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Group Theory and Solid State Physics

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Group Theory and Solid State Physics

A TRANSLATION OF THE MONOGRAPH ENTITLED
Groupes Finis de Symétrie
et Recherche de Solutions
de l'Équation de Schroedinger

L. MARIOT

Maitre de Conférences
á la Faculte des Sciences de Dijon

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PRENTICE-HALL, INC., ENGLEWOOD CLIFFS, N. J. 1962

Library of Congress Catalog Card No. 62-19495

Printed in the United States of America

36544-C

Preface

The determination of the energy levels of the valence and conduction bands in a crystal is a problem which has not been rigorously solved; it is necessary to use approximation methods to find the solutions to the Shroedinger equation.

The methods used up to the present are based on a variational principle and result in the necessity of solving a high-order secular equation if acceptable accuracy is to be obtained. Several essential points must be examined:

(a) How to determine the potential $V(r)$ of interaction of the electrons and nuclei, as well as that for the electrons among themselves.

(b) What trial functions should be chosen.

(c) How to reduce in a practical way a determinant of high order.

We propose to study in detail the last two points and to show the absolute necessity for the use of group theory in tackling this problem. It is no exaggeration to say that this discipline is an essential mathematical tool in the modern theory of the solid state.

The first chapter is a brief review of the fundamental definitions of group theory; the second treats in some detail the representations of finite groups; and in the third, we indicate the essential properties of space groups associated with crystals.

After having given briefly in Chap. 4 the principle of the Ritz variational method, we study in Chap. 5 the symmetry properties of the eigenfunctions of the Schroedinger equation applied to a system with which we associate a finite symmetry group. Then we show how to choose the trial functions involved in the Ritz method, thus finding the symmetric functions which enable us to factor the secular determinant and solve the problem.

The principle of the fertile method of plane waves is developed in Chap. 6. Finally, we apply these ideas to an example: the determination of energy levels in a diamond-type crystal.

The idea for this work is due to Professor Pierre Aigrain. To him, we express our heartiest thanks for the help and fruitful counsel given. In addition, we wish to acknowledge the friendly and lucid communication by Dr. F. Herman and Dr. T. O. Woodruff of their personal, unedited work on these questions.

Translator's Foreword

The author of this monograph assumes that the reader is familiar with quantum theory, crystal structure, and matrix algebra. For those whose preparation in any of these areas is somewhat weak, it is suggested that the following references might be helpful:

A. Nussbaum, *Semiconductor Device Physics*, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1962).

A discussion of the Schroedinger equation, lattice symmetry, Brillouin zones, etc. (plus the associated mathematics) at an introductory level.

A. J. Dekker, *Solid State Physics*, Prentice-Hall, Inc., Englewood Cliffs, N. J. (1957).

A more advanced treatment of many of the topics considered in this monograph.

J. S. Blakemore, *Semiconductor Statistics*, Pergamon Press, London (1962).

A thorough, sophisticated review of energy band theory.

H. Jones, *The Theory of Brillouin Zones and Electronic States*

in Crystals, North-Holland Publishing Co., Amsterdam (1960).

Provides a detailed discussion of some of the applications of group theory.

A. Nussbaum, *Group Theory and the Energy Band Structure of Semiconductors*, Proc. IRE 50, xxx 1762–1781 (1962).

This is a simple introduction to the algebra of groups. Tellurium and beta-brass are used as examples for energy band calculations.

M. Hamermesh, *Group Theory and Its Application to Physical Problems*, Addison-Wesley, Reading, Mass. (1962).

This recent book gives a rigorous treatment of group theory from the viewpoint of its physical applications.

The final version of this translation was typed by Irene B. Urffer, whose care and patience are deeply appreciated.

Contents

1

Elements of group theory

1. THE IDEA OF A GROUP

In this chapter, we shall merely review a number of fundamental definitions necessary for the understanding of the remainder of this book.

(a) An *ensemble* is a finite or infinite collection of arbitrary mathematical objects. These objects are called the *elements* of the ensemble.

If an arbitrary element of an ensemble E possesses a property, those elements of E possessing the same property form a new ensemble called a *proper part* of E.

(b) Being given an ensemble E, a *law of combination* of two arbitrary elements x and y is a rule which determines a third element z of E. We write

$$z = x \cdot y$$

and, in general, $x \cdot y \neq y \cdot x$.

(c) A *group* G is then an ensemble whose law of combination satisfies the following three conditions:

(1) the law is *associative*

$$C_j \cdot (C_k \cdot C_l) = (C_j \cdot C_k) \cdot C_l$$

(C_j, C_k, and C_l being members of G)

(2) the law requires a *unit element* E (from the German *einheit*, unity) such that

$$E \cdot C_k = C_k \cdot E = C_k$$

(3) every element C_i has an inverse $(C_i)^{-1}$ such that

$$C_i \cdot (C_i)^{-1} = (C_i)^{-1} \cdot C_i = E$$

Examples. The whole numbers—positive, negative, and zero—form a group for which the law of combination is addition

$$a + 0 = 0 + a = a$$

and 0 is the unit element. Then $(a)^{-1} = -a$ since $-a + a = 0$.

Consider three non-coplanar vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$. The ensemble of vectors $\boldsymbol{r} = L_1\boldsymbol{a}_1 + L_2\boldsymbol{a}_2 + L_3\boldsymbol{a}_3$, where the L_i are integers (positive, negative, or zero), forms a group.

These groups contain an infinite number of elements, hence they are *infinite groups*. On the other hand, a *finite group of order g* has g elements. The four numbers 1, -1, i, $-i$ under the ordinary law of multiplication form a group of order 4. Again, the ensemble of permutations of the three letters a, b, c is a group of order 6.

(d) *Abelian group.* If the law of combination is also commutative ($A \cdot B = B \cdot A$), the group is said to be *commutative* or *abelian*. The first three examples are abelian but

the permutation group is not. However, the group of displacements in ordinary space is abelian.

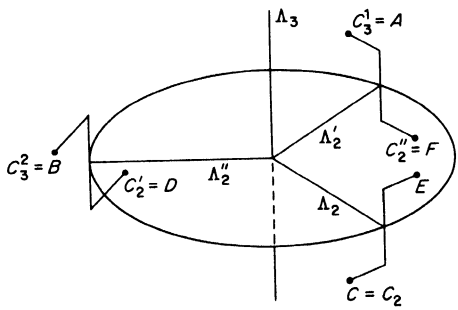
2. THE MULTIPLICATION TABLE. ISOMORPHISM

Let us take as an example the *dihedral group* D_3 of order 6; this is the symmetry group of a solid with a principal axis of symmetry Λ_3 of order 3 and three two-fold axes Λ_2 perpendicular to Λ_3. The symmetry elements are

E, $A = C_3$ (a rotation of $2\pi/3$ around Λ_3)
$B = C_3^2$ (a rotation of $4\pi/3$ around Λ_3)
$C = C_2$ $D = C_2'$ $F = C_2''$ (rotations of π around each of the three two-fold axes)

It is then easy to construct the following multiplication table:

	E	A	B	C	D	F
E	E	A	B	C	D	F
A	A	B	E	D	F	C
B	B	E	A	F	C	D
C	C	F	D	E	B	A
D	D	C	F	A	E	B
F	F	D	C	B	A	E



Thus

$$C \cdot B = F \qquad B \cdot C = D$$

For every group, such a table can be set up in the same manner.

