(\frac{\partial T}{\partial \dot{Q}_r}\right) - \frac{\partial T}{\partial Q_r} = - \frac{\partial V}{\partial Q_r}.$$

This reduces to $\ddot{Q}_r = - \lambda_r Q_r$. A function Q_r of the co-ordinates of a dynamical system for which $\ddot{Q}_r = - \lambda_r Q_r$ is called a normal co-ordinate and the mode of oscillation described by Q is called a normal mode of oscillation. It follows from such equations of motion that each normal co-ordinate corresponds to an independent mode of vibration of the system. If some of the quantities $\lambda_1, \lambda_2, \dots, \lambda_n$ are not positive, the normal co-ordinates Q which correspond to such values of λ do not represent vibrations about an equilibrium configuration and the equilibrium configuration is unstable. If all the constants λ are positive, the equilibrium configuration is stable. An equilibrium configuration is therefore stable if the potential energy of the system is a positive definite form.

λ_r is related to the frequency ν_r of vibration by the equation

$$\lambda_r = 4\pi^2 \nu_r^2.$$

If the coefficient λ of any normal co-ordinate Q is distinct from the other λ's the corresponding normal mode is said to be non-degenerate. On the other hand, if two or more Q's have the same coefficient, the corresponding modes are said to be degenerate and the number of Q's which have the same frequency is called the degree of degeneracy. In such a case the choice of Q's is not unique.

It may now be seen that if the system is referred to any other set of co-ordinates which are not normal co-ordinates, such co-ordinates are linear functions of the normal co-ordinates. Thus every conceivable vibration of the system may be regarded as the superposition of some or all of the independent normal vibrations.

In order to obtain the normal modes and frequencies in an actual case, we have to first set up the general quadratic forms for the potential and kinetic energies and find out suitable combinations of the variables so that the potential and kinetic energies expressed in terms of the altered variables may not contain cross terms. When the number of particles in a system is small, the above procedure may conveniently be followed. The method, however, becomes increasingly complicated with increasing number of particles in a dynamical system. Group theoretical methods greatly simplify the work and we shall deal with them in this Chapter in some detail.

Orthogonality Relation between the Normal Co-ordinates.— In a normal mode of oscillation Q_a, every particle vibrates with the same frequency say ν_a about its equilibrium position. If $\delta_{xi}{}^a$ is the displacement of the ith particle in the x direction corresponding to the normal co-ordinate Q_a, it may be described by the equation

$$Q_a = \Sigma \delta_{xi}{}^a x_i$$

and we have

$$\delta_{xi}{}^a = A \cos (2\pi\nu_a t + \epsilon).$$

A varies with the particle i, and the equation of motion of the ith particle is taken in the form

$$4\pi^2\nu_a{}^2 m_i \delta_{xi}{}^a = F_x{}^i,$$

where $F_x{}^i$ is the total force acting on the particle i in the direction x. Denoting the x component of the force on the *i*th particle due to a unit displacement in the *y* direction of the *j*th particle by the symbol $K_{xy}{}^{ij}$, the above equation takes the form

$$4\pi^2 \nu_a{}^2 m_i \delta_{xi}{}^a = \Sigma\, K_{xy}{}^{ij} \delta_{yj}{}^a, \qquad i, j = 1, 2, \ldots, N.$$

If Q_b is another normal co-ordinate with a different frequency say ν_b, we have similarly the equation

$$4\pi^2 \nu_b{}^2 m_i \delta_{xi}{}^b = \Sigma\, K_{xy}{}^{ij} \delta_{yj}{}^b, \qquad i, j = 1, 2, \ldots \ldots, N.$$

Multiplying the former by $\delta_{xi}{}^b$ and the latter by $\delta_{xi}{}^a$, subtracting one from the other and summing up this result for all i and x, we obtain

$$4\pi^2 (\nu_a{}^2 - \nu_b{}^2) [\Sigma m_i \delta_{xi}{}^a \delta_{xi}{}^b] = \Sigma K_{xy}{}^{ij} [\delta_{xi}{}^b \delta_{yj}{}^a - \delta_{xi}{}^a \delta_{yj}{}^b] = 0$$

as the terms on the right side cancel in pairs by virtue of the relation $K_{xy}{}^{ij} = K_{yx}{}^{ji}$. Since $\nu_a \neq \nu_b$, it follows that

$$\Sigma m_i\, \delta_{xi}{}^a\, \delta_{xi}{}^b = 0.$$

This result is known as the orthogonality relation between the normal co-ordinates.

If ν_a corresponds to a set of degenerate normal co-ordinates, suitable linear combinations of these co-ordinates may be chosen so that the resulting set is orthogonal. Thus, a complete set of normal co-ordinates which are mutually orthogonal may be ascribed to a given system.

Symmetry Properties of Normal Modes.—Let Q_1, Q_2, $\ldots$, Q_p be a complete set of normal co-ordinates of a dynamical system. We consider a configuration in which all the normal co-ordinates, except one say Q_r with frequency ν_r, vanish. As explained in the previous Section, we use the symbol Q_r to denote also the configuration of the system. By this we mean that if $Q_r = a_1 q_1 + a_2 q_2 + \ldots, + a_n q_n$, the co-ordinates q_1, q_2, $\ldots$, q_n of the particles in the system take the values $a_1, a_2, \ldots, a_n$. The following argument holds good for any configuration but as we are primarily interested in normal modes and normal frequencies, we take a configuration corresponding to a normal mode. If we now perform a sysmmetry operation R of the point group appropriate to the given dynamical system, we obtain a new configuration which we represent by the symbol RQ_r. Since a symmetry operation is only a particular case of a movement already defined as an operation in which the distance between any two points remains unaltered, the configuration RQ_r has the same potential energy as Q provided the potential energy remains invariant whenever the mutual distances between all points of the body remain unaltered. This is, of course, true even if R is a movement and not necessarily a symmetry operation of the point group. But RQ_r is not a normal co-ordinate of the original system as the individual particles are no longer in the neighbourhood of their equilibrium positions. In fact, the motion described in RQ_r is such that a particle leaves the neighbourhood of its equilibrium position and goes over into the neighbourhood of the equilibrium position of one of its equivalents if R is a symmetry operation. We can however derive from the configuration RQ_r, a geometrically identical configuration $\bar{R}Q_r$ in the following way. If by means of the operation R the lth particle in the configuration RQ_r goes over into the kth particle, we shall suppose that the kth particle remains in its own neighbourhood but gets the motion of the lth particle. By doing the same for every particle, we keep all of them in their own original neighbourhoods, thus ensuring the invariance of the kinetic energy, and obtain a configuration of the system which is geometrically identical with RQ_r. This new configuration may be denoted by $\bar{R}Q_r$. The potential and kinetic energies in the configuration $\bar{R}Q_r$ are the same as in Q_r. Therefore $\bar{R}Q_r$ represents a normal co-ordinate having the same frequency ν_r as that of Q_r. Adopting this procedure for all the symmetry operations of the point group G appropriate to the system, we obtain the several normal co-ordinates $\bar{R}Q_r$ which have the same frequency ν_r. But all these normal co-ordinates $\bar{R}Q_r$ need not be linearly independent. Let $Q_1, Q_2, \ldots, Q_f$ be a complete set of linearly independent normal co-ordinates chosen from all the co-ordinates $\bar{R}Q_r$. Then the oscillation of frequency ν_r is said to be f-fold degenerate. Similarly, we take another normal co-ordinate independent of the above set and as before obtain a set of linearly independent normal co-ordinates of frequencies, say ν_s. In general $\nu_s \neq \nu_r$. If, however, they are equal, the corresponding degeneracy is called accidental degeneracy. This degeneracy cannot be anticipated from symmetry considerations. Proceeding thus, we divide all the normal co-ordinates of the system into linearly independent sets, each set containing only normal co-ordinates of the same frequency.

The above process separates the manifold of normal oscillations into irreducible sub-manifolds. Each irreducible sub-manifold may be associated with an irreducible representation of the group of symmetry operations. The transformation matrices corresponding to an irreducible sub-manifold having $Q_1, Q_2, \ldots, Q_f$ as the basis can be written from the equations

$$\bar{R}Q_i = \Sigma {}^1R_{ik}Q_k \; (i, k = 1, 2, \ldots, f).$$

The reducible representation Γ defined by all the normal co-ordinates will then be given by the following correspondence where ${}^1R_{ik}$, ${}^2R_{mn}\ldots$ denote the matrices in the irreducible representation of R corresponding to the 1st, 2nd, etc., sets:

$$R \sim \bar{R} \sim \left|\begin{array}{ccccc} {}^1R_{ik} & 0 & 0 & \cdot & 0 \\ 0 & {}^2R_{mn} & 0 & \cdot & 0 \\ \cdot & \cdot & \cdot & \cdot & \cdot \end{array}\right|$$

Representation defined by the Cartesian Co-ordinates.— Take any set of three mutually perpendicular axes X, Y, Z and through the equilibrium position of each particle in the given system, choose three axes parallel to the X, Y, Z system. Let x_r, y_r, z_r be the co-ordinates of the rth particle in its displaced position with reference to the axes through its equilibrium position. A dynamical system consisting of n particles is completely defined by the $3n$ co-ordinates

$x_1, y_1, z_1, \ldots, x_n, y_n, z_n$. It has already been stated that all the normal co-ordinates may be expressed as linear functions of the $3n$ Cartesian co-ordinates. The relation between the two sets of co-ordinates may be given by a transformation matrix in the form

$$\begin{vmatrix} Q_1 \\ Q_2 \\ \cdot \\ \cdot \\ \cdot \\ \\ Q_{3n} \end{vmatrix} = |T| \begin{vmatrix} x_1 \\ y_1 \\ \cdot \\ \cdot \\ \cdot \\ \\ z_n \end{vmatrix};$$

where T is a matrix of $3n$ rows and $3n$ columns. T is not an orthogonal matrix but if the masses of the particles are absorbed in the co-ordinates, *i.e.* if x_i stands for $\grave{x}_i = m_i^{\frac{1}{2}} x_i$, T can be taken as an orthogonal matrix. We have shown in the previous Section that the $3n$ Q's define a representation Γ of the point group. The above equation shows that the Cartesian co-ordinates define an equivalent representation Γ' of the point group. In fact if a symmetry operation R induces the transformation $Q' = MQ$, it induces the transformation $x' = T^{-1}MTx$, since $x' = T^{-1}Q' = T^{-1}MQ = T^{-1}MTx$. Thus the matrices of Γ' are transforms of the matrices of Γ by T. Consequently, the character of any operation R in the two representations Γ and Γ' is the same. It is easy to calculate the character of an operation R from the reducible representation defined by the $3n$ Cartesian co-ordinates. If the symmetry operation R takes over the particle l into the position of particle k, we have in general a relation of the type

$$Rx_k = ax_l + by_l + cz_l$$

and the character arising from x_k is zero. Similarly the characters arising from y_k and from z_k are zero. If, on the other hand, the kth particle is invariant under the operation R, we have

$$Rx_k = x_k \cos \phi - y_k \sin \phi$$
$$Ry_k = x_k \sin \phi + y_k \cos \phi$$
$$Rz_k = \pm z_k,$$

the + or − sign in the last relation being used according as R is a pure rotation or a rotation-reflection through ϕ. In the above equations, the axis of rotation is taken as the Z-axis itself and the X and Y axes lie in a plane perpendicular to it. This choice of axes may not coincide with that taken in the beginning but it will not affect the character arising from a given R as two different co-ordinate systems give equivalent representations. It, therefore, follows that $1+2 \cos \phi$ and $-1+2\cos\phi$ are the characters for a pure rotation and a rotation-reflection respectively. We thus arrive at the result that an invariant point under the operation R gives rise to the character $\pm 1 + 2 \cos \phi$ whereas points which are not invariant do not contribute anything to the character. Hence in the reducible representation Γ' defined by the Cartesian co-ordinates, the character of any operation R is $U_R (\pm 1 + 2 \cos \phi_R)$ where U_R is the number of particles that remain in their original positions when R is performed.

It has already been pointed out that the representations defined by the normal co-ordinates and the Cartesian co-ordinates are equivalent. The character of an operation R is therefore the same in the two representations. In the previous paragraph we obtained the character of an operation R in the representation defined by the Cartesian co-ordinates. The same expression, namely, $U_R (\pm 1 + 2 \cos \phi_R)$, should therefore be equal to the character of the operation R in the representation Γ defined by the normal co-ordinates $Q_1, Q_2, \ldots, Q_{3n}$. We have seen that the normal co-ordinates can be divided into sets of irreducible manifolds and each set corresponds to an irreducible representation Γ_i. If there are n_i such sets that belong to a particular irreducible representation Γ_i, it follows that n_i is the number of times the representation Γ_i is contained in the representation Γ. To obtain the number n_i we use the formula (Appendix I)

$$n_i = \frac{1}{N} \Sigma h_\rho \chi_\rho' (R) \chi_i (R),$$

where N is the order of the point group G. $\chi_\rho'(R)$ is the compound character and stands for the expression $U_R (\pm 1 + 2 \cos \phi_R)$ and $\chi_i (R)$ is the character of the operation R in the ith irreducible representation of the group G.

The number derived in this manner includes the normal co-ordinates relating to translations and rotations of the point system as a whole. We can, however, exclude them by removing from $\chi_\rho'(R)$ the character arising from translations and rotations. In a translation all the particles get the same displacement and therefore the normal co-ordinates Q_x, Q_y and Q_z corresponding to the three translations transform under a symmetry operation R in the same way as the three unit vectors X, Y, Z along the co-ordinate axes. The unit vectors X, Y, Z relating to the three translations transform under R as

$$RX = X \cos \phi - Y \sin \phi$$

$$RY = X \sin \phi + Y \cos \phi$$

$$RZ = \pm Z,$$

the + or − sign in the last relation being used according as R is a pure rotation or a rotation-reflection. Hence the character arising from the normal co-ordinates corresponding to translations is $\pm 1 + 2 \cos \phi$. It may be noted that in this case there is no distinction between R and $\bar{R}$.

Let $Q\omega_x$, $Q\omega_y$, $Q\omega_z$ represent the normal co-ordinates corresponding to the three rotations about the co-ordinate axes. The displacement vector of a particle with position vector r in a configuration obtained by an infinitesimal rotation ω is given by the cross product $r \times \omega$. Hence $Q\omega_x$, $Q\omega_y$, $Q\omega_z$ transform in the same way as the displacement vector l. The three components of l are

$$l_x = y\delta z - z\delta y \ ; \ l_y = z\delta x - x\delta z \ ; \ l_z = x\delta y - y\delta x \ ;$$

if δx, δy, δz are the components of the rotation vector, l transforms under a rotation through ϕ around the Z-axis to l' where

$$
\begin{aligned}
l_x' &= l_x \cos\phi + l_y \sin\phi \\
l_y' &= -\, l_x \sin\phi + l_y \cos\phi \\
l_z' &= l_z.
\end{aligned}
$$

If the operation is a rotation-reflection through ϕ, the transformations will be

$$
\begin{aligned}
l_x' &= -\, l_x \cos\phi - l_y \sin\phi \\
l_y' &= l_x \sin\phi - l_y \cos\phi \\
l_z' &= l_z.
\end{aligned}
$$

Thus the character arising from a pure rotation is $1 + 2\cos\phi$ and from a rotation-reflection is $1 - 2\cos\phi$. Finally from the formula

$$n_i = \frac{1}{N} \Sigma\, h_\rho \chi_\rho'(R)\, \chi_i(R),$$

we obtain (1) the number of normal modes coming under Γ_i including translations and rotations, (2) the number of translations only, (3) the number of rotations only, (4) the number of normal modes excluding the translations and rotations if we use respectively for $\chi_\rho'(R)$ the four expressions

$$
\begin{aligned}
&(1)\quad \chi_\rho'(R) = U_{\mathrm{R}}(\pm 1 + 2\cos\phi_{\mathrm{R}}) \\
&(2)\quad \chi_\rho'(R) = \pm 1 + 2\cos\phi_{\mathrm{R}} \\
&(3)\quad \chi_\rho'(R) = 1 \pm 2\cos\phi_{\mathrm{R}} \\
&(4)\quad \chi_\rho'(R) = (U_{\mathrm{R}}-2)(1+2\cos\phi_{\mathrm{R}}) \text{ or } U_{\mathrm{R}}(-1+2\cos\phi_{\mathrm{R}}).
\end{aligned}
$$

In the last case, the first alternative corresponds to a pure rotation and the second to a rotation-reflection. The six co-ordinates T_x, T_y, T_z; R_x, R_y and R_z are called external co-ordinates.

Determination of the Normal Co-ordinates.—In order to obtain the normal co-ordinates that belong to an irreducible representation Γ_i of degree one, we start with the most general linear expression Q in the $3n$ Cartesian co-ordinates. If R is a group operation and λ is the character of the same in Γ_i we obtain RQ and write the equation

$$RQ = \lambda Q.$$

We get one such relation corresponding to each operation R of the group. If the number of modes of oscillation coming under Γ_i is only one, the normal co-ordinate Q is uniquely determined. On the other hand, if the number n_i is greater than one, the corresponding normal co-ordinates cannot in general be written uniquely without further information. We may express Q in the form

$$Q = a_1S_1 + a_2S_2, \ldots, + a_nS_n,$$

where $a_1, a_2, \ldots, a_n$ are arbitrary constants and $S_1, S_2, \ldots, S_n$ are functions of the $3n$ Cartesian co-ordinates which transform separately under the various operations R in the same way as Q. The actual normal co-ordinates in such a case cannot be obtained without a knowledge of the forces operating on the point system. The functions $S_1, S_2, \ldots, S_n$ are called the symmetry co-ordinates and the normal co-ordinates are obtained from the above relations by forming independent combinations of these functions with coefficients which depend upon the force constants.

The normal co-ordinates corresponding to translations and rotations can be written down independently and their transformation properties under group operations R can be checked with the help of the group characters. If through the equilibrium position of each particle we take three axes parallel to a parent system of rectangular axes, the three translations can be described by the normal co-ordinates

$$T_x = x_1 + x_2, \ldots + x_n,$$

$$T_y = y_1 + y_2, \ldots + y_n,$$

$$T_z = z_1 + z_2, \ldots + z_n.$$

To obtain the displacements of the particles in the normal modes corresponding to pure rotations, we note that for a small rotation about any axis, the displacement vector of a particle is given by the cross product $(r \times \omega)$ where, r is the position vector of the particle and ω is an infinitesimal vector in the direction of the axis of rotation. In some cases it may be convenient to adopt systems of axes which are not parallel to any parent system. In such cases suitable modifications must be made. If any of the translations or rotations come under a given irreducible representation, we form n_i' new functions which together with the normal co-ordinates relating to translations and rotations, if any, in Γ_i form a set of n_i mutually orthogonal co-ordinates.

In order to obtain the normal co-ordinates belonging to an irreducible representation of dimension r greater than 1, we take r general linear expressions $Q_1, Q_2, \ldots, Q_r$ in the Cartesian co-ordinates. This corresponds to a normal mode which is r-fold degenerate. As before, if R is a group operation and (a_{ik}) is the matrix representing R in the irreducible representation, we obtain $\bar{R}Q_i$ and equate it to $\sum\limits_k a_{ik}Q_k$. From these relations it follows that if there are n_i frequencies that belong to this representation, every one of these Q's will involve the same set of n_i functions $S_1, S_2, \ldots, S_{ni}$ with n_i arbitrary coefficients. As before, we allow for the normal co-ordinates corresponding to translations and rotations and form n_i' sets of mutually orthogonal symmetry co-ordinates, each set containing r expressions. We must make sure that the resulting sets transform themselves according to the transformation matrix $|a_{ik}|$. The n_i normal co-ordinates that belong to this representation are then obtained as before. It may, however, be mentioned that in this case the normal co-ordinates are not unique. Group theory helps us to determine the symmetry co-ordinates only.

Splitting of the Secular Equation.—It follows from the result of the previous Section that if $2T$ and $2V$ are expressed in terms of the symmetry co-ordinates, no cross products occur between co-ordinates that belong to different irreducible representations or between co-ordinates transforming according to different rows of the matrices in the same representation Γ^i. In view of these important properties, we can simplify the procedure of calculating the frequencies by considering the symmetry co-ordinates belonging to each irreducible representation separately.

After obtaining the symmetry co-ordinates, the problem remains to form the kinetic and potential energy expressions. We express the $3n$ Cartesian co-ordinates in terms of the symmetry co-ordinates and evaluate the kinetic and potential energies in the usual manner. The secular equation is of degree n_i. It may be noted that the transition to Cartesian co-ordinates is simple if the transformation matrix giving the symmetry co-ordinates in terms of the Cartesian co-ordinates is taken as orthogonal (which we can always do). The degrees n_i of the smaller equations into which the $3n$ by $3n$ secular equation is split, may be further reduced to degrees n_i' if we use a set of internal co-ordinates ($3n - 6$ in number in general and $3n - 5$ in the case of linear molecules). General formulae for writing the kinetic and potential energies in terms of internal co-ordinates are given in the next Section.

F and G Matrices.—Since the potential energy V of vibration of a molecule is usually expressed in terms of the variations from equilibrium values in the interatomic distances and angles between the bonds, it is sometimes* convenient to take the internal quantities (variations) as co-ordinates. If R_k are $3n - 6$ independent internal co-ordinates of a molecule consisting of n atoms, the potential energy may be written as

$$2V = \sum_{kl} F_{kl} R_k R_l \qquad k, l = 1, \ldots, 3n - 6.$$

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* E. B. Wilson, Jr., J. C. Decius and P. C. Cross, *Molecular Vibrations*, 1955.

In matrix notation, this may be written as $2V = R^\dagger F R$. The matrix of force constants $| F_{kl} |$ is called the F-matrix.

The kinetic energy T in rectangular Cartesian displacement co-ordinates x_i is given by

$$2T = \sum_i m_i \dot{x}_i^2 \qquad i = 1, \ldots, 3n$$

$$= \sum_i \dot{\hat{x}}_i^2 \qquad \hat{x}_i = (m_i)^{\frac{1}{2}}\, x_i$$

where m_i is the mass associated with x_i. We shall express the kinetic energy in terms of the internal co-ordinates. Suppose the internal co-ordinates are given by the equations

$$R_k = \sum_i d_{ki}\, \hat{x}_i \qquad k = 1, \ldots, 3n - 6$$

$$i = 1, \ldots, 3n$$

and the external co-ordinates (corresponding to the translations and rotations of the molecule as a whole) by the equations

$$(R_0)_k = \sum_i d_{ki}\, \hat{x}_i \qquad k = 3n - 5, \ldots, 3n$$

$$i = 1, \ldots, 3n.$$

In matrix notation the above two sets of equations may be written as

$$\left| \frac{R}{R_0} \right| = \left| \frac{D}{D_0} \right| (\hat{x}).$$

If $| C \,|\, C_0 |$ is the inverse matrix of $\left| \frac{D}{D_0} \right|$, we have

$$| \hat{x} | = | C \,|\, C_0 | \left| \frac{R}{R_0} \right| = | CR + C_0 R_0 |.$$

The kinetic energy may be written as

$$2T = | \dot{\hat{x}} |^\dagger | \dot{\hat{x}} | = | \dot{R}^\dagger C^\dagger + \dot{R}_0^\dagger C^\dagger_0 | \, | C\dot{R} + C_0 \dot{R}_0 |.$$

Since we are interested in writing the kinetic and potential energies in terms of the internal co-ordinates, we put $| R_0 | = | 0 |$ in the above equation. Then

$$2T = \dot{R}^\dagger C^\dagger C \dot{R}.$$

But we have $CD + C_0D_0 = E_{3n}$ and $DC = E_{3n-6}$. Here E_{3n} and E_{3n-6} are unit matrices of degrees $3n$ and $3n - 6$ respectively. We have

$$DD^\dagger C^\dagger C = E_{3n-6} \text{ and } 2T = R^\dagger \mid DD^\dagger \mid^{-1} R.$$

The matrix $DD^\dagger$ is denoted by the letter G and is called the G-matrix. The matrix element $G_{rs} = \sum_i d_{ri}d_{si}$. The kinetic energy is given by

$$2T = R^\dagger G^{-1} R.$$

The secular equation then takes the form

$$\mid F - (G^{-1})\, \lambda \mid = 0 \text{ or } \mid FG - E\lambda \mid = 0.$$

If we write the internal co-ordinate R_k in terms of the unweighted Cartesian co-ordinates x_i instead of the weighted co-ordinates $\hat{x}_i$ in the form

$$R_k = \Sigma B_{ki} x_i;$$

we have

$$B_{ki} = d_{ki} \sqrt{m_i}.$$

The quantities G_{rs} take the form

$$G_{rs} = \sum_i \mu_i B_{ri} B_{si} \qquad i = 1, 2, \ldots, 3n$$

where $\mu_i = 1/m_i$. Let the three Cartesian co-ordinates x_i pertaining to an atom t be taken as the components of a vector ρ_t and let the corresponding three coefficients B_{ki} in the expression for R_k be taken as the components of a vector S_{kt}. R_k may then be written as

$$R_k = \sum_1^n S_{kt} \cdot \rho_t$$

Here $S_{kt} \cdot \rho_t$ denotes the scalar product of the two vectors S_{kt} and ρ_t. The elements of the G-matrix may be given as

$$G_{rs} = \sum_t \mu_t \, S_{rt} . S_{st}.$$

The dot here again denotes the scalar product. General expressions for the S vectors can be easily derived and they are given below for a few typical cases.

In Fig. 5, the internal co-ordinates are taken as changes either in bond lengths or in the bond angle. Let the atoms 1, 2 and 3 form an angle 2α at the atom 1 in the equilibrium position and Q_{ij} be the reciprocal of the equilibrium distance between the atoms i and j. If the internal co-ordinate under consideration is the increase in the length of the bond formed by the atoms 1 and 2, we have

$$S_{k1} = e_{21} = -e_{12} \text{ and } S_{k2} = e_{12} = -e_{21}$$

e_{12} stands for a unit-vector from atom 1 to atom 2 and similar notation is adopted for unit vectors in other directions. If the internal co-ordinate under consideration is the variation of the angle 2α from its equilibrium value, we have

$$S_{k2} = Q_{12}\,(e_{31} + e_{12}\cos 2\alpha)/\sin 2\alpha$$

$$S_{k3} = Q_{13}\,(e_{21} + e_{13}\cos 2\alpha)/\sin 2\alpha$$

$$S_{k1} = -\,(S_{k2} + S_{k3}).$$

Using these S vectors and remembering that $e_{31}.e_{31} = 1$; $e_{21}.e_{21} = 1$; $e_{31}.\ e_{21} = \cos 2\alpha$, the matrix elements G_{rs} can be evaluated in the following form. The superscripts on the G's denote the number of atoms common to the bonds and bond angles indicated by the subscripts.

$$G_{rr}{}^{(2)} = \mu_1 + \mu_2$$

$$G_{rr}{}^{(1)} = \mu_1 \cos 2\alpha$$

$$G_{r\phi}{}^{(2)} = -\,\mu_1\,Q_{12}\sin 2\alpha$$

$$G_{\phi\phi}{}^{(3)} = \mu_2 Q_{12}{}^2 + \mu_3 Q_{13}{}^2 + \mu_1\,(Q_{12}{}^2 + Q_{13}{}^2 - 2\cos 2\alpha Q_{12}\,Q_{13})$$

It is not always possible to limit the choice of internal co-ordinates in a molecule to $3n - 6$, consistent with its symmetry. For example, in a molecule like CH_4, if we chose the variation in the length of one of the edges of the tetrahedron as a co-ordinate, we shall have to choose the variations in the lengths of the other five edges also as co-ordinates. The same applies to the angles at the centre. We can only make an arbitrary choice out of these twelve internal co-ordinates, if we restrict the number to $3n - 6$ which in

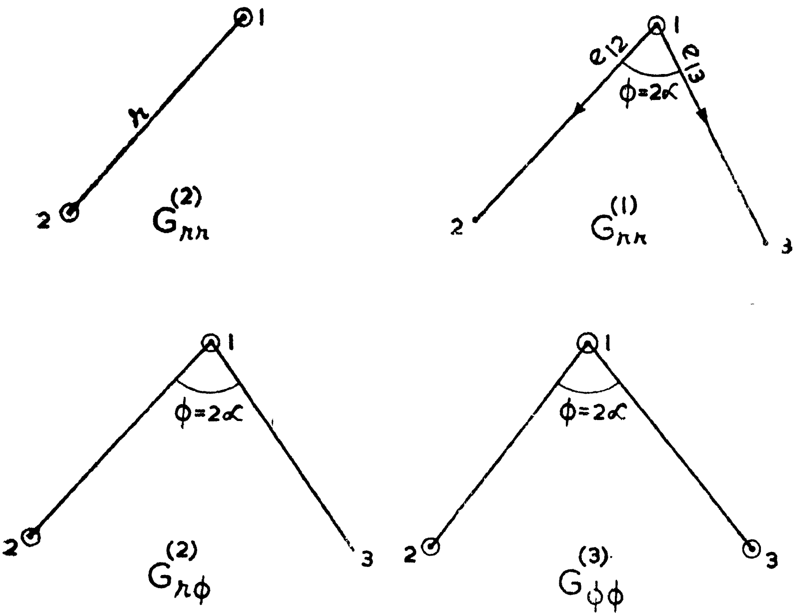

FIG. 5

this case is nine. In fact, this is so for most molecules, simpler ones being the only exceptions. Even in a simple case like a structure forming an equilateral triangle, we note that the variations in the three lengths and in the three angles have all a claim for being chosen as internal co-ordinates. In such a case, as we need only three internal co-ordinates, the choice of three out of the available total of six introduces an element of arbitrariness. Out of the larger number of co-ordinates, say *m* in a general case, we could make a selection of $3n - 6$ independent combinations and regard the rest as redundant. The *F* and *G* matrix method is formally used by taking all the *m* co-ordinates and omitting finally the rows and the columns in these matrices corresponding to the redundant co-ordinates in evaluating the normal frequencies. It is often difficult to weed out the redundant co-ordinates. For this reason, we give the alternative *F* and *G* matrix method in addition to the usual one, only in the case of some simple molecules.

CHAPTER VIII

VIBRATIONAL RAMAN EFFECT AND INFRA-RED ABSORPTION

The Molecule as a Dynamical System.—Every molecule in general may be regarded as a system of particles, namely, the atomic nuclei, which are bound together by various kinds of forces tending to keep the system in stable equilibrium. All that has been said in the foregoing Chapter on small oscillations about an equilibrium configuration of a dynamical system applies to the case of molecules. On account of the fact that there are electrons attached to the various nuclei which are in some way connected with the binding forces in a molecule, whenever a molecule finds itself in the field of an incident electromagnetic radiation, it begins to react with the field in a variety of ways. A detailed study of such a reaction furnishes the mechanism by which radiation and matter interact with each other. We shall now primarily concern ourselves with two major phenomena, namely, the Raman scattering and Infra-red absorption, because nuclear vibrations of the molecular system exhibit themselves most prominently in these two instances. Of these two, Raman scattering has an additional advantage from an experimental point of view as it is easily accessible for observation when studied in the visible region.

Raman Scattering by a Diatomic Molecule.—The general principles underlying the behaviour of a vibrating molecule in the field of a light wave may easily be understood by studying the simple case of a diatomic system. If the equilibrium nuclear distance is r_0, the kinetic and potential energies in a displaced position where the nuclear distance is $r_0 + q$ may be written as

$$2T = \mu\dot{q}^2; \quad 2V = Kq^2,$$

if harmonic forces are assumed. μ is the reduced mass of the nuclei and K is the constant characteristic of the binding between them. The corresponding equation of motion will be $q = -(K/\mu)\,q$. There is only one normal co-ordinate namely q and the corresponding normal frequency ν of vibration is given by $4\pi^2\nu^2\mu = K$. An incident electric vector $E = E_0 \sin 2\pi\nu_0 t$ may be regarded as inducing an electric moment vector $P = \alpha E_0 \sin 2\pi\nu_0 t$ in the molecule.* The molecule then behaves as a Hertzian oscillator and radiates energy in the form of electromagnetic waves of frequency ν_0. If α is a constant and does not vary with time, nothing else happens but if α is influenced by the normal oscillation of the molecule, it is altered periodically with the normal frequency ν and the electric moment of the oscillator at any given instant may be represented by the expression

$$E_0 \sin 2\pi\nu_0 t \left[\alpha_0 + \left(\frac{d\alpha}{dq}\right)_0 \sigma \cos(2\pi\nu t + \epsilon) + \tfrac{1}{2}\left(\frac{d^2\alpha}{dq^2}\right)_0 \sigma^2 \cos^2(2\pi\nu t + \epsilon) \ldots\right]$$

α_0 is the electric moment induced in the molecule in its equilibrium position by a unit incident radiation field and σ is the amplitude of the normal co-ordinate q. ϵ represents the phase of the molecular oscillation whose value is arbitrary. Taking only the first two terms of the above expression, they may be split up and written as

$$\alpha_0 E_0 \sin 2\pi\nu_0 t + \left(\frac{d\alpha}{dq}\right)_0 \sigma \frac{E_0}{2}\left[\sin\{2\pi(\nu_0+\nu)\,t+\epsilon\} + \sin\{2\pi(\nu_0-\nu)\,t-\epsilon\}\right].$$

The first term gives radiation of the same frequency as the incident field (Rayleigh scattering) and the second and the third terms give rise to radiations of frequencies $\nu_0 + \nu$ and

---

* α is a quantity connecting two vectors, namely, the incident electric vector and the induced moment vector. It is a tensor of the second order if P is regarded, to a first approximation, as being linear in E.

$\nu_0 - \nu$ (Raman scattering of the anti-Stokes and Stokes type respectively).

The extension of the above simple picture to a more complicated molecule possessing several normal modes of oscillation and corresponding normal frequencies is a formal one, chiefly because the normal modes are mutually independent.† It may, however, be mentioned that the existence of a term $(d\alpha/dq)_0$ is responsible and may be regarded as a necessary condition for this type of interaction between a nuclear system and radiation resulting in first order Raman scattering. Similarly, the second order Raman scattering when it exists in the case of a harmonic oscillator, should be regarded as arising from the existence of a term $(d^2\alpha/dq^2)_0$.

Infra-Red Absorption and Electric Moment.—In the foregoing Section, we considered a phenomenon in which the light wave falling on a molecule produces or induces in it an electric moment. The induced electric moment, besides the periodicity which it inherently possesses on account of the inducing light wave being itself periodic, also acquires superposed periodicities due to the vibrations of the molecular system about its equilibrium configuration. If, on the other hand, the molecular system has a permanent dipole moment quite apart from that induced by radiation, we are confronted with a different situation which gives rise to direct absorption under suitable conditions. The permanent dipole moment is a vector and if the molecule in its equilibrium state has a configuration resulting in such a moment, as in HCl for example, it is easily seen that when it rotates in the field of a light wave, a corresponding periodic variation in the interaction energy between the radiation field and the dipole moment is introduced and absorption occurs. Even if the molecule in its equilibrium state has no dipole moment, as in CO_2 for example, it is possible that in a normal oscilla-

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† A quantum mechanical theory of Raman scattering based on the Kramers Heisenberg dispersion formula is given in Appendix III.

tion by an unsymmetrical movement of the nuclei, the system will acquire an electric dipole moment which during the oscillation will vary with time in a periodic manner about the zero value, the periodicity being that of the normal oscillation itself. Absorption of energy in the corresponding region will again occur. Only, the region of frequency will be of the order of molecular rotations and molecular oscillations and such absorption accordingly is confined to the infra-red range of the electromagnetic spectrum. More details will be worked out in the following Sections by considering the electric moment as a matrix.

Selection Rules for Fundamentals.—In this Section, we confine ourselves to transitions in which changes occur only in the vibrational quantum number relating to molecular systems. The assumption that the potential energy is a quadratic function of the atomic displacements implies that the restoring forces are always proportional to the displacements. The corresponding oscillations about the equilibrium position are consequently simple harmonic and as has been shown in Chapter VI the eigenfunctions are normalized Hermite polynomials with the normal co-ordinates as the parameters. The appearance or otherwise of a spectral line in absorption resulting from a transition of the molecule from a vibrational state with quantum number v_1 to that with quantum number v_2 will depend upon the element $M_{v_1 v_2}(Q)$ which is equal to

$$\int \psi_{v_1}{}^* (Q)\, M(Q)\, \psi_{v_2}(Q)\, dQ.$$

$M(Q)$ in the above integral is the operator corresponding to a general linear combination of the components M_x, M_y, M_z of the electric moment vector appropriate to the molecule in the configuration Q, considered, for simplicity, as belonging to a non-degenerate normal mode Q. Since it contains only terms in the co-ordinates and does not contain the momenta, it may be written anywhere in the integral sign. If the integral vanishes, the corresponding line does not appear. If the integral does not vanish, the corresponding line will appear.

ψ_{v1} and ψ_{v2} are Hermite polynomials of degree v_1 and v_2 respectively. If we confine ourselves to $\Delta v = \pm 1$, it is easily seen that v_2 is even when v_1 is odd and *vice versa*. If Q changes sign as a result of the symmetry operation R of the molecule, the product $\psi_{v1}^* (Q) \psi_{v2} (Q)$ will also change sign. $M (Q)$ should then also change sign if the integral as a whole is to remain invariant. The latter condition has to be fulfilled because R is a symmetry operation. These statements hold good equally well for all R constituting the point group G appropriate to the molecule and we conclude that the integral will have a non-vanishing value only if $M (Q)$ has the same character under each symmetry operation R of the group as the normal co-ordinate Q itself. In the degenerate case also, it follows from the orthogonality of the irreducible representations of the group of symmetry operations of the molecule, that the integral vanishes unless M belongs to a representation contained in the representation defined by the products $\psi^*_{v1} (Q) \psi_{v2} (Q)$. The problem of finding out which normal co-ordinates can give rise to absorption or emission lines, therefore, reduces to finding out suitable linear combinations of M_x, M_y, M_z transforming under the various symmetry operations as particular sets of normal co-ordinates. This is the same thing as discovering the irreducible sets into which the manifold of M_x, M_y, M_z will fall with reference to the point group. The character of an operation in the representation defined by the manifold M_x, M_y, M_z is easily seen to be $\pm 1 + 2 \cos \phi$ because M_x, M_y, M_z which are components of a vector, transform themselves as the Cartesian co-ordinates. The number of basis elements in each irreducible set for such a case is given by the formula

$$\frac{1}{N} \Sigma h_p (\pm 1 + 2 \cos \phi_R) \chi_i (R).$$

When this number vanishes, it means that no combination of M's transforms in the same way as the set of normal co-ordinates coming under the irreducible representation Γ_i

and all the corresponding normal modes of oscillation may be classed as inactive. When it is not zero, we can get combinations of M's transforming as the normal co-ordinates and all the corresponding normal modes of oscillation in such a case may be classed as active. This condition is only necessary for the appearance of the line but not sufficient because its intensity is governed by additional factors. By substituting the Taylor expansion

$$M(Q) = M_0 + \left(\frac{\partial M}{\partial Q}\right)_0 Q + \frac{1}{2}\left(\frac{\partial^2 M}{\partial Q^2}\right)_0 Q^2 + \ldots,$$

in the foregoing integral and neglecting higher powers, we notice that the portion involving M_0 vanishes on account of the orthogonality of eigenfunctions, the intensity finally depending upon

$$\int \left(\frac{\partial M}{\partial Q}\right)_0 Q\psi_v(Q)\,\psi^*_{v+1}(Q)\,dQ.$$

Substituting for $\psi_v(Q)$ from Chapter VI and using the property $H_{v+1} - 2SH_v + 2vH_{v-1} = 0$ of the Hermite polynomials,* we have the integral written after simplification, as

$$\frac{1}{2^v v!\,\pi^{\frac{1}{2}}\sqrt{2(v+1)}}\int \left(\frac{\partial M}{\partial Q}\right)_0 \cdot \frac{ae^{-S^2}}{2} H_{v+1}(S)\,H^*_{v+1}(S)\,dS.$$

S is a new variable and is equal to Q/a. Substituting the value of the integral and simplifying, we have the intensity proportional to

$$\frac{a^2}{2}\left(\frac{\partial M}{\partial Q}\right)_0^2 (v+1).$$

Thus, a normal oscillation will give rise to an absorption line of finite intensity, if permitted to do so by the selection rules, only when there is a first order variation of the electric moment or any of its components with respect to the normal co-ordinate.

Since the components M_x, M_y, M_z transform themselves as the co-ordinates x, y, z; we can, by starting with a general linear expression $ax + by + cz$ and proceeding as in the case of the determination of normal co-ordinates, actually write down linear combinations of M_x, M_y, M_z coming under each of the one-dimensional irreducible representations of the point group of the molecule. For representations of higher dimensions also, the procedure is the same as in the case of normal co-ordinates.

Similarly, the appearance or otherwise of a spectral line in Raman scattering resulting from a transition of the molecule from a vibrational state with a quantum number v_1 to that with a quantum number v_2 will depend upon the survival or the vanishing of

$$\int a\,(Q)\,\psi^*_{v1}\,(Q)\,\psi_{v2}\,(Q)\,dQ,$$

where $a\,(Q)$ is a linear combination of the components a_{xx}, a_{yy}, a_{zz}, a_{xy}, a_{yz}, a_{zx} of the symmetric tensor relating to the polarizability of the molecule in a configuration Q. If we confine ourselves to $\Delta v = \pm 1$, arguments already outlined will lead to the conclusion that the problem of finding out which normal co-ordinates can give rise to Raman lines reduces to finding out suitable linear combinations of a_{xx}, a_{yy}, etc., transforming under the various symmetry operations exactly as particular sets of normal co-ordinates. This requires the evaluation of the character of an operation R in the representation defined by the six basic tensor components. Taking the axis of rotation as the Z axis, we obtain the following equations of transformation when R is a rotation through ϕ.

$$Ra_{xx} = a_{xx}\cos^2\phi + a_{yy}\sin^2\phi + 2a_{xy}\sin\phi\cos\phi$$

$$Ra_{xy} = -\,a_{xx}\sin\phi\cos\phi + a_{xy}\,(\cos^2\phi - \sin^2\phi) + a_{yy}\sin\phi\cos\phi$$

$$Ra_{xz} = a_{xz}\cos\phi + a_{yz}\sin\phi$$

. . . .

. . . .

$$Ra_{zz} = a_{zz}.$$

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* See Appendix V.

Similar expressions with the signs of the terms α_{xz} and α_{yz} changed are obtained when R is a rotation-reflection through ϕ. From these relations, it follows that the character of the operation R in the reducible representation defined by the polarizability tensor components is $2\cos\phi_R\,(\pm 1 + 2\cos\phi_R)$ the + or − sign being used according as the operation is a rotation or a rotation-reflection. The number of basis elements in each irreducible set for such a case is therefore given by the formula

$$\frac{1}{N}\,\Sigma h_\rho\, 2\cos\phi_R\,(\pm 1 + 2\cos\phi_R)\,\chi_i(R)$$

When this number vanishes, it means that no combination of α's transforms in the same way as the set of normal co-ordinates coming under the irreducible representation Γ_i and all the corresponding normal modes of oscillation may be classed as inactive in Raman effect. When it is not zero, we can get combinations of α's transforming as the normal co-ordinates and all the corresponding normal modes of oscillation in such a case may be classed as active. As in the case of infra-red absorption, the intensity of a Raman line is governed by additional factors. By substituting the Taylor expansion

$$\alpha(Q) = \alpha_0 + \left(\frac{\partial\alpha}{\partial Q}\right)_0 Q + \tfrac{1}{2}\left(\frac{\partial^2\alpha}{\partial Q^2}\right)_0 Q^2 + \ldots$$

in the integral and neglecting higher powers, we notice that the portion involving α_0 vanishes as before if the oscillations are simple harmonic. The intensity depends only on

$$\int\left(\frac{\partial\alpha}{\partial Q}\right)_0 Q\psi_v(Q)\,\psi_{v+1}{}^*(Q)\,dQ.$$

Effecting the same simplification as in the case of infra-red absorption, we obtain the intensity as proportional to

$$\frac{a^2}{2}\left(\frac{\partial\alpha}{\partial Q}\right)_0^2 (v+1).$$

A normal oscillation will give rise to a Raman line of finite intensity, if permitted to do so by the selection rules, only when there is a first order variation of the polarizability with respect to the normal co-ordinate.

As in the case of the electric moment vector, we can find out the linear combinations of the tensor components coming under each irreducible representation of the point group of the molecule by starting with general homogeneous expressions of the second degree in x, y, z because we are now dealing with a symmetric tensor.

Overtone and Combination Lines.—Let Q_1, Q_2 be two normal co-ordinates corresponding to a two-fold degenerate frequency ν. The eigenfunction of the vth harmonic will contain the product of two Hermite polynomials of total degree v and may be written as

$$\psi = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_{v1}(S_1) H_{v2}(S_2)$$

The corresponding energy is

$$E = (v_1+\tfrac{1}{2}+v_2+\tfrac{1}{2})\,h\nu = (v+1)\,h\nu, \text{ where } v = v_1+v_2.$$

If we confine ourselves only to the first overtones where $v = 2$ then v_1, v_2 can take the pairs of values 2, 0; 1, 1; 0, 2 and the corresponding three eigenfunctions relating to a transition energy $2h\nu$ are

$$\psi_1 = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_2(S_1) H_0(S_2);$$

$$\psi_2 = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_1(S_1) H_1(S_2);$$

$$\psi_3 = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_0(S_1) H_2(S_2).$$

These three functions form the basis of an invariant manifold under the group G. In order to find out the number of sets into which this manifold can be split up into irreducible manifolds, we have to find $\chi'(R)$ in the reducible representation defined by ψ_1, ψ_2, ψ_3.

The functions ψ_1, ψ_2, ψ_3 transform themselves as $H_2(S_1)$, $H_1(S_1)\,H_1(S_2)$, $H_2(S_2)$ because their coefficients are invariant under all operations of the group. These in turn transform in the same way as Q_1^2, Q_1Q_2, Q_2^2. The character is independent of the choice of the co-ordinate system. For a given R, we can choose the co-ordinates Q_1, Q_2 in such a manner that

$$RQ_1 = a_1Q_1; \quad RQ_2 = a_2Q_2$$

giving

$$R_{mn} = \begin{vmatrix} a_1 & 0 \\ 0 & a_2 \end{vmatrix}$$

Now $RQ_1^2 = a_1^2Q_1^2$; $RQ_1Q_2 = a_1a_2Q_1Q_2$; $RQ_2^2 = a_2^2Q_2^2$.

Hence the character for $v = 2$ is $a_1^2 + a_2^2 + a_1a_2$. In this case, $\chi'(R)$ may be represented by the symbol $\chi_f^n(R)$ where f stands for the degree of degeneracy and n stands for the order of the harmonic under consideration. We know that

$$\chi_f^1(R) = a_1 + a_2 \text{ and } \chi_f^1(R^2) = a_1^2 + a_2^2.$$

On the other hand, we have just shown that

$$\chi_f^2(R) = a_1^2 + a_2^2 + a_1a_2 = \frac{(a_1 + a_2)^2 + a_1^2 + a_2^2}{2}.$$

We, therefore, have omitting the subscript f

$$\chi^2(R) = \frac{[\chi(R)]^2 + \chi(R^2)}{2}.$$

Although, for simplicity, we have dealt with the case where $f = 2$, the proof may formally be extended to cases where $f > 2$. The non-degenerate case is even simpler. Overtones of higher order may also be dealt with in a similar manner and reference may be made to Tisaz's work in this connection.* The following relation gives C_i, the number of times the first overtone of a normal mode coming under a certain irreducible representation occurs in the irreducible representation Γ_i in the group.

$$C_i = \frac{1}{N}\Sigma h_\rho \chi_f^2(R)\, \chi_i(R).$$

By applying this test to all the irreducible representations of the group of symmetry operations, complete information as

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* *Z.f. Phys.*, Vol. 82, p. 48 (1933).

to the various types under which an overtone comes may easily be obtained. If all or some of these types are active in the fundamental, then the overtone is also active. If all the constituents are inactive, then the overtone is also inactive. These statements apply equally well to both absorption (or emission) and scattering.