Two groups G and G' are *simply isomorphic* if to each element $A, B, C, \ldots$ of G there corresponds an element $A', B', C', \ldots$ of G' such that, if $A \cdot B = C$, then $A' \cdot B' = C'$. Evidently two simply isomorphic groups have the same multiplication table.

In the preceding case, the group D_3 is simply isomorphic to the permutation group of three letters.

3. THE CONCEPT OF A CLASS

A, B, and X being three members of a group G, B is the transform of A with respect to X if $B = X^{-1} \cdot A \cdot X$ and B is said to be *conjugate* to A. The following properties are evident: every element A of G is conjugate to itself; if A is conjugate to B, B is conjugate to A; if A is simultaneously conjugate to B and C, B and C are mutually conjugate—that is, if $B = X^{-1} \cdot A \cdot X$ and if $C = Y^{-1} \cdot A \cdot Y$ (X, Y, B, and C are members of G), then $B = Z^{-1} \cdot C \cdot Z$ where $Z = Y^{-1} \cdot X$.

Fundamental Definition. All elements of the form $X^{-1} \cdot A \cdot X$, X being any element of G, constitute the *class* of A.

The unit element E of G forms a class by itself, since $X^{-1} \cdot E \cdot X = E$. Every element of an abelian group forms its own class, for

$$X^{-1} \cdot A \cdot X = X^{-1} \cdot X \cdot A = E \cdot A = A$$

On the other hand, for non-abelian groups, the concept of a class is not trivial; in this case, a class may contain many elements. For example, the group D_3 consists of the three classes E, (A,B), and (C,D,F).

4. SUBGROUPS

Definition. Given a group G, a subgroup H is a part of G obeying the following:

(a) If X and Y are members of H, then $X \cdot Y$ is also a member of H.

(b) The subgroup obeys all the laws of combination defining a group.

The unit element of H must be that of G. In fact, if E and E' are the unit elements of G and of H, if X is an element of H and X^{-1} its inverse in G, we have:

$$E' = E' \cdot E = E' \cdot X \cdot X^{-1} = X \cdot X^{-1} = E$$

Let $(H) = (E, H_1, H_2, \ldots)$ be a subgroup of G and consider an element of G. Form the ensembles:

$$X \cdot (H) = X, X \cdot H_1, X \cdot H_2, \ldots$$

$$(H) \cdot X = X, H_1 \cdot X, H_2 \cdot X, \ldots$$

If X is itself a member of H, the property $X \cdot (H) = (H) \cdot X = (H)$ is trivial, but if X does not belong to H, the ensemble of elements $X \cdot (H)$ is called the *right coset* of G associated with H. Similarly, the ensemble $(H) \cdot X$ is the *left coset* associated with H.

Theorem. The subgroup H and the coset $X \cdot H$ do not have a common element.

Suppose that $H_j = X \cdot H_k$ for j and k given. Then $X = H_j \cdot H_k^{-1}$ and X belongs to H, contrary to hypothesis. If n_1 is the order of H (H is finite), H and $X \cdot H$ contain the same number of elements.

Consider now an element Y of G, not belonging to H nor to $X \cdot H$. It is easy to show that the coset $Y \cdot H$ has no element in common with $X \cdot H$.

Then, given a subgroup H of G, an element X of G not belonging to H, an element Y of G not belonging to H nor to $X \cdot H$, and an element Z of G not belonging to H, $X \cdot H$ or $Y \cdot H$, and so forth, we have [designating the ensemble of elements of G by (G)]:

$$(G) = (H) + X \cdot (H) + Y \cdot (H) + Z \cdot (H) + \ldots \qquad (1)$$

Each coset consists only of elements of G which are not in H. If G is finite, then the number of elements n_1 in each coset (the order of H) will necessarily be a submultiple of the order n of G.

Definition. The index of the subgroup H with respect to the finite group G is the ratio of the order of G to the order of H.

The index of H equals the number of cosets in the development (1) of G with respect to H.

All the above applies equally well to left cosets, and we have:

$$(G) = (H) + (H) \cdot X + (H) \cdot Y' + \ldots \qquad (2)$$

noting in general $(H) \cdot X \neq X \cdot (H)$ and $Y \neq Y'$. To summarize:

$$\begin{aligned} (G) &= (H) \cdot [E', X, Y, \ldots] \\ (G) &= [E', X, Y', \ldots] \cdot (H) \end{aligned} \qquad (3)$$

Note that the ensembles $[E', X, Y, \ldots]$, $[E', X, Y', \ldots]$ are not necessarily groups themselves.

5. CONJUGATE AND INVARIANT SUBGROUPS

The ensemble (K) of transforms of the elements of H with respect to a given element X of G is said to be conjugate to the subgroup H. We write

$$(K) = X^{-1} \cdot (H) \cdot X \qquad (4)$$

Theorem. The ensemble K is a subgroup of G.

Let $H_i \cdot H_j = H_k$; $X^{-1} \cdot H_i \cdot X$ and $X^{-1} \cdot H_j \cdot X$ belong to K. It is evident that:

$$(X^{-1} \cdot H_i \cdot X) \cdot (X^{-1} \cdot H_j \cdot X) = X^{-1} \cdot H_i H_j \cdot X$$

belongs to K.

Further, $X^{-1} \cdot E \cdot X = E$. Finally, $X^{-1} \cdot H_j \cdot X$ is the inverse of $X^{-1} \cdot H_j^{-1} \cdot X$. K is a group called the *conjugate subgroup* of the subgroup H with respect to X.

Let us consider now the important idea of the invariant subgroup.

Definition. If $(H) = X^{-1} \cdot (H) \cdot X$ for every X in G, H is an *invariant subgroup* of G.

Let $X \cdot (H)$ and $(H) \cdot X$ be cosets associated with H. Since $X^{-1} \cdot (H) \cdot X = (H)$, then $(H) \cdot X = X \cdot (H)$ and in Eqs. (1) and (2) $Y = Y'$, $Y \cdot (H) = (H) \cdot Y$, and finally:

$$\begin{aligned} (G) &= (H) + X \cdot (H) + Y \cdot (H) + \dots \\ (G) &= (H) + (H) \cdot X + (H) \cdot Y + \dots \end{aligned} \tag{5}$$

Theorem. The ensemble $(H), X \cdot (H), Y \cdot (H), \dots$ is a *supergroup* of which the unit element is (H).

Note that the ensemble (H), $X \cdot (H)$, $Y \cdot (H)$, ... contains $X \cdot Y \cdot (H), X^{-1} \cdot (H), Y^{-1} \cdot (H), \dots$, which are not necessarily different from $X \cdot (H)$, $Y \cdot (H)$. This ensemble is then a group, since:

(a) $$\begin{aligned} X \cdot (H) \cdot Y \cdot (H) &= X \cdot (H) \cdot (H) \cdot Y \\ &= X \cdot (H) \cdot Y = X \cdot Y \cdot (H) \end{aligned}$$

(b) $$\begin{aligned} (H) \cdot X \cdot (H) & \\ &= (H) \cdot (H) \cdot X = (H) \cdot X = X \cdot (H) \end{aligned}$$

(c) $$\begin{aligned} X \cdot (H) \cdot X^{-1} \cdot (H) &= X \cdot (H) \cdot (H) \cdot X^{-1} \\ &= X \cdot (H) \cdot X^{-1} = (H) \end{aligned}$$

Equations (5) can be written:

$$(G) = (H)\cdot[E', X, Y, \ldots] = [E', X, Y, \ldots]\cdot(H) \qquad (6)$$

E' is an arbitrary element of H and $[E', X, Y,] \ldots$ is a group.

Definition. $[E', X, Y,] \ldots$ is the *factor group* of G with respect to the invariant subgroup H.

We designate the factor group by G/H and write:

$$(G) = (G/H)\cdot(H) = (H)\cdot(G/H) \qquad (7)$$

2

Representation of a group

1. LINEAR OPERATORS AND MATRICES

Let a basis of an n-dimensional (n is finite) vectorial space be composed of n linearly independent vectors $\boldsymbol{e}_1, \boldsymbol{e}_2, \ldots, \boldsymbol{e}_n$. Every vector $\boldsymbol{X}$ of this space E_n can be expressed in the form:

$$\boldsymbol{X} = \sum_{j=1}^{n} x_j \boldsymbol{e}_j \tag{1}$$

where the x_j are the components of $\boldsymbol{X}$ with respect to the basis $(\boldsymbol{e}_j)$. Let us apply to $\boldsymbol{X}$ the linear operator $\mathfrak{A}$ such that $\boldsymbol{Y} = \mathfrak{A}(\boldsymbol{X})$. The components y_k of $\boldsymbol{Y}$ with respect to the basis $(\boldsymbol{e}_j)$ are related to the components x_j of $\boldsymbol{X}$ by the relations:

$$y_k = \sum_{k=1}^{n} A_{kj} x_j \tag{2}$$

The $n \times n$ matrix with elements A_{kj} is the representation of the operator $\mathfrak{A}$ with respect to the basis $(\boldsymbol{e}_j)$. If we designate by Y the column matrix $\{y_1, \ldots, y_n\}$ and by X the column matrix $\{x_1, \ldots, x_n\}$, we can write (2) as:

$$Y = AX \tag{3}$$

Let us then accomplish the change from the basis (e_i) to a basis (e'_i) such that:

$$e_k = \sum_{j=1}^{n} P_{jk} e'_j$$

We have:

$$X = \sum_k x_k e_k = \sum_j x'_j e'_j = \sum_{jk} x_k P_{jk} e'_j$$

from which:

$$x'_j = \sum_k P_{jk} x_k$$

The components x'_i, y'_j of the vectors X and Y with respect to (e'_j) can be expressed by:

$$x'_j = \sum_k P_{jk} x_k, \qquad y'_j = \sum_k P_{jk} x_k \tag{4}$$

If we designate the column matrices $\{y'_1, \ldots, y'_n\}$ and $\{x'_1, \ldots, x'_n\}$ by Y' and X', respectively, the relations (4) become:

$$X' = PX \qquad Y' = PY \tag{5}$$

in matrix language.

If we assume the formulas (5) have inverses, the matrix P is non-singular.

From (3) and (5) we obtain:

$$Y' = PY = PAX = PAP^{-1}X'$$

so that:

$$Y' = BX' \qquad \text{with} \qquad B = PAP^{-1} \tag{6}$$

Definition. *The matrix $B = PAP^{-1}$ transformed from A by the non-singular matrix P is equivalent to the matrix A.*

The matrices A and B represent the same linear operator $\mathfrak{A}$ with respect to two different bases in E_n.

Let us recall the two important properties of equivalent matrices:

(a) The traces* of A and B are equal.
By applying the commutative property trace $(AB) =$ trace (BA), we have

$$\text{trace } B = \text{trace } (PAP^{-1}) = \text{trace } (PP^{-1}A)$$
$$= \text{trace } A$$

(b) The determinants of A and B are equal.

2. REPRESENTATION OF A GROUP

Let $M, N, \ldots, R, S, \ldots$ be the elements of a group G. Associate with each element R of G a square non-singular $n \times n$ matrix $D(R)$ such that:

$$D(R) \cdot D(S) = D(RS) \tag{7}$$

Definition. *The group of matrices $D(R)$ is an n-dimensional representation of the group G.*

The matrices $D(R)$ themselves represent non-singular linear operators defined in E_n with respect to a basis (e_n).

Remarks.

(a) $R \neq S$ does not necessarily imply $D(R) \neq D(S)$.

(b) $D(R) \equiv 0$ or 1 are the trivial representations of the group G.

(c) $$D(S^{-1}) = D^{-1}(S)$$
Using:
$$D(S^{-1})D(S) = D(S^{-1}S) = E$$

---

* The *trace* of a matrix is the sum of the diagonal elements. The trace of AB equals the trace of BA.

then:

$$D(S^{-1})D(S)D^{-1}(S) = ED^{-1}(S) = D^{-1}(S)$$

from which:

$$D(S^{-1})E = D^{-1}(S)$$

(d) The group of matrices $D(R)$ is evidently isomorphic to the group G. If we change the basis in E_n, we obtain a group of matrices $D'(R)$ equivalent to the matrices $D(R)$.

3. REDUCIBILITY

1. Let a group of regular linear operators $\mathfrak{A}$ operate in an n-dimensional linear vector space E_n.

Definitions.

(1) The subspace E_1 of E_n is an invariant space of the operator $\mathfrak{A}$ if, to *every* vector V belonging to E_1, there corresponds also a vector $\mathfrak{A}V$ belonging to E_1.

(2) E_1 is an invariant space of the *group of operators* $\mathfrak{A}$ if, to every vector V, there corresponds a vector $\mathfrak{A}V$ for every $\mathfrak{A}$ of the group.