Combinations can be dealt with in a similar manner. We shall confine ourselves, for simplicity, to the case of the fundamental of one normal mode combining with the fundamental of another normal mode. The two modes that are combining may or may not belong to the same irreducible representation. Let us consider $Q_1{}^k$, $Q_2{}^k$ as two normal co-ordinates corresponding to a twofold degenerate frequency ν coming under the irreducible representation Γ_k. The basis eigenfunctions will be written as

$$\psi_1 = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_1(S_1) H_0(S_2)$$

$$\psi_2 = Ae^{-\frac{1}{2}(S_1^2+S_2^2)} H_0(S_1) H_1(S_2).$$

Similarly, let us consider $Q_1{}^l$, $Q_2{}^l$ as two normal co-ordinates corresponding to another twofold degenerate frequency ν' coming under the irreducible representation Γ_l. The basis eigenfunctions will be written as

$$\psi_1' = Ae^{-\frac{1}{2}(S'^2_1+S'^2_2)} H_1(S_1') H_0(S_2')$$

$$\psi_2' = Ae^{-\frac{1}{2}(S'^2_1+S'^2_2)} H_0(S_1') H_1(S_2').$$

The product representation has for its basis, the four functions $\psi_1\psi_1'$, $\psi_1\psi_2'$, $\psi_2\psi_1'$, $\psi_2\psi_2'$ which transform as the products of the corresponding H functions. These in turn transform in the same way as Q_1Q_1', Q_1Q_2', Q_2Q_1', Q_2Q_2'. If we now choose the co-ordinates in such a manner that

$$RQ_1 = a_1Q_1;\ RQ_2 = a_2Q_2;\ RQ_1' = b_1Q_1';\ RQ_2' = b_2Q_2'$$

we obtain the character of the product representation as

$$a_1b_1 + a_1b_2 + a_2b_1 + a_2b_2$$

which is equal to $(a_1 + a_2)(b_1 + b_2)$. Since $a_1 + a_2$ and $b_1 + b_2$ are merely the characters of R in the irreducible representations k and l, we have, if we designate $\chi'(R)$ in this case as $\chi^{kl}(R)$,

$$\chi^{kl}(R) = \chi^{k}(R)\,\chi^{l}(R).$$

The proof may formally be extended to combinations between the harmonics of the normal modes, the harmonics being of any order and the normal modes possessing any degree of degeneracy. The following relation gives C_i, the number of times a combination between two normal modes, one coming under the irreducible representation Γ_k and the other coming under the irreducible representation Γ_l, occurs in any irreducible representation Γ_i of the group:

$$C_i = \frac{1}{N}\Sigma h_\rho \chi^{kl}(R)\,\chi_i(R).$$

The expression is valid both when l and k are the same and different. Proceeding in a manner similar to that adopted in the case of the overtones, we can express the combination as the sum of several types of motion coming under different irreducible representations. If all or some of these types are active, then the combination is active and if all the constituents are inactive, then the combination is inactive. These statements apply again to both absorption (or emission) and scattering.

It may, however, be mentioned here that the above selection rules are necessary conditions for the appearance of the overtone and combination lines but there are other factors governing the intensities of lines when they are permitted to appear. For example, an overtone line in Raman scattering from a harmonic oscillator will exhibit a finite intensity only if there is a second order variation of any one of the components of the polarizability tensor with reference to the normal co-ordinate in question. Similar remarks in respect of the electric moment vector hold good when we are dealing with infra-red absorption. Detailed expressions for the intensities of such lines have been derived elsewhere.*

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* S. Bhagavantam, *Scattering of Light and the Raman Effect* (1940).

Selection Rules in Some Special Cases.—

All modes of oscillation coming under the total symmetric classes are always Raman active. The character $\chi_i(R)$ is 1 for all R for a total symmetric class by definition. Since the combination $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$ is invariant for all R, its character is always 1 and is therefore present in the total symmetric representation of all groups. We accordingly conclude that all modes of oscillation coming under the total symmetric class are Raman active.

The first overtone of every normal mode is Raman active irrespective of whether the fundamental itself is active or not. Since we have already proved that the total symmetric oscillation is always Raman active, in order to prove this theorem, it is sufficient to show that the total symmetric irreducible representation is always one of the components into which the reducible representation corresponding to the first overtone may be resolved. From the formula

$$C_i = \frac{1}{N} \Sigma h_\rho \, \chi_f{}^2(R) \, \chi_i(R),$$

we see that this is achieved if we prove that $\Sigma h_\rho \chi_f{}^2(R) \neq 0$. In the case of non-degenerate oscillations, the character is ± 1 for all R and $[\chi(R)]^2$ as well as $\chi(R^2)$ reduce to $+1$ for all R and the above relation is at once satisfied and C_i is always equal to 1. In the case of degenerate oscillations also, the same result holds good. Thus the overtone contains at least one component coming under the total symmetric class.

If a centre of inversion is one of the elements in the group, all normal modes which are antisymmetric with respect to it are Raman inactive. This follows from the fact that all the six polarizability tensor components, being of the second order, remain invariant under the operation of inversion. Hence, no linear combination of the components which is antisymmetric with respect to the centre can be found.

All normal modes which are symmetric with respect to a centre of inversion are infra-red inactive. This theorem follows in a manner analogous to the foregoing one if we consider the behaviour of the vector components.

If a group possessing a p-gonal symmetry has a plane of reflection σ_h as one of its elements, it follows that a centre of inversion is also an element when p is even and the foregoing rule applies as such.

All Raman active normal modes combine with each one of the modes coming under the total symmetric class to give Raman active combination tones. On the other hand, the combination of an inactive mode with a mode belonging to the total symmetric class is also inactive. This follows from the fact that the product representation corresponding to the combination of any mode with one coming under the total symmetric class is equivalent to the original irreducible representation under which the mode appears.

CHAPTER IX

MOLECULAR STRUCTURE AND NORMAL MODES

Triatomic Molecules.—In this Chapter we shall proceed to consider some specific cases of molecules and deal with the normal modes of oscillation, the selection rules for fundamental, overtone and combination lines in the Raman and infra-red spectra. These depend only on the symmetry of the structure and not on the forces that bind the atoms in the molecule. Evaluation of the actual frequencies, which depends on the forces postulated, will be dealt with in the next Chapter. The case of diatomic and other linear molecules is somewhat complicated on account of the existence of an infinite fold rotational axis of symmetry and will be taken up later. Some examples, such as H_2O, D_2O, SO_2, H_2S, etc., of bent symmetrical triatomic molecules will now be considered. These come under the point group* C_{2v} and the appropriate character table with other details are given below.

C_{2v}	E	C_2	σ_v	σ_v'	n_i	n_i'	Raman	Infra-red
A_1	1	1	1	1	3	2	*P*	*A*
A_2	1	1	−1	−1	1	0	*D*	*f*
B_1	1	−1	1	−1	3	1	*D*	*A*
B_2	1	−1	−1	1	2	0	*D*	A
U_R	3	1	3	1				
$h\rho\chi\rho'$	9	−1	3	1				
$h\rho\psi\rho'$	3	1	3	1				
$2\cos\phi_R(\pm 1 + 2\cos\phi_R)$	6	2	2	2				
$\pm 1 + 2\cos\phi_R$	3	−1	1	1				

* Symbols in respect of various point groups are given in a later Chapter.

In the above table χ_ρ' is the character of an operation R from the ρth conjugate class containing h_ρ elements in the representation defined by the normal co-ordinates including translations and rotations and n_i is the corresponding number of normal co-ordinates coming under the ith irreducible representation. On the other hand, ψ_ρ' is the character of R in the representation defined by the normal co-ordinates excluding translations and rotations and n_i' is the corresponding number. P and D under the column 'Raman' signify that the normal modes coming under those irreducible representations are active in their fundamentals in scattering and give rise respectively to polarized and depolarized lines. All modes coming under the total symmetric class give rise to polarized Raman lines and the rest give rise to depolarized lines.* Under the column Infra-red, the letter A signifies that the normal modes coming under those irreducible representations are active in their fundamentals in infra-red absorption. The letter f indicates that the corresponding modes are forbidden. We see that all such molecules should give rise to three Raman lines all of which are represented in infra-red absorption. Two of them should be well polarized and the third depolarized to the limit. SO_2, for example, gives three Raman lines at 526, 1146 and 1340 all of which are represented in infra-red absorption. 1340 has been found to be depolarized to the limit.

It may be noted that $|A_1|^2 = A_1$, $|B_1|^2 = A_1$ and $A_1 \times B_1 = B_1$. Consequently, any two of the three fundamentals can combine and give a line which is active both in Raman scattering and infra-red absorption. Similarly first overtones of all the three fundamentals are active in both spectra.

Pyramidal Molecules.—Examples under this group are: (*a*) tetratomic pyramidal molecules like ammonia and the trichlorides of P, As, Sb, Bi, etc., and (*b*) molecules of the

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* For details regarding the polarization characters, reference may be made to Bhagavantam, *Scattering of Light and the Raman Effect* (1940).

type XY_3Z such as chloroform, bromoform, methyl chloride, $POCl_3$, etc. In molecules of the latter type, it is assumed that the X and Z atoms are both on the axis of the pyramid whereas the Y atoms are at the corners of its base. All these structures possess the symmetry characters appropriate to the point group C_{3v} and the character table and other necessary data for these two types of molecules are given below.

Normal Modes of PCl_3, etc.

C_{3v}	E	$2C'$	3σ	n_i	n_i'	Raman	Infra-red
A_1	1	1	1	3	2	*P*	*A*
A_2	1	1	−1	1	0	*f*	*f*
E	2	−1	0	4	2	*D*	A
U_R	4	1	2				
$h_p \chi_{p'}$	12	0	6				
$h_p \psi_{p'}$	6	0	6				
$2 \cos \phi_R (\pm 1 + 2 \cos \phi_R)$	6	0	2				
$\pm 1 + 2 \cos \phi_R$	3	0	1				

Normal Modes of $CHCl_3$, etc.

C_{3v}	E	$2C'$	3σ	n_i	n_i'	Raman	Infra-red
A_1	1	1	1	4	3	*P*	*A*
A_2	1	1	−1	1	0	*f*	*f*
E	2	−1	0	5	3	*D*	A
U_R	5	2	3				
$h_p \chi_{p'}$	15	0	9				
$h_p \psi_{p'}$	9	0	9				
$2 \cos \phi_R (\pm 1 + 2 \cos \phi_R)$	6	0	2				
$\pm 1 + 2 \cos \phi_R$	3	0	1				

Molecules of the type (*a*) should give rise to four Raman lines, all of which are represented in infra-red absorption. Two of these should be well polarized and the other two depolarized to the limit. Raman spectra of trichlorides of phosphorus, arsenic, antimony, etc., and of some tribromides have been examined. In all these cases, four lines have been recorded. The results available in respect of their polarization characters show that two of them are well polarized and the other two depolarized to the limit in accordance with the theory.

Molecules of type (*b*) should give rise to six Raman lines and show a complete correspondence with the infra-red absorption. Three of these Raman lines should be well polarized and the other three depolarized. The following table contains the results obtained in $CHCl_3$, $CHBr_3$, and $POCl_3$ which are typical representatives of this class. Additional lines which are very weak have been recorded in $CHCl_3$ and $CHBr_3$ and these are presumably either overtones or combinations. The letters *s*, *m* and *w* stand respectively for strong, medium and weak lines.

Raman Frequencies of $CHCl_3$, $CHBr_3$, *and* $POCl_3$

$CHCl_3$ ..	259 (s)	364 (s)	664 (s)	756 (*m*)	1214 (w)	3016 (*m*)
$CHBr_3$ ..	154 (s)	222 (s)	538 (m)	654 (m)	1146 (w)	3023 (m)
$POCl_3$ ..	192 (m)	268 (w)	338 (m)	485 (s)	583 (w)	1290 (w)

As an illustration of the polarization characters amongst this class of compounds, we may cite here the case of chloroform in which 259, 756 and 1214 are depolarized to the limit whereas the other three, namely, 364, 664 and 3016 are well polarized. This is in complete agreement with the theory.

It may be noted that $|A_1|^2 = A_1$, $|E|^2 = A_1 + A_2 + E$, $|E|^{(2)} = A_1 + E$; $A_1 \times E = E$. The characters of the representations $|E|^2$ are 4, 1, 0 whereas those of the representation $|E|^{(2)}$ are 3, 0, 1 under the three classes of the table. From the above equations it follows that we expect all the first overtones and all combination lines of any two of the fundamentals to appear in the Raman as well as in the infrared spectra.

The Nitrate and the Carbonate Ions.—In these groups the three oxygen atoms are at the corners of an equilateral triangle and the nitrogen or the carbon atom is at its centre. The symmetry is that of the point group D_{3h}. This group has to be derived from D_3 with the help of the relation $D_{3h} = D_3 \times C_s$. We shall distinguish the modes symmetric with respect to the reflection plane by one prime and modes antisymmetric with respect to the same plane by a double prime. BCl_3 is also a plane molecule and has accordingly to be classed under this group. The following table gives the relevant characters.

Normal Modes of the Nitrate and Carbonate Ions

D_{3h}	E	$2C'$	$3C_2$	σ_h	$2S'$	$3\sigma_v$	n_i	n_i'	Raman	Infra-red
A_1'	1	1	1	1	1	1	1	1	*P*	*f*
A_2'	1	1	−1	1	1	−1	1	0	*f*	*f*
E'	2	−1	0	2	−1	0	3	2	*D*	*A*
A_1''	1	1	1	−1	−1	−1	0	0	*f*	*f*
A_2''	1	1	−1	−1	−1	1	2	1	*f*	*A*
E''	2	−1	0	−2	1	0	1	0	*D*	*f*
U_R	4	1	2	4	1	2				
$h_\rho \chi_\rho'$	12	0	−6	4	−4	6				
$h\phi_\rho'$	6	0	0	4	−4	6				
$2\cos\phi_R(\pm 1 + 2\cos\phi_R)$	6	0	2	2	2	2				
$\pm 1 + 2\cos\phi_R$	3	0	−1	1	−2	1				

These models should therefore be expected to give three Raman lines, two of which are depolarized to the limit, the third one being well polarized. The experimental results are in entire agreement with these conclusions as may be seen from the following table.

Frequency	Mode	CO_3	NO_3	Active in
A_1' (ν_1)	Total symmetric	1088	1050	Raman effect
A_2'' (ν_2)	Transverse to plane	880	830	Infra-red
E' (ν_3)	Degenerate, in the plane	1438	1360	Raman effect and Infra-red
E' (ν_4)	Do.	714	720	Do.

The principal lines at 1050 in NO_3 and 1088 in CO_3 have been found to be well polarized. The other two lines in both cases are depolarized and are present also in the infra-red absorption. The frequency corresponding to A_2'' does not appear in Raman effect. Its first overtone has, however, been recorded both for the NO_3 and the CO_3 groups and this is in accordance with the selection rules given below.

It may be noted that $|A_1'|^2 = A_1'$; $A_1' \times E' = E'$; $A_1' \times A_2'' = A_2''$; $|E|^2 = A_1' + A_2' + E'$; $|E|^{(2)} = A_1' + E'$; $E' \times A_2'' = E''$; $|A_2''|^2 = A_1'$. If other factors are favourable, we may thus expect four overtone lines and three combination lines in the Raman spectrum and two overtone lines and three combination lines in the infra-red spectrum.

Diatomic and Other Linear Molecules.—Some of the examples of diatomic molecules are H_2, D_2, N_2, O_2, Cl_2, HCl, HBr, HI, CO and NO. In all these cases, we should expect only one oscillation frequency. Since the oscillation is total symmetric, the mode is Raman active. It may also be seen from the following table that it is active in infra-red absorption in the case of molecules which have no centre of inversion. On the other hand the mode is permitted only in Raman effect and forbidden in infra-red absorption for molecules having a centre of inversion.

Some of the examples of other linear molecules are CO_2, CS_2, HCN, COS, CiCN, BrCN, ICN and N_2O. Th

C_{pv}	E	$2C^1$	$2C^2$	..	$2C^{\frac{p-1}{2}}$	$p\sigma_v$	n_i	n_i'	R	I
A_1	1	1	1	..	1	1	3	2	P	A
A_2	1	1	1	..	1	−1	—	—	f	f
E_1	2	$2\cos\omega$	$2\cos 2\omega$	..	$2\cos\frac{p-1}{2}\omega$	0	3	1	D	A
E_2	2	$2\cos 2\omega$	$2\cos 4\omega$	..	$2\cos(p-1)\omega$	0	—	—	D	f
E_3	2	$2\cos 3\omega$	$2\cos 6\omega$	..	$2\cos\frac{3(p-1)}{2}\omega$	0	—	—	—	—
. . . .	. .	. . . .	. . . .	.	. . . .	.	.	.	.	.
. . . .	. .	. . . .	. . . .	.	. . . .	.	.	.	.	.
$E_{\frac{p-1}{2}}$	2	$2\cos\frac{(p-1)}{2}\omega$	$2\cos(p-1)\omega$	..	$2\cos\left(\frac{p-1}{2}\right)^2\omega$	0	—	—	—	—
U_R	3	3	3	..	3	3				
$h_p\chi_{p'}$	9	$6(1+2\cos\omega)$	$6(1+2\cos 2\omega)$	..	$6\left(1+2\cos\frac{p-1}{2}\omega\right)$	$3p$				
$h_p\phi_{p'}$	3	$2(1+2\cos\omega)$	$2(1+2\cos 2\omega)$	..	$2\left(1+2\cos\frac{p-1}{2}\omega\right)$	$3p$				
$2\cos\phi_R(\pm 1+2\cos\phi_R)$	6	$2\cos\omega(1+2\cos\omega)$	$2\cos 2\omega(1+2\cos 2\omega)$	..		2				
$\pm 1+2\cos\phi_R$ ..	3	$1+2\cos\omega$	$1+2\cos 2\omega$	..	$1+2\cos\frac{p-1}{2}\omega$	1				

linear unsymmetrical molecules come under the point group $C_{\infty v}$. The appropriate point group may be considered as the limiting case of C_{pv} (p odd),* where p tends to infinity. The relevant characters and other data applicable to the case of a triatomic unsymmetrical linear molecule like HCN are given in the foregoing table.

A marked feature of this group is the absence of a centre of symmetry. The selection rules for this group are

Infra-red active → A_1 and E_1,

Raman active → A_1 and E_1.

Accordingly, all the three fundamental modes should appear in Raman effect as well as in infra-red absorption. This conclusion is very different from what is expected of symmetrical molecules like CO_2 and CS_2. One of the three modes comes under the class E_1 and is degenerate and should accordingly be depolarized to the limit, while the other two coming under A_1 should be well polarized. We obtain the three Raman lines in ClCN, BrCN, and ICN. The three fundamental frequencies of N_2O are 2224, 1285, and 589. All the three appear in the infra-red absorption and two of them, namely 2224 and 1285, appear in the Raman effect. 589 has, however, not been recorded but should be present. 1285 has been found to be strongly polarized. This represents an oscillation in which the two outer atoms move in and out. The fact that it is infra-red active is most significant. These results lend strong support to the proposed unsymmetrical structure N–N–O for this molecule. In fact, this structure was first arrived at from the above considerations. Similarly, the third line in HCN should be present at about 712 but is presumably too weak. In COS, several lines other than the three fundamentals are recorded and these have to be explained as overtones or combinations. The weak line at 2602 in hydrocyanic acid is of special significance

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* The case p even is not appropriate, as it contains digonal axes of two different types perpendicular to the symmetry axis.

and has been attributed to the presence of a small percentage of the isomeric form H–N→C.

In this Chapter, results in respect of only a few molecules have been worked out. We can similarly deal with any other molecule. Appropriate character Tables and irreducible representations are given in Appendix VIII.

Sulphur.—As an illustration of a point group which has no crystallographic significance, we propose dealing with the case of sulphur molecule. The model assumed is that of a puckered octagon made up of two equal squares, one turned through 45° with respect to the other. The planes of the two squares are parallel and not coincident. The atoms in the molecule occupy the corners of the puckered octagon. Let these atoms be denoted by the numbers 1, 2, 3, 4, 5, 6, 7, 8 as shown in Fig. 6. The valence bonds are assumed to be (15), (25), (26), (36), (37), (47), (48), (81). Let XYZ be three rectangular axes through the centre of gravity of the molecule. X-axis is parallel to (86), Y-axis is parallel to (75) and Z-axis is perpendicular to the planes of the two squares. Let $2a$ be the side of a square and $2c$ be the distance between the two squares. The co-ordinates of the atoms, when referred to the above set of axes, can be given in terms of a and c. In this case, to illustrate an alternative choice of co-ordinates, the individual atoms will

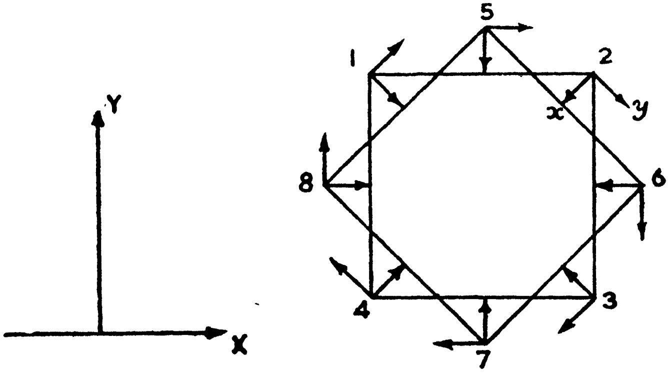

FIG. 6

be referred to a system of axes which is not parallel to the parent system. x_i, y_i, z_i are the co-ordinates of the ith atom with its equilibrium position as the origin. x_i points towards the centre of the square in which the ith atom is situated and z_i is measured perpendicular to the plane of the square and is taken positively on the side opposite to the centre of gravity of the molecule.

The symmetry operations of the model assumed for sulphur fall into seven classes. E the identity ($h = 1$), S_8 rotation-reflection by $\pm\pi/4$ about the fourfold axis ($h=2$), C_4 rotation by $\pm\pi/2$ about the fourfold axis ($h = 2$); S_3 rotation-reflection by $\pm 3\pi/4$ about the fourfold axis ($h = 2$), C_2 rotation by π about the fourfold axis ($h = 1$), σ_v reflection in a plane perpendicular to the planes of the squares and containing a diagonal of one of the squares ($h = 4$), C_2 rotation by π about an axis through the centre of gravity of the molecule and passing through the middle points of two opposite valencies such as (15) and (37) ($h = 4$).

These operations form the group which may be given as a group of permutations on the 8 symbols 1, 2, 3, 4, 5, 6, 7, 8. The elements of this group, the character table and other details are given below:

E

(15263748)

(18473625)

(1234) (5678)

(1432) (5876)

(16453827)

(17283546)

(13) (24) (47) (68)

(21) (34) (68) (7) (5)

(14) (32) (75) (6) (8)

(24) (58) (76) (1) (3)

(13) (65) (78) (2) (4)

(27) (36) (18) (45)

(37) (28) (46) (15)

(38) (47) (25) (16)

(26) (17) (35) (48)

	E	$2S^1$	$2C_4$	$2S^3$	C_2	$4\sigma_v$	$4C_2$	n_i	n_i'	ω & T	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	2	2	..	P	f
A_2 ..	1	1	1	1	1	-1	-1	1	0	ω_z	..	..
B_1 ..	1	-1	1	-1	1	1	-1	2	1	T_z	f	A
B_2 ..	1	-1	1	-1	1	-1	1	1	1	..	f	f
E_1 ..	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	3	2	T_x, T_y	f	A
E_2 ..	2	0	-2	0	2	0	0	3	3	..	D	f
E_3 ..	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0	3	2	ω_x, ω_y	D	f
U_R ..	8	0	0	0	0	2	0					
$h\rho\chi\rho'$	24	0	0	0	0	8	0					
$h\rho\psi\rho'$	18	0	-4	0	2	8	8					

It may be noted from the table that the model assumed for sulphur should be expected to give seven Raman lines, five of which are depolarized and the other two polarized. Experimental results obtained with crystalline sulphur are in general agreement with these conclusions.

CHAPTER X

MOLECULAR STRUCTURE AND NORMAL FREQUENCIES

Interatomic Forces.—The potential energy of a molecule and therefore its normal frequencies depend on the forces that come into operation when the molecule takes up different possible configurations in the neighbourhood of its equilibrium position. A considerable amount of work has been done in connection with ascertaining the nature of interatomic forces in molecules but decisive conclusions have not been reached. Some of the major types so far postulated are valence, central and intra-valence ones. Whenever a valence bond undergoes a change in length or suffers a lateral shift causing a change in the angle between two adjoining bonds, forces linearly proportional to the distortions are assumed to come into operation and these are referred to respectively as primary valence and directed valence forces. On the other hand, we can postulate forces between any two nuclei irrespective of whether they are connected by a valence bond or not such that a change in the distance between them gives rise to a proportionate restoring force. Such a system of forces is referred to as the central force system. It has often been found that neither the former type nor the latter type nor even both are able to account for the observed frequencies. Better agreement has been shown to result in some cases by postulating a third category of forces that may be called the intra-valence type resulting from cross terms between the changes in the lengths of different valence bonds. In the following Sections, we shall have occasion to refer briefly to the above types of interatomic forces.

Water.—The oscillations of the water molecule will be dealt with in some detail because it serves to explain the group theoretical notation in several aspects. This case, being inherently simple, can also be easily worked by other methods.

The molecule has a symmetrical bent structure and the appropriate character table has been given in the previous Chapter.

If we take three mutually perpendicular axes through the centre of gravity of the molecule as shown in Fig. 7,

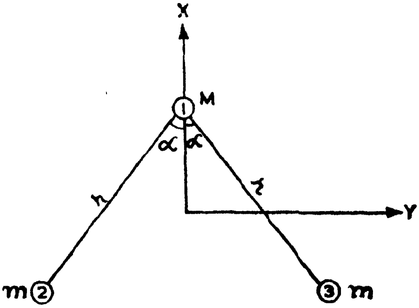

FIG. 7

the Z axis being perpendicular to the plane of the molecule, as the parent system and parallel axes through the equilibrium positions of the atoms to describe their positions for the purpose of writing down symmetry co-ordinates, the transformation properties of the various symmetry operations of the point group may be concisely given as*

$$E:\ \begin{array}{lll} 1\to 1 & x\to & x \\ 2\to 2 & y\to & y; \\ 3\to 3 & z\to & z \end{array} \qquad C_2:\ \begin{array}{lll} 1\to 1 & x\to & x \\ 2\to 3 & y\to & -y \\ 3\to 2 & z\to & -z \end{array}$$

$$\sigma_v:\ \begin{array}{lll} 1\to 1 & x\to & x \\ 2\to 2 & y\to & y; \\ 3\to 3 & z\to & -z \end{array} \qquad \sigma_v':\ \begin{array}{lll} 1\to 1 & x\to & x \\ 2\to 3 & y\to & -y \\ 3\to 2 & z\to & -z \end{array}$$

---

* The full significance of the transformations given under C_2, for example, is as follows:—

$$\begin{array}{lll} x_1\to x_1 & y_1\to -y_1 & z_1\to -z_1 \\ x_2\to x_3; & y_2\to -y_3; & z_2\to -z_3 \\ x_3\to x_2 & y_3\to -y_2 & z_3\to -z_2. \end{array}$$

Others may be similarly interpreted.

The normal co-ordinates* corresponding to the translations and rotations can be written down from their modes as follows:

$$T_x = x_1+x_2+x_3; \quad T_y = y_1+y_2+y_3; \quad T_z = z_1+z_2+z_3;$$

$$\omega_x = z_3 - z_2;$$

$$\omega_y = M(z_2+z_3) - 2mz_1;$$

$$\omega_z = \frac{\mu}{M}\cos\alpha y_1 - \sin\alpha (x_3 - x_2) - \frac{\mu}{2m}\cos\alpha (y_2+y_3).$$

μ stands for the reduced mass $2mM/(M+2m)$ and 2α is the angle between the *OH* bonds. From the transformation properties given above, it is easily verified that T_x, T_y, T_z, ω_x, ω_y, ω_z belong to the irreducible representations designated A_1, B_1, B_2, A_2, B_2 and B_1 respectively.

To obtain the two symmetry modes coming under A_1, we take the general expression

$$Q = a_1x_1+a_2x_2+a_3x_3+b_1y_1+b_2y_2+b_3y_3+c_1z_1+c_2z_2+c_3z_3.$$

The character for C_2 in A_1 is 1 and we have $C_2Q = 1.Q$. But

$$C_2Q = a_1x_1+a_2x_3+a_3x_2-b_1y_1-b_2y_3-b_3y_2-c_1z_1-c_2z_3-c_3z_2.$$

Thus from the equation $C_2Q = Q$, we have the relations

$$a_2 = a_3; \quad b_2 = -b_3; \quad c_2 = -c_3 \text{ and } b_1 = c_1 = 0.$$

Similarly from the equation $\sigma_v Q = Q$, we have the further relations $c_2 = 0$; $c_3 = 0$. From the equation $\sigma_v'Q = Q$ we do not get any new relations as σ_v' is a combination of C_2 and σ_v. So a normal co-ordinate coming under the irreducible representation A_1 must be of the form

$$a_1x_1 + a_2(x_2+x_3) + b_2(y_2 - y_3).$$

---

* It is customary to normalize the symmetry co-ordinates in such a way that the sum of the squares of the coefficients of the Cartesian (or the internal) co-ordinates in each symmetry co-ordinate is unity. This normalization is unnecessary, if we are interested only in the evaluation of the frequencies. However, if we use orthogonal and normalized symmetry co-ordinates, the corresponding transformation matrices obtained under various symmetry operations will be orthogonal.

The number of arbitrary constants is 3 corresponding to n_i in the table cited above. The symmetry co-ordinates coming under A_1 may be taken as any three orthogonal combinations of S_1, S_2, S_3 where

$$S_1 = x_1; \quad S_2 = x_2 + x_3; \quad S_3 = y_2 - y_3.$$

But we have already seen that T_x belongs to this representation. Taking one of the symmetry co-ordinates as T_x, we form two linear functions of S_1, S_2, S_3 which along with T form an orthogonal set of symmetry co-ordinates coming under A_1. One such choice is as follows:

$$T_x = x_1 + x_2 + x_3; \; Q_1 = 2mx_1 - M(x_2 + x_3);$$
$$Q_2 = y_2 - y_3.$$

Out of the three normal co-ordinates that should be expected from the representation B_1, two have been already written down, namely T_y and ω_z. Proceeding as before, the third normal co-ordinate which is unique in this case is obtained as

$$Q_3 = -\frac{2m}{M} \sin ay_1 - \cos a\,(x_3 - x_2) + \sin a\,(y_2 + y_3).$$

The symmetry modes are diagrammatically represented below n Fig. 8.

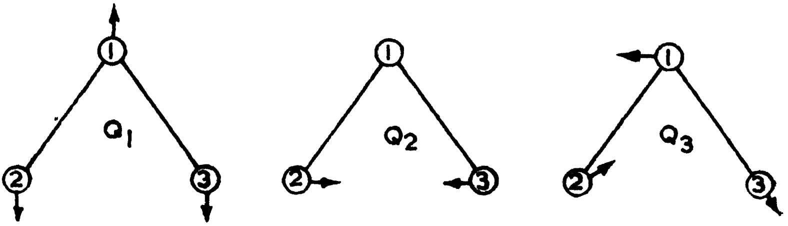

FIG. 8

If Q_1 and Q_2 are taken as having amplitudes δ and γ respectively, the co-ordinates of the atoms in the displaced positions when they take the motion corresponding to Q_1 and Q_2 simultaneously are given in the following table:—

	X	Y	Z
1	$\frac{\mu}{M} r \cos a + 2m\delta$	0	0
2	$-\frac{\mu}{2m} r \cos a - M\delta$	$-r \sin a + \gamma$	0
3	$-\frac{\mu}{2m} r \cos a - M\delta$	$r \sin a - \gamma$	0

The variations in the lengths and angles are

$$\triangle R_{12} = \triangle R_{13} = (2m + M) \cos a.\delta - \gamma \sin a; \ \triangle R_{23} = -2\gamma;$$

$$\triangle\phi_{123} = \triangle\phi_{132} = -\tfrac{1}{2}\triangle\phi_{213} = \frac{\sin a\,(2m+M)\,\delta}{r} + \frac{\gamma \cos a}{r}.$$

The kinetic and potential energies are given by

$$2T = M.4m^2\dot{\delta}^2 + 2m\,(M^2\dot{\delta}^2 + \gamma^2)$$

and

$$\begin{aligned} 2V = {} & 2K_1\,[(2m + M) \cos a.\delta - \gamma \sin a)]^2 \\ & + K_2.4\gamma^2 \\ & + K_3'\left[\frac{2}{r}\{(M + 2m) \sin a.\delta + \gamma \cos a\}\right]^2 \\ & + 2K_4'\left[\frac{1}{r}\{(M + 2m) \sin a.\delta + \gamma \cos a\}\right]^2. \end{aligned}$$

In writing down the above expressions, a change in the length of R_{12} or of R_{13} is assumed to give rise to a proportionate restoring force with the constant of proportionality equal to K_1; K_2 similarly referring to R_{23}. K_3' and K_4' are constants corresponding respectivley to changes in the angles $2\hat{1}3$ and $1\hat{2}3$ or $1\hat{3}2$. We shall replace K_3'/r^2 and K_4'/r^2 by K_3 and K_4 respectively. The Lagrangian equations give

$$\begin{vmatrix} u-(2m+M)\,2mM\lambda & v \\ v & w-2m\lambda \end{vmatrix}=0$$

where

$$u = 2K_1\,(2m+M)^2\cos^2\alpha + 4K_3\,(2m+M)^2\sin^2\alpha + 2K_4\,(2m+M)^2\sin^2\alpha$$

$$v = -2K_1\sin\alpha\cos\alpha\,(2m+M) + 4K_3\sin\alpha\cos\alpha\,(2m+M) + 2K_4\sin\alpha\cos\alpha\,(2m+M)$$

$$w = 2K_1\sin^2\alpha + 4K_2 + 4K_3\cos^2\alpha + 2K_4\cos^2\alpha.$$

If λ_1 and λ_2 are the roots of the equation, we obtain

$$\lambda_1+\lambda_2 = \frac{K_1}{m}\left[1+\frac{2m}{M}\cos^2\alpha\right]+\frac{2K_2}{m}+\left[\frac{K_4+2K_3}{m}\right]\left[1+\frac{2m}{M}\sin^2\alpha\right];$$

$$\lambda_1\lambda_2 = \frac{2}{\mu m}\,[2K_1K_2\cos^2\alpha + 2K_2K_4\sin^2\alpha + 2K_1K_3 + K_1K_4 + 4K_2K_4\sin^2\alpha].$$

In the case of the symmetry mode Q_3 with amplitude δ we obtain by a similar procedure the following expressions for the kinetic and potential energies:

$$2T = \left\{M\left(-\frac{2m}{M}\sin\alpha\right)^2 + 2m\right\}\dot{\delta}^2;$$

$$2V = 2K_1\left(\cos^2\alpha + \frac{2m}{\mu}\sin^2\alpha\right)\delta^2 + \frac{2K_4'}{r^2}\left(\cot\alpha + \frac{2m}{M}\sin\alpha\cos\alpha\right)^2\delta^2.$$

The corresponding λ is given by the equation

$$\lambda_3 = \left[\frac{1}{m}+\frac{2}{M}\sin^2\alpha\right]\left[K_1 + K_4\cot^2\alpha\right].$$

If in λ_1, λ_2 and λ_3 we put $K_2=0$ and $K_4=0$, we get expressions appropriate to the valence force system only. If we put $K_3=0$ and $K_4=0$, we get expressions appropriate to the central force system only. Expressions relating to the frequencies in other special cases such as a linear symmetrical molecule or an equilateral triangular structure and so on with specific types of forces can be derived from the above by making suitable substitutions.

In the case of symmetric linear molecules, confining ourselves to central forces only, by putting $2\alpha = 180°$, $K_3 = K_4 = 0$ in the above equations, we obtain

$$\lambda_1 = 0,\ \lambda_2 = \frac{K_1 + 2K_2}{m} \text{ and } \lambda_3 = \frac{2K_1}{\mu}.$$

However, experimental results in symmetric linear molecules like CO_2 and CS_2 show a fairly high frequency corresponding to the transverse mode λ_1 thus demonstrating the inadequacy of the central force system.

A second example which may be usefully cited to demonstrate this aspect is the case of an equilateral triangular structure. Putting $2\alpha = 60°$, $K_3 = K_4 = 0$ and $m = M$, we obtain

$$\lambda_1 = \lambda_3 = \frac{3K_1}{2m} \text{ and } \lambda_2 = \frac{3K_1}{m}.$$

The frequency of the total symmetric mode thus comes out as $\sqrt{2}$ times that of the degenerate frequency irrespective of the value of m. Experimental results do not strictly conform with this conclusion.

To calculate the normal frequencies by the F and G Matrix method, we choose the internal co-ordinates as the changes r_1 and r_2 of the bond lengths r and the change $\Delta\phi$ in the bond angle 2α (Fig. 9). r and 2α denote the equilibrium values of the bond length and the bond angle.

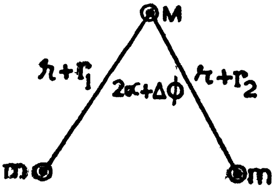

Fig. 9

Let f_r, f_{rr}, $f_{r\phi}$ and f_ϕ be taken as the force constants (coefficients in the potential energy) corresponding to the quadratic terms r_1^2 (or r_2^2), r_1r_2, $r_1\Delta\phi$ (or $r_2\Delta\phi$) and $\Delta\phi^2$. f_r and f_ϕ/r^2 here correspond to force constants K_1 and K_3 respectively. The following table bringing out the F matrix may readily be constructed.

	r_1	r_2	$\Delta\phi$
r_1	f_r	f_{rr}	$f_{r\phi}$
r_2	f_{rr}	f_r	$f_{r\phi}$
$\Delta\phi$	$f_{r\phi}$	$f_{r\phi}$	f_ϕ

The G matrix may be written in the form

$$G = \left| \begin{array}{ccc} G_{rr}^{(2)} & G_{rr}^{(1)} & G_{r\phi}^{(2)} \\ G_{rr}^{(1)} & G_{rr}^{(2)} & G_{r\phi}^{(2)} \\ G_{r\phi}^{(2)} & G_{r\phi}^{(2)} & G_{\phi\phi}^{(3)} \end{array} \right|$$

where

$$G_{rr}^{(2)} = \frac{1}{m} + \frac{1}{M}; \quad G_{rr}^{(1)} = \frac{1}{M} \cos 2a;$$

$$G_{r\phi}^{(2)} = -\frac{1}{r} \cdot \frac{1}{M} \sin 2a;$$

$$G_{\phi\phi}^{(3)} = \frac{1}{r^2}\left[\frac{2}{m} + \frac{2(1-\cos 2a)}{M}\right].$$

These expressions are easily verified to be the same as those given in Chapter VII if we note that for this particular case $\mu_2 = \mu_3 = 1/m$; $\mu_1 = 1/M$; $Q_{12} = Q_{13} = 1/r$. The secular equation in the general case will be

$$| FG - E\lambda | = 0.$$

We shall attempt the solution for a particular case of valence forces only as an illustration. For such a case, all elements except f_r and f_ϕ in the F matrix vanish and we have

$$\begin{vmatrix} f_r & 0 & 0 \\ 0 & f_r & 0 \\ 0 & 0 & f_\phi \end{vmatrix} \begin{vmatrix} G_{rr}^{(2)} & G_{rr}^{(1)} & G_{r\phi}^{(2)} \\ G_{rr}^{(1)} & G_{rr}^{(2)} & G_{r\phi}^{(2)} \\ G_{r\phi}^{(2)} & G_{r\phi}^{(2)} & G_{\phi\phi}^{(3)} \end{vmatrix} - E\lambda = 0$$

After expansion and simplification and by substituting K_1 for f_r and K_3 for f_ϕ/r^2, we obtain for the three roots λ_1, λ_2 and λ_3 the following relationships:

$$\begin{aligned} \lambda_1 + \lambda_2 &= f_r\,[G_{rr}^{(2)} + G_{rr}^{(1)}] + f_\phi G_{\phi\phi}^{(3)} \\ &= K_1\left[\frac{1}{m} + \frac{2\cos^2\alpha}{M}\right] + 2K_3\left[\frac{1}{m} + \frac{2\sin^2\alpha}{M}\right]. \\ \lambda_1\lambda_2 &= f_r f_\phi G_{\phi\phi}^{(3)}\,[G_{rr}^{(2)} + G_{rr}^{(1)}] - 2f_r f_\phi\,[G_{r\phi}^{(2)}]^2 \\ &= \frac{4K_1K_3}{m}\left(\frac{M + 2m}{2mM}\right) \\ \lambda_3 &= f_r\,[G_{rr}^{(2)} - G_{rr}^{(1)}] \\ &= K_1\left[\frac{1}{m} + \frac{2\sin^2\alpha}{M}\right]. \end{aligned}$$

These relationships are identical with those derived earlier for the water molecule by putting $K_2 = K_4 = 0$ and rendering the general case applicable to the valence force system. It should now be pointed out that these expressions for λ do not contain the stretching force constant between atoms 2 and 3. We could, however, introduce such a force if we had started with the variations in the three distances as internal co-ordinates. In such an alternative, forces involving the variations in bond angles get eliminated and we would have had what has been called the central force system.

Phosphorus.—The structure assumed for this molecule is that of a regular tetrahedron, the atoms being situated at its corners. The model belongs to the tetrahedral point group, the conventional symbol for which is T_d. If the four corners of the tetrahedron are numbered 1, 2, 3 and 4, this group can be written as a permutation group in the following manner:

E .. (1) (2) (3) (4)
$8C_3$ .. (1) (234); (1) (243); (2) (134); (2) (143);
(3) (124); (3) (142); (4) (123); (4) (132)
$3C_2$ .. (12) (34); (13) (24); (14) (23)
6σ .. (12) (3) (4); (13) (2) (4); (14) (2) (3);
(24) (1) (3); (34) (1) (2); (23) (1) (4)
$6S_4$ .. (1234); (1432); (1342); (1243); (1423); (1324).

The first 18 permutations are easily written out by reference to the figure but there may be some difficulty in the case of $6S_4$. They can be obtained by forming the product elements between $3C_2$ and 6σ.

The character table and the selection rules appropriate to this group are given below:

T_d	E	$8C_3$	$3C_2$	6σ	$6s_4$	n_i	n_i'	ω & T	Raman	Infra red
A_1 ..	1	1	1	1	1	1	1	..	P	f
A_2 ..	1	1	1	-1	-1	0	0	..	..	..
E ..	2	-1	2	0	0	1	1	..	D	f
F_1 ..	3	0	-1	-1	1	1	0	ω	..	..
F_2 ..	3	0	-1	1	-1	2	1	T	D	A
U_R ..	4	1	0	2	0					
$h\rho\chi\rho'$ ..	12	0	0	12	0					
$h\rho\phi\rho'$ ..	6	0	6	12	0					

It is seen from the table that we should expect three normal frequencies, one of them being single, one doubly degenerate and one triply degenerate. All the three are active in Raman effect whereas only one is active in infra-red absorption. Of the three lines that are to be accordingly expected in Raman effect, the single frequency coming under the total symmetric class A_1 should be polarized and the remaining two should be completely depolarized. The experimental results in respect of the Raman effect in phosphorus are in entire agreement with the above conclusions.

The principal axes, X, Y, Z, are shown in Fig. 10. They are obtained by joining the middle points of opposite edges of the tetrahedron and the positive directions are indicated by the letters X, Y, Z. The co-ordinates of each atom in any mode of oscillation are expressed with respect to a parallel co-ordinate system with the equilibrium position of the atom as the origin. The two operations C_3 (234) and σ (12) may be taken as a set of generating elements of the point group T_d. The transformations of co-ordinates under these two operations may be given as

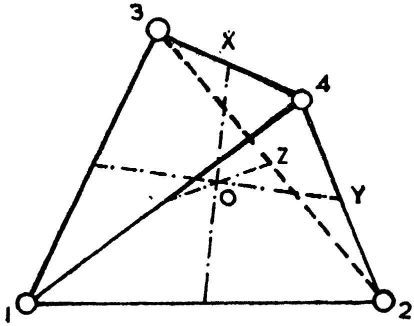

FIG. 10

$$\begin{array}{llll} & 1 \rightarrow 1 & x \rightarrow y & & 1 \rightarrow 2 & x \rightarrow x \\ C_3: & 2 \rightarrow 3 & y \rightarrow z & \sigma: & 2 \rightarrow 1 & y \rightarrow -z \\ & 3 \rightarrow 4 & z \rightarrow x & & 3 \rightarrow 3 & z \rightarrow -y \\ & 4 \rightarrow 2 & & & 4 \rightarrow 4 & \end{array}$$

The symmetry co-ordinates derived from the character table (Appendix VIII) are given below.* The first six relate to pure translations and rotations:

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* As has already been explained, the choice of degenerate Q's is not unique. For example, Q_{2a} and Q_{2b} may alternatively be taken as

$$Q_{2a} = x_1 + x_2 - x_3 - x_4 - z_1 + z_2 + z_3 - z_4$$
$$Q_{2b} = y_1 - y_2 + y_3 - y_4 - z_1 + z_2 + z_3 - z_4.$$

$$\left.\begin{aligned}T_x &= x_1 + x_2 + x_3 + x_4\\ T_y &= y_1 + y_2 + y_3 + y_4\\ T_z &= z_1 + z_2 + z_3 + z_4\end{aligned}\right] \quad \cdots \quad \cdots \quad \cdots \quad F_2\,(3)$$

$$\left.\begin{aligned}\omega_x &= y_1 - y_2 - y_3 + y_4 - z_1 + z_2 - z_3 + z_4\\ \omega_y &= x_1 - x_2 - x_3 + x_4 - z_1 - z_2 + z_3 + z_4\\ \omega_z &= x_1 - x_2 + x_3 - x_4 - y_1 - y_2 + y_3 + y_4\end{aligned}\right] \quad \cdots \quad F_1\,(3)$$

$$Q_1 = x_1+x_2-x_3-x_4+y_1-y_2+y_3-y_4+z_1-z_2-z_3+z_4 \qquad A_1$$

$$\left.\begin{aligned}Q_{2a} &= y_1 - y_2 + y_3 - y_4 - z_1 + z_2 + z_3 - z_4\\ Q_{2b} &= 2\,(x_1+x_2-x_3-x_4)-y_1+y_2-y_3+y_4-z_1+z_2+z_3-z_4\end{aligned}\right]$$

$$\left.\begin{aligned}Q_{3a} &= y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4\\ Q_{3b} &= x_1 - x_2 - x_3 + x_4 + z_1 + z_2 - z_3 - z_4\\ Q_{3c} &= x_1 - x_2 + x_3 - x_4 + y_1 + y_2 - y_3 - y_4.\end{aligned}\right] \quad \cdots \quad F_2\,(3)$$

If the potential energy function chosen involves primary valence and directed valence forces,* it is given by

$$\begin{aligned}2V = {} & K_1\,[(\triangle R_{12})^2 + (\triangle R_{13})^2 + (\triangle R_{14})^2 + (\triangle R_{23})^2 + (\triangle R_{24})^2\\ & + (\triangle R_{34})^2]\\ & + K_2\,[(\triangle\phi_{213})^2 + (\triangle\phi_{214})^2 + (\triangle\phi_{314})^2 + (\triangle\phi_{123})^2 + (\triangle\phi_{124})^2\\ & + (\triangle\phi_{321})^2 + (\triangle\phi_{132})^2 + (\triangle\phi_{134})^2 + (\triangle\phi_{234})^2 + (\triangle\phi_{142})^2\\ & + (\triangle\phi_{143})^2 + (\triangle\phi_{243})^2]\end{aligned}$$

where R_{ij} denotes the distance between the *i*th and the *j*th atoms and ϕ_{ijk} is the angle between the two valence bonds *ij* and *jk*. In all the three normal modes, the variations $\triangle R$ and $\triangle\phi$ are then calculated in the usual manner and the potential energies evaluated. The corresponding kinetic energies are written down and the following relations obtained from the equations of motion:

$$\lambda_1 = \frac{4K_1}{m}\ ;\ \lambda_2 = \frac{1}{m}\left[K_1 + \frac{6K_2}{R^2}\right]\ ;\ \lambda_3 = \frac{1}{m}\left[2K_1 + \frac{8K_2}{R^2}\right]\ ;$$

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* For a discussion of the force constants, *see* N. B. Slater, *Trans. Farad. Soc.*, **50**, 207 (1954).

where R is the length of each valence bond and m is the mass of the phosphorus atom. ν_1, ν_2 and ν_3 corresponding respectively to the representations A_1, E and F_2 may now easily be obtained from the relation $\lambda = 4\pi^2\nu^2$.

In the F and G matrix method, this molecule may be studied by choosing the six internal co-ordinates r_{ij} as the variations of the bond lengths connecting the particles i and j. The symmetry co-ordinates are

$$S_1^{A_1} = (r_{12} + r_{13} + r_{14} + r_{23} + r_{24} + r_{34})\frac{1}{\sqrt{6}}$$

$$\left.\begin{aligned} S_{11}^{E} &= \frac{1}{2\sqrt{3}}(r_{12} + r_{23} + r_{34} + r_{41} - 2r_{13} - 2r_{24}) \\ S_{21}^{E} &= \frac{1}{2}(r_{12} - r_{23} + r_{34} - r_{14}) \end{aligned}\right\}$$

$$\left.\begin{aligned} S_{11}^{F_2} &= \frac{1}{\sqrt{2}}(r_{14} - r_{23}) \\ S_{21}^{F_2} &= \frac{1}{\sqrt{2}}(r_{12} - r_{34}) \\ S_{31}^{F_2} &= \frac{1}{\sqrt{2}}(r_{13} - r_{24}) \end{aligned}\right\}$$

We have here $G_{rr}{}^{(2)} = 2/m$ and $G_{rr}{}^{(1)} = \frac{1}{2m}$. The F matrix for the A_1 vibration is $f_r + 4f_{rr}$ and the corresponding secular equation is $\lambda_1 = \frac{4}{m}(f_r + 4f_{rr})$. Taking the symmetry co-ordinate S_{21}^{E}, the F matrix for E vibration is $f_r + 2f_{rr}$ which gives $\lambda_2 = \frac{1}{m}(f_r - 2f_{rr})$. Finally the F matrix corresponding to the F vibration is f_r which gives $\lambda_3 = \frac{2}{m}f_r$. f_r is the same force constant as K_1.