Consider the invariant subspace E_1 of the group with dimensions $m < n$. Let us choose a basis $(e_1, \ldots, e_m, e_{m+1}, \ldots, e_n)$ of E_n such that the first m vectors are in E_1. With respect to such a basis, the group of operators $\mathfrak{A}$ is represented by the group of matrices A. Let us calculate $Ae_j (j = 1, 2, \ldots, m)$:

$$Ae_j = \begin{bmatrix} A_{11} & A_{12} & \ldots & A_{1n} \\ \cdot & \cdot & \ldots & \cdot \\ A_{j1} & & \ldots & \\ \cdot & & \ldots & \cdot \\ A_{n1} & & \ldots & A_{nn} \end{bmatrix} \cdot \begin{bmatrix} 0 \\ \cdot \\ 1 \\ \cdot \\ 0 \end{bmatrix} = \begin{bmatrix} A_{1j} \\ \cdot \\ A_{jj} \\ \cdot \\ A_{nj} \end{bmatrix}$$

The vector Ae_j must belong to E_1, so that the $(n - m)$ last elements of the jth column of $A (j = 1, 2, \ldots, m)$ are zero, and:

$$A = \begin{pmatrix} A_{m,m} & \alpha_{m,n-m} \\ 0 & A_{n-m,n-m} \end{pmatrix} \tag{8}$$

where $A_{m,m}$ is a square matrix with m rows and m columns, $\alpha_{m,n-m}$ is a rectangular matrix with m rows and $n - m$ columns, 0 is the rectangular null matrix with $n - m$ rows and m columns, and $A_{n-m,n-m}$ is a square matrix with $n - m$ rows and $n - m$ columns. All the matrices A of the group can be placed in the form (8). *We say that the group of the matrix A is reducible.* In the opposite case, it will be said to be *irreducible.*

If there exists in addition a second subspace E_2 of E_n, an invariant space of the group of operators $\mathfrak{A}$ and a complementary space of E_1 of dimension $(n - m)$, let us choose a basis of E_n such that the first n vectors are in E_1 while the last $(n - m)$ vectors are in E_2. The vectors $Ae_j (j = 1, 2, \ldots, m)$ belong to E_1 while the vectors Ae_p $(p = m + 1, \ldots, n)$ belong to E_2. The matrices A representing the operators $\mathfrak{A}$ of the group with respect to the basis will have the form:

$$A = \begin{pmatrix} A_{m,m} & 0 \\ 0 & A_{n-m,n-m} \end{pmatrix} = \begin{pmatrix} A^1 & 0 \\ 0 & A^2 \end{pmatrix} \tag{9}$$

We say that the group of matrices A is completely reducible. Complete reducibility implies reducibility but, in general, the inverse is not true ([3],* Chap. 2, page 57). However, if one considers only *finite groups*, the two notions are equivalent. In the following, since we

* See Bibliography on p. 109.

are studying only finite groups, we shall simply say that a matrix is *reducible* or *irreducible.*

Definition. *The matrix A is the direct sum of the matrices* A^1 and A^2:

$$A = A^1 + A^2$$

It may be that a new decomposition of A^1 and A^2 into direct sums is possible, etc. The process ends when the matrix A is decomposed to the direct sum of irreducible matrices A^γ:

$$A = A^1 + A^2 + \ldots + A^\gamma + \ldots + A^\rho$$

2. Suppose now that the group of matrices $\overline{D}(R)$ is an n-dimensional representation $\overline{\Gamma} = \{\overline{D}(R)\}$ of a finite group G of elements $M, N, \ldots, R, S, \ldots$. The group of matrices $\overline{D}(R)$ is a representation with respect to a given basis of E_n of a group of linear operators $\mathfrak{A}$.

If the group of operators $\mathfrak{A}$ does not permit any invariant subspaces, the representation $\overline{\Gamma}$ is necessarily irreducible. If not, by choice of an appropriate basis it is possible to find the matrices $D(R)$ *equivalent* to the matrices $\overline{D}(R)$ such that:

$$D(R) = \begin{pmatrix} D^1(R) & 0 \\ 0 & D^2(R) \end{pmatrix}$$

In this case, the representation $\overline{\Gamma} = \{\overline{D}(R)\}$ is equivalent to a reducible representation $\Gamma = \{D(R)\}$. Further, it is easy to verify that:

$$D(R \cdot S) = D(R) \cdot D(S) = \begin{pmatrix} D^1(R) \cdot D^1(S) & 0 \\ 0 & D^2(R) \cdot D^2(S) \end{pmatrix}$$

The groups of matrices $D^1(R)$ and $D^2(R)$ are two representations Γ^1 and Γ^2 of the group G, respectively having the dimensions n and $n - m$. We write:

$$D(R) = D^1(R) + D^2(R) \qquad \text{and} \qquad \Gamma = \Gamma^1 + \Gamma^2$$

The sign + is commutative; in fact, let us transform $D(R)$ by the permutation matrix P:

$$P^{-1}D(R)P = \begin{pmatrix} D^2(R) & 0 \\ 0 & D^1(R) \end{pmatrix} = D^2(R) + D^1(R)$$

The matrix P simply permutes the vectors of the basis, the representation $P^{-1}\Gamma P$ being identical to the representation Γ and:

$$\Gamma = \Gamma^1 + \Gamma^2 = \Gamma^2 + \Gamma^1$$

In:

$$\Gamma^1 + \Gamma^1 + \ldots + \Gamma^1 = p\Gamma^1$$

it will always be possible to decompose the representation Γ into a direct sum of *irreducible* representations, so that:

$$\Gamma = n_1\Gamma^1 + n_2\Gamma^2 + \ldots + n_\gamma\Gamma^\gamma + \ldots + n_\rho\Gamma^\rho \qquad (10)$$

the n_γ being positive whole numbers or zeroes. In what follows, we shall omit the dot over the sign +, since the operational symbol + is commutative as is the customary symbol +.

Remark. There does not exist a general method for finding the transformation matrix taking the matrices $\overline{D}(R)$ into the matrices $D(R)$ if the representation Γ is not irreducible.