Normal frequencies and selection rules for Raman and infra-red spectra for other molecules can similarly be worked out. Below are given typical examples of molecules belonging to other point groups. The point group appropriate to each molecule is given in brackets. HOD, (C_s);

H_2O_2, (C_2); CHCl = CHCl, (C_{2h}), NH_3, (C_{3v}), C_2H_4, (D_{2h}), $CH_2 = C = CH_2$, (S_{4v}); C_3H_6, (D_{3h}); C_6H_{12}, (S_{6v}); C_6H_6, (D_{6h}); SF_6, (O_h); N_2O, $(C_{\infty v})$; CO_2, $(D_{\infty h})$. The molecule CH_3OH has no element of symmetry other than E.

By comparing the calculated values with the observed frequencies in the infra-red and Raman spectra of molecules such as those cited above, approximate figures for the force constants have been obtained and some of them are given below. These may be used to make a rough assignment of the modes of oscillation and the observed frequencies in other molecules. The approximate force constants* corresponding to valency bonds HO, DO, CH, HCl, NH, NO, CO are respectively 7·76, 7·94, 4·77, 5·15, 6·5, 9·13, 5·4 $\times 10^5$ dynes/cm. and the *HOH*, *HNH*, *HCH* and *OCO* angle force constants are 0·69, 0·5, 0·46 and $0{\cdot}57 \times 10^5$ dynes/cm.

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* G. Herzberg, *Infra-red and Raman Spectra* (1944).

CHAPTER XI

LATTICES IN THREE DIMENSIONS

Space Lattices.—A set of points all of which can be reached by starting from any one of them and by performing primitive translations T_x, T_y, T_z or integral (positive or negative) multiples thereof is said to constitute a lattice in three dimensions. The X, Y and Z axes parallel to which the basic translations are to be performed may be called the principal axes of the lattice. They are not necessarily rectangular. The volume element bounded by T_x, T_y, T_z is the smallest cell that may be regarded as repeated in space for covering the entire lattice. If we locate the origin at one of the lattice points and attempt to make the Z axis in turn an axis of rotational symmetry, it has been proved that its order can be only 2, 3, 4 or 6. In three-dimensional lattices, axes of rotation of order 3 with particular distribution in space and in combination with other elements result in a type of symmetry called the cubic symmetry and this has to be considered as a special case.

For investigating the possible types of lattices, we shall consider first the possible types of symmetry. The parameters are the primitive translations T_x, T_y, T_z and α, β, γ the angles between YZ, ZX, XY axes respectively. T_x and T_y build up a two-dimensional network of points, the symmetry properties of which have already been dealt with in Chapter III. T_z is now to be located suitably with reference to the two-dimensional network. By choosing T_z so that it is normal to the XY plane, we get one lattice from each one of the five two-dimensional networks already described. The fifth one is not a distinct type but only falls under the category of the orthorhombic system and this fact can be made evident if a suitable choice of axes is made. No additional elements of symmetry are introduced by adjusting the length of T_z except in the fourth or the tetragonal system. If here, we make $T_z = T_x = T_y$, we get a new type possessing cubic symmetry. By choosing T_z so that it is not normal to the XY plane, we can again examine each case and find that only two new types of symmetry arise. One of them is the triclinic and can be derived from any of the five networks by choosing an arbitrary length and inclination for T_z. The second is the trigonal or the rhombohedral and can be derived from the fifth network if we choose T_z so that it is equal to T_x and T_y and makes the same angle with T_x and with T_y as between T_x and T_y. The possible types of symmetry are now exhausted. Their names, the values of the parameters and the appropriate symmetry elements are enumerated below.—

Crystal system	Axes	Angles	Symmetry elements
Triclinic ..	T_x, T_y, T_z	$\alpha \neq \beta \neq \gamma$	Ei
Monoclinic ..	T_x, T_y, T_z	$\alpha = \beta = 90°$ $\gamma \neq 90° \neq 120°$	$EC_2 i\sigma_h$
Orthorhombic	$T_x \neq T_y \neq T_z$	$\alpha = \beta = \gamma = 90°$	$EC_2C_2'C_2''i\sigma_h\sigma_v'\sigma_v''$
Tetragonal ..	$T_x = T_y \neq T_z$	$\alpha = \beta = \gamma = 90°$	$E2C_4C_2 2C_2' 2C_2''$ $i2S_4\sigma_h 2\sigma_v' 2\sigma_v''$
Rhombohedral	$T_x = T_y = T_z$	$\alpha = \beta = \gamma \neq 90°$ $\neq 60° \neq \cos^{-1}$ $-\frac{1}{3}$	$E2C_3 3C_2 i2S_6 3\sigma$,
Hexagonal ..	$T_x = T_y, = T_z$	$\alpha = \beta = 90°$; $\gamma = 120°$	$E2C_6 2C_3 C_2 3C_2' 3C_2''$ $i2S_6 2S_3 \sigma_h 3\sigma_v' 3\sigma_v''$
Cubic ..	$T_x = T_y = T_z$	$\alpha = \beta = \gamma = 90°$	$E8C_3 3C_2 6C_2 6C_4$ $i8S_6 3\sigma 6\sigma 6S_4$

These are the seven well-known crystal systems and all the lattices should fall under one or other of these categories. In Fig. 11, the fourteen Bravais lattices are represented diagrammatically. The first, second, fourth, eighth, tenth, eleventh and the twelfth lattices are the simplest. The manner in which the additional ones are derived (one under the monoclinic system, three under the orthorhombic system,

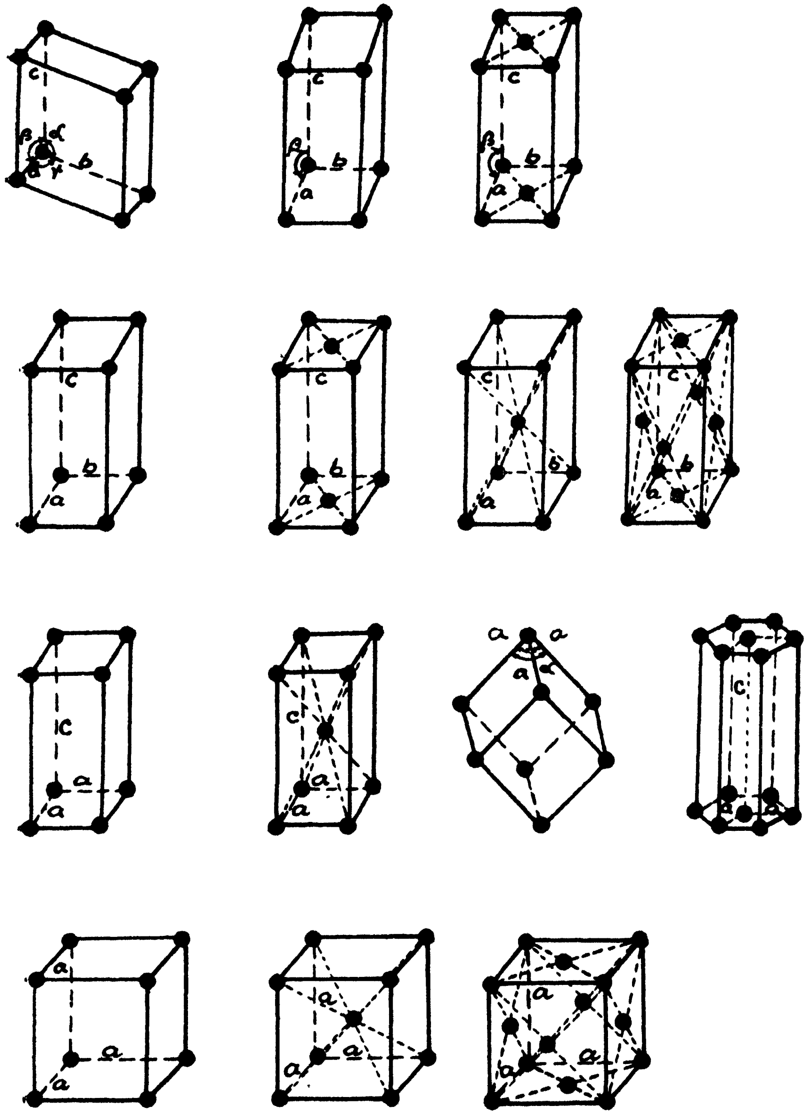

FIG. 11

one under the tetragonal system and two under the cubic system) needs some explanation. We may consider in each case the possibility of locating additional points at suitable places such as the face centres or the cell centres consistent with the requirement, that all such points along with the original ones may be fitted into a single lattice by a suitable choice of three new basic translations, the lattice itself not suffering a deterioration in symmetry. In the case where additional points are located at the centres of one pair of faces only (parallel to *XY*), the new basic translations will be $\frac{T_x \pm T_y}{2}$ and T_z. In the case where they are located at the centres of all the three pairs of faces, the new basic translations will be $\frac{T_x + T_y}{2}$; $\frac{T_y + T_z}{2}$; $\frac{T_z + T_x}{2}$. When the cell centres are filled, the basic translations will be $\frac{T_x + T_y - T_z}{2}$, $\frac{T_x - T_y - T_z}{2}$; $\frac{-T_x + T_y + T_z}{2}$. Some alternative ways of locating points are not permissible because they do not all go on a single lattice. For example, it may be seen that such a situation arises when we locate points at the centres of two pairs of faces only. Other alternative ways which are not permissible are those in which the new set of points along with the original ones, when referred to the new basic translations, give rise to a unit cell which conforms to the original symmetry type. For example, a body centred triclinic lattice can be viewed as a simple triclinic by referring it to the new basic translations. In this way, after eliminating repetitions and such of those which do not conform to the definition of a lattice, we get some new lattices under four of the seven systems which are characterized by the fact that when they are referred to the new basic translations, the unit cell appears to belong to another system of a lower symmetry and these have to be regarded as distinct ones. For example, the two additional lattices under the cubic system may be regarded as special rhombohedral types in which $T_x = T_y = T_z$; $\alpha = \beta = \gamma = 60^\circ$ or $\cos^{-1} - \frac{1}{3}$ as the case may be. The total number thus obtained is fourteen. As has already been mentioned, seven of these are of the simple type and the other seven are derived ones. In the following table, the numbers in respect of the derived ones and the original lattices from which they are derived are shown. Dashes indicate that the corresponding cases are either inconsistent with the symmetry requirements and therefore not permissible or mere repetitions of the simple types of lattices from which each case is derived. Every derived lattice may thus be regarded as a side centred or body centred or face centred simple lattice. The directions which define the corresponding simple cell bring out additional elements of symmetry and are called the crystallographic axes.

Lattice	Simple	Side centering	Body centering	Face centering
Triclinic	1	—	—	—
Monoclinic ..	2	3	—	—
Orthorhombic ..	4	5	6	7
Tetragonal ..	8	—	9	—
Rhombohedral ..	10	—	—	—
Hexagonal ..	11	—	—	—
Cubic	12	—	13	14

Crystal Classes.—It has been shown that space lattices can be divided from symmetry considerations into seven systems. Apart from the translational symmetry, which is common to all, each system possesses symmetry elements characteristic of a point group. These have been given in the foregoing Section. Taking each one of the 14 Bravais lattices, we can locate at every lattice point a point group possessing all the symmetry elements of the lattice and obtain a pattern whose symmetry is the same as that of the lattice. Such a symmetry is called the holohedral symmetry of the lattice. By locating subgroups of the holohedral symmetry group at the lattice points, we obtain patterns of that lower symmetry, if we ignore for the moment translational type of symmetry elements. Similarly, if the lattice points are filled up by point groups having symmetry elements not contained in the holohedral symmetry of the lattice, the pattern cannot acquire these new elements of symmetry but possesses only the symmetry elements which are common to the lattice and the point group used. For

Crystal system	No.	Symbol		Symmetry operations
		Hermann-Mauguin	Schönflies	
Triclinic ..	1	1	C_1	E
	2	1	C_i	Ei
Monoclinic ..	3	m	C_s	$E\sigma_h$
	4	2	C_2	EC_2
	5	$2/m$	C_{2h}	$EC_2i\sigma_h$
Orthorhombic ..	6	$2\,mm$	C_{2v}	$EC_2\sigma_v\sigma_v'$
	7	2 2 2	D_2	$EC_2C_2'C_2''$
	8	$2/m\ 2/m\ 2/m$	D_{2h}	$EC_2C_2'C_2''i\sigma_h\sigma_v'\sigma_v''$
Tetragonal ..	9	4	C_4	$E2C_4C_2$
	10	$\bar{4}$	S_4	$E2S_4C_2$
	11	$4/m$	C_{4h}	$E2C_4C_2i2S_4\sigma_h$
	12	$4\,mm$	C_{4v}	$E2C_4C_22\sigma_v2\sigma_v'$
	13	$\bar{4}\,2\,m$	S_{4v}	$EC_22C_22S_42\sigma_v$
	14	4 2 2	D_4	$E2C_4C_22C_2'2C_2''$
	15	$4/m\ 2/m\ 2/m$	D_{4h}	$E2C_4C_22C_2'2C_2''$ $i2S_4\sigma_h2\sigma_v'2\sigma_v''$
Rhombohedral ..	16	3	C_3	$E2C_3$
	17	$\bar{3}$	S_6	$E2C_3i2S_6$
	18	$3\,m$	C_{3v}	$E2C_33\sigma_v$
	19	3 2	D_3	$E2C_33C_2$
	20	$\bar{3}\ 2/m$	D_{3d}	$E2C_33C_2i2S_63\sigma_v$
Hexagonal ..	21	$3/m$	C_{3h}	$E2C_3\sigma_h\ 2S_3$
	22	6	C_6	$E2C_62C_3C_2$
	23	$6/m$	C_{6h}	$E2C_62C_3C_2i2S_62S_3\sigma_h$
	24	$\bar{6}\ 2m$	D_{3h}	$E2C_33C_2\sigma_h2S_3\ 3\sigma_v$
	25	$6\,mm$	C_{6v}	$E2C_62C_3C_23\sigma_v'3\sigma_v''$
	26	6 2 2	D_6	$E2C_62C_3C_23C_2'3C_2''$
	27	$6/m\ 2/m\ 2/m$	D_{6h}	$E2C_62C_3\ C_23C_2'3C_2''$ $i2S_62S_3\sigma_h3\sigma_v'3\sigma_v''$
Cubic ..	28	23	T	$E3C_28C_3$
	29	$2/m\ \bar{3}$	T_h	$E3C_28C_3i3\sigma8S_6$
	30	$4\ 3\ m$	T_d	$E8C_33C_26\sigma6S_4$
	31	4 3 2	O	$E8C_33C_26C_26C_4$
	32	$4/m\ \bar{3}\ 2/m$	O_h	$E8C_33C_26C_26C_4$ $i8S_63\sigma6\sigma6S_4$

this reason, point groups involving fivefold, sevenfold, etc., axes of symmetry cannot be used for filling up the corners of a space lattice in three dimensions in a manner so as to impart that degree of symmetry to the lattice itself. Point groups built from the holohedral symmetry and its subgroups of each one of the space lattices only are therefore of crystallographic significance. They are 32 in number and the above table divides them into seven sets. At the end of each set is a full group denoting the holohedral symmetry of that system and the rest of the members in the set could be regarded as subgroups of the full group in the set. It may be noted that in each set, subgroups, already enumerated in an earlier one, have been omitted. For example the two groups E; Ei; are subgroups of the group $E\sigma_h iC_2$ and are not included in the second set as they have been already taken into account in the first set.

Space Groups.—As in the case of one and two-dimensional space groups, here also translational symmetry introduces the possibility of obtaining patterns whose symmetry is isomorphous with that of one of the 32 point groups considered in the previous Section, because glide reflection planes and screw axes can come in, in the place of ordinary reflection planes and rotation axes. The total number of space groups is 230 and these are enumerated below.

The 230 *Three-Dimensional Space Groups*

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
Triclinic ..	1	$P1$	1	C_1^1	X, Y, Z
	2	$P\bar{1}$	1	C_1^1	$\bar{X}, \bar{Y}, \bar{Z}$
Monoclinic	3	$P2$	2	C_2^1	$\bar{X}, Y+\beta, \bar{Z}$
	4	$P2_1$	2	C_2^2	β
	5	$C2$	3	C_2^3	
	6	Pm	2	C_s^1	$X, \bar{Y}, \ddot{Z}+\gamma$
	7	Pc	2	C_s^2	γ

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	8	*Cm*	3	C_s^3	. .
	9	*Cc*	3	C_s^4	γ
	10	*P*2/*m*	2	C_{2h}^1	$\bar{X}, Y+\beta, \bar{Z}+\gamma$; $\bar{X}, \bar{Y}, \bar{Z}$
	11	$P2_1/m$	2	C_{2h}^2	β
	12	*C*2/*m*	3	C_{2h}^3	. .
	13	*P*2/*c*	2	C_{2h}^4	γ
	14	$P2_1/c$	2	C_{2h}^5	$\beta\gamma$
	15	*C*2/*c*	3	C_{2h}^6	γ
Ortho-rhombic	16	*P*222	4	D_2^1	$X+\alpha, \bar{Y}+\beta, \bar{Z}$; and $\bar{X}+\alpha'$, $Y+\beta', \bar{Z}+\gamma'$
	17	$P222_1$	4	D_2^2	γ'
	18	$P2_12_12$	4	D_2^3	$\alpha\beta\alpha'\beta'$
	19	$P2_12_12_1$	4	D_2^4	$\alpha\beta\beta'\gamma'$
	20	$C222_1$	5	D_2^5	γ'
	21	*C*222	5	D_2^6	. .
	22	*F*222	7	D_2^7	. .
	23	*I*222	6	D_2^8	. .
	24	$I2_12_12_1$	6	D_2^9	$\alpha\beta\beta'\gamma'$
	25	*Pmm*2	4	C_{2v}^1	$\bar{X}+\alpha, \bar{Y}+\beta$, $Z+\gamma$; and $\bar{X}+\alpha', Y+\beta'$ $Z+\gamma'$
	26	$Pmc2_1$	4	C_{2v}^2	γ
	27	*Pcc*2	4	C_{2v}^3	γ'
	28	*Pma*2	4	C_{2v}^4	α'
	29	$Pca2_1$	4	C_{2v}^5	$\gamma\alpha'\gamma'$
	30	*Pnc*2	4	C_{2v}^6	$\beta'\gamma'$
	31	$Pmn2_1$	4	C_{2v}^7	$\alpha\gamma$
	32	*Pba*2	4	C_{2v}^8	$\alpha'\beta'$
	33	$Pna2_1$	4	C_{2v}^9	$\gamma\alpha'\beta'\gamma'$
	34	*Pnn*2	4	C_{2v}^{10}	$\alpha'\beta'\gamma'$
	35	*Cmm*2	5	C_2^{11}	
	36	$Cmc2_1$	5	C_{2v}^{12}	γ
	37	*Ccc*2	5	C_{2v}^{13}	γ'
	38	*Cmm*2	5	C_{2v}^{14}	$X+\alpha, \bar{Y}, \bar{Z}+\gamma$; and $X+\alpha'$, $Y+\beta', \bar{Z}+\gamma'$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	39	*Cbm2*	5	C_{2v}^{15}	β'
	40	*Cmc2*	5	C_{2v}^{16}	γ'
	41	*Cbc2*	5	C_{2v}^{17}	$\beta'\gamma'$
	42	*Fmm2*	7	C_{2v}^{18}	..
	43	*Fdd2*	7	C_{2v}^{19}	$\alpha'/2, \beta'/2, \gamma'/2$
	44	*Imm2*	6	C_{2v}^{20}	...
	45	*Iba2*	6	C_{2v}^{21}	γ'
	46	*Ima2*	6	C_{2v}^{22}	α'
	47	*Pmmm*	4	D_{2h}^{1}	$X + \alpha, \bar{Y} + \beta, \bar{Z} + \gamma; \bar{X} + \alpha', Y + \beta', \bar{Z} + \gamma';$ and $\bar{X}, \bar{Y}, \bar{Z}$
	48	*Pnnn*	4	D_{2h}^{2}	$\beta\gamma\alpha'\gamma'$
	49	*Pccm*	4	D_{2h}^{3}	$\gamma\gamma'$
	50	*Pban*	4	D_{2h}^{4}	$\beta\alpha'$
	51	*Pmma*	4	D_{2h}^{5}	α
	52	*Pnna*	4	D_{2h}^{6}	$\beta\gamma\alpha'\beta'\gamma'$
	53	*Pmna*	4	D_{2h}^{7}	$\alpha'\gamma'$
	54	*Pcca*	4	D_{2h}^{8}	$\alpha\gamma\gamma'$
	55	*Pbam*	4	D_{2h}^{9}	$\alpha\beta\alpha'\beta'$
	56	*Pcc*	4	D_{2h}^{10}	$\alpha\gamma\beta'\gamma'$
	57	*Pbcm*	4	D_{2h}^{11}	$\beta\beta'\gamma'$
	58	*Pnnm*	4	D_{2h}^{12}	$\alpha\beta\gamma\alpha'\beta'\gamma'$
	59	*Fmmn*	4	D_{2h}^{13}	$\alpha\beta'$
	60	*Pbcn*	4	D_{2h}^{14}	$\alpha\beta\gamma'$
	61	*Pbca*	4	D_{2h}^{15}	$\alpha\beta\beta'\gamma'$
	62	*Pnam*	4	D_{2h}^{16}	$\alpha\beta\gamma\beta'$
	63	*Cmcm*	5	D_{2h}^{17}	γ'
	64	*Cmca*	5	D_{2h}^{18}	$\beta'\gamma'$
	65	*Cmmm*	5	D_{2h}^{19}	
	66	*Cccm*	5	D_{2h}^{20}	$\gamma\gamma'$
	67	*Cmma*	5	D_{2h}^{21}	α'
	68	*Ccca*	5	D_{2h}^{22}	$\alpha\gamma\alpha'\beta'\gamma'$
	69	*Pmmm*	7	D_{2h}^{23}	..
	70	*Fddd*	7	D_{2h}^{24}	$\beta/2, \gamma/2, \alpha'/2$
	71	*Immm*	6	D_{2h}^{25}	..
	72	*Ibam*	6	D_{2h}^{26}	$\gamma\gamma'$
	73	*Ibca*	6	D_{2h}^{27}	$\gamma\alpha'$
	74	*Imma*	6	D_{2h}^{28}	β'
Tetragonal	75	*P4*	8	C_4^{1}	$\bar{Y} + \alpha, X, Z + \gamma$
	76	$P4_1$	8	C_4^{2}	$\gamma/2$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	77	$P4_2$	8	C_4^3	γ
	78	$P4_3$	8	C_4^4	$3\gamma/2$
	79	$I4$	9	C_4^5	..
	80	$I4$	9	C_4^6	$\beta, \gamma/2$
	81	$P\bar{4}$	8	S_4^1	$Y, \bar{X}, \bar{Z}$
	82	$I\bar{4}$	9	S_4^2	..
	83	$P4/m$	8	C_{4h}^1	$\bar{Y} + \alpha, X + \beta, Z + \gamma$; and $\bar{X}, \bar{Y}, \bar{Z}$
	84	$P4_2/m$	8	C_{4h}^2	γ
	85	$P4/n$	8	C_{4h}^3	α
	86	$P4_2/n$	8	C_{4h}^4	$\beta\gamma$
	87	$I4/m$	9	C_{4h}^5	..
	88	$I4_1/a$	9	C_{4h}^6	$3\gamma/2, \beta/2, \gamma/$
	89	$P422$	8	D_4^1	$\bar{Y} + \alpha, X + \beta, Z + \gamma$; and $X + \alpha', \bar{Y} + \beta', \bar{Z} + \gamma'$
	90	$P42_12$	8	D_4^2	$\alpha\beta\alpha'\beta'$
	91	$P4_122$	8	D_4^3	$\gamma/2, \gamma'$
	92	$P4_12_12$	8	D_4^4	$\alpha\beta\gamma/2, \alpha'\beta'\gamma'/2$
	93	$P4_222$	8	D_4^5	γ
	94	$P4_22_12$	8	D_4^6	$\alpha\beta\gamma\alpha'\beta'\gamma'$
	95	$P4_322$	8	D_4^7	$3\gamma/2, \gamma'$
	96	$P4_32_12$	8	D_4^8	$\alpha\beta3\gamma/2, \alpha'\beta'\gamma'/2$
	97	$I422$	9	D_4^9	..
	98	$I4_122$	9	D_4^{10}	$\beta\gamma/2, \beta'\gamma'/2$
	99	$P4mm$	8	C_{4v}^1	$\bar{Y} + \alpha, X + \beta, Z + \gamma$; and $\bar{X} + \alpha', Y + \beta', Z + \gamma'$
	100	$P4bm$	8	C_{4v}^2	$\alpha'\beta'$
	101	$P4_2cm$	8	C_{4v}^3	$\gamma\gamma'$
	102	$P4_2nm$	8	C_{4v}^4	$\alpha\beta\gamma\alpha'\beta'\gamma'$
	103	$P4cc$	8	C_{4v}^5	γ'
	104	$P4nc$	8	C_{4v}^6	$\alpha'\beta'\gamma'$
	105	$P4_2mc$		C_{4v}^7	γ
	106	$P4_2bc$	8	C_{4v}^8	$\gamma\alpha'\beta'$
	107	m	9	C_{4v}^9	
	108	cm	9	C_{4v}^{10}	$\alpha'\beta'$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	109	$I4_1md$	9	C_{4v}^{11}	$\beta\gamma/2$
	110	$I4_1cd$	9	C_{4v}^{12}	$\beta\gamma/2\ \gamma'$
	111	$P\bar{4}2m$	8	D_{2d}^{1}	$Y + \alpha, \bar{X} + \beta,$ $\bar{Z} + \gamma$; and $X + \alpha', \bar{Y} + \beta',$ $\bar{Z} + \gamma'$
	112	$P\bar{4}2c$	8	D_{2d}^{2}	γ'
	113	$P\bar{4}2_1m$	8	D_{2d}^{3}	$\alpha'\beta'$
	114	$P\bar{4}2_1c$	8	D_{2d}^{4}	$\alpha'\beta'\gamma'$
	115	$P\bar{4}m2$	8	D_{2d}^{5}	$Y + \alpha, \bar{X} + \beta,$ $\bar{Z} + \gamma$; and $\bar{X} + \alpha'', Y+\beta'',$ $Z + \gamma''$
	116	$P\bar{4}c2$	8	D_{2d}^{6}	γ''
	117	$P\bar{4}b2$	8	D_{2d}^{7}	$\alpha''\beta''$
	118	$P\bar{4}n2$	8	D_{2d}^{8}	$\alpha''\beta''\gamma''$
	119	$I\bar{4}m2$	9	D_{2d}^{9}	..
	120	$I\bar{4}c2$	9	D_{2d}^{10}	γ''
	121	$I\bar{4}2m$	9	D_{2d}^{11}	..
	122	$I\bar{4}2d$	9	D_{2d}^{12}	$\beta'\gamma'/2$
	123	$P4/mmm$	8	D_{4h}^{1}	$\bar{Y} + \alpha, X + \beta,$ $Z + \gamma$; $X + \alpha',$ $\bar{Y} + \beta', \bar{Z} + \gamma'$; and $\bar{X}, \bar{Y}, \bar{Z}$
	124	$P4/mcc$	8	D_{4h}^{2}	γ'
	125	$P4/nbm$	8	D_{4h}^{3}	$\alpha\beta'$
	126	$P4/nnc$	8	D_{4h}^{4}	$\alpha\beta'\gamma'$
	127	$P4/mbm$	8	D_{4h}^{5}	$\alpha'\beta'$
	128	$P4/mnc$	8	D_{4h}^{6}	$\alpha'\beta'\gamma'$
	129	$P4/nmm$	8	D_{4h}^{7}	$\alpha\alpha'$
	130	$P4/ncc$	8	D_{4h}^{8}	$\alpha\alpha'\gamma'$
	131	$P4/mmc$	8	D_{4h}^{9}	γ
	132	$P4_2/mcm$	8	D_{4h}^{10}	$\gamma\gamma'$
	133	$P4_2/nbc$	8	D_{4h}^{11}	$\alpha\gamma\beta'$
	134	$P4_2/nnm$	8	D_{4h}^{12}	$\alpha\gamma\beta'\gamma'$
	135	$P4_2/mbc$	8	D_{4h}^{13}	$\gamma\alpha'\beta'$
	136	$P4_2/mnm$	8	D_{4h}^{14}	$\alpha\beta'$
	137	$P4_2/nmc$	8	D_{4h}^{15}	$\alpha\gamma\alpha'$
	138	$P4_2/ncm$	8	D_{4h}^{16}	$\alpha\gamma\alpha'\gamma'$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	139	$I4/mmm$	9	D_{4h}^{17}	..
	140	$I4/mcm$	9	D_{4h}^{18}	γ'
	141	$I4_1/amd$	9	D_{4h}^{19}	$3\alpha/2\ \beta/2\ 3\gamma/2$
	142	$I4_1/acd$	9	D_{4h}^{20}	$3\alpha/2, \beta/2, 3\gamma/2, \gamma'$
Trigonal	143	$P3$	10	C_3^1	$Y, X - Y, Z + Y$
	144	$P3_1$	10	C_3^2	$\gamma = \frac{1}{3}$
	145	$P3_2$	10	C_3^3	$\gamma = \frac{2}{3}$
	146	$R3$	10	C_3^4	Z, X, Y
	147	$P\bar{3}$	10	C_{3i}^1	$\bar{Y}, X - Y, Z$; and $\bar{X}, \bar{Y}, \bar{Z}$
	148	$R\bar{3}$	10	C_{3i}^2	Z, X, Y; and $\bar{X}, \bar{Y}, \bar{Z}$
	149	$P312$	10	D_3^1	$\bar{Y}, X - Y, Z+\gamma''$; and $X, X - Y, \bar{Z}$
	150	$P321$	10	D_3^2	$\bar{Y}, X - Y, Z+\gamma$; and $X - Y, \bar{Y}, \bar{Z} + \gamma'$
	151	$P3_112$	10	D_3^3	$\gamma'' = \frac{1}{3}$
	152	$P3_121$	10	D_3^4	$\gamma = \frac{1}{3}, \gamma' = \frac{2}{3}$
	153	$P3_212$	10	D_3^5	$\gamma'' = \frac{2}{3}$
	154	$P3_221$	10	D_3^6	$\gamma = \frac{2}{3}, \gamma' = \frac{1}{3}$
	155	$R32$	10	D_3^7	$Z, X, Y; \bar{Y}, \bar{X}, \bar{Z}$
	156	$P3m1$	10	C_{3v}^1	$\bar{Y}, X - Y, Z$; and $Y - X, Y, Z + \gamma$
	157	$P31m$	10	C_{3v}^2	$\bar{Y}, X - Y, Z$; and $\bar{X}, Y - X, Z + \gamma'$
	158	$P3c1$	10	C_{3v}^3	..
	159	$P31c$	10	C_{3v}^4	γ'
	160	$R3m$	10	C_{3v}^5	Z, X, Y; and $Y + \alpha, X + \alpha, Z + \alpha$
	161	$R3c$	10	C_{3v}^6	α
	162	$P\bar{3}1m$	10	D_{3d}^1	$Y, Y - X, \bar{Z}+\gamma$; and $X, X - Y, \bar{Z} + \gamma'$
	163	$P\bar{3}1c$	10	D_{3d}^2	$\gamma' = \frac{1}{2}$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	164	$P\bar{3}m1$	10	D_{3d}^3	$Y, Y-X, \bar{Z}+\gamma$; and $X-Y, \bar{Y}, \bar{Z}+\gamma''$
	165	$P\bar{3}c1$	10	D_{3d}^4	$\gamma'' = \frac{1}{2}$
	166	$R\bar{3}m$	10	D_{3d}^5	$\bar{Z}, \bar{X}, \bar{Y}$; and $Y+a, X+a, Z+a$
	167	$R\bar{3}c$	10	D_{3d}^6	a
	168	$P6$	10	C_6^1	$X-Y, X, Z+\gamma$
	169	$P6_1$	10	C_6^2	$\gamma = \frac{1}{6}$
	170	$P6_5$	10	C_6^3	$\gamma = 5/6$
	171	$P6_2$	10	C_6^4	$\gamma = \frac{1}{3}$
	172	$P6_4$	10	C_6^5	$\gamma = \frac{2}{3}$
	173	$P6_3$	10	C_6^6	$\gamma = \frac{1}{2}$
Hexagonal	174	$P\bar{6}$	11	C_{3h}^1	$Y-X, \bar{X}, \bar{Z}$
	175	$P6/m$	11	C_{6h}^1	$X-Y, X, Z+\gamma$; and $\bar{X}, \bar{Y}, \bar{Z}$
	176	$P6_3/m$	11	C_{6h}^2	$\gamma = \frac{1}{2}$
	177	$P622$	11	D_6^1	$X-Y, X, Z+\gamma$; and $X-Y, \bar{Y}, \bar{Z}$
	178	$P6_122$	11	D_6^2	$\gamma = \frac{1}{6}$
	179	$P6_522$	11	D_6^3	$\gamma = \frac{5}{6}$
	180	$P6_222$	11	D_6^4	$\gamma = \frac{1}{3}$
	181	$P6_422$	11	D_6^5	$\gamma = \frac{2}{3}$
	182	$P6_322$	11	D_6^6	$\gamma = \frac{1}{2}$
	183	$P6mm$	11	C_{6v}^1	$Y-X, Y, Z+\gamma$; and $X-Y, X, Z+\gamma'$
	184	$P6cc$	11	C_{6v}^2	γ
	185	$P6_3cm$	11	C_{6v}^3	$\gamma\gamma'$
	186	$P6_3mc$	11	C_{6v}^4	γ'
	187	$P\bar{6}m2$	11	D_{3h}^1	$Y-X, \bar{X}, \bar{Z}+\gamma$; and $X, X-Y, \bar{Z}$
	188	$P\bar{6}c2$	11	D_{3h}^2	$\gamma = \frac{1}{2}$
	189	$P\bar{6}2m$	11	D_{3h}^3	$Y-X, \bar{X}, \bar{Z}+\gamma'$; and $X-Y, \bar{Y}, \bar{Z}$
	190	$P\bar{6}2c$	11	D_{3h}^4	$\gamma' = \frac{1}{2}$

System	No.	Hermann-Mauguin	Lattice No.	Schoenflies	Generating Elements
	191	$P6/mmm$	11	D_{6h}^{1}	$X-, Y, \bar{Y}\bar{Z}+\gamma$; $X-Y, X$, $Z+\gamma'$; and $\bar{X}, \bar{Y}, \bar{Z}$
	192	$P6/mcc$	11	D_{6h}^{2}	γ
	193	$P6_3/mcm$	11	D_{6h}^{3}	γ'
	194	$P6_3/mmc$	11	D_{6h}^{4}	$\gamma\gamma'$
Cubic	195	$P23$	12	T^{1}	$X+\alpha, \bar{Y}+\beta, \bar{Z}$; and Z, X, Y
	196	$F23$	14	T^{2}	..
	197	$I23$	13	T^{3}	..
	198	$P2_13$	12	T^{4}	$\alpha\beta$
	199	$I2_13$	13	T^{5}	$\alpha\beta$
	200	$Pm3$	12	T_h^{1}	$Z+\alpha, X+\beta$, $Y+\gamma, X+\alpha'$, $\bar{Y}+\beta', \bar{Z}+\gamma'$, and $\bar{X}, \bar{Y}, \bar{Z}$
	201	$Pn3$	12	T_h^{2}	$\beta'\gamma'$
	202	$Fm3$	14	T_h^{3}	..
	203	$Fd3$	14	T_h^{4}	$\beta'/2\ \gamma'/2$
	204	$Im3$	13	T_h^{5}	..
	205	$Pa3$	12	T_h^{6}	$\alpha'\beta'$
	206	$Ia3$	13	T_h^{7}	γ'
	207	$P43$	12	O^{1}	Y, Z, X and $\bar{X}+\alpha$ $\bar{Z}+\beta, Y+\gamma$
	208	$P4_232$	12	O^{2}	α, β, γ
	209	$F432$	14	O^{3}	..
	210	$F4_132$	14	O^{4}	λ, β, γ
	211	$I432$	13	O^{5}	..
	212	$P4_332$	12	O^{6}	$3\alpha/2\ \beta/2\ 3\gamma/2$
	213	$P4_132$	12	O^{7}	$\alpha/2\ 3\beta/2\ \gamma/2$
	214	$I4_132$	13	O^{8}	$3\alpha/2\ \beta/2\ 3\gamma/2$
	215	$P\bar{4}3m$	12	T_d^{1}	Y, Z, X; and $X+\alpha, \bar{Z}+\beta$, $\bar{Y}+\gamma$
	216	$F\bar{4}3m$	14	T_d^{2}	..
	217	$I\bar{4}3m$	13	T_d^{3}	..
	218	$P\bar{4}3n$	12	T_d^{4}	α, β, γ
	219	$F\bar{4}3c$	14	T_d^{5}	γ

System	No.	Hermann-Mauguin	Lattice No.	Schöenflies	Generating Elements
	220	$I\bar{4}3d$	13	T_d^6	$3\alpha/2\ \beta/2\ 3\gamma/2$
	221	$Pm3m$	12	O_h^1	$X + \alpha$, $\bar{Z} + \beta$, $\bar{Y} + \gamma$, $Y + \alpha'$, $Z + \beta'$, $X + \gamma'$, and $\bar{X}$, $\bar{Y}$, $\bar{Z}$
	222	$Pn3n$	12	O_h^2	α
	223	$Pm3n$	12	O_h^3	α, β, γ
	224	$Pn3m$	12	O_h^4	β, γ
	225	$Fm3m$	14	O_h^5	..
	226	$Fm3c$	14	O_h^6	γ
	227	$Fd3m$	14	O_h^7	$\beta/2\ \gamma/2$
	228	$Fd3c$	14	O_h^8	$\beta/2\ 3\gamma/2$
	229	$Im3m$	13	O_h^9	..
	230	$Ia3d$	13	O_h^{10}	$3\alpha/2\ \beta/2\ 3\gamma/2$

For further details reference may be made to the *International Tables for X-ray Crystallography*, 1952. The Hermann-Mauguin notation for the various symmetry operations is the following. X and $\bar{X}$ stand respectively for an X-fold axis of rotation and of rotation-reflection. X takes the values 1, 2, 3, 4 and 6. X_r stands for a screw in which the fractional translation is rT/X where T is the basic translation along the screw axis. m stands for a pure reflection. a, b, c stand for glide planes of reflection, the glides being respectively along the x, y and z directions. n stands for a diagonal plane and d stands for a glide plane of the type $(T_x \pm T_y)/4$ in the derived lattices. The twofold axis in X_2 or $\bar{X}_2$ is normal to the rotation axis X, whereas, a rotation axis X with a reflection plane m parallel to it is denoted by Xm. When the reflection plane is perpendicular to the rotation axis X, it is denoted by X/m. The symbol X/mm denotes that X is perpendicular to one reflection plane and parallel to the other. Similarly the symbol X/mmm denotes that X is perpendicular to one reflection plane and is parallel to the other two.

The generating elements in Column 6 are to be taken as the operations which transform the point *X*, *Y*, *Z* into the point whose co-ordinates are given in that column. The co-ordinates are taken with respect to the crystallographic axes. The co-ordinates of the transformed point are given explicitly for the first space group in each typical class and are described in terms of certain parameters in all the other space groups belonging to that class. The parameters take the value zero in the first space group of each class, where they are first introduced, and only the non-vanishing parameters in the case of the other space groups are given. These operations along with the translations generate the complete space group in each case.

P stands for the simple lattice except when in the rhombohedral system *R* is used, it also stands for the same. *C*, *I* and *F* stand respectively for side centred, body centred and face centred lattices.

We have thus been enabled to build 230 space groups* in three dimensions utilizing 32 point groups and fourteen space lattices coming under seven systems of symmetry. Just as we used three-dimensional motives on two-dimensional lattices and obtained 80 space groups, instead of 17 with two-dimensional motives, we could use similarly four or even higher dimensional motives on the three-dimensional lattices. For example, we could distinguish between two otherwise identical structures, if the orientations of the spins are also taken into account.

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* Detailed derivation of the 230 space groups may be obtained from [illegible] *Theory of X-Ray Diffraction in Crystals* (1946).

CHAPTER XII

RAMAN AND INFRA-RED SPECTRA OF CRYSTALS

The Internal Structure of a Crystal.—A crystal may be looked upon as having been obtained by locating groups of atoms, molecules or ions at every lattice point of a given lattice. The symmetry of such a structure as a whole depends on the symmetry of the group chosen for repetition and the symmetry of the lattice itself. If this group contains p atoms, it is easily seen that the structure is composed of p interpenetrating monatomic Bravais lattices and the smallest unit cell, which is not necessarily the same as that bounded by the crystallographic axes, contains p atoms. If the crystallographic unit cell is different from the smallest possible unit cell, as it will be the case with all the side centred, face centred and body centred lattices, it will contain Kp atoms where the volume of the crystallographic cell chosen is K times that of the Bravais cell and K is equal to either 2 or 4.

It is customary to use the word lattice to denote an arrangement in which only one atom is located at each of the lattice points. A structure, on the other hand, denotes an arrangement in which a group of two or more atoms is located at each of the lattice points and has, therefore, to be looked upon as made up of a set of interpenetrating lattices.

Application of Group Theory.—As has already been mentioned, in the case of crystals, in addition to pure rotations and rotation-reflections, we have translatory type of symmetry operations such as pure translations, screw axes of rotation and glide planes of reflection. In spite of this, the Raman and infra-red spectra of crystals resemble closely those obtained with molecules and convenient and simplifying assumptions may be made if we are interested in the first order lines. As far as translations are concerned, the transformation properties of the components of the polarizability tensor and the electric moment vector may be assumed to be the same as for the identity element. With this extension, the usual formulæ already derived for molecules can still be used for crystals to find the normal modes of oscillation, the selection rules, etc. This, however, implies that all translations in the group of symmetry operations are being regarded as equivalent to the identity and the factor group thus obtained is isomorphic with one of the 32 point groups. Much useful information may be gathered by studying a crystal in the above manner. In many cases, this has been done and we shall illustrate it by a few applications.

There will be $3p - 3$ oscillations and they may be classified as external and internal ones. The external ones are referred to as the lattice oscillations. Such a distinction is not a very clear-cut one but the following may serve as useful criteria in the two cases. The possibility of the oscillations being classified in this manner rests on our being able to divide the p non-equivalent points into s groups such that the forces between one group and the other are comparatively feeble, whereas the forces that exist between the members of any one group are quite strong. In such a case, all the oscillations involving a movement of the s groups, only as entities, will generally exhibit low frequencies and may be termed external. The others, involving also movements of the individual members in each of the groups against themselves, will generally exhibit high frequencies and may be termed internal. The external oscillations may further be subdivided into two classes, namely, rotational and translational, according as the movements of the groups are of a rotatory type or translatory type. In complicated crystals, where a full and detailed analysis is very difficult to carry through, a classification in this manner is likely to be of great help in explaining the results. We shall now derive some important theorems and apply them to specific cases of practical interest.

The symmetry operations characteristic of the p non-equivalent atoms and the character table of the group may easily be written out. The relation which enables us to find n_i, the number of times a particular irreducible representation Γ_i is contained in another representation Γ, if the group characters in both the representations are known has already been given as

$$n_i = \frac{1}{N} \sum h_\rho \chi_\rho' (R)\, \chi_i (R),$$

$\chi_i (R)$ and $\chi_\rho' (R)$ are respectively the characters of the group operation R in the representations Γ_i and Γ and N is the order of the group and h_ρ is the number of group operations falling under the class ρ. By suitably choosing the representation Γ and utilizing the characters $\chi_\rho' (R)$ appropriate to it, we can confine ourselves to one or other of the several types of normal oscillations.

For example, if Γ is a representation defined by all the $3p$ Cartesian co-ordinates which account for the entire freedom possessed by the non-equivalent points in the unit cell, then

$$\chi_\rho' (R) = U_R (\pm 1 + 2 \cos \phi_R)$$

and n_i, obtained by substituting this will include all types of normal modes, namely translations, translatory and rotatory types of external oscillations and internal oscillations. U_R is the number of atoms that remain invariant under the operation R and the plus or the minus sign is to be taken according as R is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. This relation has been extensively used in earlier Chapters.

If we want to confine ourselves only to translations, it is clear that U_R is to be put equal to unity for all R because the whole group moves as one entity in these modes. In other words, Γ is defined by only three Cartesian co-ordinates and it is easily seen that

$$\chi_\rho' (R) = \pm 1 + 2 \cos \phi_R.$$

n_i obtained by substituting this may be denoted as $n_i\,(T)$, as the results now refer to translations only. Confining ourselves to the translatory type of external oscillations only, as has already been explained before, if s is the number of groups into which the non-equivalent points may be divided, with due regard to the magnitudes of the forces that exist between them, we have

$$\chi_\rho'\,(R) = [U_R\,(s) - 1]\,(\pm\,1 + 2\cos\phi_R).$$

$U_R\,(s)$ represents the number of such groups that remain invariant out of the number s under an operation R. The derivation of the above formula is quite simple. Each one of the groups s has 3 degrees of translational freedom and the representation in this case is defined by $3s$ Cartesian co-ordinates. $U_R\,(s)\,(\pm\,1 + 2\cos\phi_R)$ will be the character of an operation R in such a representation. If the pure translations that have already been taken account of are to be excluded from this, we have to subtract $\pm\,1 + 2\cos\phi_R$ from $U_R\,(s)\,(\pm\,1 + 2\cos\phi_R)$ and we get the above relation.

If we confine ourselves to the rotatory type of external oscillations, we get

$$\chi_\rho'\,(R) = [U_R\,(s - v)]\,(1 \pm 2\cos\phi_R).$$

v stands for the number of groups in s, which are constituted by single atoms only. Such monatomic groups have no rotational degrees of freedom and $s - v$ is, therefore, the number of groups with each of which we have to associate three degrees of rotational freedom. $U_R\,(s - v)$ represents the number that remain invariant out of the number $s - v$ under an operation R. The character of an operation R, in a representation defined by the three components of a displacement vector, is $1 \pm 2\cos\phi_R$, the $+$ or the $-$ sign being used according as R is a pure rotation through ϕ or a rotation through ϕ accompanied by a reflection. This is evident from the transformations already given and repeated below for convenience.

$$l_x \rightarrow \pm\, l_x \cos\phi \pm l_y \sin\phi;\quad l_y \rightarrow \mp\, l_x \sin\phi \pm l_y \cos\phi;\quad l_z \rightarrow l_z$$

l_x, l_y and l_z are the components of the vector l and the series of signs given on the top are to be taken when the operation R is a pure rotation around the Z axis. The alternative set relates to the case where R is a rotation accompanied by a reflection. If there are $U_R(s - v)$ separate units, each of which has three degrees of rotational freedom, the representation will be that defined by $3U_R(s - v)$ components of the vector l and the character of an operation R in such a representation is that given by the above formula. Those groups which are not invariant under the operation R do not contribute to the character as before.

In order to get n_i', the number of internal oscillations under each representation, we merely have to eliminate those given under the above categories from n_i. This is formally achieved by writing out the character as given below and using it in the general formula. The result may also be obtained by direct subtraction of the numbers under the categories of translation and translatory and rotatory types of external oscillations from the total number under each representation.

$$\begin{aligned}\chi_p'(R) = {} & [U_R - U_R(s)](\pm 1 + 2\cos\phi_R) \\ & - U_R(s - v)(1 \pm 2\cos\phi_R).\end{aligned}$$

Lattice Oscillations in Calcite and Sodium Nitrate.—In order that the utility of the method outlined in the foregoing Chapter may be fully appreciated, we shall first apply it to the cases of calcite and sodium nitrate in this Section. These two substances have the same crystal structures and their space group is D_{3d}^6. Exactly similar considerations apply to both. The unit cell which is shown in Fig. 12 is an elongated rhombohedron and contains two molecules. The lattices are ionic and the co-ordinates of the atoms in the case of calcite are given below.