4. FUNDAMENTAL THEOREMS CONCERNING THE REPRESENTATIONS OF FINITE GROUPS

Theorem 1. *Every representation of a finite group is equivalent to a unitary representation.*

Let there exist a finite group of elements $S_1, S_2, \ldots, S_j \ldots$. It is necessary to show that the matrices $D(S_j)$ are simultaneously transformable into unitary matrices. Consider the hermitian matrix F:

$$F = \sum_{j=1}^{g} D(S_j)D\dagger(S_j) \qquad (*) \tag{11}$$

g being the order of the group. Thus, every hermitian matrix S is transformable into a diagonal matrix Λ with real coefficients by a unitary matrix U:

$$\Lambda = UFU^{-1}$$

from which:

$$\Lambda = U \sum_j D(S_j)U^{-1}UD\dagger(S_j)U^{-1}$$

$$= [U \sum_j D(S_j)U^{-1}] \cdot [UD(S_j)U^{-1}]\dagger$$

Since U is unitary, $U\dagger = U^{-1}$. Then:

$$\Lambda = \sum_j K(S_j)K\dagger(S_j) \qquad K(S_j) = UD(S_j)U^{-1} \tag{12}$$

The matrices $K(S_j)$ form a representation equivalent to the matrices $D(S_j)$. In noting that $\Lambda^{-1/2}\Lambda\Lambda^{-1/2} = E$ and that $(\Lambda^{1/2})\dagger = \Lambda^{1/2}$, one is able to write:

$$\Lambda^{-1/2} \sum_j K(S_j)K\dagger(S_j)\Lambda^{-1/2} = E \tag{13}$$

We then form the matrix $H(S_j) = \Lambda^{-1/2}K(S_j)\Lambda^{1/2}$ and we show that the matrices $H(S_j)$ form a unitary representation, that is:

$$H(S_j)H\dagger(S_j) = E \tag{14}$$

Let us replace $H(S_j)$ by its value:

$$H(S_j)H\dagger(S_j) = \Lambda^{-1/2}K(S_j)\Lambda^{1/2} \cdot E \cdot \Lambda^{1/2}K\dagger(S_j)\Lambda^{-1/2}$$

In this equation we replace E by the expression (13):

$$H(S_j)H\dagger(S_j) = \Lambda^{-1/2}K(S_j)\Lambda^{1/2}\Lambda^{-1/2} \sum_k K(S_k)K\dagger(S_k)\Lambda^{-1/2}\Lambda^{1/2}K\dagger(S_j)\Lambda^{-1/2}$$

$$= \Lambda^{-1/2} \sum_k K(S_j)K(S_k)[K(S_j)K(S_k)]\dagger\Lambda^{-1/2}$$

---

* The transpose of A is the matrix $\overline{A}$ such that $(\overline{A})ij = Aji$. The conjugate of A is the matrix A^* such that $(A^*)ij$ is the complex conjugate of $(A)ij$. The adjoint of A is the matrix $A\dagger = \overline{A}^*$. A matrix is hermitean if $A\dagger = A$.

Thus the matrices $K(S_j)$ form a representation of the group G, $K(S_j) \cdot K(S_k) = K(S_l)$ and:

$$H(S_j)H\dagger(S_j) = \Lambda^{-1/2} \sum_l K(S_l)K\dagger(S_l)\Lambda^{-1/2} = E$$

in view of (12). Then the matrices $D(S_j)$ are transformed into unitary matrices by the matrix $\Lambda^{-1/2}U$, U transforming F into the diagonal matrix Λ:

$$H(S) = \Lambda^{-1/2}U \cdot D(S) \cdot (\Lambda^{-1/2}U)^{-1} \tag{15}$$

Theorem 2. *Every matrix C commuting with all the matrices $D(S)$ of an irreducible representation of a finite group is scalar.**

Because of the preceding theorem, we are always able to take the matrices $D(S)$ as unitary. By hypothesis:

$$D(S) \cdot C = C \cdot D(S) \tag{16}$$

from which:

$$\begin{aligned} C\dagger D\dagger(S) &= D\dagger(S)C\dagger \\ C\dagger D^{-1}(S) &= D^{-1}(S)C\dagger \\ C\dagger D(S^{-1}) &= D(S^{-1})C\dagger \end{aligned}$$

Putting $S^{-1} = R$, we have:

$$D(R)C = CD(R) \qquad \text{and} \qquad D(R)C\dagger = C\dagger D(R)$$

Then the hermitian matrices $(C + C\dagger)$ and $i(C - C\dagger)$ commute with the matrices $D(R)$. It suffices to show then that every hermitian matrix H commuting with the matrices $D(R)$ is scalar.

H can be diagonalized by a unitary matrix U which transforms $D(R)$ into $F(R)$:

$$\Lambda = UHU^{-1} \qquad \text{and} \qquad F(R) = UD(R)U^{-1} \tag{17}$$

It is a consequence of the commutivity hypothesis that:

---

* Λ is said to be scalar if $\Lambda = \lambda E$.

$$\Lambda \cdot F(R) = F(R) \cdot \Lambda \tag{18}$$

If Λ is not scalar, it has at least two unequal elements Λ_{rr} and Λ_{ss}, and (18) then results in:

$$\Lambda_{rr} F_{rs} = F_{rs} \Lambda_{ss}$$

where $\Lambda_{rr} \neq \Lambda_{ss}$ requires that $F_{rs} = 0$. The matrix F is reducible which is contrary to hypothesis.

Corollary. *Every irreducible representation of a finite abelian group is necessarily one-dimensional.*

In fact, every matrix of an irreducible representation of a finite abelian group commutes with all the matrices of the same representation of the group; thus they are scalar matrices. This implies complete reducibility, contrary to hypothesis, unless every matrix is one-dimensional.

Theorem 3. (Schur's Lemma). *If* $\Gamma^1 = D^1(R)$ *and* $\Gamma^2 = D^2(R)$ *are irreducible representations of respective dimensions* m *and* n *of a finite group* G, *and if there exists a matrix* $X(m \times n)$ *such that* $X \cdot D^2(R) = D^1(R) \cdot X$ *for every element* R *of* G: (*a*) X *is the null matrix* $(m \times n)$; *or* (*b*) X *is square* $(m = n)$ *and non-singular and the representation* Γ^2 *is equivalent to the representation* Γ^1.

The hypothesis is:

$$X \cdot D^2(R) = D^1(R) \cdot X \tag{19}$$

Let us take the adjoint of both sides, the matrices $D^1(R)$ and $D^2(R)$ being assumed to be unitary, so that we have:

$$[D^2]^{-1}(R) \cdot X\dagger = X\dagger \cdot [D^1]^{-1}(R)$$

or:

$$D^2(R^{-1}) \cdot X\dagger = X\dagger \cdot D^1(R^{-1})$$

$$D^2(S) \cdot X\dagger = X\dagger \cdot D^1(S) \tag{20}$$

If we multiply (19) on the right by $X\dagger S$ and (20) on the left by X and on the right by S, we see that:

$$XX\dagger D^1(S) = D^1(S)XX\dagger \tag{21}$$

Since $XX\dagger$ commutes with the unitary matrices $D^1(S)$ forming an irreducible representation of G, then it is a scalar matrix and equal to λE.

(a) Γ^1 and Γ^2 are equivalent ($m = n$) and $\det(XX\dagger) = \lambda^n$. If $\lambda \neq 0$, X^{-1} exists and X is a non-singular square matrix. If $\lambda = 0$, X is the null matrix.

(b) If $m \neq n$, the matrix X is not square, and we easily see that it is the null matrix.

Theorem 4. *Being given a group G of order g with elements $M, N, \ldots, R, S, \ldots$ and two irreducible representations Γ^γ and $\Gamma^{\gamma'}$, of respective dimensions d_γ and $d_{\gamma'}$, we have*

$$\sum_R D^{\gamma}_{ij}(R) \cdot D^{\gamma'}_{kl}(R) = \delta_{ik} \cdot \delta_{jl} \cdot \delta_{\gamma\gamma'} \cdot \frac{g}{d_\gamma} \tag{22}$$

where $\delta_{i,j}$ is the Kronecker delta, defined by:

$$\delta_{i,j} = 1 \quad \text{when} \quad i = j$$

$$\delta_{i,j} = 0 \quad \text{when} \quad i \neq j$$

and where the summation is taken over all operations R in the group.

We are, of course, assuming that the representations are unitary. It is impossible to multiply square matrices whose orders are different, but it is possible to form the $(d_\gamma \times d_{\gamma'})$ matrix A by considering the product:

$$A = \sum_R D^\gamma(R) \cdot B \cdot D\dagger^{\gamma'}(R)$$

where B is an arbitrary $(d_\gamma \times d_{\gamma'})$ matrix.

Multiplying A on the left by $D^\gamma(S)$, this becomes:

$$D^{\gamma}(S)\cdot A = \sum_{R} D^{\gamma}(S)D^{\gamma}(R)\cdot B\cdot D\dagger^{\gamma'}(R)$$

$$D^{\gamma}(S)\cdot A = \sum_{R} D^{\gamma}(S)D^{\gamma}(R)\cdot B\cdot D\dagger^{\gamma'}(R)\cdot D\dagger^{\gamma'}(S)D^{\gamma'}(S) \quad (23)$$

and $D^{\gamma'}(S)$ being unitary, we have $D\dagger^{\gamma'}(S)D^{\gamma'}(S) = E$, so that (23) becomes:

$$D^{\gamma}(S)\cdot A = \sum_{R} D^{\gamma}(SR)\cdot B\cdot D\dagger^{\gamma'}(SR)\cdot D^{\gamma'}(S)$$

from which:

$$D^{\gamma}(S)\cdot A = A\cdot D^{\gamma'}(S) \qquad \text{(for every } S \text{ in } G) \quad (24)$$

We can then apply Schur's lemma to A, as follows:

1. If the representations Γ^{γ} and $\Gamma^{\gamma'}$ are non-equivalent, A is the null matrix, and:

$$A_{im} = \sum_{R}\sum_{jl} D^{\gamma}_{ij}(R)\cdot B_{jl}\cdot D^{\dagger\gamma'}_{lm}(R) = 0 \quad (25)$$

Now, B is a completely arbitrary matrix; choose it so that its terms are zero, except for $B_{jl} = 1$. Then (25) becomes:

$$\sum_{R} D^{\gamma}_{ij}(R)\cdot D^{\dagger\gamma'}_{lm}(R) = 0$$

and taking the complex conjugate:

$$\sum_{R} D^{*\gamma}_{ij}(R)\cdot D^{\gamma'}_{ml}(R) = 0 \quad (26)$$

2. If the representations Γ^{γ} and $\Gamma^{\gamma'}$ are equivalent, then A is a scalar matrix, $A_{im} = \delta_{im}\cdot\lambda$, and:

$$A_{im} = \delta_{im}\cdot\lambda = \sum_{R} D^{\gamma}_{ij}(R)\cdot B_{jl}\cdot D^{\dagger\gamma}_{lm}(R)$$

With a convenient choice of B_{jl}, we can write:

$$\delta_{im}\cdot\lambda = \sum_{R} D^{\gamma}_{ij}(R)\cdot D^{\dagger\gamma'}_{lm}(R) \quad (27)$$

Letting $i = m$ and summing the two sides of (27) over i (i runs from 1 to d_{γ}), the left side gives:

$$\sum_{i=1}^{d_{\gamma}} \delta_{ii}\cdot\lambda = \lambda\cdot d_{\gamma}$$

while the right becomes:

$$\sum_R \sum_{i=1}^{d_\gamma} D_{ii}^{\dagger\gamma}(R) \cdot D_{ij}^{\gamma}(R) = \sum_R (E)_{lj} = g \cdot \delta_{lj}$$

from which:

$$\lambda \cdot d_\gamma = g \cdot \delta_{lj}$$

Equation (25) becomes, by taking complex conjugate quantities:

$$\sum_R D_{ij}^{*\gamma}(R) \cdot D_{ml}^{\gamma}(R) = \delta_{im} \cdot \delta_{jl} \cdot \frac{g}{d_\gamma} \tag{28}$$

Finally, Eqs. (26) and (28) can be combined to give Eq. (22), which is thus established.

5. DIRECT PRODUCT OF TWO REPRESENTATIONS

1. We define the *direct product* of an $(m \times m)$ matrix A with an $(n \times n)$ matrix B as the $(mn \times mn)$ matrix C such that:

$$A_{jk} B_{pq} = C_{jp,kq}$$

Thus, the direct product of a third-order and a second-order matrix is a sixth-order one:

$$A \times B = \begin{vmatrix} a_{11} & a_{12} & a_{13} \\ a_{21} & a_{22} & a_{23} \\ a_{31} & a_{32} & a_{33} \end{vmatrix} \times \begin{vmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{vmatrix} = \begin{vmatrix} a_{11}b_{11} & a_{11}b_{12} & a_{12}b_{11} & a_{12}b_{12} & a_{13}b_{11} & a_{13}b_{12} \\ a_{11}b_{21} & a_{11}b_{22} & . & . & . & . \\ a_{21}b_{11} & . & . & . & . & . \\ . & . & . & . & . & . \end{vmatrix}$$

2. Properties of the direct product:

   (a) It is associative.

   (b) It is not commutative.

$$A \times B \neq B \times A$$

   (c) Let A_1 and A_2 be two $(m \times m)$ matrices and B_1 and B_2 be two $(n \times n)$ matrices. Form the product:

$$[(A_1 \times B_1)\cdot(A_2 \times B_2)]_{jp,kq} = \sum_{\alpha\beta} (A_1 \times B_1)_{jp,\alpha\beta}(A_2 \times B_2)_{\alpha\beta,kq}$$

which becomes:

$$\begin{aligned}\sum_{\alpha\beta} (A_1 \times B_1)_{jp,\alpha\beta}(A_2 \times B_2)_{\alpha\beta,kq} &= \sum_{\alpha\beta} (A_1)_{j\alpha}(B_1)_{p\beta}(A_2)_{\alpha k}(B_2)_{\beta q} \\ &= (A_1A_2)_{jk}(B_1B_2)_{pq} \\ &= [(A_1\cdot A_2) \times (B_1\cdot B_2)]_{jp,kq}\end{aligned}$$

Then:

$$(A_1 \times B_1)\cdot(A_2 \times B_2) = (A_1\cdot A_2) \times (B_1\cdot B_2) \qquad (29)$$

The consequences of the equality (29) are interesting. For example, suppose A and B are two regular, square matrices of dimensions m and n:

$$(A \times B)\cdot(A^{-1} \times B^{-1}) = AA^{-1} \times BB^{-1} = E_m \times E_n = E_{mn}$$

The matrix $A \times B$ is thus regular and has an inverse $A^{-1} \times B^{-1}$. We can also verify that $(A \times B)\dagger = A\dagger \times B\dagger$. Finally, if we take two unitary matrices U and V, we have:

$$\begin{aligned}(U \times V)\dagger(U \times V) &= (U\dagger \times V\dagger)(U \times V) \\ &= U\dagger U \times V\dagger V = E_{mn}\end{aligned}$$

and $U \times V$ is also unitary.