Ca (1, 2): $\frac{1}{4}\,\frac{1}{4}\,\frac{1}{4}$; $\frac{3}{4}\,\frac{3}{4}\,\frac{3}{4}$;
C (3, 4): 0 0 0; $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$;
O (5 to 10):

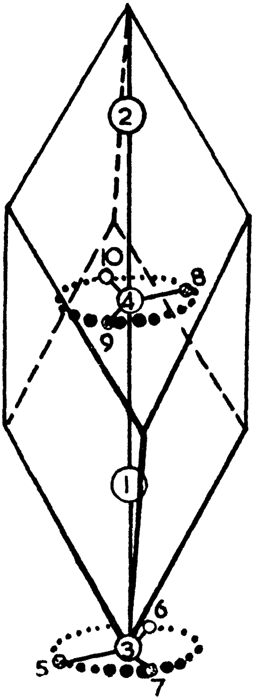

FIG. 12

In our notation $p = 10$, $s = 4$ and $v = 2$ for this case. If as a result of symmetry operation, an atom moves into the position of one of its equivalents, it should be regarded as invariant.

The operations of this group may be expressed as follows:

E (Identity)

$$2S_6 \begin{cases} (1)\ (2)\ (3, 4)\ (5, 9, 7, 8, 6, 10) \\ (1)\ (2)\ (3, 4)\ (5, 10, 6, 8, 7, 9) \end{cases}$$

$$2C_3 \begin{cases} (1)\ (2)\ (3)\ (4)\ (8, 10, 9)\ (5, 7, 6) \\ (1)\ (2)\ (3)\ (4)\ (8, 9, 10)\ (5, 6, 7) \end{cases}$$

$$(1)\ (2)\ (3, 4)\ (5, 8)\ (6, 9)\ (7, 10)$$

$$3\sigma v \text{ (glide) } \left\{ \begin{array}{l} (1, 2)\,(3, 4)\,(5, 8)\,(6, 10)\,(7, 9) \\ (1, 2)\,(3, 4)\,(5, 10)\,(6, 9)\,(7, 8) \\ (1, 2)\,(3, 4)\,(5, 9)\,(6, 8)\,(7, 10) \end{array} \right.$$

$$3C_2 \left\{ \begin{array}{l} (1, 2)\,(3)\,(4)\,(5)\,(8)\,(6, 7)\,(9, 10) \\ (1, 2)\,(3)\,(4)\,(6)\,(9)\,(5, 7)\,(8, 10) \\ (1, 2)\,(3)\,(4)\,(7)\,(10)\,(5, 6)\,(8, 9) \end{array} \right.$$

The character table and the values of n_i, n_i', etc., are given below.

n_i, T, T', R' and n_i' stand for the total number of oscillations, translations, translatory type of external oscillations, rotatory type of external oscillations and the internal oscillations respectively. $\chi_p'(n_i)$, $\chi_p'(T)$, $\chi_p'(T')$ and $\chi_p'(R')$

D_{3d}^6	E	$2S_6$	$2C_3$	i	$3\sigma_v$	$3C_2$	n_i	T	T'	R'	n_i'	Raman	Infra-red
A_1 ..	1	1	1	1	1	1	1	0	0	0	1	*p*	*f*
A_2 ..	1	1	1	1	−1	−1	3	0	1	1	1	*f*	*f*
B_1 ..	1	−1	1	−1	1	−1	4	1	1	1	1	*f*	*p*
B_2 ..	1	−1	1	−1	−1	1	2	0	1	0	1	*f*	*f*
E_1 ..	2	1	−1	−2	0	0	6	1	2	1	2	*f*	*p*
E_2 ..	2	−1	−1	2	0	0	4	0	1	1	2	*p*	*f*
$U_R(n_i)$ ..	10	2	4	2	0	4							
$U_R(s)$ ..	4	2	4	2	0	2							
$U_R(s-v)$	2	0	2	0	0	2							
$h_p\chi_p'(n_i)$ ..	30	0	0	−6	0	−12							
$h_p\chi_p'(T)$ ..	3	0	0	−3	3	−3							
$h_p\chi_p'(T')$ ..	9	0	0	−3	−3	−3							
$h_p\chi_p'(R')$ ..	6	0	0	0	0	−6							

have been obtained in accordance with the values given for them in the previous Chapter. *p* denotes that all the oscillations coming under that representation are permitted to appear and f denotes that they are forbidden. The following features may now be noted. Because there are two CO_3 ions in the unit cell, each internal oscillation of the free CO_3 ion splits into two in the crystal. The extent of splitting will naturally depend upon the forces that are present in the crystal. Since $s = 4$, besides the translations which represent the acoustic series, there are present a large number of external oscillations, both of the rotatory type and the translatory type. If we are not immediately interested in the internal oscillations, it is quite easy to picture the external modes coming under each representation in them, because all the four groups are to be regarded as entities. Only the CO_3 ions take part in the rotatory type of external oscillations as the calcium ions (monatomic groups) come under the v class. As an example, we give below the symbolic representation of the two external modes coming under the representation E_2. These are Raman active.

$$\left.\begin{aligned} T'(a) &= x_3 - x_4 \\ T'(b) &= y_3 - y_4 \\ R'(a) &= l_x^3 + l_x^4 \\ R'(b) &= l_y^3 + l_y^4 \end{aligned}\right] \quad \cdot\cdot \qquad \cdot\cdot \quad E_2$$

$T'(a)$ and $T'(b)$ and similarly $R'(a)$ and $R'(b)$ are degenerate. Z axis is taken along the trigonal axis and the X and Y axes may lie anywhere in the plane perpendicular thereto. x_3 indicates that the group containing atom 3 undergoes a displacement of one unit in the direction of the X axis. x_3, y_3, etc., occurring in the normal co-ordinates relating to the T type, are to be similarly interpreted. l_x^3 indicates that the group containing atom 3 undergoes a rotation such that it possesses unit angular momentum around the X axis. l_x^3, l_y^4, etc., occurring in the normal co-ordinates relating to the R' type, are to be similarly interpreted. With the help of the group operations and the transformation matrices for x, y, z and l_x, l_y, l_z already given in a foregoing Section, it may be verified that the characters of the normal co-ordinates given above for various R are just those given under the irreducible representation E_2.

In a similar manner, we can write down the normal co-ordinates relating to all the external oscillations without much trouble and without reference to the internal modes. In fact, if only the external modes and their classification are needed, the group operations also could have been written in a much simpler manner utilizing the symbols 1, 2, 3, 4 only.

Some Special Cases.—Such a simplification will be particularly useful, when experimental results show that the intermolecular forces in the crystal are not very important. This may easily be inferred, especially in cases where there is no degradation of symmetry from the free molecule to the crystal, if we find that the Raman lines obtained in the liquid exhibit a general one to one correspondence with those obtained in the same substance in the crystalline state even though there may be two or more molecules per unit cell in the latter.* In such cases, no more information will be obtained by making a detailed study of the internal frequencies for a group of molecules than that available from a study of the single molecule. On the other hand, much of the interest will centre round the lattice oscillations and the special methods outlined in the foregoing pages will be useful. The classification of the lattice oscillations into the translatory and the rotatory type is also of some help, if the following principles are borne in mind in interpreting the experimental results. The translatory type of oscillations are likely to give rise to relatively low frequencies in most cases and even these will be of low intensity in Raman scattering as the changes caused in the polarizability of the crystal cannot be appreciable. On the other hand, the

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* The resemblance referred to is of a general nature. One or two of the lines that occur in the crystal may not appear in the liquid and *vice versa* on account of the different symmetries in the two cases. The essential point is that there is no splitting of the majority of the lines as we pass from the liquid to the crystal.

rotatory type of oscillations will result in intense Raman lines, if the rotating groups are strongly optically anisotropic.

If there is only one molecule per unit cell and if centre of inversion is a symmetry operation of the structure, the crystal may exhibit three lattice oscillations of the rotatory type if there is no degeneracy. This result easily follows from the fact that the three oscillations of the rotatory type are symmetric to the operation of inversion. For crystals of trigonal, tetragonal and hexagonal systems, this number reduces to two and for crystals of the cubic type, it reduces to one merely as a result of the symmetry. As the intensity will also be governed by the optical anisotropy of the molecule, the only lattice line in the case of cubic crystals will have zero intensity because the molecule itself should possess cubic symmetry and one of the lattice lines (non-degenerate one) in the trigonal, tetragonal and hexagonal types will also have zero intensity.

If there are two molecules per unit cell and if the centre of inversion is located at one of the molecules, all lattice oscillations of the translatory type will be Raman inactive. Some of them may be infra-red active. This follows from the fact that the normal co-ordinates, relating to such oscillations, are always antisymmetric to the operation of inversion.

If in the above case, the centre of inversion is located midway between the two molecules, all lattice oscillations of the translatory type will be symmetric to the operation of inversion and some of them may be Raman active. All of them will be infra-red inactive.

Lattice Oscillations in Some Organic Crystals.—We shall choose, in this Section, organic substances like naphthalene and diphenyl which crystallize in the monoclinic prismatic class having the space group C_{2h}^5. The unit cell in each case contains two molecules. Such a choice has specially been made with a view to bring out the fact that the crystal structure plays a major part in determining the character of the low frequency Raman spectrum while the exact chemical nature of the substance has only a secondary influence on it. We start by noting that these crystals melt at comparatively low temperatures and that the Raman lines of the liquid state show a one to one correspondence with those obtained in the crystal. Lines do not show any systematic doubling even though there are two molecules in the unit cell. A study of the internal oscillations may, therefore, be confined with advantage to the free molecule. We shall now apply the methods of the foregoing Sections to these cases and obtain the results that are to be expected in the low frequency region of the Raman spectrum. Figure 13 represents the unit cell for naphthalene which is a typical representative of this class. The two molecules are numbered 1 and 2. In our notation $s = 2$ and $v = 0$. These molecules have their lengths roughly parallel to the c axis and their planes

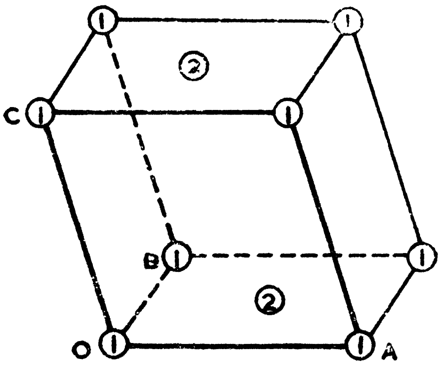

FIG. 13

making angles of about $+ 65°$ and $- 65°$ with the (010) plane. The group operations may be written out as

E: (1) (2)
C_2^s: (1, 2)
i: (1) (2)
σ_h^s: (1, 2)

The character table and other relevant features are given below:

C_{2h}^5	E	C_2	i	σ_h	T	T'	R'	Raman	Infra-red
A_1	1	1	1	1	0	0	3	p	f
A_2	1	−1	1	−1	0	0	3	p	f
B_1	1	1	−1	−1	1	2	0	f	p
B_2	1	−1	−1	1	2	1	0	f	p
$U_R(s)$	2	0	2	0					
$U_R(s-v)$	2	0	2	0					
$h_p\chi_p'(T)$	3	−1	−3	1					
$h_p\chi_p'(T')$	3	1	−3	−1					
$h_p\chi_p'(R')$	6	0	6	0					

Centre of inversion in this case is located at the molecule 1 and it comes under one of the special cases dealt with in the previous Section. We do not get any Raman-active lattice oscillations of the translatory type. We should, however, expect six oscillations of the rotatory type. The corresponding normal co-ordinates may easily be written out in the following manner:

$$\left.\begin{matrix} l_x^1 - l_x^2 \\ l_y^1 - l_y^2 \\ l_z^1 - l_z^2 \end{matrix}\right] \quad \ldots \quad A_1; \qquad \left.\begin{matrix} l_x^1 + l_x^2 \\ l_y^1 + l_y^2 \\ l_z^1 + l_z^2 \end{matrix}\right] \quad \ldots \quad A_2.$$

The symmetry axis is chosen as the Z axis and any two mutually perpendicular directions in the *ac* plane may be chosen as the X and Y axes. It may be seen that the three modes coming under A_1 differ from those coming under A_2 only in the matter of the relative phase difference between the two molecules. For example, while in A_1, both molecules are rotating about the z axis in phase, in A_2, they do so in opposite phases. As has already been said, if the intermolecular forces are not appreciable, the frequencies of these two types of motion cannot differ very much from each other and we can only expect to record three broad bands. The lattice oscillations observed in naphthalene, diphenyl, *p*-dichlorobenzene and *p*-dibromobenzene, all of which belong to this class, are given below:

Naphthalene	45	73	109 and 124
Diphenyl	49	75	150
p-Dichlorobenzene ..	43	55	82
p-Dibromobenzene ..	38	..	93

The figures given are in cm.$^{-1}$ and in most cases, the lines are broad. The general similarity is clear. A line at about 20 cm.$^{-1}$, recorded by Vuks in the last two substances, is not included in the above table as it has not been confirmed by other investigators. The highest frequency in naphthalene has split into two, apparently because of its nearness to the sum of the other two frequencies at 45 and 73. Since all the three lines are expected to be complex in structure and as they all come under the same representation, it will be incorrect to assign any one of the frequencies to a particular mode. Consequently, one may not expect in these cases, such a clear-cut classification of the lattice oscillations into the symmetric, the antisymmetric and the degenerate types as has been obtained in simpler structures like calcite and sodium nitrate.

Raman Spectra and Different Crystalline Modifications.— Several attempts have been made to detect changes in the Raman spectrum of a substance as we pass from one crystalline modification to another. On account of experimental difficulties, these have been mostly confined hitherto, to the internal oscillations although prominent changes are not to be expected in that region but should be looked for only in the low frequency region. In order to illustrate this point we shall consider here the case of aragonite. The crystal structure of aragonite bears to that of calcite, the same relationship as that existing between the structures of potassium nitrate and sodium nitrate and so similar considerations apply to potassium nitrate. However, the lattice oscillations of these substances have not been studied in detail in their Raman spectra and only meagre and conflicting results are available. Nevertheless, the analysis is given here as the structures are of great importance.

The space group of aragonite is V_h^{16} and the unit cell of the smallest size, a projection of which is shown in Fig. 14, contains four molecules of $CaCO_3$. Since we are interested only in the lattice oscillations, we need consider 8 groups ($s = 8$) on the whole, of which 4 ($v = 4$) are monatomic.

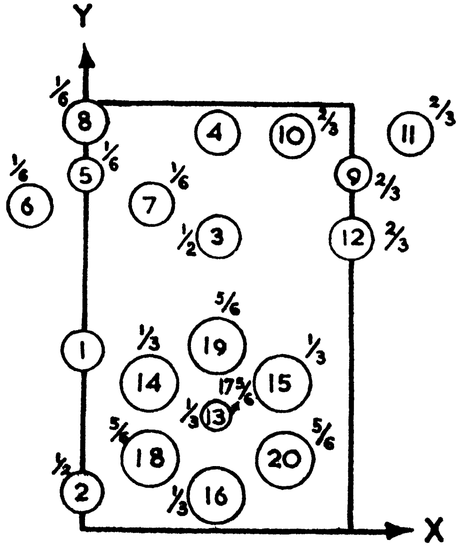

FIG. 14

The groups are numbered as follows:

Ca: 1, 2, 3 and 4;
CO_3: 5, 9, 13 and 17.

Atoms numbered 6, 7, 8, 10, 11, 12, 14, 15, 16, 18, 19, 20 are the oxygens and they need not be considered separately as they go with the corresponding carbons.

The operations of the group are

E (Identity)	
C_2 (Screw $\|^l$ to Z) ..	(1, 2) (3, 4) (5, 9) (13, 17)
C_2' (Screw $\|^l$ to Y) ..	(1, 4) (2, 3) (5, 17) (9, 13)
C_2'' (Screw $\|^l$ to X) ..	(1, 3) (2, 4) (5, 13) (9, 17)
i ..	(1, 2) (3, 4) (5, 9) (13, 17)
σ_h ..	(1) (2) (3) (4) (5) (9) (13) (17)
σ_v (glide) ..	(1, 3) (2, 4) (5, 13) (9, 17)
σ_v' (glide) ..	(1, 4) (2, 3) (5, 17) (9, 13)

The character table and other relevant features are given below:

V_k^{16}	E	C_2	C_2'	C_2''	i	σ_h	σ_v	σ_v'	T	T'	R'	Raman	Infra-red
A_{1g} ..	1	1	1	1	1	1	1	1	0	4	1	p	f
A_{2g} ..	1	−1	1	−1	1	−1	1	−1	0	2	2	p	f
B_{1g} ..	1	1	−1	−1	1	1	−1	−1	0	4	1	p	f
B_{2g} ..	1	−1	−1	1	1	−1	−1	1	0	2	2	p	f
A_{1u} ..	1	1	1	1	−1	−1	−1	−1	0	2	2		f
A_{2u} ..	1	−1	1	−1	−1	1	−1	1	1	3	1		p
B_{1u} ..	1	1	−1	−1	−1	−1	1	1	1	1	2	f	p
B_{2u} ..	1	−1	−1	1	−1	1	1	−1	1	3	1	f	p
$U_R(s)$ ..	8	0	0	0	0	8	0	0					
$U_R(s-v)$	4	0	0	0	0	4	0	0					
$h_p\chi_p'(T)$	3	−1	−1	−1	−3	1	1	1					
$h_p\chi_p'(T')$	21	1	1	1	3	8	−1	−1					
$h_p\chi_p'(R')$	12	0	0	0	0	−4	0	0					

We see from the table, that, besides a large number of translatory type of oscillations, we should expect to get in the Raman spectrum, six oscillations of the rotatory type under different classes. These six normal co-ordinates are easily written down in the following manner:

$$\begin{array}{ll}
l_z^5 + l_z^9 - l_z^{13} - l_z^{17} & A_{1g} \\
\left.\begin{array}{l} l_x^5 + l_x^9 - l_x^{13} - l_x^{17} \\ l_y^5 + l_y^9 + l_y^{13} + l_y^{17} \end{array}\right] & A_{2g} \\
l_z^5 + l_z^9 + l_z^{13} + l_z^{17} & B_{1g} \\
\left.\begin{array}{l} l_x^5 + l_x^9 + l_x^{13} + l_x^{17} \\ l_y^5 + l_y^9 - l_y^{13} - l_y^{17} \end{array}\right] & B_{2g}
\end{array}$$

Normal co-ordinates coming under A_{1g} and B_{1g}, although Raman-active, involve rotations of the CO_3 groups about the Z axis and since the XY plane is nearly a plane of optical symmetry, we can confidently conclude that these modes will not produce appreciable intensities in Raman scattering. Under A_{2g} and B_{2g} we should expect four lines appearing as two close doublets or two broad bands covering the whole series. Besides these, we may expect a few lines arising from the translatory type of oscillations, characterized by comparatively low frequencies. Thus the results that are to be expected of aragonite are quite different from those obtained in the case of calcite, particularly in the low frequency region.

Splitting of Degenerate Modes in Crystals of Lower Symmetry.—The Raman spectra of anhydrite and gypsum have been studied by a number of investigators. The frequencies observed are given below:

Raman frequencies

Substance	Lattice	Internal to SO_4 ion				Water bands
SO_4 ion ..	..	454 (v_2) double	622 (v_3) triple	983 (v_1) single	1106 (v_4) triple	..
$CaSO_4$ .. (Anhydrite)	126 169 233 (1) (2) (1)	415 499 (1) (5*d*)	609 628 674 (2) (2) (8)	1018 (15)	1108 1128 1160 (2) (10) (5)	..
$CaSO_4.2H_2O$ (gypsum) ..	..	414 494 (5) (3)	.. 618 672 .. (2*b*) (4)	1008 (20)	1113 1135 .. (2) (10)	3402 3493 (10*d*) (20)

The case of the free SO_4 ion is also included for comparison. The frequencies have been divided into various classes, the division being self-explanatory. The degree of degeneracy and the conventional designation are indicated in each case for the frequencies of the free ion. Numbers in brackets represent estimates of relative intensities. The splitting in the crystalline state of all the degenerate frequencies belonging to the tetrahedral SO_4 ion is noteworthy. Such a splitting is to be expected since the crystals of anhydride and gypsum do not as a whole possess the high degree of symmetry that is characteristic of the SO_4 ion. This follows directly from the fact that all the irreducible representations appropriate to the crystals in question are of dimension one and there can be no degeneracy.

Special Case of Diamond.—It is well known that diamond may be regarded as having been made up of two interpenetrating cubic face-centred lattices. Each atom of one lattice is at the centre of the tetrahedron formed by its four nearest neighbours of the other lattice. The positions of the atoms in the lattice are usually given with reference to the edges of the unit cube as axes. Accordingly the co-ordinates of the eight atoms in the unit cube are given by $(0, 0, 0)$; $(\frac{1}{2}, \frac{1}{2}, 0)$; $(\frac{1}{2}, 0, \frac{1}{2})$; $(0, \frac{1}{2}, \frac{1}{2})$; $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$; $(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$; $(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$; $(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$.

The above description of the structure of diamond is no doubt convenient in visualizing the lattice, but the Bravais cell is the parallelopiped formed by the edges 12, 13 and 14 and consists of two non-equivalent atoms (1 and 5) only (Fig. 15).

The symmetry operations pertaining to the point group O_h of such a lattice are

$$E,\ 8C_3,\ 3C_2,\ 6\sigma,\ 6S_4,\ i,\ 8S_6,\ \sigma,\ 6C3_2 \text{ and } 6C_4.$$

The corresponding character table is given on next page.

The selection rules for this group require that the lines coming under the class F_{2g} should be Raman active and infra-red inactive. The mode coming under F_{2u} is a pure

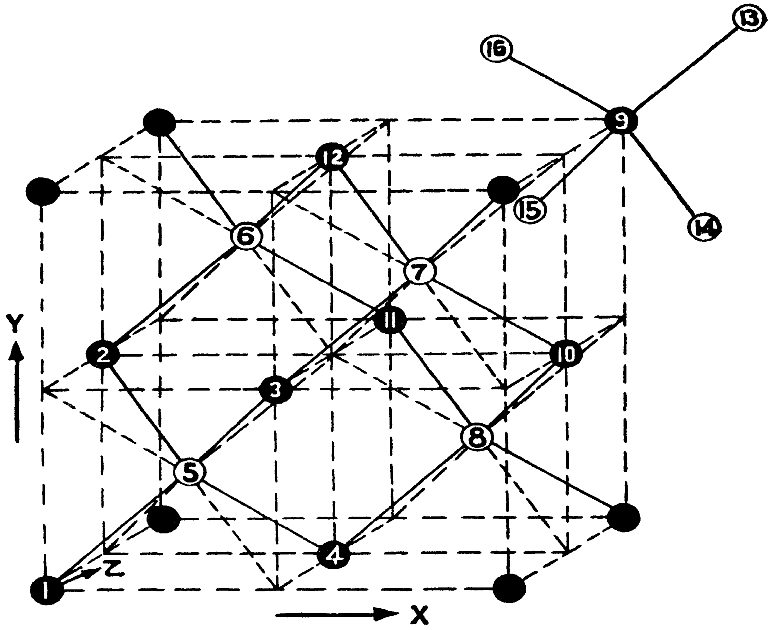

FIG 15

O_h	E	$8C_3$	$3C_2$	6σ	$6S_4$	i	$8S_6$	3σ	$6C_2$	$6C_4$	n_i
A_{1g} ..	1	1	1	1	1	1	1	1	1	1	0
A_{2g} .	1	1	1	-1	-1	1	1	1	-1	-1	0
E_g ..	2	-1	2	0	0	2	-1	2	0	0	0
F_{1g} ..	3	0	-1	-1	1	3	0	-1	-1	1	0
F_{2g} ..	3	0	-1	1	-1	3	0	-1	1	-1	1
A_{1u} ..	1	1	1	1	1	-1	-1	-1	-1	-1	0
A_{2u} ..	1	1	1	-1	-1	-1	-1	-1	1	1	0
E_u ..	2	-1	2	0	0	-2	1	-2	0	0	0
F_{1u} ..	3	0	-1	-1	1	-3	0	1	1	-1	0
F_{2u} ..	3	0	-1	1	-1	-3	0	1	-1	1	1
U_R ..	2	2	2	2	2	0	0	0	0	0	
$h_\rho \chi_\rho'$ ..	6	0	-6	12	-12	0	0	0	0	0	

*

translation. We thus see that the diamond lattice has only one principal normal mode of oscillation which is Raman active and infra-red inactive. The normal co-ordinates corresponding to this triply degenerate oscillation and the translation are

$$\left.\begin{array}{l} Q_a = x_1 - x_5 \\ Q_b = y_1 - y_5 \\ Q_c = z_1 - z_5 \end{array}\right] F_{2g}; \quad \left.\begin{array}{l} T_x = x_1 + x_5 \\ T_y = y_1 + y_5 \\ T_z = z_1 + z_5 \end{array}\right] F_{2u}.$$

The normal co-ordinates show that the two interpenetrating lattices are oscillating against each other, the direction of oscillation being arbitrary.

The potential energy function may be formed in terms of three types of forces, namely the primary valence, the directed valence, and the repulsive forces between the distant atoms. If N is the total number of atoms in the lattice, the kinetic and potential energies are given by

$$2T = Nm\dot{\delta}^2; \quad 2V = N\left[\frac{8K_1}{3} + \frac{64K_2}{3l^2}\right]\delta^2;$$

where m, l respectively stand for the mass of a carbon atom and the length of a valence bond (15), K_1 and K_2 are the primary and the directed valence force constants. The constant relating to the repulsive force between distant atoms does not enter the energy expression V. The frequency of oscillation is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{8}{3m}\left(K_1 + \frac{8K_2}{l^2}\right)}.$$

CHAPTER XIII

CRYSTAL SYMMETRY AND PHYSICAL PROPERTIES

General Considerations.—Physical properties of substances generally express the relation between two quantities. These may be scalars, vectors, second- or higher-order tensors. Voigt made the transformation properties of the quantities involved in a physical relation the basis for the classification of crystal properties, thus distinguishing scalar-scalar relations, vector-vector relations, tensor-tensor relations and so on. Density, pyro-electricity, dielectric polarization and elasticity are respectively simple examples of physical properties arising from such relations. Each of these relations requires a number of independent coefficients connecting the components of the quantities involved, and, without assuming any symmetry of the crystal, the number of independent coefficients in the case of linear relations is the product of the numbers of independent components of the quantities being related. In crystals with symmetry elements, this maximum number of coefficients will be reduced. In order to find the reduction produced by a symmetry element, Voigt transforms the axes of reference according to the symmetry element and demands that this transformation should keep invariant the values of the coefficients expressing the relation of the physical quantities. It follows by this direct method of transformation that a number of coefficients may be zero, while others are related to each other. The systems of non-vanishing as well as of independent constants for various properties were thus derived in considerable detail by Voigt and by Pockels. Love, Wooster, Cady, Mason and others have subsequently dealt with the subject.

The fact that the symmetry operations of a crystal form a group allows the application of group theory to the study of the effect of symmetry on the physical properties of crystals. This method can be used as a valuable check on the direct process of deriving the non-vanishing constants in each of the 32 crystal classes. Jahn made use of group theory for deducing the number of independent parameters and the non-vanishing constants of crystals. A somewhat different method by which group theory can be used for deriving the numbers of independent constants in the 32 crystal classes for any property will be described here. It is possible to apply it in a general manner to all the physical properties, already measured or otherwise, which depend on the crystallographic symmetry.

Crystal Optics.—The Fresnel ellipsoid plays an important part in describing the optics of crystals. The principal refractive indices are the reciprocals of the lengths of the principal axes of the ellipsoid. The orientation of the ellipsoid gives the manner in which these principal axes are related to the crystallographic axes. The phenomenon of refraction is connected with the property of the medium acquiring an optic moment which is a vector when it is acted on by the electric field of an incident light wave which is also a vector. In general, the direction of the induced vector does not coincide with the direction of the inducing vector and this results in double refraction. The optical coefficients C_{ik} of a crystal give us the relation between the three components of the incident light vector and those of the induced optic moment vector. They should accordingly be 9 in number but reduce to 6 on account of the relation $C_{ik}=C_{ki}$. While their number remains at 6 in crystals of the triclinic system, a further reduction takes place when higher symmetry is present as the latter involves mutual relationships between the various coefficients.

Let a_{xx}, a_{yy}, a_{zz}, a_{yz}, a_{zx} and a_{xy} represent the set of 6 independent coefficients of a crystal. Under an operation R consisting of a rotation through ϕ or a rotation-reflection through ϕ, these coefficients which constitute a tensor transform as products of Cartesian co-ordinates. The equations connecting the optic moments with the components of the incident light vector should remain invariant under a symmetry operation. This requirement imposes certain restrictions on the coefficients and those or such combinations of those which remain invariant for all the symmetry operations alone will survive. The problem is to find the number of such surviving terms for each class of crystal symmetry and in this case is simple.

Results of applying the general method described below to all the 32 classes of crystals are given in a table in a following Section under the column 3 (*a*). The number obtained in each case is well known and can easily be verified. In the case of a triclinic crystal, we require 6 constants and this implies that three refractive indices as well as the orientation of the principal optical directions with reference to the crystallographic axes requiring three independent parameters have to be specified. On the other hand, in the case of an orthorhombic crystal, only 3 constants are required and it is well known that these three may be chosen as the refractive indices themselves along the principal directions which in this case coincide with the crystallographic axes. All the other crystal systems may be dealt with in this manner.

Elasticity and Photoelasticity.—Before we take up the general method, we shall deal with elasticity and photoelasticity as another illustration. The moduli of elasticity for a crystal give the relation between the six components of the stress tensor on the one hand and the six components of the strain tensor on the other. These could accordingly be 36 in number but reduce to 21 even in triclinic crystals on account of the relation $C_{ik} = C_{ki}$. The stress-optical coefficients deal with the photoelastic behaviour and give the relation between the optical coefficients of the crystal and the components of an applied stress tensor. Their maximum number is 36 and this number remains undiminished in the triclinic system of crystals because the relation $C_{ik} = C_{ki}$ does not generally hold good for stress-optical coefficients. As in the case of optical coefficients, the largest number of moduli of elasticity and of stress-optical coefficients that are required in each case depends on the symmetry properties of the crystal in question. The usual methods of ascertaining the number of coefficients required for each crystal system are known and described in standard treatises.*

Results for all the 32 classes of crystals are given in a following table under the columns 8 and 8 (*a*). Numbers in respect of elastic properties agree with the known results in all cases. Numbers in respect of photoelasticity agree with those given by Pockels in all cases except C_4, S_4 and C_{4h} of the tetragonal system, C_3, S_6, C_{3h}, C_6 and C_{6h} of the trigonal system and T and T_h of the cubic system.

It is not clear how the extra coefficients in the classes cited above have been regarded by Pockels as vanishing. An important result relates to the T and T_h classes of the cubic system. It will be noticed that they require 4 stress-optical coefficients for the description of their photoelastic behaviour while the rest of the classes under the cubic system require only 3. Such a distinction does not occur in respect of elastic moduli.†

Description of the General Method.—Consider the transformation properties under any symmetry operation of a scalar, a vector, a second-order symmetric tensor and a second-order general tensor. A scalar remains unchanged, the components of a vector transform as the Cartesian co-ordinates, the components of a symmetric tensor as the products of Cartesian co-ordinates with some additional conditions, the components of general tensor as simple products of Cartesian co-ordinates. Thus, under an operation R_ϕ consisting of a rotation about the z axis through ϕ or a rotation-reflexion through ϕ, the components of a vector,

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* Reference may be made to Love, *Mathematical Theory of Elasticity*, for literature relating to the elastic moduli. The subject of photoelasticity in crystals is dealt with by Cocker and Filon in their *Treatise on Photoelasticity* and by Szivessy in *Handbuch der Physik*, Vol. 21, p. 832 (1929). These authors have, however, only quoted the earlier and pioneering work on the subject by Pockels contained in *Lehrbuch der kristalloptik* (1906).

† For a detailed discussion of this phenomenon and the related experimental results, see J. F. Nye, *Physical Properties of Crystals* (1957).

a symmetric tensor and a general tensor transform according to the equations (1), (2) and (3) respectively. The upper and lower sign, where an alternative occurs, refer respectively to a pure rotation and a rotation-reflexion.

$$\left.\begin{aligned} &p_x \rightarrow p_x \cos\phi + p_y \sin\phi, \\ &p_y \rightarrow -p_x \sin\phi + p_y \cos\phi,\ p_z \rightarrow \pm p_z; \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} &a_{xx} \rightarrow a_{xx}\cos^2\phi + a_{yy}\sin^2\phi + 2a_{xy}\sin\phi\cos\phi, \\ &a_{yy} \rightarrow a_{xx}\sin^2\phi + a_{yy}\cos^2\phi - 2a_{xy}\sin\phi\cos\phi, \\ &a_{zz} \rightarrow a_{zz}, \\ &a_{yz} \rightarrow \pm a_{yz}\cos\phi \mp a_{zx}\sin\phi, \\ &a_{zx} \rightarrow \pm a_{yz}\sin\phi \pm a_{zx}\cos\phi, \\ &a_{xy} \rightarrow - a_{xx}\sin\phi\cos\phi + a_{yy}\sin\phi\cos\phi \\ &\qquad\qquad + a_{xy}(\cos^2\phi - \sin^2\phi); \end{aligned}\right\} \quad (2)$$

$$\left.\begin{aligned} &\beta_{xx} \rightarrow \beta_{xx}\cos^2\phi + \beta_{yy}\sin^2\phi + (\beta_{xy}+\beta_{yx})\sin\phi\cos\phi, \\ &\beta_{yy} \rightarrow \beta_{xx}\sin^2\phi + \beta_{yy}\cos^2\phi - (\beta_{xy}+\beta_{yx})\sin\phi\cos\phi, \\ &\beta_{zz} \rightarrow \beta_{zz}, \\ &\beta_{yz} \rightarrow \mp \beta_{xz}\sin\phi \pm \beta_{yz}\cos\phi, \\ &\beta_{zy} \rightarrow \mp \beta_{zx}\sin\phi \pm \beta_{zy}\cos\phi, \\ &\beta_{zx} \rightarrow \pm \beta_{zx}\cos\phi \pm \beta_{zy}\sin\phi, \\ &\beta_{xz} \rightarrow \pm \beta_{xz}\cos\phi \pm \beta_{yz}\sin\phi, \\ &\beta_{xy} \rightarrow - \beta_{xx}\sin\phi\cos\phi + \beta_{yy}\sin\phi\cos\phi \\ &\qquad\qquad + \beta_{xy}\cos^2\phi - \beta_{yx}\sin^2\phi, \\ &\beta_{yx} \rightarrow - \beta_{xx}\sin\phi\cos\phi + \beta_{yy}\sin\phi\cos\phi \\ &\qquad\qquad - \beta_{xy}\sin^2\phi + \beta_{yx}\cos^2\phi. \end{aligned}\right\} \quad (3)$$

These transformations may be regarded as linear substitutions. The characters of the three transformation matrices are easily seen to be respectively,

$$(2\cos\phi \pm 1), \quad (4\cos^2\phi \pm 2\cos\phi)$$
$$(4\cos^2\phi \pm 4\cos\phi + 1).$$

Similarly, the transformation matrix and the respective character for a tensor of a higher order representing any given physical property can be deduced. It will be noted that the character for a tensor having nine components is the square of the character for the vector of three components. Similarly, the character for a third-order tensor (piezo-electric constants giving the relation between a vector and a symmetric tensor) is the product of the characters appropriate to a vector and a symmetric tensor, and so on. When special relations exist between the various components, the character has, however, to be deduced by writing down the full transformation matrix itself. For example, the elastic coefficients show how a stress tensor (second-order symmetric) gives rise to a strain tensor (second-order symmetric), but the maximum number of such coefficients is only 21, and not 36, because of the special relations* $c_{ik} = c_{ki}$, and the character in such a case has to be evaluated independently. Similar considerations apply to the higher-order elastic coefficients which reduce to 56 from being 126. These characters are given in column 3 of the adjoining table.

Considering, for example, the above symmetric tensor of six components, the linear substitutions (2) constitute a reducible representation of the group G of symmetry operations of any crystal class. Six mutually orthogonal and independent linear combinations of the above components may be found in such a way that they fall into six or less number of sets, the members in each set transforming among themselves by every operation of the group G. These will constitute the basis for a new and completely reducible representation of the group G. The character appropriate to any element R in this representation will be the same as that obtained before, since the two are equivalent. It is now easy to find n_i, the number of times a particular irreducible representation repeats itself, in the representation consisting of the new variables with the help of the general formula

$$n_i = \frac{1}{N} \sum_j h_j \chi_j'(R)\, \chi_i(R). \tag{4}$$

---

* Voigt's notation is used: i and k run from 1 to 6.

N is the total number of elements of the group G, and h_j is the number of elements in the jth class. $\chi_j'(R)$ is the character of the appropriate transformation matrix relative to the operation R, as given in the table, and $\chi_i(R)$ is the character relative to the operation R in the particular irreducible representation.

By the application of Voigt's condition, it follows that in the case of any specified physical property represented by such a tensor (row 3 *a* of table) only those combinations of parameters in respect of any particular crystal can survive which have the entire symmetry of the crystal. Thus we want to know the number of combinations that remain invariant for all operations R of the crystallographic group G. This means that we need only find the value of n_i appropriate to the total symmetric irreducible representation. This is characterized by the fact that $\chi_i(R) = 1$ for all R. In this case $\chi_j'(R)$ has already been shown to be equal to $(4\cos^2\phi \pm 2\cos\phi)$.

Similar arguments hold for the various coefficients describing other phenomena. In each case, the number n_i represents the number of independent constants needed to describe the phenomenon in the particular crystal class.

Results.—The following table gives the physical properties arranged systematically in order of increasing complexity and is self-explanatory. Rows 1 to 10 refer to first-order phenomena, whereas rows 11, 12 and 13 are representative of higher-order phenomena.* The list of physical properties in any row is only representative and is not complete. Where no representative physical property is known to exist, a line is drawn.

In the following table are given the 32 crystal classes or point groups with their well-known symbols. Symbols representing the symmetry elements under each crystal class

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* Recently, Fumi, *Phys. Rev.*, **83**, 1274 (1951) using the direct inspection method and Hearmon, *Act. Cryst.*, 6, 331 (1953) using the principle of invariance of strain energy have given the numbers as well as the actual schemes of third order elastic constants for all the crystal classes.

Classification of Physical Properties

No.	Physical property represents the relation between	Character $\chi_j'(R)$	Maximum number of constants	Physical properties known, if any
1	Scalar and scalar	1	1	Density
2	Scalar and vector	$2c \pm 1$	3	Pyro-electricity; production of charges by hydrostatic pressure (Cady, 1946)
3	Scalar and symmetric tensor	$4c^2 \pm 2c$	6	Thermal expansion
3 (*a*)	Vector and vector ($c_{ik} = c_{ki}$: and k run from 1 to 3)	$4c^2 \pm 2c$	6	Optical, dielectric and (dia- and para-) magnetic polarisation; thermal and electrical conductivities; thermo-electricity
4	Scalar and unsymmetric tensor	$4c^2 \pm 4c + 1$	9	—
5	Vector and vector	$4c^2 \pm 4c + 1$	9	—
6	Vector and symmetric tensor	$8c^3 \pm 8c^2 + 2c$	18	Piezo-electricity; electro-optical Kerr effect
7	Vector and unsymmetric tensor	$8c^3 \pm 12c^2 + 6c \pm 1$	27	—
8 (*a*)	Symmetric tensor and symmetric tensor ($c_{ik} = c_{ki}$: i and k run from 1 to 6)	$16c^4 \pm 8c^3 - 4c^2 + 1$	21	Elasticity
8	Symmetric tensor and symmetric tensor	$16c^4 \pm 16c^3 + 4c^2$	36	Photo-elasticity; effect of pressure on electrical conductivity (Cookson, 1935)
9	Symmetric tensor and unsymmetric tensor	$16c^4 \pm 24c^3 + 12c^2 \pm 2c$	54	—
10	Unsymmetric tensor and unsymmetric tensor	$16c^4 \pm 32c^3 + 24c^2 \pm 8c + 1$	81	—
11	Vector and square of symmetric tensor ($c_{ik} = c_{ki}$: i and k run from 1 to 6)	$32c^5 \pm 32c^4 \mp 4c^2 + 2c \pm 1$	63	Piezo-electric coefficients
12	Symmetric tensor and square of symmetric tensor ($c_{ikl} = c_{kil} = c_{ilk} = c_{ckli}$, etc.: i, k and l run from 1 to 6)	$64c^6 \pm 32c^5 - 48c^4 \mp 8c^3 + 16c^2$	56	Elastic coefficients (Birch, 1947)
13	Symmetric tensor and square of symmetric tensor ($c_{ik} = c_{ki}$: i and k run from 1 to 6)	$64c^6 \pm 64c^5 \mp 8c^3 + 4c^2 \pm 2c$	126	Photo-elastic coefficients

c in the above table indicates $\cos\phi$.

have the usual significance. The numbers of independent constants for each of the properties needed by the 32 classes, as derived from formula (4), are given here. The elements of symmetry given in column 5 for each of the point groups are divided into conjugate classes of the group. In the sub-columns headed by 8 and 12 are given the photo-elastic coefficients and the third-order elastic coefficients, in which discrepancies were noticed and pointed out first by the application of this method. The division of the 32 crystal classes into 11 *Obergruppen* in all cases when we are dealing with centro-symmetrical properties is especially evident in sub-columns headed by 8 and higher numbers. Each of these *Obergruppen* consists of a class with centre of inversion as one of the symmetry operations, and of all its immediate subgroups.

Enantiomorphism and Optical Activity.—For the properties dealt with above we have to find the value of n_i appropriate to the total symmetric irreducible representation because we want to know the number of combinations that remain invariant for all operations R of the crystallographic group G. In addition, there are other properties for which we have to find the number of combinations that remain invariant for operations of pure rotations, and change sign for operations of rotation-reflexions. Enantiomorphism and optical activity are examples of such phenomena.

Enantiomorphism is the existence of forms which are mirror images of each other. This is obviously represented by a single constant. Optical activity is represented by a second-order symmetric tensor which is the gyration tensor with six components. The sign of rotation of the plane of polarization remains invariant under an operation of pure rotation and changes sign for a rotation-reflexion. In order, therefore, to find the number of independent constants required to specify the gyration tensor, we should find the number of independent and orthogonal linear combinations of the components which will transform so as to remain

Number af coefficients in each of the 32 crystal classes

Crystal Class No. *	Number of independent constants for the physical property														
	1	2	3 & 3 (*a*)	4 & 5	6	7	8 (*a*)	8	9	10	11	12	13	En.	Op. A.
1	1	3	6	9	18	27	21	36	54	81	63	56	126	1	6
2	1	0	6	9	0	0	21	36	54	81	0	56	126	0	0
3	1	2	4	5	10	14	13	20	28	41	34	32	68	0	2
4	1	1	4	5	8	13	13	20	28	41	29	32	68	1	4
5	1	0	4	5	0	0	13	20	28	41	0	32	68	0	0
6	1	1	3	3	5	7	9	12	15	21	17	20	39	0	1
7	1	0	3	3	3	6	9	12	15	21	12	20	39	1	3
8	1	0	3	3	0	0	9	12	15	21	0	20	39	0	0
9	1	1	2	3	4	7	7	10	14	21	15	16	34	1	2
10	1	0	2	3	4	6	7	10	14	21	14	16	34	0	2
11	1	0	2	3	0	0	7	10	14	21	0	16	34	0	0
12	1	1	2	2	3	4	6	7	8	11	10	12	22	0	0
13	1	0	2	2	2	3	6	7	8	11	7	12	22	0	1
14	1	0	2	2	1	3	6	7	8	11	5	12	22	1	2
15	1	0	2	2	0	0	6	7	8	11	0	12	22	0	0
16	1	1	2	3	6	9	7	12	18	27	21	20	42	1	2
17	1	0	2	3	0	0	7	12	18	27	0	20	42	0	0
18	1	1	2	2	4	5	6	8	10	14	13	14	26	0	0
19	1	0	2	2	2	4	6	8	10	14	8	14	26	1	2
20	1	0	2	2	0	0	6	8	10	14	0	14	26	0	0
21	1	0	2	3	2	2	5	8	12	19	10	12	24	0	0
22	1	1	2	3	4	7	5	8	12	19	11	12	24	1	2
23	1	0	2	3	0	0	5	8	12	19	0	12	24	0	0
24	1	0	2	2	1	1	5	6	7	10	5	10	17	0	0
25	1	1	2	2	3	4	5	6	7	10	8	10	17	0	0
26	1	0	2	2	1	3	5	6	7	10	3	10	17	1	2
27	1	0	2	2	0	0	5	6	7	10	0	10	17	0	0
28	1	0	1	1	1	2	3	4	5	7	4	8	13	1	1
29	1	0	1	1	0	0	3	4	5	7	0	8	13	0	0
30	1	0	1	1	1	1	3	3	3	4	3	6	9	0	0
31	1	0	1	1	0	1	3	3	3	4	1	6	9	1	1
32	1	0	1	1	0	0	3	3	3	4	0	6	9	0	0

* These numbers have the same significance as in Chapter XI.

invariant if the symmetry operation is a pure rotation and change sign if the symmetry operation is a rotation-reflexion.

Hence the appropriate irreducible representation for which the number of combinations has to be found is not the total symmetric one but the antisymmetric irreducible representation with character $\chi_i = \pm 1$, the upper sign referring to pure rotations and the lower referring to rotation-reflexions. The character χ_j' of the transformation matrix for the gyration tensor is again $(4\cos^2\phi \pm 2\cos\phi)$, and for enantiomorphism it is unity. Using the general formula (4) with the new character, the numbers of constants for the 32 classes are easily obtained. They are given in the sub-columns headed by En. and Op. A. They all agree with the known numbers.

This principle can also be extended to the other characters. Voigt has considered the cases of what he calls a pseudo-scalar, axial vector and axial tensor, and physical properties represented by these and the combination of these with the usual polar vector and polar tensor. He has deduced the schemes of non-vanishing constants for these properties irrespective of whether these properties have a real existence or not. The numbers in all these cases agree with those that would be obtained by combining the value of ± 1 for $\chi_i(R)$ with the $\chi_j'(R)$ in the first six rows of the preceding table, namely, 1, $(2\cos\phi \pm 1)$, $(4\cos^2\phi \pm 2\cos\phi)$, $(4\cos^2\phi \pm 4\cos\phi + 1)$ and $(8\cos^3\phi \pm 8\cos^2\phi + 2\cos\phi)$. Numbers in these cases, except for enantiomorphism and optical activity, are not given here as they are not all represented by known physical properties. Voigt claims that the second and the last of the above are represented by pyromagnetism and piezo-magnetism respectively. An extension of this principle to some of the more complicated tensors is easy, but it is doubtful whether the results represent any possible physical phenomena.

Isotropic Solids.—Amorphous substances like glass are examples of isotropic solids. Polycrystalline aggregates with randomly oriented constituents also behave like isotropic solids under certain conditions. The group $R_\infty{}^i$ of symmetry operations of an isotropic solid contains all rotations about all axes, reflections in all planes and a centre of inversion. The number n_i of physical constants is given by the formula

$$n_i = \frac{1}{2\pi}\int_0^\pi (\chi'_+\chi_- + \chi'_-\chi_+)\, d\phi$$

where $\chi'_\pm$ stands for the character of the physical property and $\chi_\pm = 1 \pm \cos\phi$, the upper sign holding for rotations and the lower for rotation-reflections. For example, in the case of elasticity,

$$\chi'_\pm = 16\cos^4\phi \pm 8\cos^3\phi - 4\cos^2\phi + 1$$

and the above formula gives $n_i = 2$.

If we are dealing with the special case of an isotropic solid not possessing a centre of inversion, the group will be represented by R_∞ and the formula becomes

$$n_i = \frac{1}{\pi}\int_0^\pi \chi'_+\chi_-\, d\phi.$$

These two formulæ follow directly from the orthogonality relations between the characters of the irreducible representations of the respective groups.* They may be used for readily obtaining the number of constants relating to each physical property as 1, 0, 1, 1, 0, 0, 2, 2, 2, 3, 0, 3, 4, 0 and 0 for the first case and 1, 0, 1, 1, 0, 1, 2, 2, 2, 3, 0, 3, 4, 1 and 1 for the second case given in the order followed earlier for the 32 crystal classes in this Chapter. Identical results have been obtained by Jahn‡ using a slightly different method. Similar results in respect of the other infinite groups C_∞, $C_{\infty v}$, $C_\infty{}^h$, D_∞ and $D_\infty{}^h$ have been given by Rahman.§

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[*] E. P. Wigner, *Gruppentheorie*, p. 167.

[‡] H. A. Jahn, *Acta Cryst.*, **2**, 30 (1949).

[§] A. Rahman, *Acta Cryst.*, **6**, 426 (1953).