3. Returning to the representations of a group, if Γ^1 is an m-dimensional representation with matrices $D^1(S)$ and Γ^2 is n-dimensional with matrices $D^2(S)$, the direct product $D^1(S) \times D^2(S)$ is also a representation Γ of the group:

$$\Gamma = \Gamma^1 \times \Gamma^2$$

Also, the matrix $D^1(S) \times D^2(S)$ is regular since $D^1(S)$ and $D^2(S)$ are both regular, and in addition:

$$\begin{aligned}&[D^1(R) \times D^2(R)]\cdot[D^1(S) \times D^2(S)] \\ &\quad = [D^1(R)\cdot D^1(S)] \times [D^2(R)\cdot D^2(S)] = D^1(RS) \times D^2(RS)\end{aligned}$$

Note. It can be shown ([3], Chap. 3, p. 69) that:

$$\Gamma = \Gamma^1 \times \Gamma^2 = \Gamma^2 \times \Gamma^1$$

6. CHARACTERS OF THE REPRESENTATION OF A FINITE GROUP

It is a tedious job to find the irreducible representations constituting the completely reducible representation equivalent to a known representation Γ of a finite group G. Fortunately, for physical applications, it suffices to find the traces of the matrices.

Definition. *The numbers χ_R expressing the traces of the matrices $D(R)$ forming the representation Γ of the group G are called the characters of the representation Γ:*

$$\chi_R = \sum_i D_{ii}(R)$$

Some immediate consequences of this definition are:

(a) Two equivalent representations of the same group have the same characters, since the traces of two equivalent matrices are equal.

(b) All the elements in a given class of a group have the same character, for if A is an element of a class, the other elements have the form $X^{-1}AX$ and the corresponding matrices have equal traces.

(c) The character of the representation of the unit element E of the group equals the dimensionality of the representation since the matrix corresponding to E is the unit matrix.

Properties of Characters. Concerning this topic, we state four fundamental theorems. Consider a finite group G of order g comprising p classes $\mathcal{C}_1 = E, \mathcal{C}_2, \ldots, \mathcal{C}_p$.

Theorem I. *The number of irreducible representations of a finite group is equal to the number p of classes.*

Theorem II. *The sum of the squares of the dimensions d_γ of the irreducible representations of a finite group equals the order g of the group:*

$$\sum_{\gamma=1}^{p} d_\gamma^2 = g$$

We will omit the proofs of these theorems, which are lengthy. (See [3], Chap. 3, p. 83.)

Theorem III. *The characters χ_R^γ and $\chi_R^{\gamma'}$ associated with two irreducible representations Γ^γ and $\Gamma^{\gamma'}$ of the same finite group are connected by the orthogonality relation:*

$$\sum_R \chi_R^{*\gamma} \cdot \chi_R^{\gamma'} = g \cdot \delta_{\gamma\gamma'} \qquad (30)$$

The relation (30) is an immediate consequence of Eq. (22); in that equation put $i = j$, $k = l$, and sum over i and k, obtaining:

$$\sum_R \chi_R^{*\gamma} \cdot \chi_R^{\gamma'} = \delta_{\gamma\gamma'} \sum_{ik} (\delta_{ik})^2 \cdot \frac{g}{d_\gamma}$$

But:

$$\sum_{ik} (\delta_{ik})^2 = d_\gamma$$

from which we obtain (28).

Theorem IV. *If χ^{Γ^1} is the character of a representation Γ^1 of the group G and χ^{Γ^2} is the character of a representation Γ^2 of G, the character χ^Γ of the direct product $\Gamma = \Gamma^1 \times \Gamma^2$ is equal to the product $\chi^{\Gamma^1} \cdot \chi^{\Gamma^2}$.*

Thus:

$$[D^\Gamma(R)]_{jp,kq} = [D^1(R)]_{jk} [D^2(R)]_{pq}$$

and:

$$\sum_{jp} [D^\Gamma(R)]_{jp,jp} = \sum_j [D^1(R)]_{jj} \sum_p [D^2(R)]_{pp}$$

which is equivalent to:

$$\chi^\Gamma = \chi^{\Gamma^1} \cdot \chi^{\Gamma^2} \qquad (31)$$

The first three theorems and the notion of the function of a class, which we have not considered here ([13], Chap. 4, Secs. 48 and 49), enables us to find the irreducible representations of a given finite group and thus construct the character tables. This has been done for the point groups and the space groups of crystallography [9]. Unfortunately, the symbols vary among authors. One-dimensional irreducible representations are said to be nondegenerate and those of higher dimension are degenerate.

7. DECOMPOSITION OF A REPRESENTATION. AN EXAMPLE

1. Given a representation Γ' of a finite group G, it is essential in applications to know the nature and number of irreducible representations constituting the completely reduced representation Γ equivalent to Γ'. The use of characters permits a simple solution of the problem, if we initially form the table for all the possible irreducible representations of the group G.

2. The characters $X_R^{\Gamma'}$ and X_R^{Γ} of the representations Γ' and Γ are identical since the matrices forming the representations are equivalent. Let us suppose that the irreducible representations $\Gamma^1, \Gamma^2, \ldots, \Gamma^\gamma, \ldots, \Gamma^\rho$ appear $n_1, n_2, \ldots, n_\gamma, \ldots, n_\rho$ times, respectively, in Γ (n_γ is a positive integer or zero), so that we have:

$$\chi_R^{\Gamma'} = \chi_R^{\Gamma} = \sum_{\gamma=1}^{\rho} n_\gamma \chi_R^\gamma \tag{32}$$

χ_R^γ being the character of the element R in the irreducible representation Γ^γ.