CHAPTER XIV

ROTATION GROUPS

The Rotation Groups in Two and Three Dimensions.—The set of rotations characteristic of a body like a circular disc about the symmetry axis perpendicular to its own plane forms an infinite group. If we take a system of rectangular axes in which the axis of rotation is taken as the Z axis, the substitutions corresponding to a rotation through an angle ω may be given as

$$S(\omega) :— \quad \begin{aligned} x' &= x \cos \omega + y \sin \omega \\ y' &= - x \sin \omega + y \cos \omega \\ z' &= z. \end{aligned}$$

All the members of this group designated as R_2 commute with one another, a result which may be expressed by writing

$$S(\omega)\, S(\omega') = S(\omega')\, S(\omega) = S(\omega + \omega').$$

The group is thus Abelian and is a one parameter continuous group. The range of values of ω can be taken as $0 \leqslant \omega < 2\pi$.

For a system with spherical symmetry, all possible rotations about axes passing through its centre satisfy the group postulates and hence constitute an infinite group which may be called the rotation group and designated as R_3.

In Fig. 16, $OXYZ$ is a system of rectangular axes fixed in space. X, Y and Z are the points at which these axes cut the surface of a sphere with its centre at O. If the sphere is assumed to be rotated about a certain axis, these points of intersection move to three new positions X', Y' and Z', respectively. The Eulerian angles of such a rotation are $90 + \phi$, θ and $90 - \psi$, where ϕ, θ and ψ are as shown in the Figure. The rotation itself may be designated by the symbol $R(\phi\theta\psi)$. The relationships given below for the various cosines easily follow. For example, from the spherical triangle XAX', we have $\cos XX' = \cos XA \cos X'A + \sin XA \sin X'A \cos XAX' = \cos (90 + \phi) \cos (90 - \psi) + \sin (90 + \phi) \sin (90 - \psi) \cos \theta$ which is the first row first column element in the following table.

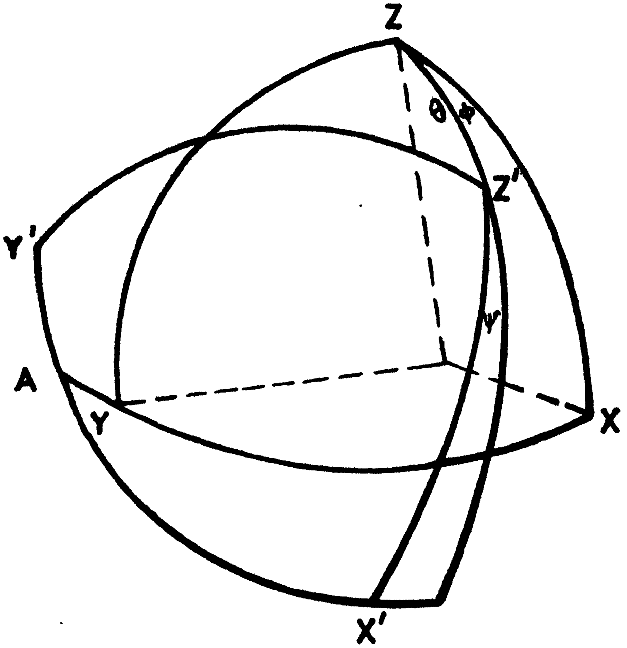

FIG. 16

	X	Y	Z
X'	$\cos\psi \cos\phi \cos\theta - \sin\psi \sin\phi$	$\sin\psi \cos\phi + \cos\psi \sin\phi \cos\theta$	$-\sin\theta \cos\psi$
Y'	$-\sin\psi \cos\phi \cos\theta - \cos\psi \sin\phi$	$\cos\psi \cos\phi - \sin\psi \sin\phi \cos\theta$	$\sin\theta \sin\psi$
Z'	$\sin\theta \cos\phi$	$\sin\theta \sin\phi$	$\cos\theta$

The rotation R may be regarded as transforming the coordinates X, Y, Z of a point to X', Y', Z' and the above table furnishes the transformation matrix appropriate to such a case. Let $S(\psi)$ and $S(\phi)$ denote rotations through ψ and ϕ respectively about the Z-axis. Similarly $T(\theta)$ is a rotation through θ about the Y-axis. It can now be verified that $R\ (\phi\theta\psi) = S(\psi)\ T(\theta)\ \ S(\phi)$ by noting the equality between the transformation matrix appropriate to the operation R and the product given below:

$$\begin{vmatrix} \cos\psi & \sin\psi & 0 \\ -\sin\psi & \cos\psi & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} \cos\theta & 0 & -\sin\theta \\ 0 & 1 & 0 \\ \sin\theta & 0 & \cos\theta \end{vmatrix} \begin{vmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

The rotations on the right-hand side are performed in the order $R(\phi)$, $T(\theta)$ and $R(\psi)$. The following relationships correspond to the first two matrices in the product.

$$S(\psi): \quad \begin{aligned} x' &= x\cos\psi + y\sin\psi \\ y' &= -x\sin\psi + y\cos\psi \\ z' &= z \end{aligned}$$

$$T(\theta): \quad \begin{aligned} x' &= x\cos\theta - z\sin\theta \\ y' &= y \\ z' &= x\sin\theta + z\cos\theta. \end{aligned}$$

The third matrix similarly corresponds to $S(\phi)$. If the transformation corresponding to the operation $R(\phi\theta\psi)$ is written in the form

$$\begin{aligned} x' &= l_1x + l_2y + l_3z \\ y' &= m_1x + m_2y + m_3z \\ z' &= n_1x + n_2y + n_3z \end{aligned}$$

it follows that

$$l_1m_1 + l_2m_2 + l_3m_3 = 0;\ m_1n_1 + m_2n_2 + m_3n_3 = 0;\ n_1l_1 + n_2l_2 + n_3l_3 = 0;$$

$$l_1^2 + l_2^2 + l_3^2 = m_1^2 + m_2^2 + m_3^2 = n_1^2 + n_2^2 + n_3^2 = 1;$$

$$\begin{vmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \\ n_1 & n_2 & n_3 \end{vmatrix} = 1,$$

because $S(\psi)$, $T(\theta)$, $S(\phi)$ as well as $R(\phi\theta\psi)$ are orthogonal transformations. The irreducible representations of the rotation group R_3 can be easily obtained from those of the unimodular unitary substitution group U_2 of two variables and this will be dealt with in the following Sections.

Unitary Substitutions of Two Variables.—A 2×2 unitary unimodular matrix D may be taken in the form

$$D = \begin{vmatrix} a & b \\ -b^* & a^* \end{vmatrix}$$

With the condition $aa^* + bb^* = 1$. The star indicates the complex conjugate. The totality of all such matrices D constitutes the unimodular unitary group U_2. The carrier space for these matrices is the two-dimensional complex linear vector space, which is also called the spin space. A vector (ξ, η) in this space is called a two-component spin vector or spinor. Since D is unitary, $\xi\xi^* + \eta\eta^*$ is invariant under the transformations D. On account of the relation $aa^* + bb^* = 1$, a and b should be of the form $\cos \alpha . e^{i\beta}$ and $\sin \alpha . e^{i\gamma}$. However, we take a and b as

$$a = \cos \frac{\theta}{2} . e^{\frac{i(\phi+\psi)}{2}}$$

$$b = \sin \frac{\theta}{2} . e^{\frac{i(-\phi+\psi)}{2}} .$$

Each set of values for ϕ, θ and ψ corresponds to one substitution. If the linear substitution matrix corresponding to ϕ, θ, ψ is designated by the symbol $D(\phi\theta\psi)$ it can be verified that $D(\phi\theta\psi) = D(\psi 00)\, D(0\theta 0)\ \ D(\phi 00)$ by noting the equality between the matrix

$$\begin{vmatrix} \cos \frac{\theta}{2} e^{\frac{i(\phi+\psi)}{2}} & \sin \frac{\theta}{2} e^{\frac{i(-\phi+\psi)}{2}} \\ -\sin \frac{\theta}{2} e^{\frac{i(\phi-\psi)}{2}} & \cos \frac{\theta}{2} e^{\frac{-i(\phi+\psi)}{2}} \end{vmatrix}$$

and the product

$$\begin{vmatrix} e^{\frac{i\psi}{2}} & 0 \\ 0 & e^{\frac{-i\psi}{2}} \end{vmatrix} \begin{vmatrix} \cos\frac{\theta}{2} & \sin\frac{\theta}{2} \\ -\sin\frac{\theta}{2} & \cos\frac{\theta}{2} \end{vmatrix} \begin{vmatrix} e^{\frac{i\phi}{2}} & 0 \\ 0 & e^{\frac{-i\phi}{2}} \end{vmatrix}.$$

The group is a three parameter continuous one. The range of the parameters ϕ, θ and ψ should be restricted in such a manner that there must correspond one and only one set of values to each transformation matrix in the group. Without loss of generality, $\cos\theta/2$ and $\sin\theta/2$ may be given any positive values which fix the range for $\theta/2$ as 0 to $\pi/2$. It is then easily verified that for a given value of ψ, $\phi/2$ can take any value in the range 0 to 2π. Similarly, $\psi/2$ can take any value in the range 0 to π for a given value of ϕ without giving rise to a matrix which is already in the set. The range of the parameter is thus

$$0 < \theta < \pi;\ 0 < \phi < 4\pi;\ 0<\psi<2\pi \text{ and } 0\leqslant\theta\leqslant\pi;\ \psi=\phi=0.$$

The quantities a and b will then assume all pairs of values satisfying $aa^*+bb^*= 1$, each set of values occurring only once. a and b are called the Cayley-Klein parameters.

Irreducible Manifolds with respect to U_2.—Let us now consider functions of the type

$$u_p = \xi^p\eta^q \, (p + q = n,\ p = 0,\ 1 \ldots n).$$

The $n + 1$ such functions will constitute the basis of all homogeneous polynomials of the nth degree in ξ, η, and the polynomials form a linear manifold of $n + 1$ dimensions. This manifold is invariant under the group $D\,(\phi\theta\psi)$ because the operation of D on any homogeneous polynomial of the nth degree is a linear substitution which gives rise to another homogeneous polynomial of the same degree within the manifold. We shall now show that this manifold is irreducible. If it is not irreducible, it should contain an invariant sub-manifold. Let u be a member of this sub-manifold and therefore also a member of the original manifold enabling us to write

$$u = \sum_{p=0}^{p=n} a_p u_p.$$

In this expression some of the coefficients a_p may be zero but not all. Since the matrix corresponding to $D(\omega 00)$ is $\begin{vmatrix} e^{\frac{i\omega}{2}} & 0 \\ 0 & e^{\frac{-i\omega}{2}} \end{vmatrix}$, it follows that

$$D(\omega 00)\, u_p = e^{\frac{i\omega}{2}(p-q)}\, u_p = e^{\frac{\omega}{2}(2p-n)}\, u_p.$$

Therefore, we have

$$D(\omega 00)\, u = \sum_{p=0}^{p=n} a_p e^{\frac{i\omega}{2}(2p-n)}\, u_p.$$

Since $D(\omega 00)$ is an element of the group, the sum on the right-hand side must be a member of the invariant sub-manifold for all values of ω. ω may now be assigned suitable values and linear combinations of the resulting sums may be formed so as to show that u_p for the range $p = 0$ to $p = n$ are all individually members of the sub-manifold. It has already been remarked that in the expression for u, there will be found at least one coefficient a_p which is different from zero and therefore, there is at least one member u_p belonging to the sub-manifold. Operating on this u_p by $D\left(0\frac{\pi}{2}0\right)$, we have

$$D\left(0\frac{\pi}{2}0\right) u_p = \left(\frac{\xi+\eta}{\sqrt{2}}\right)^p \left(\frac{-\xi+\eta}{\sqrt{2}}\right)^q$$

which is again a member of the sub-manifold. This sum contains a term ξ^{p+q} with a non-vanishing coefficient and, by the above argument, ξ^{p+q} must be a member of the sub-manifold. Operating on this member again by $D\left(0\frac{\pi}{2}0\right)$, we have

$$D\left(0\tfrac{\pi}{2}0\right)\xi^{p+q}=\left(\frac{\xi+\eta}{\sqrt{2}}\right)^{n}$$

This sum contains all the $n+1$ basis elements of the original manifold with non-vanishing coefficients and all of them, by the same argument, are members of the sub-manifold. So the sub-manifold which was postulated to be contained in the original manifold is the same as the original manifold and the original manifold is therefore irreducible. Thus for a given integral value of n, we get a set of $n+1$ functions forming the basis of an invariant manifold which is irreducible. Putting $n=2l$, $p=l+m$, $q=l-m$, the basis functions can be written as

$$u_m{}^l=\xi^{l+m}\eta^{l-m}$$

and are $2l+1$ in number.

Irreducible Representations of U_2.—The irreducible manifolds define irreducible representations of the unitary group. In order that we may obtain the representations of U_2 in the unitary form, the basis functions have to be written as in the following:

$$u_m{}^l=\frac{\xi^{l+m}\,\eta^{l-m}}{[(l+m)\,!\,(l-m)\,!]^{\frac{1}{2}}},$$

where $l=0,\ \frac{1}{2},\ 1,\ \frac{3}{2},\ \ldots$ etc., since $2l$ should be an integer and $m=p-l$ where p can take all integral values from 0 to n or $2l$. It is now obvious that

$$D\,(\phi\theta\psi)\,u_m{}^l=\frac{(a\xi+b\eta)^{l+m}\,(-b^*\xi+a^*\eta)^{l-m}}{[(l+m)\,!\,(l-m)\,!\,]^{\frac{1}{2}}}.$$

The right-hand side may be expanded and expressed as the sum of the basis polynomials. As m varies from $-l$ to l, we obtain $2l+1$ such equations for a specified value of l. The coefficients in the equations form a matrix which will be designated ${}^lD_{mn}$. The matrices thus obtained are unitary and constitute a representation ${}^lD$ of U_2. We shall work out the two special cases of $l=\frac{1}{2}$ and $l=1$. In the former case $n=1$ and $m=\pm\frac{1}{2}$. The basis functions are $u_{\frac{1}{2}}{}^{\frac{1}{2}}=\xi$ and $u_{-\frac{1}{2}}{}^{\frac{1}{2}}=\eta$.

$$D\,(\phi\theta\psi)\,u_{\frac{1}{2}}^{\frac{1}{2}} = (a\xi + b\eta)$$
$$D\,(\phi\theta\psi)\,u_{-\frac{1}{2}}^{\frac{1}{2}} = (-\,b^*\xi + a^*\eta).$$

The corresponding transformation matrix is $\begin{vmatrix} a & b \\ -b^* & a^* \end{vmatrix}$ and this has already been dealt with. In the latter case $n = 2$ and the basis consists of three functions. $m = 1,\ 0,\ -1$ and the functions may be designated u_1^1, u_0^1, u_{-1}^1.
We have

$$u_1^1 = \frac{\xi^2}{\sqrt{2}};\quad u_0^1 = \xi\eta;\quad u_{-1}^1 = \frac{\eta^2}{\sqrt{2}}\,.$$

$$D\,(\phi\theta\psi)\,u_1^1 = \frac{(a\xi + b\eta)^2}{\sqrt{2}} = a^2\frac{\xi^2}{\sqrt{2}} + \sqrt{2}\,ab\xi\eta + b^2\frac{\eta^2}{\sqrt{2}};$$

$$D\,(\phi\theta\psi)\,u_0^1 = (a\xi + b\eta)\,(-\,b^*\xi + a^*\eta)$$
$$= -\sqrt{2}ab^*\frac{\xi^2}{\sqrt{2}} + (aa^* - bb^*)\,\xi\eta + \sqrt{2}a^*b\frac{\eta^2}{\sqrt{2}};$$

$$D\,(\phi\theta\psi)u_{-1}^1 = \frac{(-\,b^*\xi + a^*\eta)^2}{\sqrt{2}}$$
$$= b^{*2}\frac{\xi^2}{\sqrt{2}} - \sqrt{2}a^*b^*\xi\eta + a^{*2}\frac{\eta^2}{\sqrt{2}}\,.$$

The corresponding transformation matrix is

$$\begin{vmatrix} a^2 & \sqrt{2}ab & b^2 \\ -\sqrt{2}ab^* & (aa^* - bb^*) & \sqrt{2}a^*b \\ b^{*2} & -\sqrt{2}a^*b^* & a^{*2} \end{vmatrix}$$

This may be verified to be unitary in character.

In the general case, that the matrix ${}^{l}D_{mn}$ is unitary follows from the fact that it keeps the form

$$\sum_{m=-l}^{l} (u_m^l)^*\,(u_m^l) = \sum_{m=-l}^{l} \frac{(\xi\xi^*)^{l+m}\,(\eta\eta^*)^{l-m}}{(l+m)!\,(l-m)!}$$
$$= \frac{1}{2l!}\,(\xi\xi^* + \eta\eta^*)^{2l}$$

invariant.

Characters of the Group U_2.—$D(\phi\theta\psi)$ has been taken to denote a unitary matrix of the type $\begin{vmatrix} a & b \\ -b^* & a^* \end{vmatrix}$. If one such matrix is given, it is always possible to find (Appendix II) another unitary matrix A of the same type such that the transform $A^{-1}\begin{vmatrix} a & b \\ -b^* & a^* \end{vmatrix}A$ is a diagonal matrix $\begin{vmatrix} p & 0 \\ 0 & p^* \end{vmatrix}$. A is an element of the group and it follows from the definition of conjugate classes that $\begin{vmatrix} a & b \\ -b^* & a^* \end{vmatrix}$ and $\begin{vmatrix} p & 0 \\ 0 & p^* \end{vmatrix}$ belong to the same class. $\begin{vmatrix} p^* & 0 \\ 0 & p \end{vmatrix}$ is equivalent to the latter and belongs to the same class. We have $pp^* = 1$ and p is of the form $e^{\frac{i\omega}{2}}$, $a + a^* = p + p^* = 2\cos\omega/2$ because of the invariance of the spur of the matrices belonging to a conjugate class. Since $a + a^* = 2\cos\theta/2\,\cos(\phi + \psi)/2$, we have $\cos\omega/2 = \cos\theta/2\cos(\phi + \psi)/2$. All unitary matrices corresponding to the set of values ϕ, θ, ψ satisfying the above relation when ω takes a specified value from a class. This class contains the element $D(\omega 00)$. Since

$$D_1 u_m{}^l = e^{i\frac{\omega}{2}(2p-2l)} = e^{i\omega m},$$

the trace of the matrix $({}^lD_{mn})$ is

$$\sum_{m=-l}^{l} e^{i\omega m} = \sin(2l + 1)\frac{\omega}{2}\ \sin\frac{\omega}{2}\,.$$

Hence the character of the representation ${}^lD$ is given by

$${}^l\chi\,(\omega) = \sin(2l + 1)\frac{\omega}{2}\sin\frac{\omega}{2}\,.$$

The orthogonality relations for the representations may be given by

$$\int_{\phi=0}^{4\pi}\int_{\theta=0}^{\pi}\int_{\psi=0}^{2\pi} {}^lD_{mn}\,{}^\lambda D_{\mu v}\ V(\phi, \theta, \psi)\,d\phi\,d\theta\,d\psi$$

$$= \frac{1}{2\lambda + 1}\,\delta_{l\lambda}\delta_{m\mu}\delta_{nv}$$

where the volume element $V(\phi\, \theta\, \psi) = (\sin\theta)/(4\pi)^2$. The constant in the volume element is so chosen that the integral of $V(\phi, \theta, \psi)$ is unity.

The orthogonality relations for the characters may be given by

$$\int_{\phi=0}^{4\pi} \int_{\theta=0}^{\pi} \int_{\psi=0}^{2\pi} {}^l\chi(\omega)^\lambda\chi(\omega)\, V(\phi, \theta, \psi)\, d\phi\, d\theta\, d\psi = \delta_{l\lambda}$$

in which ϕ, θ, ψ satisfy the relation $\cos\theta/2 \cos(\phi + \psi)/2 = \cos\omega/2$. These relations reduce to the form

$$\int_0^{4\pi} {}^l\chi(\omega)^\lambda\chi(\omega)\, \rho(\omega)\, d = \delta_{l\lambda}$$

where $\rho(\omega)$ is obtained by integrating $V(\phi, \theta, \psi)$ over all values of ϕ, θ, ψ for which ω has a fixed value.

The Irreducible Components of ${}^lD\times{}^\lambda D$.—Suppose ${}^lD$ and ${}^\lambda D$ are two irreducible representations of the group U_2. The irreducible components of the direct product representation ${}^lD\times{}^\lambda D$ may be obtained with the help of the characters. If

$${}^l\chi(\omega) \sum_{m=-l}^{l} = e^{im\omega}$$

and

$${}^\lambda\chi(\omega) = \sum_{\mu=-\lambda}^{\lambda} e^{i\mu\omega}$$

the character $\chi(\omega)$ of the product representation is given by the relation

$$\chi(\omega) = \sum_{m=-l}^{l} \sum_{\mu=-\lambda}^{\lambda} e^{i(m+\mu)\omega}.$$

This may be transformed into

$$\sum_{l=|l-\lambda|}^{l+\lambda} \sum_{M=-l}^{l} e^{iM\omega} = \sum_{l=|l-\lambda|}^{l+\lambda} {}^l\chi(\omega).$$

Thus

$${}^lD\times{}^\lambda D = {}^{l+\lambda}D + {}^{l+\lambda-1}D + \dots + {}^{|l-\lambda|}D$$

Isomorphism between the Rotation and the Unitary Groups.—We shall now consider the following three real functions of the two complex variables ξ, η.

$$x = \xi^*\eta + \xi\eta^*$$

$$y = \frac{1}{i}(\xi^*\eta - \xi\eta^*)$$

$$z = \xi\xi^* - \eta\eta^*.$$

x', y', z' may be similarly formed in terms of ξ' and η'. Let ξ, η be subjected to the substitution $D(\psi 00)$ explained in the previous Section and x', y', z' be written in terms of x, y, z. We have

$$x' = x\cos\psi + y\sin\psi$$

$$y' = -x\sin\psi + y\cos\psi$$

$$z' = z$$

which is the same as $S(\psi)$. This correspondence may be expressed by stating that $D(\psi 00)$ induces the rotation $S(\psi)$. Similarly $D(0\theta 0)$ may be shown to induce the rotation $T(\theta)$. It may also be verified that the product $D(\psi 00)\ D(0\theta 0)$ induces the rotation $S(\psi)\ T(\theta)$. By extending this principle, it may be proved more generally that $D(\phi\theta\psi)$ which has been shown to be identical with $D(\psi 00)\ D(0\theta 0)\ D(\phi 00)$ will induce a rotation $S(\psi)\ T(\theta)\ S(\phi)$. The latter is equivalent to a rotation $R(\phi\theta\psi)$. It may further be verified that the product D_1D_2 of any two unitary transformations D_1 and D_2 will induce a product rotation R_1R_2 of the corresponding rotations R_1 and R_2. Thus it is clear that a multiplicative correspondence exists between the elements of the D group and those of the rotation group.* The correspondence is not unique for if a rotation is induced by $D(\phi\theta\psi)$, the same is also induced by $D(\phi + 2\pi,\ \theta,\ \psi)$.

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* It may be shown that the spin co-ordinates define the unitary substitutions D, where the Cartesian co-ordinates define the corresponding substitutions R.

The irreducible representations of the rotation group can be picked out from those of the *D* group by confining ourselves to integral values of *l*. Half odd-integral values of *l* lead to a correspondence in which each element of the rotation group is associated with two matrices and are therefore not to be counted as representations, in the usual sense. However, they are called the spin or two valued representations.†

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† An alternative method for obtaining these representations has been given by Gel'fand, I. M. and Šapiro, Z. Ya, *American Math. Soc. Translations*, **2**, 207 (1956).

CHAPTER XV

APPLICATION TO PROBLEMS OF ATOMIC SPECTRA

Solutions of the Wave Equation.—In a system consisting of a single electron moving in a central field of force, the potential energy V is a function of the distance only of the electron from the centre. The Hamiltonian operator H for such a system is given by

$$H = -\frac{\hbar^2}{2m}\left(\frac{\partial}{\partial x^2} + \frac{\partial}{\partial y^2} + \frac{\partial}{\partial z^2}\right) + V(r).$$

If R denotes a rotation about an axis passing through the centre of force, H remains invariant under R. Operating on the wave equation

$$H\psi = W\psi$$

of the system by R, since $R(H\psi) = H(R\psi)$ and W is a constant, we obtain

$$H(R\psi) = W(R\psi).$$

This shows that if ψ is a solution of the wave equation for some value of W, $R\psi$ is also a solution of the equation for the same value of W. If ψ satisfies certain boundary conditions, $R\psi$ also generally satisfies the same boundary conditions. Consequently the eigenfunctions of the wave equation corresponding to a definite eigenvalue W form an invariant manifold with respect to the rotation group. The invariant manifold of the eigenfunctions appropriate to any eigenvalue W may be split up into irreducible manifolds each of which defines an irreducible representation of the rotation group. The results stated so far hold good even for systems consisting of several electrons, provided the force field is of the central type. The ψ functions will then involve $x_1, y_1, z_1 \ldots x_n, y_n, z_n$, the co-ordinates of all the n electrons in the system.

Angular Momentum Operators.—It has been mentioned in the foregoing Chapter that $S(\psi)$ and $T(\theta)$ denote rotations of ψ and θ about the Z and Y axes respectively. Similarly we may denote a rotation about the X axis by U and write down the following relations:

$$U(\omega):\ x' = x,\ y' = y + z\omega,\ z' = -y\omega + z;$$

$$T(\omega):\ x' = x - z\omega,\ y' = y,\ z' = x\omega + z;$$

$$S(\omega):\ x' = x + y\omega,\ y' = -x\omega + y,\ z' = z;$$

where ω is an infinitesimal angle. If a system is composed of n particles, the ψ functions are expressible in terms of their co-ordinates x_a, y_a, z_a where a runs from 1 to n. Regarding U as an operator, we write

$$U\psi(x_a, y_a, z_a) = \psi(x_a, y_a + z_a\omega, -y_a\omega + z_a)$$

$$= \psi(x_a, y_a, z_a) + \omega \sum_{a=1}^{n}\left(z_a\frac{\partial\psi}{\partial y_a} - y_a\frac{\partial\psi}{\partial z_a}\right).$$

If the total angular momentum of the system is L with components L_x, L_y and L_z, we have

$$L_x = \sum_{a=1}^{n}(y_a p_{z_a} - p_{y_a} z_a)$$

and similar expressions of L_y and L_z. As has already been mentioned, the components of the angular momentum may be regarded as operators on ψ functions and obtained by replacing p_x, p_y, p_z by $h/2\pi i\ \partial/\partial x$, $h/2\pi i\ \partial/\partial y$, $h/2\pi i\ \partial/\partial z$ respectively.

We therefore have

$$L_x\psi = \sum_{a=1}^{n}\frac{h}{2\pi i}\left(y_a\frac{\partial\psi}{\partial z_a} - z_a\frac{\partial\psi}{\partial y_a}\right)$$

and similar expressions for $L_y\psi$ and $L_z\psi$. If L_x, L_y, L_z are operators corresponding to the angular momentum components expressed in units of $h/2\pi$, we obtain the relations

$$U = E - i\omega L_x;\quad T = E - i\omega L_y;\quad S = E - i\omega L_z.$$

Thus the infinitesimal rotation operators are expressible in terms of angular momentum operators. E in the above relations is the identity operator. The three rotations $U(\omega)$, $T(\omega)$, $S(\omega)$ about the co-ordinate axes are equivalent to $R(3\pi/2\ \omega\ \pi/2)$, $R(0\omega 0)$, $R(00\omega)$ respectively. One set of corresponding unitary substitutions is given by $D(-\pi/2\ \omega\ \pi/2)$, $D(0\omega 0)$, $D(00\omega)$ and the Cayley-Klein parameters are obtained in the following manner because ω is an infinitesimal angle.

$$U\colon\ a = 1,\ b = \frac{i\omega}{2}$$

$$T\colon\ a = 1,\ b = \frac{\omega}{2}$$

$$S\colon\ a = 1 + \frac{i\omega}{2},\ b = 0.$$

Out of the invariant manifold of eigenfunctions appropriate to the eigenvalue W let us choose $a\psi$ belonging to an irreducible manifold of dimension $2l + 1$. If $u_m{}^l$ is a member of the irreducible manifold of polynomial functions of the same dimension, namely $2l + 1$, from the results of the foregoing Chapter and neglecting higher powers of ω in the operators U, T, S as above, we can write

$$\begin{aligned} Uu_m{}^l &= \frac{\left(\xi + \frac{i\omega\eta}{2}\right)^{l+m}\left(\frac{i\omega\xi}{2} + \eta\right)^{l-m}}{[(l+m)!\,(l-m)!]^{\frac{1}{2}}} \\ &= u_m{}^l + \frac{i\omega}{2}\,[(l-m+1)^{\frac{1}{2}}\,(l+m)^{\frac{1}{2}}\,u^l{}_{m-1} \\ &\qquad + (l+m+1)^{\frac{1}{2}}\,(l-m)^{\frac{1}{2}}\,u^l{}_{m+1}], \end{aligned}$$

$$\begin{aligned} Tu_m{}^l &= \frac{\left(\xi + \frac{\omega}{2}\eta\right)^{l+m}\left(-\frac{\omega}{2}\,\xi + \eta\right)^{l-m}}{[(l+m)!\,(l-m)!]^{\frac{1}{2}}} \\ &= u_m{}^l + \frac{\omega}{2}\,[(l-m+1)^{\frac{1}{2}}\,(l+m)^{\frac{1}{2}}\,u^l{}_{m-1} \\ &\qquad - (l+m+1)^{\frac{1}{2}}\,(l-m)^{\frac{1}{2}}\,u^l{}_{m+1}], \end{aligned}$$

$$Su_m{}^l = \frac{\left(\xi + \frac{i\omega\xi}{2}\right)^{l+m}\left(\eta - \frac{i\omega\eta}{2}\right)^{l-m}}{[(l+m)!\,(l-m)!]^{\frac{1}{2}}}$$
$$= u_m{}^l + i\omega m\, u_m{}^l.$$

Since the matrix of transformation of the $2l+1$ polynomial functions can be taken without loss of generality as the matrix of transformation of the $(2l+1)$ ψ functions, the corresponding equation of transformation for the ψ functions can be written as

$$U\psi_m{}^l = \psi_m{}^l + \frac{i\omega}{2}\,[(l-m+1)^{\frac{1}{2}}(l+m)^{\frac{1}{2}}\,\psi^l{}_{m-1}$$
$$+ (l+m+1)^{\frac{1}{2}}(l-m)^{\frac{1}{2}}\,\psi^l{}_{m+1}],$$

$$T\psi_m{}^l = \psi_m{}^l + \frac{\omega}{2}\,[(l-m+1)^{\frac{1}{2}}(l+m)^{\frac{1}{2}}\,\psi^l{}_{m-1}$$
$$- (l+m+1)^{\frac{1}{2}}(l-m)^{\frac{1}{2}}\,\psi^l{}_{m+1}],$$

$$S\psi_m{}^l = \psi_m{}^l + i\omega m\psi_m{}^l.$$

Comparing the above equations with the expressions for U, T and S in terms of the angular momentum operators, we have*

$$(L_x - iL_y)\,\psi_m{}^l = -\,(l+m+1)^{\frac{1}{2}}(l-m)^{\frac{1}{2}}\;\psi^l{}_{m+1},$$
$$(L_x + iL_y)\,\psi_m{}^l = -\,(l-m+1)^{\frac{1}{2}}(l+m)^{\frac{1}{2}}\;\psi^l{}_{m-1},$$
$$L_z\psi_m{}^l = -\,m\,\psi_m{}^l$$

or
$$L^2\,\psi_m{}^l = (L_x{}^2 + L_y{}^2 + L_z{}^2)\,\psi_m{}^l$$
$$= \tfrac{1}{4}[2(l+m)(l-m+1) + 2\,(l-m)(l+m+1) + 4m^2]\,\psi_m{}^l$$
$$= l\,(l+1)\,\psi_m{}^l.$$

The value for $L_x{}^2 + L_y{}^2$ may be obtained by putting it equal to

$$\tfrac{1}{2}\,[(L_x - iL_y)(L_x + iL_y) + (L_x + iL_y)(L_x - iL_y)]$$

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* The eigenvalue m in the equation for L_z has a minus sign because we have regarded the clockwise rotations as positive.

or by obtaining directly the result of operating with L_x twice and adding it to that obtained by operating with L_y twice.

Quantization of Angular Momentum and its Components.—The most significant relationships deduced in the previous Section are

$$L_z \psi_m{}^l = - m \psi_m{}^l,$$
$$L^2 \psi_m{}^l = l\,(l + 1)\, \psi_m{}^l.$$

It may be recalled that in formulating the polynomial basis functions, l takes the values 0, $\frac{1}{2}$, 1, . . . etc., and $m = p - 1$ where p can take all integral values from 0 to $2l$.

For a given l, there are $2l + 1$ possible values for m. The second of the above equations is to be interpreted by saying that $l\,(l + 1)$ is the value which the square of the total angular momentum of the system characterized by the eigenfunction $\psi_m{}^l$ can assume. This is independent of m and is the same for all states characterized by the set of eigenfunctions $\psi_m{}^l$ in which m runs through its permitted range $+ l$ to $- l$. The system has a $2l + 1$ fold rotational degeneracy.

The first equation is similarly to be interpreted by saying that $- m$ is the value which the component I_z of the angular momentum can take. There is no degeneracy here as each possible value of m for a given l corresponds to a single ψ function. This is the well-known law of space quantization restricting the projection of an angular momentum vector l along a specific direction Z in space to a set of $2l + 1$ discrete values.

Vector Addition of Angular Momenta.—If the angular momentum quantum numbers in respect of two component parts of a system are l_1 and l_2, it is of great importance for the subject of atomic spectra to find out the possible values which the resultant angular momentum quantum number can assume in respect of the whole system. The basis eigenfunctions in the two cases may be written respectively as

$$\psi^{l_1}{}_{m_1} = \frac{\xi_1{}^{l_1+m_1} \eta_1{}^{l_1-m_1}}{c\,(l_1 m_1)}\,; \quad \phi^{l_2}{}_{m_2} = \frac{\xi_2{}^{l_2+m_2} \eta_2{}^{l_2-m_2}}{c\,(l_2 m_2)}$$

where $c(l_1m_1)$ and $c(l_2m_2)$ are the normalization factors and respectively equal to $[(l_1+m_1)!\ (l_1-m_1)!]^{\frac{1}{2}}$ and $[(l_2+m_2)!\,(l_2-m_2)!]^{\frac{1}{2}}$. It has already been pointed out that every operation D in respect of each one of the above manifolds gives rise to a unitary matrix and the set of such matrices constitute an irreducible representation of the D group. These representations have been designated ${}^{l_1}D$ and ${}^{l_2}D$. If the interaction energy of the two component parts is neglected, the basis eigenfunctions of the system are merely products of the individual basis eigenfunctions and therefore polynomials of degree $2(l_1+l_2)$ and are $(2l_1+1)(2l_2+1)$ in number. They define a manifold of $(2l_1+1)(2l_2+1)$ dimensions invariant under the D group. These basis elements give rise to a new reducible representation of the D group which may be designated the product representation ${}^{l_1}D\times{}^{l_2}D$, capable of being split up into a set of irreducible representations in the following manner.

$${}^{l_1}D\times{}^{l_2}D={}^{l_1+l_2}D+{}^{l_1+l_2-1}D+\ldots+{}^{|l_1-l_2|}D.$$

The indices on the left-hand corners of the component irreducible representations denote the values which the total angular momentum quantum number can assume. Thus

$$l=l_1+l_2;\ \ l_1+l_2-1;\ \ldots\ |\,l_1-l_2\,|.$$

The rule obtained above is applicable to the combination of two angular momenta, both arising from either the orbital type or the spin type or one arising from the orbital and the other from the spin. In the last case, if l_1 stands for the total orbital angular momentum of an atom (usually denoted by L) and l_2 stands for the total spin angular momentum (usually denoted by S), we get the well-known result for the total angular momentum l (usually denoted by J) of an atom given by

$$J=L+S;\ \ L+S-1;\ldots\ |\,L-S\,|.$$

There are $2S+1$ different possible values of J for a given value of S when it is less than L and this represents the multiplicity of the J value.

Reduction of the Product Manifold.—If we denote by $\Phi_M{}^J$ the basis eigenfunctions of the product manifold corresponding to an irreducible representation J_D, we have

$$R\Phi_M{}^J = \Sigma^J D_{MN}\Phi_N{}^J.$$

$\Phi_M{}^J$ are linear combinations of the product functions and are homogeneous polynomials of degree $2l_1$ in $\xi_1\eta_1$ and $2l_2$ in $\xi_2\eta_2$. To find these polynomials, let us start with functions of the type

$$f_M{}^J = \frac{\xi_3{}^{J+M}\,\eta_3{}^{J-M}}{C\,(JM)}$$

ξ_3, η_3 transform as ξ_1, η_1 and ξ_2, η_2 and are functions thereof.

Therefore $f_M{}^J$ can be written as

$$f_M{}^J = \frac{(\xi_1 + x\xi_2)^{J+M}\,(\eta_1 + x\eta_2)^{J-M}}{C\,(JM)}$$

Since the value of x is arbitrary, the coefficients of powers of x, if the above is expanded as such, will also be functions satisfying the equation. If we pick out the coefficient of x^p and designate it $f_M{}^{J_p}$, it will be a polynomial of degree $2J - p$ in $\xi_1\eta_1$ and p in $\xi_2\eta_2$. In order to get the required degree in both cases, an additional factor which remains invariant under R has to be introduced. Accordingly, we write

$$\Phi_M{}^J = C\,f_M{}^{J_p}\,(\xi_1\eta_2 - \xi_2\eta_1)^q,$$

where

$$p = J - (l_1 - l_2);\; q = (l_1 + l_2) - J.$$

$\Phi^J{}_M$'s are now polynomials of degree $2J - p + q = 2l_1$ in $\xi_1\eta_1$ and $p + q = 2l_2$ in $\xi_2\eta_2$ and are therefore of the desired degree. They also satisfy the equation because C is simply a constant and $(\xi_1\eta_2 - \xi_2\eta_1)^q$ transforms into itself by any operation of the D group.

We shall now consider the particular case* in which $l_2 = 1$. J can assume three values, namely, $l_1 \pm 1$ and l_1. If we pick out the case where $J = l_1 - 1$, we have $p = 0$; $q = 2$ and

$$f_m^{J_p} = \frac{\xi_1^{l_1+m-1}\eta_1^{l_1-m-1}}{C(l_1 - 1, m)}$$

and

$$\underset{(J=l_1-1)}{\Phi_m^J} = \frac{C\xi_1^{l_1+m-1}\,\eta_1^{l_1-m-1}\,(\xi_1\eta_2 - \xi_2\eta_1)^2}{C(l_1 - 1, m)}$$

After expanding and simplifying, we can write

$$\begin{aligned}\underset{(J=l_1-1)}{\Phi_m^J} = {} & \left[\frac{(l_1 + m)(l_1 + m + 1)}{2l_1(2l_1 + 1)}\right]^{\frac{1}{2}} \psi^{l_1}{}_{m+1}\,\phi_{-1}{}^1 \\ & - \left[\frac{(l_1+m)(l_1 - m}{l_1(2l_1+1)}\right]^{\frac{1}{2}} \psi_m{}^{l_1}\phi_0{}^1 \\ & + \left[\frac{(l_1 - m)(l_1 - m + 1)}{2l_1(2l_1 + 1)}\right]^{\frac{1}{2}} \psi^{l_1}{}_{m-1}\phi^1{}_1.\end{aligned}$$

The constant C has been so adjusted that the sum of the squares of the coefficients on the right-hand side becomes unity because that is the requirement for the $\Phi^J{}_M$'s to be

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* The coefficients $C^{Jl_1l_2}_{Mm_1m_2}$ in the expansion

$$\Phi^J_M = \Sigma\, C^{Jl_1l_2}_{Mm_1m_2}\,\psi^{l_1}_{m_1}\,\phi^{l_2}_{m_2}$$

are zero if $M \neq m_1 + m_2$. When $M = m_1 + m_2$, omitting the suffixes l_1, l_2 and M, the coefficients $C^J{}_{m_1m_2}$ are given by the general formula

$$C^J{}_{m_1m_2} = C_1 \times C_2$$

where

$$C_1{}^2 = \frac{(2J+1)(J+l_1-l_2)!\,(J-l_1+l_2)!\,(l_1+l_2-J)!\,(J+m_1+m_2)!\,(J-m_1-m_2)!}{(J+l_1+l_2+1)!\,(l_1-m_1)!\,(l_1+m_1)!\,(l_2-m_2)!\,(l_2+m_2)!}$$

and

$$C_2 = \sum_k (-1)^{k+l_2+m_2} \frac{(J+l_2+m_1-k)!\,(l_1-m_1+k)!}{(J-l_1+l_2-k)!\,(J+m_1+m_2-k)!\,k!\,(k+l_1-l_2-m_1-m_2)!}.$$

k takes all integral values which do not make the argument of any factorial negative. In this book, we have dealt with particular cases of interest to atomic and Raman spectra only. For a derivation of this formula and for a description of the symmetry properties of these coefficients, reference may be made to Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, p. 191 (1959).

normalized. Similarly by working out the remaining two cases in which $J = l_1$, and $J = l_1 + 1$ we have,

$$\underset{(J=l_1)}{\Phi_m^J} = \left[\frac{(l_1 - m)(l_1 + m + 1)}{2l_1(l_1 + 1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+1}\,\phi^1_{-1} + \frac{m}{[l_1(l_1+1)]^{\frac{1}{2}}}\,\psi^{l_1}_{m}\,\phi^1_0 - \left[\frac{(l_1+m)(l_1 - m+1)}{2l_1(l_1+1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m-1}\,\phi^1_1$$

$$\underset{(J=l_1+1)}{\Phi_m^J} = \left[\frac{(l_1 - m + 1)(l_1 - m)}{2(l_1 + 1)(2l_1 + 1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+1}\,\phi^1_{-1} + \left[\frac{(l_1 + m + 1)(l_1 - m + 1)}{(l_1 + 1)(2l_1 + 1)}\right]^{\frac{1}{2}} \psi_m^1\,\phi_0^1 + \left[\frac{(l_1 + m + 1)(l_1 + m)}{2(l_1 + 1)(2l_1 + 1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m-1}\,\phi^1_1.$$

The coefficients in the above equations form an orthogonal matrix. Its inverse is therefore obtained by interchanging the rows and columns. Consequently, the product functions can be expressed as linear combinations of the single functions as follows:

$$\psi^{l_1}_{m+1}\,\phi^1_{-1} = \left[\frac{(l_1 + m)(l_1 + m + 1)}{2l_1(2l_1 + 1)}\right]^{\frac{1}{2}} \Phi_m^{l_1-1} + \left[\frac{(l_1 - m)(l_1 + m + 1)}{2l_1(l_1 + 1)}\right]^{\frac{1}{2}} \Phi_m^{l_1} + \left[\frac{(l_1 - m + 1)(l_1 - m)}{2(l_1 + 1)(2l_1 + 1)}\right]^{\frac{1}{2}}$$

$$\psi^{l_1}_m\phi_0^1 = -\left[\frac{(l_1+m)(l_1 - m)}{l_1(2l_1 + 1)}\right]^{\frac{1}{2}} \Phi_m^{l_1-1} + \frac{m}{[l_1(l_1 + 1)]^{\frac{1}{2}}}\Bigg]\Phi_m^{l_1} + \left[\frac{(l_1 + m + 1)(l_1 - m+1)}{(l_1 + 1)(2l_1 + 1)}\right]^{\frac{1}{2}} \Phi_m^{l_1+1}.$$

$$\psi^{l_1}_{m-1}\,\phi_1^1 = \left[\frac{(l_1 - m)(l_1 - m + 1)}{2l_1(2l_1 + 1)}\right]^{\frac{1}{2}} \Phi_m^{l_1-1}$$

$$-\left[\frac{(l_1+m)(l_1-m+1)}{2l_1(l_1+1)}\right]^{\frac{1}{2}}\Phi_m^{l_1}$$

$$+\left[\frac{(l_1+m+1)(l_1+m)}{2(l_1+1)(2l_1+1)}\right]^{\frac{1}{2}}\Phi_m^{l_1+1}.$$

Selection Rules and Intensities of Spectral Lines.—The intensity of the spectral line resulting from a transition from the state $\Phi_{M_1}^{J_1}$ to $\Phi_{M_2}^{J_2}$ depends on $\int\Phi_{M_1}^{J_1}\, M\Phi_{M2}^{J_2*}\, dV$, where M stands for a general linear combination of the components M_x, M_y, M_z of the electric moment. If X, Y, Z are the components of a vector along the co-ordinate axes, we form the functions

$$\frac{1}{\sqrt{2}}(-X+iY);\quad Z;\quad \frac{1}{\sqrt{2}}(X+iY)$$

out of such components. If these functions are further taken to represent the vector sums of the co-ordinates of the various electrons, their mean values multiplied by the electronic charge will determine the electric moments M_x, M_y, M_z and hence the problem of finding spectral intensities reduces to the problem of finding the mean values of the above functions. If we are interested in relative intensities, the electronic charge which is a constant factor can be conveniently omitted. The above functions transform under an operation D in the same way as $\xi^2/\sqrt{2}$; $\xi\eta$ and $\eta^2/\sqrt{2}$. The corresponding transformation matrix is given at the end of the previous Chapter. The latter have already been designated in our terminology ϕ_1^1; ϕ_0^1; and ϕ_{-1}^1 respectively. If we now take ϕ_1^1; ϕ_0^1 and ϕ_{-1}^1 to represent $1/\sqrt{2}\ (-X+iY)$; Z and $1/\sqrt{2}\ (X+iY)$ respectively, the problem of finding intensities reduces to the evaluation of $\int\Phi_{M_1}^{J_1}\,\phi_1^1\,\phi_{M_2}^{J_2*}dV$; $\int\Phi_{M_1}^{J_1}\,\phi_0^1\,\Phi_{M_2}^{J_2*}dV$ and $\int\Phi_{M_1}^{J_1}\,\phi_{-1}^1\,\Phi_{M_2}^{J_2*}dV$.

From the first integral, using the expressions given in the foregoing Section, we have

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* Eckart, *Rev. Mod. Phys.*, **2**, p. 331 (1930).

$$\int \Phi_{M_1}{}^{J_1}\phi_1{}^1\Phi_{M_2}{}^{J_2 *}dV =$$

$$\int\left[\frac{(J_1 - M_1 - 1)(J_1 - M_1)}{2J_1(2J_1 + 1)}\right]^{\frac{1}{2}} \Phi^{J_1 - 1}_{M_1+1}\, \Phi^{J_2 *}_{M_2}\, dV$$

$$-\int\left[\frac{(J_1 + M_1 + 1)(J_1 - M_1)}{2J_1(J_1 + 1)}\right]^{\frac{1}{2}} \Phi^{J_1}_{M_1+1}\, \Phi^{J_2 *}_{M_2}\, dV$$

$$+\int\left[\frac{(J_1 + M_1 + 2)(J_1 + M_1 + 1)}{2(J_1 + 1)(2J_1 + 1)}\right]^{\frac{1}{2}} \Phi^{J_1+1}_{M_1+1}\, \Phi^{J_2 *}_{M_2}\, dV.$$

ince $\Phi_M{}^J$ form the basis functions for the irreducible representations, they are orthogonal* and the above equation shows that the transition $J_1 \rightarrow J_2$; $M_1 \rightarrow M_2$ is permitted if $J_2 - J_1 = \triangle J = -1, 0, 1$ and $M_2 - M_1 = \triangle M = 1$. Dealing with the second and the third integrals in a similar manner, we obtain that the transition $J_1 \rightarrow J_2$; $M_1 \rightarrow M_2$ is also permitted if $\triangle J$ has the same values as before and $\triangle M = 0$ and -1 respectively. These constitute the selection rules for spectral lines. In the case of permitted lines, the intensities are proportional to the squares of the surviving integrals and their values, with the normalization factors, are tabulated below. The suffixes have been dropped out and J and M instead for J_1 and M_1 respectively.

M \ J	$J - 1$	J	$J + 1$
$M - 1$	$C_1 \cdot \frac{(J+M)(J+M-1)}{2J(2J+1)}$	$C_2 \cdot \frac{(J-M+1)(J+M)}{2J(J+1)}$	$C_3 \cdot \frac{(J-M+2)(J-M+1)}{2(J+1)(2J+1)}$
M	$C_1 \cdot \frac{(J+M)(J-M)}{J(2J+1)}$	$C_2 \cdot \frac{M^2}{J(J+1)}$	$C_3 \cdot \frac{(J+M+1)(J-M+1)}{(J+1)(2J+1)}$
$M + 1$	$C_1 \cdot \frac{(J-M-1)(J-M)}{2J(2J+1)}$	$C_2 \cdot \frac{(J+M+1)(J-M)}{2J(J+1)}$	$C_3 \cdot \frac{(J+M+2)(J+M+1)}{2(J+1)(2J+1)}$
C	$C_1 = \frac{2J+1}{2J-1}$	$C_2 = 1$	$C_3 = \frac{2J+1}{2J+3}$

Identical expressions were derived by Kronig and Goudsmit and others by adopting different methods. It is now known that these formulæ are well confirmed in respect of the Zeeman component intensities for a number of spectral lines.

In addition to the two selection rules just derived, namely, $\triangle J = 0$ or ± 1 and $\triangle M = 0$ or ± 1, there is yet another important rule of combinations between spectral terms known as Laporte's rule. It is easy to obtain this rule by once again considering the integral

$$\int \psi_1{}^1 \psi_{M_1}{}^{J_1} \psi^*{}_{M_2}{}^{J_2} \, dV,$$

where ψ's have been used for the Φ's as there is no need to make any further distinction. If it can be assumed that a centre of inversion is a symmetry operation for the atomic states, the spectral terms divide themselves into odd and even ones according as their corresponding eigenfunctions transform into themselves with or without a change of sign as a result of the inversion operation. The application of such an operation will transform $\psi_1{}^1$ and the other two related functions $\psi_0{}^1$ and $\psi_{-1}{}^1$ into themselves with a change of sign in each case because they are all simple linear combinations of the Cartesian co-ordinates occurring in single powers. It is thus evident that the integral as a whole will change sign when the product $\psi_{M_1}{}^{J_1} \psi_{M_2}{}^{J_2}$ does not change sign as a result of the operation of inversion. The latter will be the case if both the functions $\psi_{M_1}{}^{J_1}$ and $\psi_{M_2}{}^{J_2}$ either individually change sign or both individually do not change sign. The operation of inversion is however a symmetry operation and is to leave the integral unchanged by definition, a condition which is consistent with the above only when the integral vanishes. On the other hand, if $\psi_{M_1}{}^{J_1}$ changes sign and $\psi_{M_2}{}^{J_2}$ does not or *vice versa* as a result of the operation of inversion, their product will change sign and the above integral can have a non-vanishing value in such circumstances. If as has been pointed out already, we designate spectral terms odd and even, we can cover the above rule by stating that even terms combine only with odd terms and odd terms only with even terms. This combination rule assumes special significance in particular cases. For example, if J is an angular momentum of the orbital type only in which case it is usually designated by L, the eigenfunctions in certain simple cases such as a hydrogen atom are even if L is even and odd if L is odd and in such cases the above rule of combination gives rise to the selection principle $\triangle L = \pm 1$. In general it is not possible to lay down such a rule for J without ascertaining the nature of the corresponding eigenfunctions but the special case $J = 0 \rightarrow J = 0$ is readily excluded as a combination between two even terms.

Pauli Theory.—From the results obtained earlier in this Chapter, we can see that the components L_X, L_Y, L_Z of the angular momentum L satisfy the commutation rules

$$\begin{aligned} L_X L_Y - L_Y L_X &= iL_Z \\ L_Y L_Z - L_Z L_Y &= iL_X \\ L_Z L_X - L_X L_Z &= iL_Y. \end{aligned}$$

We shall start with the converse proposition. Let J_X, J_Y, J_Z be three operators satisfying the commutation rules given above in respect of L_X, L_Y, L_Z. If J is now defined by the relation $J^2 = J^2 + J_Y{}^2 + J_Z{}^2$, we may look upon it as a kind of general angular momentum operator. It can be verified that J^2 commutes with J_X, J_Y, J_Z and that $(J_X + iJ_Y)\,J_Z = (J_Z - 1)\;(J_X + iJ_Y)$. If ψ is an eigenfunction simultaneously of J_Z and J^2 with eigenvalues m and λ respectively, we can show that $\ldots\ldots m-2, m-1, m, m+1, m+2\ldots.$ are all eigenvalues of J_Z and each one of the corresponding eigenfunctions with respect to J_Z is also an eigenfunction of J^2 for the same eigenvalue λ of J^2. Since for any state, the average value of J^2 is the sum of the average values of $J_X{}^2$, $J_Y{}^2$, and $J_Z{}^2$, the squares of the eigenvalues of J_Z alone cannot be greater than λ. The maximum and minimum eigenvalues of J_Z can be shown to be respectively equal to

$$\pm\left[-\tfrac{1}{2} + \tfrac{1}{2}\sqrt{(1 + 4\lambda)}\right].$$

Denoting the maximum by A, which is fixed by the particular eigenvalue we assign to J^2, we see that the eigenvalues of J_Z under such circumstances are

$$-A, -A+1, -A+2, \ldots\ldots, A-1, A.$$

The difference between A and $-A$ must therefore be an integer so that $2A = n$ or $A = n/2$, where n is any positive integer. In addition to the integral eigenvalues of J_z, we thus see that half integral ones are also permissible. In the case of the electron, it is assumed that the possible values of the components s_x, s_y, s_z of spin angular momentum in any specified direction are confined to $\frac{1}{2}$ and $-\frac{1}{2}$.

In order to obtain certain convenient relations, we can form a new set of operators σ_x, σ_y, σ_z in terms of s_x, s_y, s_z with the help of the equations $s_x = \frac{1}{2}.\sigma_x$, etc. The eigenvalues of σ_x, σ_y, σ_z should be ± 1 because the eigenvalues of s_x, s_y, s_z are $\pm \frac{1}{2}$. σ_x^2, σ_y^2, σ_z^2 must therefore each have only one eigenvalue, namely $+1$. By substituting σ's for s's in the commutation rules, we obtain the following operational equations

$$\sigma_x^2 = \sigma_y^2 = \sigma_z^2 = 1;$$

$$\sigma_x\sigma_y = -\sigma_y\sigma_x; \quad \sigma_y\sigma_z = -\sigma_z\sigma_y; \quad \sigma_z\sigma_x = -\sigma_x\sigma_z.$$

The three matrices given below satisfy the above relationships if 1 is regarded as a unit matrix and may accordingly be taken as a particular representation of the σ operators.

$$\sigma_x = \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}, \qquad \sigma_y = \begin{vmatrix} 0 & -i \\ i & 0 \end{vmatrix}, \qquad \sigma_z = \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}.$$

In this notation, the operands are to be taken as two component column vectors like $\psi = \begin{vmatrix} \psi_1 \\ \psi_2 \end{vmatrix}$. Thus, every ψ should be regarded as consisting of two components ψ_1 and ψ_2 on account of the introduction of a spin angular momentum. The components ψ_1 and ψ_2 should both be bounded, continuous and single valued throughout the permitted range of the co-ordinates.

Pauli Exclusion Principle.—If there is an ensemble of n electrons all of which are assumed to be essentially indistinguishable from each other, any wave function ψ which is a function of the electron co-ordinates will transform into another function ψ' as a result of a permutation operator P operating on ψ. This result may be expressed by the equation

$$\psi' = P\psi.$$

Since P is a mere permutation of the n electrons amongst themselves, the state ψ' should be physically indistinguishable from the state ψ. This gives $\psi' = C\psi$. This C's constitute a representation of the symmetric group and are evidently matrices of order 1 being equal to ± 1 for all classes of P. As has been explained in Appendix IV, there are only two such representations for every symmetric group. The first of them which may be called the symmetric representation or the total symmetric representation corresponds to C being $+ 1$ for all classes of P. This is not of significance as the energy levels that are actually observed in atomic spectra are never characterized by such representations. The second of them which may be called the antisymmetric representation corresponds to the C's being equal to $+ 1$ for all classes consisting of even permutations and $- 1$ for all classes consisting of odd permutations giving

$$P\psi = \pm \psi.$$

This representation is the only one which needs to be considered while dealing with an ensemble of electrons, a choice which is equivalent to stating that electrons obey Fermi-Dirac statistics.

We shall now show that the Pauli exclusion principle stated in its usual form that no two electrons in a given atom can have all their four quantum numbers identical follows at once from the fact that all eigenfunctions which are symmetric with respect to every member of the permutation group have been ruled out while those which are symmetric with respect to the even members and anti-symmetric with respect to the odd members of the permutation group are the only possible ones. Consider a system composed of three electrons numbered 1, 2, 3. The individual equations

$$H_1\psi_1 = W_1\psi_1;\quad H_2\psi_2 = W_2\psi_2;\quad H_3\psi_3 = W_3\psi_3;$$

may be combined into a single equation

$$H\psi = W\psi,$$

where

$$H = H_1 + H_2 + H_3;\quad W = W_1 + W_2 + W_3;$$

$$\psi(1\,2\,3) = \psi_1(1)\,\psi_2(2)\,\psi_3(3);$$

provided the mutual interaction energy is small enough to be neglected. The permutation group generated from the symbols 1, 2, 3 is of order 6 and consists of the elements (1) (2) (3); (12) (3), (13) (2), (23) (1); (123), (132). If $\psi(123)$ is a solution of the three electron system corresponding to an eigenvalue W, the following ψ's are also seen to be solutions corresponding to the same eigenvalue

$$\begin{aligned}
\psi(123) &= \psi_1(1)\,\psi_2(2)\,\psi_3(3)\\
\psi(213) &= \psi_1(2)\,\psi_2(1)\,\psi_3(3)\\
\psi(321) &= \psi_1(3)\,\psi_2(2)\,\psi_3(1)\\
\psi(132) &= \psi_1(1)\,\psi_2(3)\,\psi_3(2)\\
\psi(231) &= \psi_1(2)\,\psi_2(3)\,\psi_3(1)\\
\psi(312) &= \psi_1(3)\,\psi_2(1)\,\psi_3(2)
\end{aligned}$$

These, however, are not the eigenfunctions because it has already been shown that an eigenfunction must be transformed either into itself by all the permutations or into itself with or without a change of sign according as the permutation applied is odd or even. In fact the two such functions, which are linear combinations of the above solutions, are

$$\psi_s = \psi(123)+\psi(213)+\psi(321)+\psi(132)+\psi(231)+\psi(312),$$

$$\psi_a = \psi(123)-\psi(213)-\psi(321)-\psi(132)+\psi(231)+\psi(312)$$

ψ_a can be put in the form of a determinant as

$$\psi_a = \begin{vmatrix} \psi_1(1) & \psi_2(1) & \psi_3(1) \\ \psi_1(2) & \psi_2(2) & \psi_3(2) \\ \psi_1(3) & \psi_2(3) & \psi_3(3) \end{vmatrix}.$$

If ψ_s's are ruled out, it is easily seen that ψ_a's can exist only when $\psi_1(1)$, $\psi_2(1)$, $\psi_3(1)$ are not all the same as $\psi_1(2)$, $\psi_2(2)$, $\psi_3(2)$ respectively. If all the four co-ordinates of electron 1 are identically the same as the four co-ordinates of electron 2, the above condition is not fulfilled and no ψ_a's exist because the determinant becomes zero.

CHAPTER XVI

OTHER APPLICATIONS

The Hydrogen Molecule.—This system consists of two electrons and two protons. If we denote the electrons as 1 and 2 and the protons as *a* and *b*, their respective masses being *m* and *M*, the Hamiltonian function in Cartesian co-ordinates may be written as

$$H = \frac{1}{2m}\left(p_{x_1}{}^2 + p_{y_1}{}^2 + p_{z_1}{}^2 + p_{x_2}{}^2 + p_{y_2}{}^2 + p_{z_2}{}^2\right)$$

$$+ \frac{1}{2M}\left(p_{x_a}{}^2 + p_{y_a}{}^2 + p_{z_a}{}^2 + p_{x_b}{}^2 + p_{y_b}{}^2 + p_{z_b}{}^2\right)$$

$$+ e^2\left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right).$$

r in each case is the distance between the pair of particles denoted by its suffixes. The Hamiltonian in this form is invariant under the operations of the rotation group. Since M is large in comparison with m, the terms involving M in the denominator can be omitted as an approximation. Substitutions of the type $h/2\pi i\ \partial/\partial x$ for p_x in the Hamiltonian expressed in Cartesian co-ordinates will lead to the appropriate operators for forming the wave equation, and we have $h^2/8\pi^2 m\,(\nabla_1{}^2 + \nabla_2{}^2)\,\psi$

$$- e^2\left(\frac{1}{r_{ab}} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{b1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b2}}\right)\psi + W\psi = 0.$$

ψ function in the above form includes co-ordinates relating to nuclear oscillations and molecular rotations besides those of the electrons. As the interaction between these three types of motion may be neglected, the function can be represented as a product of three functions in the form $\psi = \psi(v)\,\psi(R)\,\psi(e)$.

Treating r_{ab} as a constant and the nuclear axis as fixed in space, we will be eliminating those degrees of freedom and the above wave equation will give rise to eigenfunctions and eigenvalues appropriate to the electron configurations only. We then, for simplicity, drop the *e* in brackets and regard ψ to be the same as $\psi(e)$. The method adopted for solving this problem is to regard the molecule as made up of two hydrogen atoms in the first instance and introduce later the interaction terms as a perturbation. If electron 1 is on proton *a*, the corresponding wave function of the first order is

$$\psi_1 = Ae^{\frac{-r_{a1}}{r_0}}.$$

Similarly for cases where electron 1 is on proton *b*, electron 2 is on proton *a* and on proton *b*, we have respectively the wave functions ϕ_1, ψ_2, ϕ_2 given by

$$\phi_1 = Ae^{\frac{-r_{b1}}{r_0}}\ ; \quad \psi_2 = Ae^{\frac{-r_a}{r_0}}\ ; \quad \phi_2 = Ae^{\frac{-r_{b2}}{r_0}}.$$

A is the normalizing factor and r_0 the radius of the first Bohr orbit. The two possible cases of the unperturbed molecule are those in which electron 1 is on proton *a*, the second electron necessarily being on proton *b* and electron 2 is on proton *a*, the first electron necessarily being on proton *b*. The two wave functions are $\psi_1\phi_2$ and $\psi_2\phi_1$ and they correspond to the same eigenvalue and are therefore degenerate. We choose two mutually orthogonal linear combinations χ_1 and χ_2 in the form

$$\chi_1 = a_1\psi_1\phi_2 + b_1\psi_2\phi_1; \quad \chi_2 = a_2\psi_1\phi_2 + b_2\psi_2\phi_1.$$

The orthogonality and normalization requirements of χ_1 and χ_2 lead to

$$\chi_1 = A_1(\psi_1\phi_2 + \psi_2\phi_1)\ ; \quad \chi_2 = A_2(\psi_1\phi_2 - \psi_2\phi_1),$$

where A_1 and A_2 are constants. It is of importance to note that χ_1 is symmetric for an interchange of the electrons 1 and 2 whereas χ_2 is antisymmetric. The introduction of the interaction terms may be assumed to result in the perturbed eigenfunctions taking the form $\chi_1 + \chi_1'$ and $\chi_2 + \chi_2'$. These are solutions of the wave equation and by substituting them therein, the corresponding eigenvalues which will now be different from each other may be evaluated. Heitler and London have plotted the actual energy values thus obtained in the two cases against the nuclear distance r_{ab} between two neutral atoms and showed that the curve in the antisymmetric case is such that the value of the energy is always positive and goes on decreasing with increasing nuclear distance, exhibiting no turning point. This means that the nuclei always repel each other and molecule formation is not possible. On the other hand, the curve in the symmetric case exhibits a minimum so that a stable molecule of this configuration can be expected. Thus we conclude that the electronic eigenfunctions, for the hydrogen molecule in its ground state, in so far as they refer to the position co-ordinates only, should be symmetric with reference to an interchange of the electrons.

So far we have considered only the position co-ordinates of the electrons. In molecular hydrogen, there are two electrons and if with the first electron are associated two spin functions $\psi_1^{\frac{1}{2}}$ and $\psi_1^{-\frac{1}{2}}$ and with the second are associated two similar functions $\psi_2^{\frac{1}{2}}$ and $\psi_2^{-\frac{1}{2}}$, the product functions

$$\psi_1^{\frac{1}{2}}\psi_2^{\frac{1}{2}};\quad \psi_1^{\frac{1}{2}}\psi_2^{-\frac{1}{2}};\quad \psi_1^{-\frac{1}{2}}\psi_2^{\frac{1}{2}};\quad \psi_1^{-\frac{1}{2}}\psi_2^{-\frac{1}{2}}$$

constitute a reducible representation. The permutation group that can be constructed out of the two symbols 1 and 2 is Abelian and is of order 2 and consists of two conjugate classes E, (12). There will be only two irreducible representations, one of the symmetric type and the other of the antisymmetric type. It is easily seen that under the identity operation, every product function transforms into itself thus giving a character 4 whereas under the operation C_1 (12), two of them, namely, $\psi_1^{\frac{1}{2}}\psi_2^{\frac{1}{2}}$ and $\psi_1^{-\frac{1}{2}}\ \psi_2^{-\frac{1}{2}}$ transform into themselves and the other two interchange amongst themselves thus giving a character $1 + 1 + 0 + 0 = 2$. Four mutually orthogonal combinations can be found so that three of them, namely, $\psi_1^{\frac{1}{2}}\psi_2^{\frac{1}{2}}$; $\psi_1^{\frac{1}{2}}\psi_2^{-\frac{1}{2}} + \psi_1^{-\frac{1}{2}}\psi_2^{\frac{1}{2}}$; $\psi_1^{-\frac{1}{2}}\psi_2^{-\frac{1}{2}}$, constitute an irreducible manifold coming under the symmetric representation and one, namely, $\psi_1^{\frac{1}{2}}\psi_2^{-\frac{1}{2}} - \psi_1^{-\frac{1}{2}}\psi_2^{\frac{1}{2}}$, under the antisymmetric representation as per the Character Table given below:

	E	C_1	n_i
A_1	1	1	3
A_2	1	-1	1
$x'(R)$	4	2	

The three symmetrical spin functions are, however, of no avail for the ground state of the hydrogen molecule because by combining with the eigenfunction relating to the position co-ordinates which is already a symmetric one, they will give rise to functions which are on the whole symmetric in the electrons, a result which comes into conflict with the Pauli exclusion principle. They play a part only in the excited states of the hydrogen molecule. The fact that the antisymmetric spin function $\psi_1^{\frac{1}{2}}\psi_2^{-\frac{1}{2}} - \psi_1^{-\frac{1}{2}}\psi_2^{\frac{1}{2}}$ is the only permissible one means that if one of the electrons in the hydrogen molecule has its $s = +\frac{1}{2}$, the other should have its $s = -\frac{1}{2}$, giving zero for the resultant S thus making the molecule belong to the $^1\Sigma$ type in its ground state.

Rotational Specific Heat of Hydrogen.—It has been mentioned that the full wave function for a molecule is approximately expressed as

$$\psi = \psi(v)\,\psi(R)\,\psi(e).$$

$\psi(e)$ refers to the electronic portion and includes the position as well as the spin co-ordinates of the electrons. $\psi(v)$ refers to the vibrational state of the nuclei. If, for simplicity, we consider the molecule as non-vibrating, $\psi(v)$ need not be considered. $\psi(R)$ is in general a composite nuclear eigenfunction, including the position as well as the spin co-ordinates of the nuclei and its symmetry properties play an important part in determining the rotational specific heat. In the case of hydrogen molecule, the ground state is ${}^1\Sigma$. If we consider the molecule as rotating with a rotational quantum number J, the corresponding energy is $BJ(J+1)$, where $B = h^2/8\pi^2 I$. The relative eigenfunction consists of two parts P_{lm} and Q_m in the notation of Chapter VI. The operation of interchanging the nuclei is equivalent to changing θ to $\pi - \theta$ and ϕ to $\pi + \phi$ and as a result of such a change, P_{lm} may be seen to transform into $(-1)^{l-m} P_{lm}$ and Q_m into $(-1)^m Q_m$. This makes the product $P_{lm}Q_m$ transform into $(-1)^l P_{lm}Q_m$. The product eigenfunction will thus be termed symmetric or anti-symmetric in the nuclei according as l is even or odd. In the case of the hydrogen molecule in its ground state l is the same as J. Thus on account of nuclear rotation, the nuclear eigenfunctions divide themselves into the symmetric and antisymmetric types according as J is even or odd in so far as the position co-ordinates alone are concerned. To each of the two nuclei, we have, however, to ascribe a spin of $s = \pm \frac{1}{2}$. Accordingly, two spin functions $\psi_a^{\frac{1}{2}}$, $\psi_a^{-\frac{1}{2}}$ will be associated with the proton a and two other spin functions $\psi_b^{\frac{1}{2}}$, $\psi_b^{-\frac{1}{2}}$ will be associated with the proton b. Following the same argument as in the case of electrons, it may be shown that four mutually orthogonal linear combinations of the product functions

$$\psi_a^{\frac{1}{2}}\psi_b^{\frac{1}{2}},\quad \psi_a^{\frac{1}{2}}\psi_b^{-\frac{1}{2}},\quad \psi_a^{-\frac{1}{2}}\psi_b^{\frac{1}{2}},\quad \psi_a^{-\frac{1}{2}}\psi_b^{-\frac{1}{2}}$$

will be found such that three of them come under the symmetric type and one under the antisymmetric type. Total eigenfunctions referring to the position as well as the spin co-ordinates of the nuclei have to be now formed by making products of the rotational ones with those of the spin. In the case of hydrogen nuclei which are protons, they obey the Fermi-Dirac statistics. In such a case the total eigenfunctions should always be antisymmetric in the nuclei. They may accordingly be formed by combining the rotational eigenfunctions which are symmetric ($J =$ even) only with the spin eigenfunctions which are antisymmetric (one out of the possible four) and by combining the rotational eigenfunctions which are antisymmetric ($J =$ odd) only with the spin eigenfunctions which are symmetric (three out of the possible four). This gives a relative weight of 3 : 1 for the eigenfunctions with an odd J with reference to those with an even J. That these two sets are non-combining has already been shown. Remembering that the degree of degeneracy to be attributed to a rotational state J is $2J + 1$ and taking into account the above relative weight and the fact that each one of the molecules has an energy $BJ(J + 1)$, we have the following expressions for the total number of each kind of hydrogen molecules in a given assembly where $\sigma = B/KT$.

$$Q_{(J\ \text{even})} = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \ldots\ldots$$

$$Q_{(J\ \text{odd})} = 9e^{-2\sigma} + 21e^{-12\sigma} + \ldots\ldots\ldots$$

From the well-known expressions for the rotational specific heat, we have the contribution to it from each kind given by

$$\frac{C}{R} = \sigma^2 \frac{d^2}{d\sigma^2} \log Q.$$

If we denote the specific heat obtained by using $Q\,(J\,\text{odd})$ by C_a and that obtained by using $Q\,(J\,\text{even})$ by C_s, the actual specific heat C_o will be given by

$$C_o = \frac{C_a + C_s}{4}.$$

The experimental results are known to be in close agreement with the predictions contained in the above formulæ.

Nuclear Spin.—In the case of a diatomic molecule with like nuclei, each nucleus possessing a spin quantum number s, we have to associate $2s + 1$ spin functions with each of the nuclei. There are obviously $(2s + 1)^2$ ways of forming the product functions, if each product is to contain one spin function from one of the nuclei and the other from the second nucleus. If, as before, we consider the permutation group $E\,(12)$; of order 2 in respect of the nuclei a and b, the Character Table may be written in the following manner:

	E	(12)	n_i
A_1	1	1	$(s+1)(2s+1)$
A_2	1	-1	$s(2s+1)$
χ_p'	$(2s+1)^2$	$(2s+1)$	

All the $(2s+1)^2$ product functions are invariant under the operation E and therefore the character χ_p' of E in the representation defined by the $(2s+1)^2$ product functions is $(2s+1)^2$. On the other hand, in the operation (12) consisting of an interchange of the nuclei only, such of the products for which the spin vectors are the same for both nuclei remain invariant and these alone contribute to the character. They are $(2s+1)$ in number and hence the character of this operation is $(2s+1)$. Applying the general theorem for finding n_i, we notice that $(s+1)(2s+1)$ orthogonal combinations of the spin functions come under the symmetric class and $s(2s+1)$ orthogonal combinations come under the antisymmetric class. These have to combine with the rotational eigenfunctions to yield product eigenfunctions which should be antisymmetric in the nuclei if the nuclei obey Fermi-Dirac statistics and symmetric in the nuclei if they obey Bose-Einstein statistics. It has already been pointed out that rotation eigenfunctions of a diatomic molecule are symmetric in the nuclei when J is even and antisymmetric when J is odd. Thus, the product eigenfunctions for the former case can be formed either between those corresponding to even J and $s(2s+1)$ antisymmetric spin functions or between those corresponding to odd J and $(s+1)(2s+1)$ symmetric spin functions. The relative weights of rotational states with odd J and even J will therefore be as $(s+1)$: s in this cateogry. Hydrogen, which has already been dealt with, is a special case and by putting

$s = \frac{1}{2}$, we obtain the appropriate ratio of 3 : 1. In the latter, where the nuclei obey Bose-Einstein statistics, the product eigenfunctions can be formed only between those corresponding to even J and $(s+1)(2s+1)$ symmetric spin functions and between those corresponding to odd J and $s(2s+1)$ antisymmetric spin functions. The relative weights of rotational states with odd J and even J will in such a case be as $s : (s+1)$. Deuterium molecule is an example of this kind. The deuterium nucleus has a spin moment $s = 1$ and obeys Bose-Einstein statistics. Accordingly, we should expect the statistical weight of rotational states with odd J to be only half that of the rotational states with even J. The experimental results in respect of the rotational Raman spectrum of deuterium fully confirm the above expectation.

These formulæ are well known and are of wide applicability in connection with nuclear spins and their effect on rotational spectra. They have to be taken into consideration in explaining the results relating to specific heats, although the effects are most significant in the case of hydrogen on account of its low moment of inertia. It may be noted here that in addition to the spin statistical weight discussed above, an *a priori* probability $(2J+1)$ is to be associated with each rotational state J.

Intensities of Rotational Raman Lines.—The selection rules for the vibrational Raman scattering were derived in Chapter VIII. It was shown that the induced electric moment which is a tensor is influenced by the normal oscillation of a molecule in that it is altered periodically with the normal frequency. A similar periodic variation of the induced moment may be affected by the rotation of an anisotropic molecule with reference to the incident light vector. Rotational Raman lines will then result. The intensity of a Raman line of this category due to a transition $J_1 \rightarrow J_2$, $K_1 \rightarrow K_2$ is governed by an integral of the form $\int \alpha \psi_{K_1}{}^{J_1} \psi^*{}_{K_2}{}^{J_2} \, dV$, where α stands for any combination of the tensor components α_{xx}, α_{xy}, α_{xz}, α_{yy}, α_{zz}, α_{yz}. In the place of the Cartesian co-ordinates, if we use circular co-ordinates

$1/\sqrt{2}(-X+iY)$, Z, $1/\sqrt{2}(X+iY)$ and denote them by the suffixes 1, 0, -1, the corresponding tensor components may be written as α_{11}, α_{10}, α_{00}, α_{1-1}, α_{-10} and α_{-1-1}. It is easily verified that the quantities

$$\frac{\xi^4}{[4!]^{\frac{1}{2}}}, \frac{\psi^3\eta}{[3!]^{\frac{1}{2}}}, \frac{\xi^2\eta^2}{[2!\,2!]^{\frac{1}{2}}}, \frac{\xi\eta^3}{[3!]^{\frac{1}{2}}}, \frac{\eta^4}{[4!]^{\frac{1}{2}}}$$

transform under the operations of the group U_2 in the same way as the quantities

$$\frac{\alpha_{11}}{2}, \frac{\alpha_{10}}{\sqrt{2}}, \frac{\alpha_{00}+\alpha_{1-1}}{\sqrt{6}}, \frac{\alpha_{-10}}{\sqrt{2}}, \frac{\alpha_{-1-1}}{2}.$$

The corresponding transformation matrix is

$$\begin{vmatrix} a^4 & 2a^3b & \sqrt{6}a^2b^2 & 2ab^3 & b^4 \\ -2a^3b^* & a^2(aa^* - 3bb^*) & \sqrt{6}ab(aa^* - bb^*) & b^2(3aa^* - bb^*) & 2a^*b^3 \\ \sqrt{6}a^2b^{*2} & \sqrt{6}ab^*(bb^* - aa^*) & a^2a^{*2} - 4aa^*bb^* + b^2b^{*2} & \sqrt{6}a^*b(aa^* - bb^*) & \sqrt{6}b^2a^{*2} \\ -2ab^{*3} & b^{*2}(3aa^* - bb^*) & \sqrt{6}a^*b^*(bb^* - aa^*) & a^{*2}(aa^* - 3bb^*) & 2ba^{*3} \\ b^{*4} & -2a^*b^{*3} & \sqrt{6}a^{*2}b^{*2} & -2b^*a^{*3} & a^{*4} \end{vmatrix}$$

The quantities $\xi^4/[4!]^{\frac{1}{2}}$, etc., have been designated in our terminology as $\phi_2{}^2$, $\phi_1{}^2$, $\phi_0{}^2$, $\phi_{-1}{}^2$, $\phi_{-2}{}^2$. Hence complete information relating to the selection rules and intensity factors of rotational Raman lines is obtained from a study of the integrals of the type $\int \phi_a{}^2\psi_{K_1}{}^{J_1}\psi^*{}_{K_2}{}^{J_2}\,dV$, where $a=\pm 2, \pm 1, 0$. The problem thus reduces to the reduction of the representation defined by $\phi_a{}^2\psi_{K_1}{}^{J_1}$ into its irreducible components. In the notation of Chapter XV,

$$\Phi_m{}^J = Cf_{pm}{}^J(\xi_1\eta_2 - \xi_2\eta_1)^q$$

where $p = J - (l_1 - l_2)$ and $q = l_1 + l_2 - J$.

$f_{pm}{}^J$ is the coefficient of x^p in $(\xi_1 + x\xi_2)^{J+m}(\eta_1 + x\eta_2)^{J-m}$.

Here $J = l_1 + 2$ and we have $p = 4$, $q = 0$.

$$\underset{(J=l_1+2)}{\Phi_m{}^J} = Cf_m{}^{J_4}.$$

Expanding and simplifying, we can write

$$\begin{aligned}\underset{(J=l_1+2)}{\Phi_m{}^J} = & \left[\frac{(l_1-m)(l_1-m-1)(l_1-m+1)(l_1-m+2)}{4(l_1+1)(l_1+2)(2l_1+1)(2l_1+3)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+2}\,\phi^2_{-2}\\ & + \left[\frac{(l_1-m)(l_1-m+1)(l_1-m+2)(l_1+m+2)}{(l_1+1)(l_1+2)(2l_1+1)(2l_1+3)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+1}\,\phi^2_{-1}\\ & + \left[\frac{3(l_1-m+1)(l_1+m+1)(l_1-m+2)(l_1+m+2)}{2(l_1+1)(l_1+2)(2l_1+1)(2l_1+3)}\right]^{\frac{1}{2}} \psi^{l_1}_{m}\,\phi^2_{0}\\ & + \left[\frac{(l_1+m)(l_1+m+1)(l_1+m+2)(l_1-m+2)}{(l_1+1)(l_1+2)(2l_1+1)(2l_1+3)}\right]^{\frac{1}{2}} \psi^{l_1}_{m-1}\,\phi^2_{1}\\ & + \left[\frac{(l_1+m)(l_1+m-1)(l_1+m+1)(l_1+m+2)}{4(l_1+1)(l_1+2)(2l_1+1)(2l_1+3)}\right]^{\frac{1}{2}} \psi^{l_1}_{m-2}\,\phi^2_{2}.\end{aligned}$$

Similarly, we have

$$\begin{aligned}\underset{(J=l_1+1)}{\Phi_m{}^J} = & \left[\frac{(l_1-m)(l_1-m-1)(l_1-m+1)(l_1+m+2)}{2l_1(l_1+1)(l_1+2)(2l_1+1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+2}\,\phi^2_{-2}\\ & + \left[\frac{(l_1-m)(l_1-m+1)(l_1+2m+2)^2}{2l_1(l_1+1)(l_1+2)(2l_1+1)}\right]^{\frac{1}{2}} \psi^{l_1}_{m+1}\,\phi^2_{-1}\end{aligned}$$

$$+\left[\frac{3m^2(l_1+m+1)(l_1-m+1)}{l_1(l_1+1)(l_1+2)(2l_1+1)}\right]^{\frac{1}{2}}\psi^{l_1}_{m_1}\phi^2_0$$

$$+\left[\frac{(l_1-2m+2)^2(l_1+m)(l_1+m+1)}{2l_1(l_1+1)(l_1+2)(2l_1+1)}\right]^{\frac{1}{2}}\psi^{l_1}_{m-1}\phi^2_1$$

$$+\left[\frac{(l_1+m)(l_1+m-1)(l_1+m+1)(l_1-m+2)}{2l_1(l_1+1)(l_1+2)(2l_1+1)}\right]^{\frac{1}{2}}\psi^{l_1}_{m-2}\phi^2_2,$$

$$\underset{(J=l_1)}{\Phi_m^J}=\left[\frac{3(l_1-m)(l_1-m-1)(l_1+m+1)(l_1+m+2)}{2l_1(l_1+1)(2l_1-1)(2l_1+3)}\right]^{\frac{1}{2}}\psi^{l_1}_{m+2}\phi^2_{-2}$$

$$+\left[\frac{3(2m+1)^2(l_1-m)(l_1+m+1)}{2l_1(l_1+1)(2l_1-1)(2l_1+3)}\right]^{\frac{1}{2}}\psi^{l_1}_{m+1}\phi^2_{-1}$$

$$+\frac{3m^2-l_1(l_1+1)}{[l_1(l_1+1)(2l_1-1)(2l_1+3)]^{\frac{1}{2}}}\psi^{l_1}_{m}\phi^2_0$$

$$+\left[\frac{3(-2m+1)^2(l_1+m)(l_1-m+1)}{2l_1(l_1+1)(2l_1-1)(2l_1+3)}\right]^{\frac{1}{2}}\psi^{l_1}_{m-1}\phi^2_1$$

$$+\left[\frac{3(l_1+m)(l_1-m+1)(l_1-m+2)(l_1+m-1)}{2l_1(l_1+1)(2l_1-1)(2l_1+3)}\right]^{\frac{1}{2}}\psi^{l_1}_{m-2}\phi^2_2.$$

Denoting the coefficients in the equation corresponding to $J=l_1+2$ by a_{51}, a_{52}, a_{53}, a_{54}, a_{55} and those in the one corresponding to $J=l_1+1$ by a_{41}, a_{42}, a_{43}, a_{44}, a_{45} and so on, we can regard the matrix $[a_{ik}]$ as furnishing the transformation of five product functions on the right-hand side into five single functions on the left-hand side. Moreover the coefficients a_{11}, a_{12}, a_{13}, a_{14}, a_{15} in the equation corresponding to $J=l_1-2$ can be obtained respectively from a_{55}, a_{54}, a_{53}, a_{52}, a_{51} by replacing l_1 by l_1-2 and multiplying by $(2l_1-3)/(2l_1+1)$, m's in the latter set of coefficients being replaced by $m+2$, $m+1$, m, $m-1$ and $m-2$ respectively. Similarly the coefficients a_{21}, a_{22}, a_{23}, a_{24}, a_{25} in the equation, corresponding to $J=l_1-1$, can be obtained respectively from a_{45}, a_{44}, a_{43}, a_{42}, a_{41} by replacing l_1 by l_1-1 and multiplying by $(2l_1-1)/(2l_1+1)$, m's in the latter set being replaced by $m+2$, $m+1$, m, $m-1$, and $m-2$ respectively.

The coefficients in the five equations now described form an orthogonal matrix. Its inverse is therefore obtained by interchanging the rows and columns. Consequently, the product functions can be expressed as linear combinations of the single function. For example, we have

$$\phi_2^2\psi^{l_1}_{m_1-2} = \left[\frac{(l_1-m_1)(l_1-m_1-1)(l_1-m_1+1)(l_1-m_1+2)}{4\,(l_1-1)\,l_1\,(2l_1+1)\,(2l_1-1)}\right]^{\frac{1}{2}} \Phi^{l_1-2}_{m_1}$$

$$+\left[\frac{(l_1-m_1+1)(l_1-m_1)(l_1-m_1+2)(l_1+m_1-1)}{2\,(l_1-1)\,l_1\,(l_1+1)\,(2l_1+1)}\right]^{\frac{1}{2}} \Phi^{l_1-1}_{m1}$$

$$+\left[\frac{3\,(l_1+m_1)(l_1-m_1+1)(l_1-m_1+2)(l_1+m_1-1)}{2l_1\,(l_1+1)\,(2l_1-1)\,(2l_1+3)}\right]^{\frac{1}{2}} \Phi^{l_1}_{m_1}$$

$$+\left[\frac{(l_1+m_1)\,(l_1+m_1-1)(l_1-m_1+1)\,(l_1-m_1+2)}{2l_1\,(l_1+1)\,(l_1+2)\,(2l_1+1)}\right]^{\frac{1}{2}} \Phi^{l_1+1}_{m_1}$$

$$+\left[\frac{(l_1+m_1)(l_1+m_1-1)(l_1+m_1+1)(l_1+m_1+2)}{4\,(l_1+1)\,(l_1+2)\,(2l_1+1)\,(2l_1+3)}\right]^{\frac{1}{2}} \Phi^{l_1+2}_{m_1}$$

and similarly for the products ${\phi_1}^2\,{\psi^{l}}_{1m_1-1}$, ${\phi_0}^2\,{\psi^{l}}_{1m_1}$, $\phi^2_{-1}\ {\psi^{l}}_{1m_l+1}$ and ${\phi_{-2}}^2\,{\psi^{l}}_{1m_1+2}$.

As has already been mentioned, the intensity of the Raman line resulting from a transition $J_1 \rightarrow J_2$; $K_1 \rightarrow K_2$ depends on the integrals of the type $\int {\phi_2}^2 {\Phi_{K_1}}^{J_1} {\Phi_{K_2}}^{J_2*}\,dV$. Using the expressions given in the foregoing paragraphs and replacing l_1 and l_2 by J_1 and J_2 and m_1 and m_2 by K_1+2 and K_2 respectively, we have

$$\int {\Phi_{K_1}}^{J_1}\,{\phi_2}^2\,{\Phi_{K_2}}^{J_2*}dV$$

$$=\int\left[\frac{(J_1-K_1-2)(J_1-K_1-3)(J_1-K_1-1)(J_1-K_1)}{4\,(J_1-1)\,(J_1)\,(2J_1+1)\,(2J_1-1)}\right]^{\frac{1}{2}} \Phi^{J_1-2}_{K_1+2}\,\Phi^{J_2*}_{K_2}dV$$

$$+\int\left[\frac{(J_1-K_1-1)(J_1-K_1-2)(J_1-K_1)(J_1+K_1+1)}{2\,(J_1-1)\,(J_1)\,(J_1+1)\,(2J_1+1)}\right]^{\frac{1}{2}} \Phi^{J_1-1}_{K_1+2}\,\Phi^{J_2*}_{K_2}\,dV$$

$$+\int\left[\frac{3\,(J_1+K_1+2)(J_1-K_1-1)(J_1-K_1)(J_1+K_1+1)}{2J_1\,(J_1+1)\,(2J_1-1)\,(2J_1+3)}\right]^{\frac{1}{2}} \Phi^{J_1}_{K_1+2}\,\Phi^{J_2*}_{K2}\,dV$$

$$+\int\left[\frac{(J_1+K_1+2)(J_1+K_1+1)(J_1+K_1+3)(J_1-K_1)}{2J_1\,(J_1+1)\,(J_1+2)\,(2J_1+1)}\right]^{\frac{1}{2}} \Phi^{J_1+1}_{K_1+2}\,\Phi^{J_2*}_{K_2}\,dV$$

$$+\int\left[\frac{(J_1+K_1+2)(J_1+K_1+1)(J_1+K_1+3)(J_1+K_1+4)}{4\,(J_1+1)\,(J_1+2)\,(2J_1+1)\,(2J_1+3)}\right]^{\frac{1}{2}} \Phi^{J_1+2}_{K_1+2}\,\Phi^{J_2*}_{K_2}\,dV$$

Since $\Phi_K{}^J$ form the basis functions for the irreducible representations, they are orthogonal and the above equation shows that the transition $J_1 \rightarrow J_2$; $K_1 \rightarrow K_2$ is permitted if $J_2 - J_1 = \triangle J = \pm 2, \ \pm 1, \ 0$ and $K_2 - K_1 = \triangle K = 2$. Dealing with the second, third, fourth and fifth integrals in a similar manner, we obtain that the transition $J_1 \rightarrow J_2$; $K_1 \rightarrow K_2$ is also permitted if $\triangle J$ has the same set of values as in the first integral and $\triangle K = 1, 0, -1, -2$ respectively. These constitute the selection rules for rotational Raman lines. In the case of permitted lines, the intensities are proportional to the squares of the surviving integrals and their values, with the normalization factors, are tabulated below. The suffixes have been dropped out and J and K inserted for J_1 and K_1 respectively. p and q stand for $J + K$ and $J - K$ respectively. These results have been obtained earlier by Placzeck and Teller* using other methods.

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* *Zeit. f. Physik*, Vol. 81 (1930)

K' \ J'	$J-2$	$J-1$	J
$K-2$	$C_1 . p(p-1)(p-2)(p-3)$	$C_2 . p(p-1)(p-2)(q+1)$	$C_3 . 3p(p-1)(q+1)(q+2)$
$K-1$	$C_1 . 4pq(p-1)(p-2)$	$C_2 . \frac{1}{4}p(p-1)(3q-p+2)^2$	$C_3 . 3p(q+1)(p-q-1)^2$
K	$C_1 . 6pq(p-1)(q-1)$	$C_2 . \frac{3}{2}pq(p-q)^2$	$C_3 . \frac{1}{2}(p^2+q^2-4pq-p-q)^2$
$K+1$	$C_1 . 4pq(q-1)(q-2)$	$C_2 . \frac{1}{4}q(q-1)(3p-q+2)^2$	$C_3 . 3q(p+1)(q-p-1)^2$
$K+2$	$C_1 . q(q-1)(q-2)(q-3)$	$C_2 . q(q-1)(q-2)(p+1)$	$C_3 . 3q(q-1)(p+1)(p+2)$
C	$1/C_1 = 4J(J-1)(2J-1)(2J+1)$	$1/C_2 = 2J(J-1)(J+1)(2J+1)$	$1/C_3 = 2J(J+1)(2J-1)(2J+3)$

$K' \backslash J'$	$J+1$	$J+2$
$K-2$	$C_4 . p(q+1)(q+2)(q+3)$	$C_5 . (q+1)(q+2)(q+2)(q+3)(q+4)$
$K-1$	$C_4 . \frac{1}{4}(q+1)(q+2)(3p-q)^2$	$C_5\ 4(p+1)(q+1)(q+2)(q+3)$
K	$C_4 . \frac{3}{2}(p+1)(q+1)(p-q)^2$	$C_5 . 6(p+1)(p+2)(q+1)(q+2)$
$K+1$	$C_4 . \frac{1}{4}(p+1)(p+2)(3q-p)^2$	$C_5 . 4(p+1)(p+2)(p+3)(q+1)$
$K+2$	$C_4 . q(p+1)(p+2)(p+3)$	$C_5 . (p+1)(p+2)(p+3)(p+4)$
C	$1/C_4 = 2J(J+1)(J+2)(2J+1)$	$1/C_5 = 4(J+1)(J+2)(2J+1)(2J+3)$

APPENDIX I

REPRESENTATIONS OF FINITE GROUPS

Linear Vector Spaces.—Let the vectors $A_1, B_1, \ldots\ldots$ constitute an Abelian group V under the operation of addition. Let us define in some way the product xA, etc., where $x, y, \ldots.$ are numbers. If $xA \ldots.$ denote elements in V, then V is called a linear vector space (or linear manifold), if the following postulates are satisfied. $xA = Ax$; $x(A + B) = xA + xB$; $(x + y) A = xA + yA$; $x(yA) = (xy) A$ and $1.A = A$.

A set of vectors $A_1, A_2, \ldots, A_n$ are called linearly dependent, if there exist numbers, $x_1, x_2, \ldots, x_n$ not all zero such that $x_1A_1 + x_2A_2 + \ldots x_nA_n$ equals the zero vector. If no such scalars exist, the vectors are called linearly independent.

The dimension of a linear vector space V is the maximum number of linearly independent vectors in V. Suppose $A_1, A_2, \ldots, A_n$ form a set of linearly independent vectors. They may be called a basis set of vectors in V for, any vector A can be uniquely expressed in the form

$$A = x_1A_1 + \ldots + x_nA_n.$$

The vector itself may then be replaced by the row matrix $(x_1, \ldots, x_n)$ and $x_1, \ldots, x_n$ may be called the co-ordinates of the vector. In the latter description of the vectors as row (or corresponding transposed column) matrices, addition and scalar multiplication in V may be identified with corresponding operations in matrices. This description of a vector, of course, depends on the choice of the basis.

Suppose $B_1, B_2, \ldots, B_n$ is another set of basis vectors in V. Then every B_r can be expressed in terms of the basis vectors A_s in the form

$$B_r = \Sigma\, t_{rs}\, A_s.$$

The matrix $T = |t_{rs}|$ is non-singular and further, if $y_1, \ldots, y_n$, are the co-ordinates of the vector A in the new basis, we have

$$x_s = \Sigma\, y_r t_{rs}$$

or in matrix notation

$$| x_1, \ldots, x_n | = | y_1, \ldots, t_n | \, T$$

or simply $| x | = | y | \, T$. If the vector $| x |$ is taken as a column matrix instead of as a row matrix, this equation takes the form $| x | = T \, | y |$.

The Concept of Reducibility in Terms of Invariant Subspaces.—Suppose V_n is a linear vector space of dimension n. A subset of vectors in V_n satisfying all the postulates of a vector space is called a subspace of V_n. Let M be any $n \times n$ matrix. If the vectors in V_n are taken in the form $|x|$ with any basis set of vectors $A_1, A_2, \ldots, A_n$, a linear transformation mapping $f(M)$ may be associated with the matrix M by the equation

$$| x' | = | x | \, M.$$

Suppose there is a subspace V_r or dimension r in V_n such that any vector in V_r is mapped into a vector again in V_r. Then, we say that V_r is an invariant subspace of V_n under the mapping $f(M)$.

Let $\triangle$ be a set of $n \times n$ matrices. The set is called reducible if there exists an r-dimensional subspace V_r of V_n which remains invariant simultaneously under all the linear transformations defined by the set $\triangle$. If this condition is not satisfied, we say that $\triangle$ is an irreducible set of matrices. If the set of matrices in $\triangle$ defines a representation of a group G, the representation is called reducible or irreducible according as $\triangle$ is a reducible or an irreducible set. We shall now show that this definition is equivalent to the one given previously.

Choose a set of basis vectors $B_1, B_2, \ldots, B_r, \ldots, B_n$ in V_n such that the first r vectors form a basis for the subspace V_r. With the new basis, let the vectors in V_n be represented by $|y|$. We have then in the notation of the previous Section

$$|x| = |y|T$$
$$|x'| = |y'|T.$$

The mapping $f(M)$ in the new co-ordinate system will be described by the linear transformation

$$|y'| = |y|S$$

where $S = T^{-1}MT$. If V_r is an invariant subspace under the mapping $f(M)$, we have

$$|y_1', \ldots, y_r', 0, \ldots, 0| = |y_1, \ldots, y_r, 0, \ldots, 0|\, S.$$

Writing S in the form

$$\begin{bmatrix} A & B \\ C & D \end{bmatrix},$$

where A and D are square matrices of orders r and n-r respectively, Y for $(y_1, y_2, \ldots, y_r)$ and 0 for the n-r row $(0, \ldots, 0)$, the above equation may be briefly given as

$$(Y':0) = (Y:0)\begin{bmatrix} A & B \\ C & D \end{bmatrix}$$

that is

$$|Y':0| = |AY: BY|.$$

Since this equation should hold good for all Y, the matrix B is zero. That is $S = T^{-1}MT$ is of the form

$$\begin{bmatrix} A & 0 \\ C & D \end{bmatrix}.$$

If the matrices M define a representation Γ_1 of a group G, the matrices S define an equivalent representation Γ_2 the matrices of which are all of the form

$$\begin{bmatrix} A_r & 0 \\ C_r & D_r \end{bmatrix}.$$

This shows the equivalence of the two definitions of reducibility of a representation. It may be observed, that a change of basis in V_n gives rise to an equivalent representation. Thus, reducibility or irreducibility is an attribute to a class of equivalent representations rather than to a single member in it.

Schur's Lemma.—Let $\triangle_1$ and $\triangle_2$ be two irreducible sets of square matrices of respective orders m and n, and let A be a rectangular m by n matrix such that

$$\triangle_1 A = A \triangle_2.$$

Schur's Lemma states that A is either a zero matrix or a non-singular square matrix. To prove this let V_m and V_n be two vector spaces of dimensions m and n respectively. Let X and Y be a pair of matrices in $\triangle_1$ and $\triangle_2$ for which $XA = AY$. Let U_m be the vector space AV_n. U_m consists of all vectors which are obtained by operating the mapping described by the matrix A on the vectors in V_n. Under the mappings defined by the matrices X in $\triangle_1$, U_m is an invariant subspace of V_m, for

$$XU_m = XAV_n = AYV_n = A \mid YV_n \mid$$

which is included in U_m. Since $\triangle_1$ is an irreducible set, either $U_m = 0$ or V_m. In the first case, A is the zero matrix. Now consider the set of all vectors in V_n for which $AV_n = 0$. They form an invariant subspace say U_n of V_n, for

$$A \mid YU_n \mid = X \mid AU_n \mid = 0$$

so that YU_n is included in U_n. From the irreducibility of $\triangle_2$, U_n is either zero or the entire space V_n. In the latter case A is the zero matrix. The first alternative shows that the zero vector in V_n is the only vector belonging to U_n. This shows that, distinct vectors in V_n will go over into distinct vectors in V_m under the mapping defined by A. Hence if $A \neq 0$, A defines a one to one mapping of V_n on to V_m. That is A is a non-singular matrix.

A square matrix A which commutes with all matrices of an irreducible set $\triangle$ is a scalar matrix. For, let us consider the matrix $M = A - \lambda I$, where λ is a characteristic root of A. Then M is singular but commutes with all the matrices of the set $\triangle$. From Schur's Lemma M should be the zero matrix and $A = \lambda I$.

Orthogonality Relations for Irreducible Representations.—Let Γ_1 and Γ_2 be two non-singular representations of dimensions n and m of a finite group G of order N. Let the elements in G be taken as a_k $(k = 1, 2, \ldots, N)$ and the corresponding matrices in Γ_1 and Γ_2 be A_k and B_k. Let $\triangle_1$ and $\triangle_2$ respectively denote the irreducible sets of matrices A_k and B_k. Further let Y be an $m \times n$ matrix. Then the matrix M defined by the relation

$$M = \sum_s B_s^{-1} Y A_s$$

satisfies

$$M \triangle_1 = \triangle_2 M$$

for,

$$\begin{aligned} MA_k = \sum_s B_s^{-1} Y A_s A_k &= B_k \sum_s B_k^{-1} B_s^{-1} Y A_s A_k \\ &= B_k \sum_s \mid B_s B_k \mid^{-1} Y A_s A_k \\ &= B_k M. \end{aligned}$$

Hence by Schur's Lemma M is a scalar matrix λE or zero according as Γ_1 is equivalent to Γ_2 or not. That is

$$\begin{aligned} M_{ij} = \sum_{s,\, m,\, n} \mid B_s^{-1} \mid_{im} Y_{mn} \mid A_s \mid_{nj} &= 0 \qquad \text{if } \Gamma_1 \not\approx \Gamma_2 \\ &= \lambda \delta_{ij} \quad \text{if } \Gamma_1 \approx \Gamma_2 \end{aligned}$$

λ depends on Y. Choosing the matrix Y such that $Y_{mn} = \delta_{mk} \delta_{nl}$ where k and l are fixed, we have

$$\begin{aligned} \sum_{s,\, m,\, n} \mid B_s^{-1} \mid_{im} \delta_{mk} \delta_{nl} (A_s)_{nj} = \sum_s \mid B_s^{-1} \mid_{ik} \mid A_s \mid_{lj} \\ &= 0 \qquad \text{if } \Gamma_1 \not\approx \Gamma_2 \\ &= \lambda \delta_{ij} \quad \text{if } \Gamma_1 \approx \Gamma_2. \end{aligned}$$

In the latter case $\lambda = \sum_s \mid A_s \mid_{lj} \mid B_s^{-1} \mid_{ik}$. Suppose Γ_1 and Γ_2 are not only equivalent but identical then B^{-1} is the inverse of A so that

$$\sum_i \lambda = \sum_s \sum_i | A_s |_{li} | B_s^{-1} |_{is} = \sum_s \delta_{lk} = N\,\delta_{lk}$$

where N is the order of G. $\sum_i \lambda = n\lambda$ where n is the dimension of the representation. We have the orthogonality relations:

$$\sum_s | B_s^{-1} |_{ik} | A_s |_{lj} = 0 \qquad \text{if } \Gamma_1 \not\approx \Gamma_2$$

$$= \frac{N}{n}\,\delta_{ij}\delta_{kl} \quad \text{if } \Gamma_1 = \Gamma_2.$$

If Γ_1 and Γ_2 are unitary $| B_s^{-1} |_{ik}$ may be replaced by $| \bar{B}_s |_{ki}$.

Unitary Representations.—Every non-singular representation Γ of a finite group G is equivalent to a unitary representation. To prove this, let the elements of G be a_k and the corresponding non-singular matrices in Γ be A_k. Since the representation is non-singular each matrix $A_k{}^*A_k$ is a positive definite Hermitian matrix. Let $H = \sum_k A^*{}_kA_k$. H is also a positive definite Hermitian matrix. Hence it may be transformed by a unitary matrix U into a real non-singular diagonal matrix D with positive diagonal elements and $D = U^*HU$. Taking the positive square roots of each of the diagonal elements of D in the same order we form the diagonal matrix $D^{\frac{1}{2}}$ so that its square is D. Let $D^{-\frac{1}{2}}$ be the inverse of $D^{\frac{1}{2}}$ and $S = UD^{-\frac{1}{2}}$. If we take $X_k = S^{-1} A_kS$, we have

$$\begin{aligned} X_k{}^* X_k &= | S^{-1} A_kS |^* | S^{-1} A_kS | \\ &= | D^{\frac{1}{2}} U^*A_kUD^{-\frac{1}{2}} |^* | D^{\frac{1}{2}} U^*A_k UD^{-\frac{1}{2}} | \\ &= D^{-\frac{1}{2}} U^*A_k{}^* UDUA_kUD^{-\frac{1}{2}} \\ &= D^{-\frac{1}{2}} U^*A_k{}^*HA_kUD^{-\frac{1}{2}} \\ &= D^{-\frac{1}{2}} U^*A_k{}^* | \sum_s A_s{}^* A_s | A_k UD^{-\frac{1}{2}} \\ &= D^{-\frac{1}{2}} U^* \sum_s | A_sA_k |^* | A_sA_k | UD^{-\frac{1}{2}}. \end{aligned}$$

But the set of matrices A_sA_k for a fixed k and all s is the same as the set A_s and therefore,

$$X_k{}^*X_k = D^{-\frac{1}{2}} U^*HUD^{-\frac{1}{2}} = D^{-\frac{1}{2}} DD^{-\frac{1}{2}} = E$$

so that the matrices X_k define a representation Γ' which is unitary and equivalent to Γ.

A unitary reducible representation Γ_1 of a finite group G is equivalent to a completely reducible representation. For, as before let the matrices corresponding to the elements a_k in G and defining the representation Γ_1 be denoted by A_k. Let A_k be assumed to operate on vectors in an n-dimensional vector space V_n. Since Γ_1 is reducible, there exists an r-dimensional subspace V_r, which is invariant under the transformations defined by A_k. Consider the set of vectors $| b |$ in V_n which are orthogonal to all the vectors $| a |$ in V_r, that is satisfying the relation $(b, a) = | b | \ | a^* | = 0$. (b, a) is called the scalar product of the vectors b and a. This set forms a linear vector space say U_{n-r} of dimensions n-r. On account of the relation $(b, a) = 0$, there is no vector common to V_r and U_{n-r}, except the zero vector. Since the matrix A_k is unitary, we have $(bA_k, aA_k) = (b, a) = 0$. Also, since A_k is non-singular, the set aA_k covers the entire space V_r as a is taken over the whole set V_r. This shows that bA_k belongs to U_{n-r}. Thus the space V_n is split into two subspaces V_r and U_{n-r} both of which are invariant under the mappings A_k. This is the criterion for complete reducibility of a representation. We show that this definition may be identified with the one given earlier.

We have already seen that a change of basis in the space V_n leads to a similarity transformation of the matrices A_k. Let $X_1, \ldots, X_r$ and $Y_1 \ldots, Y_{n-r}$ respectively form a set of basis vectors in V_r and U_{n-r}. These $r + (n - r)$ vectors may be taken as basis vectors in V_n. Any vector in V_n will be expressed as $| X \colon Y |$ where X and Y stand for rows of the form $| x_1, \ldots, x_r |$ and $| y_1, \ldots, y_{n-r} |$. Let the mappings corresponding to A_k be now described with the new basis by the matrices $A_k' = T^{-1} A_k T$. Writing A_k' in the form

$$\begin{bmatrix} A_k'' & {}_k'' \\ C_k'' & D_k'' \end{bmatrix}$$

where A_k'' and D_k'' are square matrices of orders r and n-r

respectively, we have on account of the invariance of the subspaces V_r and U_{n-r} the following equations.

$$\begin{aligned} | X' : 0 | &= | X : 0 | \begin{bmatrix} A_k'' & B_k'' \\ C_k'' & D_k'' \end{bmatrix} \\ &= | XA_k'' : XD_k'' | \end{aligned}$$

and

$$\begin{aligned} | 0 : Y' | &= | 0 : Y | \begin{bmatrix} A_k'' & B_k'' \\ C_k'' & D_k'' \end{bmatrix} \\ &= | YC_k'' : YD_k'' | \end{aligned}$$

for arbitrary rows X and Y. This shows that the matrices B_k'' and C_k'' are zero matrices.

It may be easily verified that the matrices A_k'' define a representation of the group G. So also do the matrices D_k''. If the matrices A_k'' (or D_k'') define a reducible representation, we repeat the above process of reduction. This may be done until we arrive at a stage, where the matrices in each subdivision define an irreducible representation of G. It may be noted that at every stage we can assume the representations to be unitary.

It now follows that every non-singular representation of a finite group G is either irreducible or completely reducible into unitary irreducible representations.

Regular Representation.—Let $a_1, \ldots, a_N$ be the elements in a finite group G of order N. Consider the mapping

$$a_k \rightarrow a_k a_s,$$

where a_s is fixed and a_k varies over the elements of the group. This defines a representation of the group G for if a_r and a_s correspond to the mappings

$$a_k \rightarrow a_k a_r$$

and

$$a_k \rightarrow a_k a_s$$

then $a_r a_s$ corresponds to the mapping

$$a_k \rightarrow a_k (a_r a_s)$$

for $a_k(a_r a_s) = (a_k a_r)(a_s)$. This representation is called a right regular representation of G. The degree of this representation is N. If $a_k a_s = a_l$ the matrix A_s corresponding to the element a_s in the above representation is such that the k-th row l-th column element in it is one and all other elements in the k-th row are zero. Similarly, the representation induced by the mapping

$$a_k \rightarrow a_s a_k$$

is called a left regular representation of G. It is easy to verify that all these regular representations are equivalent. This set of representations is called a regular representation. As an example, take the group G defined by the relations $a^3 = E$, $b^2 = E$ and $ba = a^2b$ and write the elements of G in some order say $E\, a\, a^2\, b\, ab\, a^2b$. To obtain the matrix corresponding to b in a right regular representation we multiply the above elements on the right by b and obtain the following matrix equation:—

$$\begin{vmatrix} E \\ a \\ a^2 \\ b \\ ab \\ a^2b \end{vmatrix} |\, b\, | = \begin{vmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{vmatrix} \begin{vmatrix} E \\ a \\ a^2 \\ b \\ ab \\ a^2b \end{vmatrix}$$

Thus b corresponds to the above matrix. The matrices corresponding to the other elements can similarly be given. If we take a different order for the elements of G we get a representation which is equivalent to the above one.

Multiplication of Conjugate Classes.—Let C_ρ and C_σ be two conjugate classes of orders h_ρ and h_σ in a finite group G. Form the $h_\rho h_\sigma$ products by combining with the group operation the elements of C_ρ with those of C_σ. We shall refer to this set of $h_\rho h_\sigma$ elements as the product $C_\rho C_\sigma$. Suppose

u is an element of C_k and let it occur α times in $C_\rho C_\sigma$. Since $t^{-1} C_\rho C_\sigma t = t^{-1} C_\rho t . t^{-1} C_\sigma t = C_\rho C_\sigma$ for every group element t, $u' = t^{-1} ut$ occurs β times in $C_\rho C_\sigma$ by the same argument u occurs in $C_\rho C_\sigma$ at least β times. This argument holds good for every pair in C_k so that all elements in C_k occur the same number α times in $C_\rho C_\sigma$. We can therefore write

$$C_\rho C_\sigma = \sum_k \gamma_{\rho\sigma k} C_k.$$

The inverse elements of a conjugate class C_ρ form a conjugate class which may be denoted by $\bar{C}_\rho$. It is possible that $C_\rho = \bar{C}_\rho$. In the product $C_\rho C_\sigma$ the unit element $C_1 (= E)$ occurs only if $C_\sigma = \bar{C}_\rho$ and in this case it occurs h_ρ times. Hence we have

$$\begin{aligned} \gamma_{\rho\sigma 1} &= 0 \qquad \text{if } C_\sigma \neq \bar{C}_\rho \\ &= h_\rho \qquad \text{if } C_\sigma = \bar{C}_\rho. \end{aligned}$$

It may be verified that $C_\rho C_\sigma = C_\sigma C_\rho$.

Let C_ρ represent not only the collection of elements in it but the sum of all the elements in it. If in a representation Γ of a group G, M_ρ denotes the sum of the matrices in Γ which correspond to the elements in C_ρ, the relation

$$C_\rho C_\sigma = \Sigma \gamma_{\rho\sigma k} C_k$$

leads to

$$M_\rho M_\sigma = \Sigma \gamma_{\rho\sigma k} M_k.$$

The Characters of a Representation.—The sum of the diagonal elements in a matrix A is called the trace of A and is written as $tr A$. Let the matrices A_k^j define a representation Γ^j of a finite group G. The set of numbers $x_k^j = tr A_k^j$ is called the character of the representation Γ^j. x_k^j is the same for representations equivalent to Γ^j. In the orthogonality relations of the unitary irreducible representations, namely

$$\sum_s (\bar{B}_s{}^i)_{k\rho} (A_s{}^j)_{l\sigma} = 0 \qquad \text{if } \Gamma^i \not\approx \Gamma^j$$

$$= \left(\frac{N}{n}(r)\right) \delta_{\rho\sigma}\delta_{kl} \text{ if } \Gamma^i = \Gamma^j$$

put $k = \rho$ and $l = \sigma$ and sum over ρ and σ. (Here, the matrices $A_s{}^j$ define the representation Γ^j and $B_s{}^i$ define the representation Γ^i), We then have,

$$\sum_s \bar{\chi}_s{}^i \chi_s{}^j = 0 \qquad \text{if } \Gamma^i \not\approx \Gamma^j$$

$$= N \qquad \text{if } \Gamma^i = \Gamma^j \text{ or } \Gamma^i \approx \Gamma^j$$

because $(N/n) \sum_{\rho,\sigma} \delta_{\rho\sigma} = N$. The summation over s is with respect to the elements in the group. Since elements in a conjugate class have the same trace, the above relations may be replaced by

$$\sum_{\rho=1}^{q} h_\rho \bar{\chi}_\rho{}^i \chi_\rho{}^j = N\delta_{ij} \quad (i, j = 1, 2, \ldots, p).$$

Here q denotes the number of conjugate classes in G and p denotes the number of non-equivalent irreducible representations. The summation in the equation is now with respect to the conjugate classes only. If we define the normalized characters by the equation $v_\rho{}^s = \sqrt{(h_\rho/N)}\, \chi_\rho{}^s$ they satisfy the relations

$$\sum_{\rho=1}^{q} \bar{v}_\rho{}^i v_\rho{}^j = \delta_{ij} \qquad (i, j = 1, \ldots, p).$$

Hence the normalized characters v^r, considered as q-dimensional vectors, form an orthogonal set. Since there can be at most q orthogonal vectors in a q-dimensional space, we have $p \leqslant q$. We shall see later that from a similar argument $q \leqslant p$ resulting in p being equal to q.

Reduction of a Reducible Representation.—A non-singular representation Γ of a finite group G can be reduced in a unique manner (except for equivalence) into a direct sum of irreducible representations. This may be seen as follows.

We have already proved that any representation can be completely reduced into irreducible representations. Let n_i

be the number of times the irreducible representation Γ^i is contained in the reduced form of Γ. Let χ be the character of the representation Γ. Equating the characters of Γ in the two forms we have

$$\chi = \sum_i n_i \chi_r{}^i.$$

Multiply both sides by $h_\rho \chi_\rho{}^i$ and sum over r. By virtue of the orthogonality relations we have,

$$\sum_{\rho=1}^{a} h_\rho \bar{\chi}_\rho{}^i \chi = N n_i$$

Thus, the numbers n_i are uniquely determined.

We know that equivalent representations have the same character. The converse is also true. Namely, two representations are equivalent if they have the same character. This follows easily, for both the representations having the same character are equivalent to the same reduced form.

If χ is the character of a non-singular representation Γ then

$$\sum_\rho h_\rho \bar{\chi}_\rho \chi_\rho = N \qquad \text{if } \Gamma \text{ is irreducible}$$

$$> N \qquad \text{if } \Gamma \text{ is reducible.}$$

The first relation is just the orthogonality relation for an irreducible representation. In the second case, let $\chi_\rho = \sum_s n_i \chi_\rho{}^i$ then we have

$$\sum_\rho h_\rho \bar{\chi}_\rho \chi_\rho = \sum_{\rho,j,i} h_\rho (n_j \bar{\chi}_\rho{}^j)(n_i \chi_\rho{}^i) = N \sum_i n_i{}^2$$

from which the result follows.

The regular representation of a finite group G contains every irreducible representation as often as the dimension of the irreducible representation. This may be proved as follows: The character of the regular representation is given by $\chi_E = N$ and $\chi_\rho = 0$ for $C_\rho \neq E$. Hence in the reduction of the regular representation $\Gamma = \Sigma n_i \Gamma^i$

$$n_i = \frac{1}{N} \sum_{\rho=1}^{a} h_\rho \bar{\chi}_\rho{}^i \chi_\rho = \bar{\chi}_E{}^i = d_i.$$

d_i is the dimension of the irreducible representation Γ^i

We shall later use the character of the regular representation Γ in the reduced form

$$\chi_\rho = \sum_i d_i \, \chi_\rho{}^i = 0 \qquad \text{if } C_\rho \neq E$$
$$= N \qquad \text{if } C_\rho = E$$

The Number of Irreducible Representations of a Finite Group.—Let Γ^i be an irreducible representation of dimension d_i of a group G of order N. Let M_ρ denote the sum of the matrices of Γ^i which represent the elements in the conjugate class C_ρ. Since C_ρ commutes with every element in G, it follows that the matrix M_ρ commutes with every matrix of the irreducible set in Γ^i. Hence $M_\rho = \lambda^{(i)} E$. Taking the trace of this equations, we have

$$tr\, M_\rho = h_\rho \chi_\rho{}^i = \lambda^i d_i.$$

Hence

$$\lambda^{(i)} = \frac{h_\rho \chi_\rho{}^i}{d_i}$$

and

$$M_\rho = \frac{h_\rho}{d_i} \chi_\rho{}^i E.$$

From the relation

$$C_\rho C_\sigma = \Sigma \gamma_{\rho\sigma k} \, C_k,$$

we have

$$M_\rho M_\sigma = \sum_k \gamma_{\rho\sigma k} M_k.$$

Substituting the values of M_ρ, M_σ and M_k and multiplying by d_i we have

$$h_\rho h_\sigma \chi_\rho{}^i \chi_\sigma{}^i = \sum_k \gamma_{\rho\sigma k} h_\tau n_i \chi_\tau{}^i.$$

Summing over i, the right-hand side gives $\sum_k \gamma_{\rho\sigma k} h_k \left(\sum_i d_i \chi_\tau{}^i\right)$ But $\sum_i d_i \chi_\tau{}^i$ is the component of the character of the class C_τ in the regular representation and therefore equals N for $\tau = 1$ and zero otherwise. Hence

$$h_\rho h_\sigma \sum_i \chi_\rho^{\,i} \chi_\sigma^{\,i} = \gamma' ij$$

$$\begin{aligned} &= Nh_\rho \quad \text{if } C_\sigma = \bar{C}_\rho \\ &= 0 \qquad \text{if } C_\sigma \neq \bar{C}_\rho \end{aligned}$$

or

$$h_\rho h_\sigma \sum_i \bar{\chi}_\rho^{\,i}\, \chi_\sigma^{\,i} = N h_\rho \delta_{\rho\sigma}.$$

Using the normalized characters

$$v_\rho^{\,r} = \sqrt{\frac{h_\rho}{N}}\, \chi_\rho^{\,i}$$

we have

$$\sum_{i=1}^{p} \bar{v}_\rho^{\,i} v_\sigma^{\,i} = \delta_{\rho\sigma}.$$

Considering $v_\rho^{\,i}$ $(i = 1, \ldots, p)$ as a vector in a p-dimensional space, we observe that the vectors $v_\rho(\rho = 1, \ldots, q)$ form an orthogonal set. Hence $q \leqslant p$. This coupled with the previous result $p \leqslant q$ shows that the number of non-equivalent irreducible representations p of a finite group is equal to the number of conjugate classes q.

$$\begin{aligned} &\sum_\rho h_\rho \chi_\rho^{\,i} \chi_{\rho'}^{\,i} = N && \\ &\sum_\rho h_\rho \chi_\rho^{\,i} \chi_{\rho'}^{\,j} = O && (i \neq j) \\ &h_\rho \sum_i \chi_\rho^{\,i} \chi_{\rho'}^{\,j} = N && \\ &\sum_i \chi_\rho^{\,i} \chi_\sigma^{\,i} \quad = O && (\sigma \neq \rho') \end{aligned}$$

constitute the orthogonality relations between the group characters. $\chi_{\rho'}^{\,i}$ is the complex conjugate of $\chi_\rho^{\,i}$. The distinction between them disappears if the character is real which is the case when $\rho = \rho'$. The superscripts i and j refer to the irreducible representations (rows) and the subscripts σ and ρ refer to the conjugate classes (columns). In this case the first orthogonality relation means that the sum of the squares of the characters in any row multiplied by the order of the corresponding conjugate class equals the order of the group. The second relation means that the sum of the products of the corresponding characters taken from two different rows multiplied by the order of the conjugate classes in each case equals zero. The third and fourth relations give respectively the same properties as above in respect of the columns in the character table.

Suppose a and b are two elements in a group belonging to different conjugate classes C_ρ and C_σ. Then the vectors v_ρ and v_σ are orthogonal to each other so that $v_\rho{}^i = v_\sigma{}^i$ for all i cannot hold good. This means that there exists at least one representation Γ for which $\chi(a) \neq \chi(b)$. This is usually referred to as the completeness theorem for irreducible representations. We have hence proved the orthogonality, unitarity and completeness of irreducible representations of a finite group.

Group Characters.—In evaluating the characters for a group by the following general method, the first step to be done is to form the conjugate classes of elements of the group and obtain the numbers $\gamma_{\rho\sigma k}$. Let Γ^i be an irreducible representation of dimension d_i of a group G of order N. Let M_ρ denote the sum of the matrices of Γ^r representing the elements of the conjugate class C_ρ. Taking

$$\lambda_\rho{}^i = (h_\rho \chi_\rho{}^i)/d_i$$

we proved that

$$M_\rho = \lambda_\rho{}^i E.$$

We have then the following relation

$$\lambda_\rho{}^i \lambda_\sigma{}^i = \sum_k \gamma_{ijk} \lambda_k{}^i.$$

Multiplying this equation by an arbitrary coefficient A_ρ and summing with respect to ρ we have the following p equations. (p is the number of conjugate classes.)

$$x \lambda_\sigma{}^i = (\Sigma \ \gamma_{\rho\sigma k} A_\rho) \lambda_k{}^i (\sigma = 1, 2, \ldots, p)$$

where

$$x = \sum_{\rho} A_\rho \lambda_\rho^i.$$

Eliminating the p quantities λ_k^i from the above equations we have

$$\left| \sum_{\rho=1}^{p} A_\rho \gamma_{\rho\sigma k} - x\, \delta_j^k \right| = f(x, A_1, \ldots, A_p) = 0,$$

The p roots of this equation in x are the p values of $\sum_{\rho} A_\rho \chi_\rho^i$ and therefore $f(x, A_1, \ldots, A_p)$ should split up into p homogeneous linear factors. If $x - \sum_{\rho} a_\rho A_\rho$ is one of the linear factors of f, we have then the p relations

$$\frac{h_\rho \chi_\rho^i}{d_i} = a_\rho \qquad (\rho = 1, 2, \ldots, p).$$

Using these values of χ_ρ^i in the orthogonality relation

$$\sum_{\rho} h_\rho \chi_\rho^i \bar{\chi}_\rho^i = N$$

we have

$$d_i^2 \sum \frac{a_\rho \bar{a}_\rho}{h_\rho} = N.$$

This enables us to determine d_i. The character χ_ρ^i is determined from the equation

$$(h_\rho \chi_\rho^i)/d_i = a_\rho.$$

Groups which are simply isomorphous have the same characters as the numbers $\gamma_{\rho\sigma k}$ will be the same for both. We illustrate this method of calculating the table of characters for the group

$$a^3 = E, b^2 = E, a^2 b = ba,$$

which is isomorphous with the symmetry group of degree 3. The conjugate classes of this group are

$$C_1 = E; \qquad (h_1 = 1)$$
$$C_2 = (b, ab, a^2 b); \qquad (h_2 = 3)$$
$$C_3 = (a, a^2); \qquad (h_3 = 2).$$

The multiplication table of the conjugate classes is

$$C_1^2 = C_1;\ \ C_1C_2 = C_2;\ \ C_1C_3 = C_3;\ \ C_2^2 = 3C_1 + C3_3;$$
$$C_2C_3 = 2C_2;\ \ C_3^2 = 2C_1 + C_3.$$

The determinantal equation is

$$0 = \begin{vmatrix} A_1 - x & A_2 & A_3 \\ 3A_2 & A_1 + 2A_3 - x & 3A_2 \\ 2A_3 & 2A_2 & A_1 + A_3 - x \end{vmatrix}.$$

The linear factors of this equation are

$$x - A_1 - 3A_2 - 2A_3;\ \ x - A_1 + A_3;\ \ x - A_1 + 3A_2 - 2A_3.$$

The characters of the identity element in the three irreducible representations defined by these three linear factors are obtained from the relation

$$N = d_i^2 \sum \frac{a_\rho \bar{a}_\rho}{h_\rho}$$

and they are 1, 2, 1 respectively. The other characters are obtained from the relation

$$h_\rho \chi_\rho^i = a_\rho d_i.$$

The Character Table is thus completed and is seen to be identical as it should be with the one already obtained for the symmetric group of degree 3.

Direct Product Groups.—Let G_1 and G_2 be two groups not necessarily with the same group operation. Consider the set G of elements which are pairs of the form (a, b) where a and b respectively belong to G_1 and G_2. We define multiplication of elements in G by the rule

$$(a_1, b_1)\ (a_2, b_2) = (a_1a_2,\ b_1b_2)$$

where a_1 and a_2 are combined according to the group operation in G_1 and b_1 and b_2 are combined according to the group operation in G_2. The set G forms a group which is the direct product of G_1 and G_2.

If $a_2 = a^{-1}\, a_1\, a$ in G_1 and $b_2 = b^{-1}\, b_1\, b$ in G_2, then $(a_2, b_2) = (a^{-1}, b^{-1})\,(a_1, b_1)\,(a, b)$ in G. The converse also follows. This shows that if C_i and C_j' are conjugate classes in G_1 and G_2, the direct product $C_i \times C_j'$ consisting of the elements (a_1, b_j), where a_i and b_j respectively belong to C_i and C_j', is a conjugate class in G which may be denoted by the symbol C_{ij}.

Let Γ^r be an irreducible representation of G_1 in which the group elements a_k correspond to the matrices A_k and let $\triangle^s$ be an irreducible representation of G_2 in which the group elements b_l correspond to the matrices B_l. If the direct product matrix $A_k X B_l$ is made to correspond to the element (a_k, b_l) in G, this correspondence defines an irreducible representation of G which may be denoted by Γ^{rs}. If $\chi_\rho{}^i$ and $\chi_\sigma{}^j$ are the characters of the representations Γ^i and $\triangle^j$ the character of the representation Γ^{ij} is $\chi_\rho{}^i\, \chi_\sigma{}^j$ and may be denoted by the symbol $\chi_{\rho\sigma}{}^{ij}$. The irreducibility of Γ^{ij} can be seen from the relation

$$\sum_{\rho,\sigma} h_\rho h_\sigma'\, \chi_{\rho\sigma}{}^{ij} \bar{\chi}_{\rho\sigma}{}^{ij} = \Big(\sum_{\rho} h_\rho \chi_\rho{}^i \bar{\chi}_\rho{}^i\Big)\Big(\sum_{\sigma} h_\sigma'\, \chi_\sigma{}^j \bar{\chi}_\sigma{}^j\Big) = 1.1 = 1.$$

Here h_ρ and h_ρ' are the orders of the conjugate classes C_ρ and C_ρ'.

APPENDIX II

TRANSFORMATION OF MATRICES

Transformation of a Unitary Matrix into the Diagonal Form.—We prove below that any unitary matrix $|a_{ik}|$ can be transformed into the diagonal form by another unitary matrix. We first take a matrix with two rows and two columns. Let

$$A = \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix}$$

be a unitary matrix with characteristic roots λ_1 and λ_2. We can find x_{11} and x_{21}, which satisfy $x_{11} x_{11}^* + x_{21} x_{21}^* = 1$, such that

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \begin{vmatrix} x_{11} \\ x_{21} \end{vmatrix} = \lambda_1 \begin{vmatrix} x_{11} \\ x_{21} \end{vmatrix}$$

$\begin{vmatrix} x_{11} \\ x_{22} \end{vmatrix}$ is a characteristic vector of A corresponding to the characteristic root λ_1. Having taken x_{11} and x_{21}, we can find x_{12} and x_{22}, which satisfy the equations

$$x_{11} x_{12}^* + x_{21} x_{22}^* = 0$$

and

$$x_{12} x_{12}^* + x_{22} x_{22}^* = 1.$$

The product

$$\begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \begin{vmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{vmatrix}$$

is of the form

$$\begin{vmatrix} \lambda_1 x_{11} & b_{12} \\ \lambda_1 x_{21} & b_{21} \end{vmatrix}. \quad \text{The matrix} \quad \begin{vmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{vmatrix}$$

is unitary, and when multiplied by a suitable constant has its determinant equal to $+1$. The product of the three matrices

$$\begin{vmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{vmatrix}^{-1} \begin{vmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{vmatrix} \begin{vmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{vmatrix}$$

is equal to

$$\begin{vmatrix} x_{11} & x_{12} \\ x_{21} & x_{22} \end{vmatrix}^{-1} \begin{vmatrix} \lambda_1 x_{11} & b_{12} \\ \lambda_1 x_{21} & b_{22} \end{vmatrix}.$$

This product will be of the form

$$\begin{vmatrix} \lambda_1 & C \\ 0 & \lambda_2 \end{vmatrix}.$$

Here C will be equal to zero, because the matrix is unitary in character. The original matrix is thus transformed into the diagonal form by means of another unitary matrix of determinant $+1$.

Let

$$A = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix}$$

be a 3×3 unitary matrix and let X_1 be a characteristic vector corresponding to a characteristic root μ_1 of A. As before, we can choose in a variety of ways, a unitary matrix U with X_1 as its first column. Then the matrix

$$B = U^{-1} A U$$

will be of the form

$$\begin{vmatrix} \mu_1 & b_{12} & b_{13} \\ 0 & b_{22} & b_{23} \\ 0 & b_{32} & b_{33} \end{vmatrix}.$$

Since U, A and U^{-1} are unitary, B is also unitary and therefore b_{12} and b_{13} should be equal to zero. Thus, the matrix B is of the form

$$\begin{vmatrix} \mu_1 & 0 \\ 0 & B' \end{vmatrix}$$

where B' is a 2×2 unitary matrix. B' can be transformed, as has been shown above, by a unitary matrix, say V, into the diagonal form

$$\begin{vmatrix} \mu_2 & 0 \\ 0 & \mu_3 \end{vmatrix}.$$

Now the matrix

$$\begin{vmatrix} 1 & 0 \\ 0 & V \end{vmatrix} U$$

is unitary and transforms A into the diagonal form

$$\begin{vmatrix} \mu_1 & 0 & 0 \\ 0 & \mu_2 & 0 \\ 0 & 0 & \mu_3 \end{vmatrix}$$

The above argument can easily be extended to unitary matrices of any order and the proof completed by induction.

Transformation of a Real Orthogonal Matrix.—We prove that any 3×3 real orthogonal matrix may be transformed into the form

$$\begin{vmatrix} \cos\phi & \sin\phi & 0 \\ -\sin\phi & \cos\phi & 0 \\ 0 & 0 & \pm 1 \end{vmatrix}.$$

Let A be a 3×3 real orthogonal matrix. As A may be regarded as a unitary matrix also, from the results of the previous Section, we could find a unitary matrix U which transforms A into the diagonal form

$$D = \begin{vmatrix} e^{i\phi} & 0 & 0 \\ 0 & e^{-i\phi} & 0 \\ 0 & 0 & \pm 1 \end{vmatrix}$$

(The characteristic roots of a real orthogonal matrix have modulus unity and the roots occur in pairs of conjugate imaginaries.) We have thus $AU = DU$. Let C_1, C_2, C_3 be the column vectors of the matrix U. Writing the columns

C_r in the form $P_r + iQ_r$ and equating the real and imaginary parts in the equations

$$\begin{aligned} AC_1 &= e^{i\phi} \quad C_1 = (\cos\phi + i\sin\phi)\, C_1 \\ AC_2 &= e^{-i\phi} \quad C_2 = (\cos\phi - i\sin\phi)\, C_2 \\ AC_3 &= \pm\, C_3, \end{aligned}$$

we have

$$A \mid P_1\, Q_1\, P_3 \mid = \begin{vmatrix} \cos\phi & -\sin\phi & 0 \\ \sin\phi & \cos\phi & 0 \\ 0 & 0 & \pm 1 \end{vmatrix} \mid P_1\, Q_1\, P_3 \mid .$$

By virtue of the fact that U is unitary, it follows that the matrix $[\, Y = \sqrt{}2P_1 - \sqrt{}2Q_1\, P_3]$ is an orthogonal matrix and transforms A into the required form. It is obvious that the determinant of Y could be taken as $+ 1$. The orthogonal transformation Y corresponds to a change of co-ordinate system and it follows from the above result that an orthogonal transformation is equivalent to a rotation or a rotation-reflection.

Simultaneous Reduction of Two Quadratic Forms.—A quadratic form $\phi\,(x, x) = \Sigma a_{ik}x_i x_k$ is said to be real if the coefficients a_{ik} and the variables $x_1, x_2, \ldots, x_n$ are real quantities. $\phi\,(x, x)$ is called positive definite, if $\phi\,(x, x)$ is positive for all sets of values of $x_1, x_2, \ldots, x_n$ and takes the value zero, only when $x_1 = x_2, \ldots, = x_n = 0$. Associated with the form ϕ we have the matrix $[a_{ik}]$. If in the matrix $[a_{ik}]$, all the non-diagonal terms are zero, the form is said to be canonical. If all the diagonal terms are each equal to one and the non-diagonal terms are zero, the corresponding quadratic form is called normal. Let

$$\phi_1\,(x, x) = \Sigma a_{ik}x_i x_k \qquad i\, k = 1, 2, \ldots, n$$

and

$$\phi_2\,(x, x) = \Sigma b_{ik}x_i x_k \qquad i, k = 1, 2, \ldots, n$$

be two real quadratic forms of which the first one is positive definite. We show here that by a suitable linear transformation of co-ordinates, ϕ_1 can be reduced to the normal form and ϕ_2 to the canonical form. The proof consists of three steps. We shall first show that $\phi_1(x, x)$ can be reduced to a canonical form by means of an orthogonal linear transformation. This type of transformation always keeps the normal form invariant. The second step in the proof consists in transforming the canonical form of $\phi_1(x, x)$ into a normal one. When both the above transformations are performed successively, the quadratic form ϕ_1 reduces to a normal form whereas ϕ_2 may still remain as a general quadratic form. As a last step in the transformation, we may repeat the procedure of an orthogonal linear transformation reducing ϕ_2 to the canonical form but leaving the normal form of ϕ_1 unchanged.

Consider the sets of values of $x_1, x_2, \ldots, x_n$ for which $x_1^2 + x_2^2 + \ldots + x_n^2 = 1$. Among all these sets take one set $x_1, x_2, \ldots, x_n$ for which $\phi_1(x, x)$ is the greatest. Let this greatest value of $\phi_1(x, x)$ be χ_1 and $l_{11}, l_{21}, \ldots, l_{n1}$ be the corresponding set of values of $x_1, x_2, \ldots, x_n$. We have

$$l_{11}^2 + l_{21}^2, \ldots, + l_{n1}^2 = 1.$$

Next consider the totality of the sets of numbers $x_1, x_2, \ldots, x_n$ which satisfy the two conditions

$$x_1^2 + x_2^2, \ldots, + x_n^2 = 1$$

and

$$x_1 l_{11} + x_2 l_{21} \ldots + x_n l_{n1} = 0.$$

Among all these sets choose one set, say, $l_{12}, l_{22}, \ldots, l_{n2}$ for which $\phi_1(x, x)$ is greatest. We have the relations

$$l_{12}^2 + l_{22}^2 + \ldots + l_{n2}^2 = 1$$

and

$$l_{11} l_{12} + l_{21} l_{22} + \ldots + l_{n1} l_{n2} = 0.$$

Let the corresponding greatest value of $\phi_1(x, x)$ be χ_2. Proceeding in this manner we obtain n sets of values of $x_1, x_2, \ldots, x_n$, the i-th set being $l_{1i}, l_{2i}, \ldots, l_{ni}$, and the n corresponding values of $\phi_1(x, x)$ being $\chi_1, \chi_2, \ldots, \chi_n$. Now the linear transformation

$$x_i = \Sigma l_{ik}\alpha_k \qquad i, k = 1, 2, \ldots, n$$

is orthogonal. Substituting these values of $x_1, x_2, \ldots, x_n$ in $\phi_1(x, x)$ we obtain a canonical form in $\alpha_1, \alpha_2, \ldots, \alpha_n$. To prove this let $\phi_1 = \Sigma a_{ik}'\alpha_i\alpha_k$. Since $\phi_1 = \chi_1$ when $\alpha_i = 1$ and all other α's are zero, we have

$$\phi_1 = \chi_1\alpha_1^2 + \chi_2\alpha_2^2 \ldots + \chi_n\alpha_n^2 + a'_{12}\alpha_1\alpha_2 + a'_{13}\alpha_1\alpha_3 \ldots$$

Consider the function $\phi_1(x, x) - \chi_1(x_1^2 + x_2^2 + \ldots + x_n^2)$ which is on account of our choice of χ_1 is always negative for values of $x_1, x_2, \ldots, x_n$ such that $x_1^2 + x_2^2 + \ldots + x_n^2 = 1$. This function will be transformed into

$$\chi_1\alpha_1^2 + \chi_2\alpha_2^2 \ldots + \chi_n\alpha_n^2 + a'_{12}\alpha_{21}\alpha_2 + \ldots$$
$$- \chi_1(\alpha_1^2 + \alpha_2^2 \ldots \alpha_n^2).$$

Put

$$\alpha_1 = \frac{1}{\sqrt{1 + \epsilon^2}}, \alpha_2 = \frac{\epsilon}{\sqrt{1 + \epsilon^2}}, \alpha_3 = \alpha_4 \ldots = \alpha_n = 0.$$

For these values of $\alpha_1, \alpha_2, \ldots$ the above function becomes

$$\frac{\chi_1^2 + \chi_2\epsilon^2 + a'_{12}\,\epsilon - \chi_1(1 - \epsilon^2)}{1 + \epsilon^2} = \frac{\epsilon\,[a'_{12} - \epsilon(\chi_1 - \chi_2)]}{1 + \epsilon^2}.$$

The sign of $\epsilon\,[a'_{12} - \epsilon(x_1 - x_2)]$ cannot always be maintained negative unless a'_{12} vanishes. For the sign of the term $a'_{12} - \epsilon(\chi_1 - \chi_2)$ for small values of ϵ is dominated by the sign of a'_{12} and $\epsilon a'_{12}$ can be made positive by properly choosing ϵ. Thus a'_{12} is zero. In the same way we show that all the cross terms a'_{ik} $(i \neq k)$ vanish and ϕ_1 reduces to the canonical form

$$\phi_1 = \chi_1\alpha_1^2 + \chi_2\alpha_2^2 \ldots + \chi_n\alpha_n^2.$$

Since ϕ_1 is a positive definite form $\chi_1, \chi_2, \ldots, \chi_n$ are all positive and different from zero. Applying the transformation

$$\xi_i = \sqrt{\chi_i}^{\,a} \qquad i = 1, 2, \ldots, n$$

ϕ_1 becomes $\xi_1^2 + \xi_2^2 + \ldots + \xi_n^2$ and ϕ_2 transforms in general into $\Sigma c_{ik}\xi_i\xi_k$.

Proceeding as in the case of $\phi_1(x\,x)$, we can reduce $\phi_2 = \Sigma c_{ik}\xi_i\xi_k$ into the canonical form $\phi_2 = \Sigma\lambda_i\eta_i^2$ by means of an orthogonal linear transformation

$$\xi_i = \Sigma l'_{ik}\eta_k$$

which keeps the form ϕ_1 invariant. Thus writing χ's in terms of η's the two forms reduce to

$$\phi_1 = \eta_1^2 + \eta_2^2 + \,..\, + \eta_n^2$$

and

$$\phi_2 = \lambda_1\eta_1^2 + \lambda_2\eta_2^2 + \,..\, + \lambda_n\eta_n^2.$$

A second important result arising from the above transformation of co-ordinates is that $\lambda_1, \lambda_2, \ldots, \lambda_n$ are the roots of the determinantal equation

$$| \, b_{ik} - \lambda a_{ik} \, | = 0.$$

This follows from the fact that $| \, b_{ik} - \lambda a_{ik} \, |$ and

$$\begin{vmatrix} \lambda_1 - \lambda & 0 & 0 & \ldots. & 0 \\ 0 & \lambda_2 - \lambda & 0 & \ldots. & 0 \\ \ldots. & \ldots. & \ldots. & \ldots. & \ldots. \\ 0 & \ldots. & \ldots. & \ldots. & \lambda_n - \lambda \end{vmatrix}$$

are equivalent matrices and therefore have the same characteristic roots. The roots of the latter are $\lambda_1, \lambda_2, \ldots, \lambda_n$. Hence these are also the roots of the former.

APPENDIX III

KRAMERS-HEISENBERG DISPERSION FORMULA

The time dependent Schrödinger equation for a system of particles is given by (1).

$$\left(H_0 + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\Psi^0(q, t) = 0. \qquad (1)$$

Ψ^0 is a general solution and if ψ's are the various time independent eigenfunctions of the system, we have

$$\Psi^0 = \sum_r a_r \psi_r e^{-\frac{2\pi i}{h}E_r t}. \qquad (2)$$

Let the system now find itself in the field of a light wave described by (3)*.

$$E = \frac{U}{2}e^{2\pi i \nu_0 t} + \frac{U^*}{2}e^{-2\pi i \nu_0 t}. \qquad (3)$$

If M is the electric moment relating to the molecule, the additional energy due to the radiation field is $-(M\,E)$ and we have

$$\left[H_0 - (M\,E) + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right]\Psi(q, t) = 0. \qquad (4)$$

Ψ in (4) describes the condition of the perturbed system. If the system is assumed to be in the state Ψ_k^0 before perturbation, we can write to a first approximation,

$$\Psi = \Psi_k^0 + \Psi_k^{(1)}. \qquad (5)$$

Substituting (5) in (4), using the relation (1) and neglecting the terms of the second order, we get (6).

$$\left(H_0 + \frac{h}{2\pi i}\frac{\partial}{\partial t}\right)\Psi_k^{(1)} = (M\,E)\,\Psi_k^0. \qquad (6)$$

We seek for solutions of (6) in the form of (7).

$$\Psi_k^{(1)} = \Psi_k^+ e^{-\frac{2\pi i}{h}(E_k + h\nu_0)t} + \Psi_k^- e^{-\frac{2\pi i}{h}(E_k - h\nu_0)t}. \qquad (7)$$

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* In the special case where $U_x = U_y = 0$ and $U_z = E$, the incident light vector reduces to $E_0 \cos 2\pi\nu_0 t$ and represents a linearly polarized beam.

Substituting (7) and (3) in (6) and writing $\psi_k e^{-\frac{2\pi i}{h}E_k t}$ for $\Psi_k{}^0$, we obtain (8) by comparing coefficients.

$$H_0 \Psi_k{}^+ - (E_k + h\nu_0)\Psi_k{}^+ = \left(\frac{U^*M}{2}\right)\psi_k$$

$$H_0 \Psi_k{}^- - (E_k - h\nu_0)\Psi_k{}^- = \left(\frac{UM}{2}\right)\psi_k. \tag{8}$$

The right-hand side of equations (8) may be expanded in terms of the time independent eigenfunctions of the unperturbed system as in (9)

$$\left(\frac{UM}{2}\right)\psi_k = \sum \left(\frac{UM_{rk}}{2}\right)\psi_r. \tag{9}$$

In (9) $M_{rk} = \int \psi_k M \psi^*{}_r d\tau$. We shall also assume that

$$\Psi_k{}^\pm = \Sigma B_r{}^\pm \psi_r. \tag{10}$$

Substituting (10) and (9) in (8) and remembering that $H_0\psi_r = E_r\psi_r$, etc., we get the values of $B_r{}^\pm$ by comparing the coefficients of the same ψ's on either side. Using these values, relation (10) may be written as in (11)

$$\Psi_k{}^+ = \tfrac{1}{2}\sum \frac{(U^*M_{rk})\,\psi_r}{E_r - E_k - h\nu_0}$$

$$\Psi_k{}^- = \tfrac{1}{2}\sum \frac{(UM_{rk})\,\psi_r}{E_r - E_k + h\nu_0}\,. \tag{11}$$

Relation (7) may now be written as (12).

$$\Psi_k{}^{(1)} = \tfrac{1}{2}\sum \left\{\frac{(U^*M_{rk})\,\psi_r}{E_r - E_k - h\nu_0}\, e^{-\frac{2\pi i}{h}(E_k + h\nu_0)t} + \frac{(UM_{rk})\,\psi_r}{E_r - E_k + h\nu_0}\, e^{-\frac{2\pi i}{h}(E_k - h\nu_0)t}\right\}. \tag{12}$$

We are now in a position to evaluate the various matrix elements of the electric moment relating to the system in the perturbed state. The values in two typical cases are given below as (13) and (14). $M_{kk}{}^0$ in (13) refers to the permanent electric moment of the system in state k. $M_{kn}{}^0$ in (14) refers to the spontaneous transition of the system from state k to state n.

$$\begin{aligned} M_{kk} &= \int (\Psi_k^0 + \Psi_k^{(1)})^* M (\Psi_k^0 + \Psi_k^{(1)})\, d\tau \\ &= M_{kk}^0 + \frac{1}{2h}\sum \left\{ \frac{(UM_{kr})M_{rk}}{\nu_{rk}-\nu_0} + \frac{M_{kr}(UM_{rk})}{\nu_{rk}+\nu_0} \right\} e^{-2\pi i \nu_0 t} \\ &+ \frac{1}{2h}\sum \left\{ \frac{U^*M_{rk})M_{kr}}{\nu_{rk}-\nu_0} + \frac{M_{rk}(U^*M_{kr})}{\nu_{rk}+\nu_0} \right\} e^{-2\pi i \nu_0 t} \qquad (13) \end{aligned}$$

$$\begin{aligned} M_{kn} &= \int (\Psi_k^0 + \Psi_k^{(1)})^* M (\Psi_n^0 + \Psi_n^{(1)})\, d\tau \\ &= M_{kn}^0\, e^{2\pi i \nu_{kn} t} \\ &+ \frac{1}{2h}\sum \left\{ \frac{(UM_{kr})M_{rn}}{\nu_{rk}-\nu_0} + \frac{M_{kr}(UM_{rn}}{\nu_{rn}+\nu_0} \right\} e^{2\pi i (\nu_{kn}+\nu_0) t} \\ &+ \frac{1}{2h}\sum \left\{ \frac{(U^*M_{kr})M_{rn}}{\nu_{rk}+\nu_0} + \frac{M_{kr}(U^*M_{rn})}{\nu_{rn}-\nu_0} \right\} e^{2\pi i (\nu_{kn}-\nu_0) t} \end{aligned} \qquad (14)$$

Similarly, M_{nk} can be written out and easily seen to be conjugate to M_{kn}. Thus, we conclude that if a molecule finds itself in the field of a light wave

$$\frac{U}{2} e^{2\pi i \nu_0 t} + \frac{U^*}{2} e^{-2\pi i \nu_0 t}$$

a typical diagonal element of its electric moment matrix M undergoes alteration as per the scheme

$$M_{kk} = M_{kk}^0 + M_{kk}^{(1)},$$

where

$$M_{kk}^{(1)} = p_{kk}\, e^{2\pi i \nu_0 t} + p^*_{kk}\, e^{-2\pi i \nu_0 t},$$

$$p_{kk} = \frac{1}{2h}\sum_r \left\{ \frac{(UM_{kr})\, M_{rk}}{\nu_{rk}-\nu_0} + \frac{M_{kr}(UM_{rk})}{\nu_{rk}+\nu_0} \right\}.$$

M_{kk} and M_{kk}^0 are respectively the values of this element in the presence and absence of the external field. Since $M_{kk}^{(1)}$ is an oscillating moment, the molecule will emit light according to the usual laws of radiation. The frequency of the emitted radiation will be ν_0 and its intensity will be given by

$$\frac{64\pi^4 \nu_0^4}{3c^3} \mid p_{kk} \mid^2.$$

Similarly, a typical non-diagonal element of the matrix undergoes alteration as per the scheme

$$M_{kn} = M_{kn}^0 \, e^{2\pi i \nu_{kn} t} + M_{kn}^{(1)},$$

where

$$M_{kn}^{(1)} = p_{kn} e^{2\pi i (\nu_{kn} + \nu_0) t} + p'_{kn} e^{2\pi i (\nu_{kn} - \nu_0) t}$$

$$p_{kn} = \frac{1}{2h} \sum \left\{ \frac{(UM_{kr}) \, M_{rn}}{\nu_{rk} - \nu_0} + \frac{M_{kr} \, (UM_{rn})}{\nu_{rn} + \nu_0} \right\}$$

and p_{kn}' is obtained from p_{kn} by replacing U and ν_0 in it respectively by U^* and $-\nu_0$. $M_{kn}^{(1)}$ is again an oscillating moment and the molecule will emit radiation. The frequency of the emitted radiation will no longer be ν_0 but will be either $\nu_{kn} + \nu_0$ or $\nu_{kn} - \nu_0$. Thus we get a general explanation of the appearance of altered frequencies in the spectrum of the scattered light. The dashed terms are called the negative dispersion terms and the condition that scattered light relating to these terms may appear is that $\nu_{kn} - \nu_0 > 0$ or $v_k > \nu_0 + \nu_n$. If the inducing agency is visible light of frequency ν_0, the molecule will be obliged to find itself in an electronically excited state in order that these transitions may occur. Such transitions have not yet been detected. The undashed terms are the usual dispersion terms and the condition that scattered light relating to these terms may appear is that $\nu_{kn} + \nu_0 > 0$ or $\nu_n < \nu_0 + \nu_k$. Both kinds of transitions, namely those in which $\nu_n > \nu_k$ and those in which $\nu_n < \nu_k$, satisfy this condition and we accordingly get two types of Raman lines. If k is taken as the initial state, the former are called the Stokes Raman lines and the latter are called the anti-Stokes Raman lines. The frequency of the emitted radiation will be $\nu_{kn} + \nu_0$ and its intensity per molecule is given by

$$\frac{64\pi^4 (\nu_{kn} + \nu_0)^4}{3c^3} \mid p_{kn} \mid^2.$$

In order that a line of altered frequency $\nu_0 + \nu_{kn}$ may be emitted as a result of the system undergoing a transition from state k to state n, p_{kn} should not vanish. The summation in it extends over all the intermediate states r. Only such of these which are capable of combining in ordinary absorption with both the initial and final states k and n will contribute to the value of p_{kn}, as it is only then that the terms M_{kr} and M_{rn} do not vanish. The existence of a Raman line due to a transition $k \rightarrow n$ may therefore be said to depend upon the existence of some intermediate levels r such that the transitions $k \rightarrow r$ and $r \rightarrow n$ are allowed in ordinary absorption.

APPENDIX IV

EVALUATION OF GROUP CHARACTERS

Abelian Groups.—We shall first consider the case of a cyclic group. Let $A, A^2, \ldots, A^N = E$ be the N elements of a cyclic group G of order N generated by the element A. Since the group is Abelian, each element of G is a conjugate class by itself. Thus there are N conjugate classes and N irreducible representations of G. The relation

$$N = \Sigma\,(\chi_0^{\,i})^2 \qquad i = 1, 2, \ldots, N$$

shows that all the irreducible representations of G are one-dimensional. If ϵ is a primitive N-th root of unity,* the N multiplicative correspondences

$$A \sim \epsilon^a \qquad a = 0, 1, 2, \ldots, N-1$$

define the N irreducible representations of G and the character Table is thus completed. As an example we take the cyclic group A, $A^2 \ldots A^6 = E$ which is of order 6. The character Table is

	E	A	A^2	A^3	A^4	A^5
Γ_1	1	1	1	1	1	1
Γ_2	1	ϵ	ϵ^2	ϵ^3	ϵ^4	ϵ^5
Γ_3	1	ϵ^2	ϵ^4	1	ϵ^2	ϵ^4
Γ_4	1	ϵ^3	1	ϵ^3	1	ϵ^3
Γ_5	1	ϵ^4	ϵ^2	1	ϵ^4	ϵ^2
Γ_6	1	ϵ^5	ϵ^4	ϵ^3	ϵ^2	ϵ

$$\epsilon = \cos\frac{2\pi}{6} + i\sin\frac{2\pi}{6}\,.$$

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* A root ϵ is a primitive N-th root of unity, if the least power of ϵ which is equal to unity is N. ϵ may be taken as $\cos(2\pi/n) + i\sin(2\pi/n)$ or $\cos(2k\pi/n) + i\sin(2k\pi/n)$, where k and N have no common factor.

The case of a general Abelian group of finite order may now be easily dealt with. It can be proved that an Abelian group G of order N can always be expressed as the direct product of cyclic groups, $G_1, G_2, \ldots, G_r$ of orders $n_1, n_2, \ldots, n_r$ and any element S of G can be expressed in the form

$$S = S_1^{x_1} S_2^{x_2} \ldots S_r^{x_r},$$

where $S_1, S_2, \ldots, S_r$ are the generating elements of the cyclic groups $G_1, G_2, \ldots, G_r$. The N multiplicative correspondences

$$\begin{array}{ll} S_1 \sim \epsilon_1^{a_1} & a_1 = 0, 1, 2, \ldots, n_1 - 1 \\ S_2 \sim \epsilon_2^{a_2} & a_2 = 0, 1, 2, \ldots, n_2 - 1 \\ \ldots\ldots\ldots\ldots & \ldots\ldots\ldots\ldots\ldots\ldots \\ S_r \sim \epsilon_r^{a_r} & a_r = 0, 1, 2, \ldots, n_r - 1 \end{array}$$

where ϵ_k is a primitive n_k-th root of unity and k running through the values $1, 2, \ldots, r$ define $n_1, n_2, \ldots, n_r = N$ irreducible representations of G.

Symmetric Groups.—The theory of characters of symmetric groups is intimately connected with the theory of partitions. If $n = \lambda_1 + \lambda_2 + \ldots + \lambda_p$ is an equation in positive integers, then the set of numbers $(\lambda_1, \lambda_2, \ldots, \lambda_p)$ which may be denoted by the symbol (λ) is called a partition of n. It can be easily proved that the number of conjugate classes of a symmetric group of degree n is equal to the number of partitions of n. Any conjugate class C_ρ of the symmetric group can be represented by the symbol $(1^a 2^b 3^c \ldots)$, where C_ρ consists of all permutations on n symbols, each permutation consisting of a cycles of one symbol, b cycles of 2 symbols, etc. The order h_ρ of the class C_ρ is given by the relation

$$h_\rho = \frac{n!}{1^a 2^b 3^c \ldots a! b! c! \ldots}.$$

Each irreducible representation of a symmetric group of degree n may be associated with a partition of n. The characters of the symmetry groups can be quickly obtained by using the recurrence relations between S-functions. An

S-function is defined by a set of integers $\lambda_1, \lambda_2, \ldots, \lambda_p$ and may be denoted by the symbol $\{\lambda_1, \lambda_2, \ldots, \lambda_p\}$. λ's here need not be positive. A standard form of an S-function is one in which the λ's are written in the descending order. In reducing any S-function to the standard form, the following rules must be taken into account. The value of an S-function is not altered when any two consecutive parts in an S-function are interchanged and the preceding part is diminished and the succeeding part is increased by unity and the sign of the resulting S-function is changed. As an example, we have $\{10, 4, 7, 1\} = -\{10, 6, 5, 1\}$. If in any S-function, any part exceeds its preceding part by unity, the value of the S-function is zero. The value is also zero if the last part is negative. With the help of the following two theorems, the Table of characters of a symmetric group can be easily constructed.

Theorem I.[*]—If the class ρ' of a symmetric group of order $(n+r)!$ contains the same cycles as the class ρ of the symmetric group of order $n!$ together with an extra cycle of order r, then

$$\chi_{\rho'}{}^{(\mu)} = \Sigma \pm \chi_{\rho}{}^{(\lambda)}$$

summed for the characters $\chi^{(\lambda)}$ which correspond to the S-functions

$$\{\mu_1 - r, \mu_2, \ldots \mu_m\}, \{\mu_1, \mu_2 - r, \ldots \mu_m\} \ldots \{\mu_1, \mu_2, \ldots \mu_m - r\}$$

the minus sign being taken when the S-function with the parts reduced to descending order becomes negative.

Theorem II[†].—The character of the class (n) in the irreducible representations of the symmetric group of degree n corresponding to the partition $[p, 1^q]$ where $(p+q) = n$ is $(-1)^q$ for $q = 0, 1, \ldots, n-1$. The characters of the same class in the other irreducible representations are all zero.

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[*] Littlewood, *The Theory of Group Characters*, p. 142.

[†] Venkatarayudu, *Journal of the Indian Mathematical Society* (1943), p. 42.

We obtain here the characters of the symmetric groups of degrees 2, 3, 4. The symmetric group of order 2 consists of elements E, (12) and in our terminology they are represented by 1^2 and 2 respectively. It is also a cyclic group of order 2 and the character Table is easily written as follows:

Class	1^2	2
Order	1	1
[2]	1	1
$[1^2]$	1	-1

In the case of the symmetric group of degree 3, we have three irreducible representations corresponding to the three partitions [3], [21], $[1^3]$ of 3. The characters in the last column of the Table below are obtained with the help of Theorem II. The remaining characters in the first row are obtained from the corresponding characters of the symmetric group of degree 2 by means of the relation

$$\{3\} = \{2\}.$$

Similarly the characters in the second and third rows are computed respectively from the relations

$$\{21\} = \{2\} + \{1^2\} \text{ and } \{1^3\} = \{1^2\}.$$

The character Table is as follows. This has already been given as an example in Chapter III.

Class	1^3	12	3
Order	1	3	2
[3]	1	1	1
[21]	2	0	-1
$[1^3]$	1	-1	1

The character Table for the symmetric group of degree 4 is similarly constructed. The characters of the class (4) are written as before by using Theorem II. Those of classes 1^4, $1^2 2$, 13 are obtained from the characters of the corresponding classes of degree 3 by means of the recurrence relations

$$\{4\}=\{3\};\ \{31\}=\{3\}+\{21\};\ \{2^2\}=\{21\};\ \{21^2\}=\{21\}+\{1^3\};\ \{1^4\}=\{1^3\}.$$

The characters of the class 2^2 are obtained from the characters of the corresponding class of degree 2 by means of the relations

$$\{4\}=\{2\};\ \{31\}=\{1^2\};\ \{2^2\}=\{2\}-\{1^2\};\ \{21^2\}=-\{2\};\ \{1^4\}=-\{1^2\}.$$

The Table when thus completed works out as follows:

Class	1^4	$1^2 2$	13	2^2	4
Order	1	6	8	3	6
[4]	1	1	1	1	1
[31]	3	1	0	−1	−1
$[2^2]$	2	0	−1	2	0
$[21^2]$	3	−1	0	−1	1
$[1^4]$	1	−1	1	1	−1

The character Tables for symmetric groups of higher degrees can be similarly constructed.

One-Dimensional Representations of Symmetric Groups.—Let Γ be a one-dimensional representation of a symmetric group S. A transposition should correspond in Γ to either $+1$ or -1, since the square of the transposition is the identity element. All the transpositions in S belong to the same conjugate class and consequently they all correspond to the same number either $+1$ or -1 in Γ. Since any permutation is a product of transpositions, when the transpositions correspond to $+1$ in Γ, all permutations in S correspond to $+1$ and then Γ is called the symmetric representation. In the alternative case when the transpositions correspond to -1, even permutations of S correspond to $+1$ and odd permutations of S correspond to -1. Then Γ is called the anti-symmetric representation. Thus there are only two one-dimensional representations of a symmetric group. One is the symmetric representation and the other is the anti-symmetric representation.

Solvable Groups.—Let G be a group. Form the series

$$G = H_0 \supset H_1 \supset H_2 \supset \ldots \supset E$$

where H_{r+1} is a maximum self-conjugate subgroup of H_r and the symbol $\supset$ in $H_r \supset H_{r+1}$ indicates that H_r contains H_{r+1}. If the orders of the factor groups H_r/H_{r+1} are all prime numbers, we refer to G as a solvable group.

Let G be a group of a finite order and H a subgroup of G. Let

$$G = \sum_{r=1}^{k} g_r H$$

be a left coset decomposition of G with respect to H. Every element g of G could be written as $g_r h$ where h belongs to H. Consider the product $gg_i = g_r h g_i$. This element could be written uniquely as the product of some g_j belonging to the above set g_r ($r = 1$ to k) and another element h' belonging to the group H. Now construct the matrix having the i-th row j-th column element as h' and all other elements in the i-th row being zeros. It is easily verified that these matrices define a representation of the group G. These may be called the monomial representations of G. (More general representations of G could be defined* in this manner but they are not necessary for our purpose.)

For example, in the group G defined by the relations $a^3 = E$, $b^2 = E$, $a^2 b = ba$, if H is the subgroup formed by

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* Hans Zassenhaus, *Theory of Groups* (1949), p. 136.

the elements E and b, the left cosets of G with respect to H may be written as

$$G = E(E, b) + a(E, b) + a^2(E, b).$$

The corresponding monomial representation is given by

$$E \rightarrow \begin{vmatrix} E & 0 & 0 \\ 0 & E & 0 \\ 0 & 0 & E \end{vmatrix} \quad a \rightarrow \begin{vmatrix} 0 & E & 0 \\ 0 & 0 & E \\ E & 0 & 0 \end{vmatrix} \quad a^2 \rightarrow \begin{vmatrix} 0 & 0 & E \\ E & 0 & 0 \\ 0 & E & 0 \end{vmatrix}$$

$$b \rightarrow \begin{vmatrix} b & 0 & 0 \\ 0 & 0 & b \\ 0 & b & 0 \end{vmatrix} \quad ab \rightarrow \begin{vmatrix} 0 & b & 0 \\ b & 0 & 0 \\ 0 & 0 & b \end{vmatrix} \quad a^2b \rightarrow \begin{vmatrix} 0 & 0 & b \\ 0 & b & 0 \\ b & 0 & 0 \end{vmatrix}$$

If in the monomial representation of G defined with respect to H, the elements of H are replaced by the corresponding matrices in a representation Γ of H, we obtain a matrix representation of G which we may call the representation induced by H.

Let the cosets of a normal subgroup H of G be H, a_2H, a_3H, etc. Suppose $\triangle$ is an irreducible representation of the factor group G/H in which the element $a_\gamma H$ corresponds to the matrix M_γ. Now by making every element of G belonging to the coset $a_\gamma H$ correspond to the same matrix M_γ, we obtain a representation of G which may be called the representation engendered by $\triangle$.

Let g be an element of G and h be an element of the self-conjugate subgroup H of G. Let Γ be a representation of H in which the element h_γ of H corresponds to matrix M_γ. The element $g^{-1}h_\gamma g$ belongs to H as H is a self-conjugate subgroup of G. Now if we make the element $g^{-1}h_\gamma g$ correspond to the matrix M_γ, we obtain a representation of H which is called the conjugate of Γ and may be denoted by the symbol $\Gamma(g)$. The totality of elements of g belonging to G for which Γ is equivalent to $\Gamma(g)$ form a group called the little group L relative to G, H and Γ. The elements of H which correspond to the identity matrix in Γ form a group which is called the

Kernel K of the representation. K is a self-conjugate subgroup of L.

We show here how the representations of a group G may be obtained from subgroups and factor groups whose representations are known. Let H be a normal subgroup of G. We first determine all the irreducible representations of H. We divide these representations into distinct sets called the stars or orbits with respect to the elements of G as follows. An orbit of representations of H relative to G consists of the totality of non-equivalent irreducible representations of H which are mutually conjugate with respect to the elements of G. We select arbitrarily one irreducible representation Γ_i from each orbit. Let L_i be the little group relative to G, H and Γ_i and let K_i be the Kernel of representation Γ_i. We then determine all the irreducible representations $\Gamma_{i,j}$ of the factor group L_i/K_i. Each one of these representations $\Gamma_{i,j}$ of L_i/K_i engenders a representation of the group L_i. We denote these representations of L_i by $\triangle_{i,j}$. If from the elements of L_i we pick out the elements of H and take the corresponding matrices in the representation $\triangle_{i,j}$, we obtain a representation of H which is not necessarily a multiple of Γ_i, with which we started. Out of the several irreducible representations $\triangle_{i,j}$ we pick out only those which give rise to representations of H which are multiples of Γ_i. These representations $\triangle_{i,j}$ are called allowable or non-spurious representations. The representations of G induced by the allowable representations $\triangle_{i,j}$ are irreducible. Every irreducible representation of G is obtained in this manner exactly once. This may be proved with the help of the orthogonality relations for the characters.

The above method of obtaining the representations and characters of a group G is valid whether G is solvable or not. But in the case of solvable groups like point groups and space groups, the procedure is simple as it reduces to building up the representations of G from the irreducible representations of cyclic groups.

APPENDIX V

PROPERTIES OF SOME POLYNOMIAL FUNCTIONS

Hermite Polynomials.—The Hermite polynomial $H_n(S)$ of degree n is defined as the coefficient of $\frac{t^n}{n!}$ in the expansion of e^{-t^2+2ts}. Thus

$$e^{-t^2+2ts} = \sum_0^\infty \frac{H_n(S)\,t^n}{n!}$$

and

$$H_n(S) = (2S)^n - \frac{n(n-1)}{1!}(2S)^{n-2} + \cdots$$

$$+ \frac{(-1)^k n(n-1)\ldots(n-2k+1)}{k!}(2S)^{n-2k} + \ldots$$

The first five polynomials are

$$H_0(S) = 1, \qquad H_1(S) = 2S,$$

$$H_2(S) = 4S^2 - 2, \qquad H_3(S) = 8S^3 - 12S,$$

$$H_4(S) = 16S^4 - 48S^2 + 12.$$

Differentiating with respect to t the defining relation and equating the coefficient of t^n on both sides, we obtain the recurrence relation

$$H_{n+1} - 2SH_n + 2n\,H_{n-1} = 0.$$

Differentiating with respect to S and equating the coefficient of t^n we obtain $H'_n(S) = 2n\,H_{n-1}$.

$H_n(S)$ can be shown to be given by the equation

$$H_n(S) = (-1)^n e^{S^2} \frac{d^n}{dS^n}(e^{-S^2}).$$

Using this expression for $H_n(S)$ in

$$I = \int_{-\infty}^{\infty} H_m(S)\,H_n(S)\,e^{-S^2}\,dS$$

and integrating by parts, we have

$$I = (-1)^{n+1} \int_{-\infty}^{\infty} H'_m(S) \frac{d^{n-1}}{dS^{n-1}} e^{-S^2}\, dS$$

$$= (-1)^{n+1}\, 2m \int_{-\infty}^{\infty} H_{m-1}(S) \frac{d^{n-1}}{dS^{n-1}} e^{-S^2} dS.$$

Repeating the process m times, we obtain

$$\int_{-\infty}^{\infty} H_m(S)\, H_n(S)\, e^{-S^2}\, dS = 0 \qquad \text{if } m < n$$

$$\left.\begin{aligned} &= 2^n . n!\int_{-\infty}^{\infty} e^{-S^2}\, dS \\ &= 2^n\, n!\, \sqrt{\pi} \end{aligned}\right\} \quad \text{if } m = n.$$

The above integral is used for orthogonalization and normalization of Hermite polynomials. The normalized Hermite polynomial of degree n is

$$\frac{H_n(S)}{\sqrt{2^n\, n!\, \sqrt{\pi}}}\, e^{-\frac{S^2}{2}}.$$

Legendre Polynomials.—The Legendre polynomial $P_n(S)$ of degree n is defined as the coefficient of t^n in the expansion of

$$\frac{1}{\sqrt{1 - 2tS + t^2}}.$$

Thus

$$\frac{1}{\sqrt{1 - 2tS + t^2}} = \sum_{0}^{\infty} P_n(S)\, t^n$$

and

$$P_n(S) = \sum (-1)^k \frac{1.3.5.\ldots.(2n - 2k - 1)}{2^k\, k!\, (n - 2k)!} (S)^{n-2k}.$$

The first five polynomials are

$$P_0(S) = 1, \qquad P_1(S) = S,$$

$$P_2(S) = \tfrac{3}{2}S^2 - \tfrac{1}{2}, \qquad P_3(S) = \tfrac{5}{2}S^3 - \tfrac{3}{2}S,$$

$$P_4(S) = \tfrac{35}{8}S^4 - \tfrac{15}{4}S^2 + \tfrac{3}{8}.$$

Differentiating with respect to t the defining relation and equating the coefficient of t^n on both sides, we obtain the recurrence relation

$$(n+1)P_{n+1} - (2n+1)SP_n - nP_{n-1} = 0.$$

$P_n(S)$ can be shown to be given by the equation

$$P_n(S) = \frac{1}{2^n\, n!}\frac{d^n}{dS^n}(S^2-1)^n.$$

Using this expression for $P_n(S)$ in

$$I = \int_{-1}^{1} P_m(S)\, P_n(S)\, dS$$

and integrating by parts, we have

$$I = \int_{-1}^{1} P_m(S)\, P_n(S)\, dS = 0 \qquad (m < n)$$

$$= \frac{2}{2n+1} \qquad (m = n).$$

The above integral is used for orthogonalization and normalization of Legendre polynomials. The normalized Legendre polynomial of degree n is

$$\sqrt{\frac{2n+1}{2}}\, P_n(S).$$

An associated Legendre polynomial $P_{nm}(S)$ is derived from the Legendre polynomial $P_n(S)$ by the relation

$$P_{nm}(S) = (1-S^2)^{\frac{m}{2}}\, P_n{}^m(S) = (1-S^2)^{\frac{m}{2}}\frac{d^m}{dS^m}[P_n(S)].$$

It can be verified that

$$P_{11}(S) = (1-S^2)^{\frac{1}{2}};\ P_{21}(S) = 3S(1-S^2)^{\frac{1}{2}}, \text{ etc.}$$

The integral used for normalizing the associated functions is

$$\int_{-1}^{1} P_{nm}(S)\, P_{km}(S)\, dS = 0 \qquad (n \neq k)$$

$$= \frac{2}{2n+1}\frac{(n+m)!}{(n-m)!} \ldots (n=k)$$

Laguerre Polynomials.—The Laguerre polynomial $L_k(S)$ of degree k is defined as the coefficient of $\frac{t^k}{k!}$ in the expansion of

$$\frac{e^{-\frac{St}{1-t}}}{1-t}.$$

Thus

$$\frac{e^{-\frac{St}{1-t}}}{1-t} = \sum_{0}^{\infty} L_k(S)\frac{t^k}{k!}$$

and

$$L_k(S) = (-1)^k \left\{S^k - \frac{k^2}{1!}S^{k-1} + \dots \right.$$
$$\left. + (-1)^{k\ r}\frac{[k(k-1)\dots(k-r+1)]^2}{r!}S^{k-r} + \dots \right.$$

The first five polynomials are

$$L_0(S) = 1, \qquad L_1(S) = -S + 1,$$
$$L_2(S) = S^2 - 4S + 2, \quad L_3(S) = -S^3 + 9S^2 - 18S + 6,$$
$$L_4(S) = S^4 - 16S^3 + 72S^2 - 96S + 24.$$

Differentiating with respect to t the defining relation and equating the coefficient of t^k on both sides, we obtain the recurrence relation

$$L_{k+1}(S) - (2k + 1 - S)L_k(S) + k^2 L_{k-1}(S) = 0.$$

$L_k(S)$ can be shown to be given by the equation

$$L_k(S) = e^S \frac{d^k}{dS^k}(S^k e^{-S}).$$

Using this expression for $L_k(S)$ in

$$\int_0^\infty e^{-S} L_k(S) L_m(S)\, dS$$

and integrating by parts, we have

$$\int_0^\infty e^{-S} L_k(S)\, L_m(S)\, dS = 0 \qquad (m < k)$$

$$= (k!)^2 \qquad (m = k)$$

The above integral is used for orthogonalization and normalization of Laguerre polynomials. The normalized Laguerre polynomial of degree k is

$$\frac{e^{-\frac{S}{2}} L_k(S)}{k!}.$$

The generalized Laguerre polynomial $L_k{}^n(S)$ is given by

$$L_k{}^n(S) = \frac{d^n}{dS^n} L_k(S).$$

The integral used for normalizing the generalized polynomial functions is

$$\int_0^\infty S^{2l+1} e^{-S} L_{n+l}^{2l+1}(S)\, L_{m+l}^{2l+1}(S)\, dS = 0 \qquad (m \neq n)$$

$$= \frac{[(n+l)!]^3}{(n-l-1)!} \ldots (m = n).$$

APPENDIX VI

LAPLACIAN OPERATOR

If ϕ is a scalar function of position and $\triangle$ is the Laplacian Operator, we have by definition

$$\triangle\,\phi = \text{div grad}\,\phi.$$

We obtain here an expression for $\triangle$ in a general orthogonal co-ordinate system. If u, v, w are the co-ordinates in an orthogonal system, the surface characterised by constant values for u, v, w intersect orthogonally. The surfaces $v =$ constant, $w =$ constant, intersect along a curve in which u alone varies. Let dS_u be a small distance measured along this curve from a point P whose co-ordinates are u, v, w and let $dS_u = \frac{1}{h_1}\,du$, h_1 is in general a function of u, v, w. Similarly we write $dS_v = \frac{1}{h_2}\,dv$ and $dS_w = \frac{1}{h_3}\,dw$. In this system of co-ordinates grad ϕ will have the components $\frac{\partial\phi}{\partial S_u}, \frac{\partial\phi}{\partial S_v}, \frac{\partial\phi}{\partial S_w}$. If $\vec{A}$ is put equal to grad ϕ, we have for the components A_u, A_v, A_w of $\vec{A}$

$$A_u = \frac{\partial\phi}{\partial S_u} = \frac{\partial\phi}{du}\,h_1$$

$$A_v = \frac{\partial\phi}{\partial S_v} = \frac{\partial\phi}{\partial v}\,h_2$$

and

$$A_w = \frac{\partial\phi}{\partial S_w} = \frac{\partial\phi}{\partial w}\,h_3.$$

To obtain the divergence of $\vec{A}$, consider the infinitesimal rectangular parallelopiped whose edges are dS_u, dS_v and dS_w. Its volume is

$$dS_u\,dS_v\,dS_w = \frac{1}{h_1 h_2 h_3}\,du\,dv\,dw.$$

The surface integral of the vector A over the surface enclosed by the parallelopiped is

$$\sum_{u,\,v,\,w}[(A_u\,dS_v\,dS_w)_{u+du}-(A_u\,dS_v\,dS_w)_u]$$

$$=\sum_{u,\,v,\,w}\left[\left(A_u\frac{1}{h_2h_3}\,dv\,dw\right)_{u+du}-\left(A_u\frac{1}{h_2h_3}\,dv\,dw\right)_u\right]$$

$$=\sum_{u,\,v,\,w}\frac{\partial}{\partial u}\left(A_u\frac{1}{h_2h_3}\,du\,dv\,dw\right).$$

Therefore

$$\operatorname{div} A=h_1h_2h_3\left[\sum_{u,\,v,\,w}\frac{\partial}{\partial u}\left(A_u\frac{1}{h_2h_3}\right)\right]$$

and $\triangle\psi=\operatorname{div}\operatorname{grad}\psi$

$$=h_1h_2h_3\left[\frac{\partial}{\partial u}\left(\frac{h_1}{h_2h_3}\frac{\partial\psi}{\partial u}\right)+\frac{\partial}{\partial v}\left(\frac{h_2}{h_3h_1}\frac{\partial\psi}{\partial v}\right)\right.$$

$$\left.+\frac{\partial}{\partial w}\left(\frac{h_3}{h_1h_2}\frac{\partial\psi}{\partial w}\right)\right].$$

The form of this operator in special cases may easily be worked out.

In Cartesian rectangular co-ordinates for example, u, v, w are x, y, z respectively and $h_1=h_2=h_3=1$ and

$$\triangle\psi=\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}.$$

Similarly in polar co-ordinates u, v, w are r, θ, ϕ and $h_1=1$, $h_2=\frac{1}{r}$, $h_3=\frac{1}{r\sin\theta}$ and

$$\triangle\psi=\frac{1}{r^2\sin\theta}\left[\frac{\partial}{\partial r}\left(r^2\sin\theta\frac{\partial\psi}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{\partial}{\partial\theta}\left(\frac{1}{\sin\theta}\frac{\partial\psi}{\partial\theta}\right)\right]$$

$$=\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}.$$

PARAMETER GROUPS

Volume Element in Parameter Groups.—Suppose the general element x of a group G can be described by n real parameters $(x_1, x_2, \ldots, x_n)$ and that x is a differentiable function of each of the variables x_r. Let $y = ax$, where a is a fixed element of G. This equation is said to define the left translation of the group G induced by the element a. We assume that the parameters $(y_1, y_2, \ldots, y_n)$ of y are analytic functions of the parameters of the elements a and x. We denote the $n \times n$ matrix $\frac{\partial y}{dx} \equiv \left| \frac{\partial (y_r)}{\partial (x_s)} \right|$ by $F(y, x)$. We have then

$$F(z, x) = F(z, y)\, F(y, x),$$

$$F(x, y)\, F(y, x) = E_n \text{ (the unit } n \times n \text{ matrix)}$$

and

$$F(z, x) = F(z, e)\, F(e, x),$$

where e is the identity element and z is an arbitrary element of G. If we write $F(x, e) = F(x)$, we have $F(e) = E_n$, $F(e, x) = F^{-1}(x)$ and $F(z, x) = F(z)\, F^{-1}(x)$. Since

$$\left| \frac{\partial y}{\partial x} \right| = F(y, x) = F(y) . F^{-1}(x),$$

it follows that

$$\begin{aligned} \text{det. } F^{-1}(x) . dx &= \text{det. } F^{-1}(y) . dy \\ &= \text{det. } F^{-1}(ax) . d(ax). \end{aligned}$$

If we write det. $F^{-1}(x)\, dx = V_l(x)\, dx$, we find that $V_l(x)\, dx$ is invariant under an arbitrary left translation of the group. $V_l(x)$ may be called the left invariant volume element of G.

To determine $\mathrm{V}_l(x)$ explicitly, take the equation $y = ax$. Differentiating partially with respect to x_r and using summation convention, we have

$$\frac{\partial y}{\partial y_q}\,\frac{\partial y_q}{\partial x_r} = a\,.\,\frac{\partial x}{\partial x_r}\,.$$

When $y = e, a = x^{-1}$ and the above equation gives

$$M_q\left(\frac{\partial y_q}{\partial x_r}\right)_{y=e} = x^{-1}\left(\frac{\partial x}{\partial x_r}\right).$$

Here

$$M_q = \left(\frac{\partial y}{\partial y_q}\right)_{y=e} = \left(\frac{\partial x}{\partial x_q}\right)_{x=e} \qquad (q = 1, 2, \ldots, n)$$

and M_q are called the characteristic elements of G. This shows that $\partial y_q/\partial x_r$ is the coefficient $c_r{}^q$ of M_q in the expansion of $x^{-1}(\partial x/\partial x_r)$ and that $F(e, x)$ or $F^{-1}(x)$ is the matrix $C = | c_r{}^q |$. Hence the volume element is (det. C) dx. We have to take the absolute value of the determinant C to make sure that the volume element is always positive.

Suppose $f(x)$ is a real continuous function on a compact topological group satisfying the second axiom of countability, then

$$\int f(x)\, V_l(x)\, dx = \int f(ax)\, V_l(ax)\, d(ax) = \int f(ax)\, V_l(x)\, dx$$

on account of the left invariance of $V_l(x)\,dx$ where the integrals are now ordinary definite integrals, the range of integration being specified by the variability domain of the group parameters. (In compact groups, the parameter range and also the value of the above integrals are finite.) The volume element can be multiplied by a suitable constant to ensure that $\int V_l(x)\,dx = 1$. $\int f(x)\, V_l(x)\, dx$ satisfies conditions 1 to 5 of the uniqueness theorem and therefore coincides with $Mf(x)$.

Starting with the equation $y = xa$, we can define analogously a right invariant volume element $V_r(x)$. [In non-compact groups $V_l(x) \neq V_r(x)$ in general.] With the help of $V_r(x)$, we can define (right invariant) integration satisfying conditions 1 to 4 and 6. By the (analogous) uniqueness theorem, $\int f(x)\, V_r(x)\, dx$ coincides with $Mf(x)$. Since $\int f(x)\, V_l(x)\, dx = \int f(x)\, V_r(x)\, dx$ for all functions $f(x)$, we may write $V_r(x) = V_l(x) = V(x)$.

Invariant integration on G may now be extended to complex valued functions also.

Volume Element of U_2.—A 2×2 unimodular unitary matrix may be taken in the form

$$X = \begin{bmatrix} x_4 - ix_3 & -x_2 - ix_1 \\ x_2 - ix_1 & x_4 + ix_3 \end{bmatrix}$$

where $x_1^2 + x_2^2 + x_3^2 + x_4^2 = 1$. The three real quantities x_1, x_2, and x_3 may be taken as the parameters of the group elements. The identity element of U_2 corresponds to $x_1 = x_2 = x_3 = 0$ and $x_4 = 1$. Since $x_1dx_1 + x_2dx_2 + x_3\,dx_3 + x_4dx_4$ element of U_2 corresponds to $x_1 = x_2x_3 = 0$ and $x_3 = 1$. $= 0$, $dx_4 = 0$ at the identity element. The three characteristic matrices of U_2 are:

$$M_1 = \begin{bmatrix} 0 & -i \\ -i & 0 \end{bmatrix};\ M_2 = \begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix};\ M_3 = \begin{bmatrix} -i & 0 \\ 0 & i \end{bmatrix}.$$

Now writing

$$X^{-1}\,dX = \begin{bmatrix} x_4 + ix_3 & x_2 + ix_1 \\ -x_2 + ix_1 & x_4 - ix_3 \end{bmatrix}\begin{bmatrix} dx_4 - idx_3 & -dx_2 - idx_1 \\ dx_2 - idx_1 & dx_4 + idx_3 \end{bmatrix}$$

in the form $\sum\limits_{k=1}^{3} c^k M_k$, we obtain

$$c^1 = -x_3dx_1 + x_4dx_2 + x_1dx_3 - x_2dx_4$$

$$c^2 = x_4dx_1 + x_3dx_2 - x_2dx_3 - x_1dx_4$$

$$c^3 = x_2dx_1 - x_1dx_2 + x_4dx_3 - x_3dx_4.$$

Putting the value of dx_4 in terms of dx_1, dx_2 and dx_3 in the above equations, the determinant of the matrix $(c_j{}^i)$ simplifies into $1/x_4\, dx_1.\, dx_2\, dx_3$ which is the required volume element of U_2.

If we take the element of the matrix x in the form

$$\begin{bmatrix} a & b \\ -b^* & a^* \end{bmatrix}$$

with $a = \cos \alpha \exp i\beta$ and $b = \sin \alpha \exp i\gamma$, the jacobian of the transformation from the parameters x_1, x_2 and x_3 into the parameters α, β, γ is $\sin \alpha \cos^2 \alpha \cos \beta$ and the volume element is $\sin \alpha \cos \alpha$ or any constant multiple of $\sin \alpha \cos \alpha$. The constant is so chosen that the integral of unity over the entire parameter range is unity.

APPENDIX VIII

CHARACTER TABLES AND IRREDUCIBLE REPRESENTATIONS IN RESPECT OF VARIOUS POINT GROUPS

Characters.—In this Appendix, the following additional notation is adopted for convenience. $2C(\phi)$ denotes an infinite-fold rotation axis and rotations of $\pm\phi$ about such an axis. $2C^k$ denotes rotations through $\pm\frac{2k\pi}{p}$ about a p-fold axis. Similarly $2S^k$ denotes rotation-reflections of $\pm\frac{2k\pi}{p}$ about a p-fold axis. The Tables given below will enable us to write down explicitly the characters in respect of several of the point groups. ω in Tables III and IV stands for $\frac{2\pi}{p}$.

Table I

C_i, C_s and C_2

C_i	E	i
C_s	E	σ
C_2	E	C_2
A_1	1	1
A_2	1	-1

Table I enables us to get the characters for the groups C_i, C_s and C_2. The Character Table in respect of C_{2h} may be obtained from the relation $C_{2h} = C_2 \times C_i$ by regarding it as a direct product group. Character Tables for C_{3v} and D_3 can be obtained from Table III. Since $D_{3d} = D_3 \times C_i$ and $D_{3h} = D_3 \times C_s$, the Character Tables for these two groups can also be derived from Table III. Character Tables

TABLE II

$C_{\infty v}$ and D_{∞}

D_{∞} $C_{\infty v}$	E E	$2C(\phi)$ $2C(\phi)$	$\cdots$ $\cdots$	C_2 σ_v
A_1	1	1	$\cdots$	1
A_2	1	1	$\cdots$	-1
E_1	2	$2\cos\phi$	$\cdots$	0
E_2	2	$2\cos 2\phi$	$\cdots$	0
.	.	.	$\cdots$	.
.	.	.	$\cdots$	.
E_l	2	$2\cos l\phi$	$\cdots$	0

TABLE III

C_{pv} and D_p where p is odd

D_p C_{pv}	E E	$2C^1$ $2C^1$	$\cdots$ $\cdots$	$2C^{\frac{p-1}{2}}$ $2C^{\frac{p-1}{2}}$	pC_2 $p\sigma_v$
A_1	1	1	$\cdots$	1	1
A_2	1	1	$\cdots$	1	-1
E_1	2	$2\cos\omega$	$\cdots$	$2\cos\left(\frac{p-1}{2}\right)\omega$	0
E_2	2	$2\cos 2\omega$	$\cdots$	$2\cos(p-1)\omega$	0
.	.	.	$\cdots$	.	.
.	.	.	$\cdots$	.	.
$E_{\frac{p-1}{2}}$	2	$2\cos\left(\frac{p-1}{2}\right)\omega$	$\cdots$	$2\cos\left(\frac{p-1}{2}\right)^2\omega$	0

for C_{2v}, C_{4v}, C_{6v}, D_2, D_4, D_6 and S_{4v} can be obtained from Table IV. Since $D_{2h} = D_2 \times C_i$, $D_{4h} = D_4 \times C_i$ and $D_{6h} = D_6 \times C_i$, the Character Tables for these three groups can also be derived from Table IV. Table V enables us to get the characters for O, T_d and $O \times C_i = O_h$. Table VI enables us to get the characters for C_3, $C_3 \times C_i = S_6$ and $C_3 \times C_s = C_{3h}$. Table VII enables us to get the characters for C_4, S_4 and $C_4 \times C_s = C_{4h}$. Table VIII enables us to get the characters for C_4 and $C_6 \times C_s = C_{6h}$. Table IX

TABLE IV

C_{pv}, D_p and S_{pv} when p is even

D_p	E	$2C^1$	$\cdots$	$C^{\frac{p}{2}}$	$\frac{p}{2}C_2$	$\frac{p}{2}C_2'$
C_{pv}	E	$2C^1$	$\cdots$	$C^{\frac{p}{2}}$	$\frac{p}{2}\sigma_v$	$\frac{p}{2}\sigma_{v'}$
S_{pv}	E	$2S^1$	$\cdots$	$C^{\frac{p}{2}}$	$\frac{p}{2}\sigma_v$	$\frac{p}{2}C_2$
A_1	1	1	$\cdots$	1	1	1
A_2	1	1	$\cdots$	1	-1	-1
B_1	1	-1	$\cdots$	$(-1)^{\frac{p}{2}}$	1	-1
B_2	1	-1	$\cdots$	$(-1)^{\frac{p}{2}}$	-1	1
E_1	2	$2\cos\omega$	$\cdots$	$2\cos\frac{p}{2}\omega$	0	0
E_2	2	$2\cos 2\omega$	$\cdots$	$2\cos p\omega$	0	0
.	.	.	. . .	.	.	.
.	.	.	. . .	.	.	.
$E_{p}{}_{-1}$	2	$2\cos\left(\frac{p}{2}-1\right)\omega$	$\cdots$	$2\cos\frac{p}{2}\left(\frac{p}{2}-1\right)\omega$	0	0

TABLE V

O and T_d

O	E	$8C_3$	$3C_2$	$6C_2$	$6C_4$
T_d	E	$8C_3$	$3C_2$	6σ	$6S_4$
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
F_1	3	0	-1	-1	1
F_2	3	0	-1	1	-1

TABLE VI

C_3

$$\left(\epsilon = e^{\frac{2\pi i}{3}}\right)$$

C_3	E	C_3	C_3^2
A_1	1	1	1
E	1 1	ϵ ϵ^2	ϵ^2 ϵ

enables us to get the characters for T and $T \times C_s = T_h$. The Character Table for C_1 is merely 1. This list completes the groups of crystallographic significance. Other point groups are also covered by the Tables II, III and IV.

In some groups, the characters are complex quantities. These do not have much significance in physical applications of interest to us. In such cases, a pair of complex conjugate representations may be combined to give real representations and characters.

TABLE VII

C_4 and S_4

$(i = \sqrt{-1})$

C_4	E	C_2	C_4	C_4^3
S_4	E	C_2	S_4	S_4^3
A_1	1	1	1	1
A_2	1	1	-1	-1
E	1 1	-1 -1	i $-i$	$-i$ i

TABLE VIII

C_6

$\left(\epsilon = e^{\frac{2\pi i}{6}}\right)$

C_6	E	C_6	C_6^2	C_6^3	C_6^4	C_6^5
A_1	1	1	1	1	1	1
A_2	1	-1	1	-1	1	-1
E_1	1 1	ϵ^2 ϵ^4	ϵ^4 ϵ^2	1 1	ϵ^2 ϵ^4	ϵ^4 ϵ^2
E_2	1 1	ϵ $-\epsilon^2$	ϵ^2 $-\epsilon$	-1 -1	$-\epsilon$ ϵ^2	$-\epsilon^2$ ϵ

Irreducible Representations.—Let us first consider the case of the dihedral groups C_{pv}, D_p (p odd or even) and S_{pv}

TABLE IX

T

T	E	$3C_2$	$4C_3$	$4C_3'$
A	1	1	1	1
E	$\left(\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}1\\1\end{matrix}$	$\begin{matrix}\epsilon\\\epsilon^2\end{matrix}$	$\left.\begin{matrix}\epsilon^2\\\epsilon\end{matrix}\right)$
F	3	-1	0	0

(p even). The abstract form of these groups is given by the following relations. a and b are the generating elements.

$$a^p = e; \quad b^2 = e; \quad ab = ba^{-1}.$$

p is a positive integer and $2p$ is the order of the group G. Let us first take the case p odd. The conjugate classes of G are $(p+3)/2$ in number and they are

$$e; \quad (a^r, a^{-r}), r = 1 \text{ to } (p-1)/2; \text{ and } (b, ba, \ldots, ba^{p-1}).$$

Hence there are $(p+3)/2$ non-equivalent irreducible representations of G. If we use the orthogonality relation

$$N = \sum_i h_i \chi_i^r \overline{\chi_i^r}$$

for the class e in the form

$$N = n_1^2 + n_2^2 + \ldots + n_q^2$$

where $n_r (= \chi_1^r)$ is the dimension of the representation Γ^r and q is the number of non-equivalent irreducible representations (or conjugate classes in G), we find from the unique representation of $2p$ as sums of squares of integers

$$2p = \tfrac{1}{2}(p-1)\,2^2 + 2.1^2$$

that the group has two one-dimensional representations and $(p-1)/2$ two-dimensional representations. It may be observed that in a representation it is sufficient to give the matrices corresponding to the generating elements as the matrices corresponding to the other elements can be deduced from them. The one-dimensional representations of G may be given as

$$a \rightarrow 1 \text{ and } b \rightarrow \pm 1.$$

The possibility $a \rightarrow -1$ is excluded as it is not compatible with the generating relations of the group.

In order to obtain the two-dimensional representations, we first note that the matrix A corresponding to a can be taken without loss of generality in the diagonal form as

$$\begin{vmatrix} \epsilon^r & 0 \\ 0 & \epsilon^s \end{vmatrix}$$

where $\epsilon = \cos 2\pi/p + i \sin 2\pi/p$. If we take the matrix B corresponding to the element b in the form

$$\begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix}$$

and use the condition $AB = BA^{-1}$ we find $s = -r \bmod p$; $b_{11} = b_{22} = 0$ and $b_{12} = b_{21} = 1$ or -1. Thus a set of non-equivalent irreducible representations of G are given by

	a	b
A_1	1	1
A_2	1	-1
E_r	$\begin{vmatrix} \epsilon^r & 0 \\ 0 & \epsilon^{-r} \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}$

$r = 1, 2, \ldots, (p-1)/2$.

The case p even can be similarly treated. In this case the conjugate classes are $\frac{1}{2}p + 3$ in number and they are (e); (a^r, a^{-r}), $r = 1, \ldots \frac{1}{2}p - 1$; $(a^{p/2})$; $(b, ba^2, \ldots ba^{p-2})$; and

$(ba, ba^3, \ldots ba^{p-1})$. The unique representation of $2p$ as sums of squares is

$$2p = 4.1^2 + (\tfrac{1}{2}p - 1)\,2^2.$$

This shows that the group has 4 one-dimensional representations and $\frac{1}{2}p - 1$ two-dimensional representations. They are described below:—

	a	b
A_1	1	1
A_2	1	$X-1$
B_1	-1	1
B_2	-1	-1
E_r	$\begin{vmatrix} \epsilon^r & 0 \\ 0 & \epsilon^{-r} \end{vmatrix}$	$\begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}$

$r = 1, 2, \ldots p/2 - 1.$

We shall take the two-dimensional representations E_r in both cases p odd and p even in an equivalent form

$$E_r: \quad a \rightarrow \begin{vmatrix} \cos\dfrac{2\pi r}{p} & -\sin\dfrac{2\pi r}{p} \\ \sin\dfrac{2\pi r}{p} & \cos\dfrac{2\pi r}{p} \end{vmatrix}$$

$$b \rightarrow \begin{vmatrix} 0 & 1 \\ 1 & 0 \end{vmatrix}$$

in which the matrices are real.

We next consider the representations of the groups 0 and T_d. These groups are isomorphous with the symmetric group of degree four. The group H formed by the permutations E, (12) (34), (13) (24) and (14) (23) is a self-conjugate subgroup of S_4 and the factor group S_4/H is isomorphic with S_3. We have thus obtained three irreducible representations of S_4. S_4 has in addition two three-dimensional irreducible representations. They may be obtained as follows. Subject the four variables x_1, x_2, x_3 and x_4 connected by the relation $x_1 + x_2 + x_3 + x_4 = 0$ to the permutations of S_4. We then obtain one of the three-dimensional representations. If in this representation, we reverse the signs of the matrices corresponding to odd permutations we obtain the other three-dimensional representation. We give below all the non-equivalent irreducible representations of S_4 in a different form. The permutations (12) and (234) may be taken as a set of generating elements of S_4. The representations are completely defined if the matrices corresponding to the generating elements are given. Further, for applications later it is sufficient to know the matrices for the generating elements only. The symbols A, B, E, F are the conventional ones used in point groups and stand for one-dimensional (A and B), two-dimensional (E) and three-dimensional (F) representations.

	S_4	
	(12)	(234)
A_1	1	1
A_2	-1	1
E	$\begin{vmatrix} 0 & 0 \\ 1 & 0 \end{vmatrix}$	$\begin{vmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$
F_1	$\begin{vmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{vmatrix}$	$\begin{vmatrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{vmatrix}$
F_2	$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{vmatrix}$	$\begin{vmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{vmatrix}$

The irreducible representations of T_d give also the irreducible representations of T. In the case of T, F_1 and F_2 become indistinguishable. Since $O_h = O \times C_i$ and $T_h = T \times C_s$, the irreducible representations of O_h (or T_h) are obtained by making in addition the basis element of C_i (or C_s) represent the matrices I_n and $-I_n$ successively.

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