Multiply equation (32) by $\chi_R^{*\gamma'}$ and sum over all the elements R of the group G:

$$\sum_R \chi_R^{\Gamma} \chi_R^{*\gamma'} = \sum_R \sum_\gamma n_\gamma \chi_R^\gamma \chi_R^{*\gamma'}$$

By virtue of Eq. (30):

$$\sum_R \chi_R^{\Gamma} \chi_R^{*\gamma'} = \sum_\gamma n_\gamma \delta_{\gamma\gamma'} g = n_{\gamma'} \cdot g$$

giving:

$$n_\gamma = \frac{1}{g} \sum_R \chi_R^{\Gamma} \cdot \chi_R^{*\gamma} \tag{33}$$

Since the characters of the elements of the same class are equal, Eq. (33) transforms into:

$$n_\gamma = \frac{1}{g} \sum_{j=1}^{\rho} g_j \chi_j^{\Gamma} \cdot \chi_j^{*\gamma} \tag{34}$$

Here the summation is with respect to different classes of the group, g_j designating the number of elements in class $\mathfrak{C}_j$. Formula (34) readily permits us to find the composition of Γ, the completely reduced representation equivalent to the given representation Γ'.

Example. Let C_{3v} denote the crystallographic point group of order $g = 6$. The symmetry elements are a three-fold axis of rotation A_3 and three symmetry-planes containing this axis. The symmetry operations are (1) E, the identity, (2)–(3) C_3 and C_3^2, rotations of $2\pi/3$ and $4\pi/3$ about the ternary axis, and (4)–(6) reflections σ_v, σ_v' and σ_v'', reflections in the three symmetry-planes. The classes are then (E), (C_3, C_3^2), and $(\sigma_v, \sigma_v', \sigma_v'')$. Since there are three classes, there are three irreducible representations (Theorem I, Sec. 6). Also, Theorem II, Sec. 6, gives the degree of these representations (1, 1, and 2), and the character table is [9]:

(T)		E	$2C_3$	$3\sigma_v$	
	χ^{γ_1}	1	1	1	$g = 6$
	$\chi^{\gamma_1'}$	1	1	−1	$g_E = 1$
	χ^{γ_2}	2	−1	0	$g_{C_3} = 2$
					$g_{\sigma_v} = 3$

Consider now the ammonia molecule NH_3. Taking the ternary axis through the N atom:

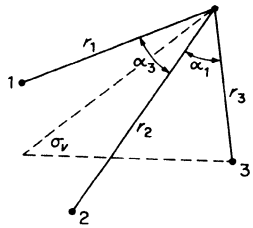


FIG. 1

and the symmetry planes through this axis and each of the H atoms, we see that the molecule is invariant under the operations of the group C_{3v}. The ensemble of coordinates r_1, r_2, r_3, α_1, α_2, α_3 constitutes a sixth-order representation of the group C_{3v}, since they transform among themselves in accordance with the operations of the group. Let us find the irreducible representations composing the equivalent completely reduced representation. We note that:

E leaves invariant all 6 coordinates, so that $\chi_E^{\Gamma} = 6$

C_3 interchanges all 6 coordinates, so that $\chi_{C_3}^{\Gamma} = 0$

σ_v, σ_v', σ_v'' leave 2 coordinates invariant, giving $\chi_{\sigma_v}^{\Gamma} = 2$

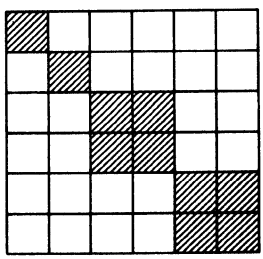
From Eq. (34):

$$n_\gamma = \tfrac{1}{6}[6\chi_E^{*\gamma} + 6\chi_{\sigma_v}^{*\gamma}]$$

which gives:

$$n_{\gamma_1} = 2 \qquad n_{\gamma_1'} = 0 \qquad n_{\gamma_2} = 2$$

Every matrix of the representation Γ is of the form:



The two linear combinations $S_1 = r_1 + r_2 + r_3$ and $S_4 = \alpha_1 + \alpha_2 + \alpha_3$ belong to the irreducible, nondegenerate representation γ_1, since:

E_1 applied to $r_1 + r_2 + r_3$ gives $r_1 + r_2 + r_3$

C_3 applied to $r_1 + r_2 + r_3$ gives $r_1 + r_2 + r_3$

σ_v applied to $r_1 + r_2 + r_3$ gives $r_1 + r_2 + r_3$

The combinations $S_2 = 2r_1 - r_2 - r_3$ and $S_3 = 2r_2 - r_3 - r_1$ belong to the degenerate representation γ_2, since:

$$\begin{cases} ES_2 = S_2 \\ ES_3 = S_3 \end{cases} \quad \begin{cases} C_3S_2 = S_3 \\ C_3S_3 = -S_2 - S_3 \end{cases} \quad \begin{cases} \sigma_vS_2 = S_3 \\ \sigma_vS_3 = S_2 \end{cases} \tag{35}$$

The traces of the matrices of transformation (35) are 2, −1, 0, which are the characters of the representation γ_2 (see Table T). Further, $S_4 = 2\alpha_1 - \alpha_2 - \alpha_3$ and $S_5 = 2\alpha_2 - \alpha_3 - \alpha_1$ are also combinations belonging to the irreducible degenerate representation γ_2.

The six combinations $S_1, S_2, \ldots, S_6$ then form the basis of the completely reduced six-dimensional representation Γ of C_{3v}. To within a normalization factor, these six combinations constitute the "symmetric coordinates" of the molecule NH_3. We shall not give here the rules which permit the automatic determination of the combinations S_i for any arbitrary finite group [9].

For the same example, let us consider the idea of the direct product of two representations. From Table T and Eq. (31), we can see immediately that:

$$\Gamma^{\gamma_1} \times \Gamma^{\gamma_1} = \Gamma^{\gamma_1}$$
$$\Gamma^{\gamma_1'} \times \Gamma^{\gamma_1'} = \Gamma^{\gamma_1'}$$
$$\Gamma^{\gamma_1} \times \Gamma^{\gamma_1'} = \Gamma^{\gamma_1'}$$
$$\Gamma^{\gamma_1} \times \Gamma^{\gamma_2} = \Gamma^{\gamma_2}$$
$$\Gamma^{\gamma_1'} \times \Gamma^{\gamma_2} = \Gamma^{\gamma_2}$$

But we notice that $\Gamma^{\gamma_2} \times \Gamma^{\gamma_2}$ is not irreducible; in fact, the characters are 4, 1, 0 and Eq. (34) gives

$$n_\gamma = \tfrac{1}{6}[4\chi_E^{*\gamma} + 2\chi_{C_3}^{*\gamma}]$$

from which:

$$n_{\gamma_1} = 1, \qquad n_{\gamma_1'} = 1, \qquad n_{\gamma_2} = 1$$

Then:

$$\Gamma^{\gamma_2} \times \Gamma^{\gamma_2} = \Gamma^{\gamma_1} + \Gamma^{\gamma_1'} + \Gamma^{\gamma_2}$$

3

Space groups

1. THE LINEAR GROUP OF EUCLIDEAN SPACE E_3

Let us consider a transformation of the linear group which associates with the point $P(x_1, x_2, x_3)$ of E_3 the transformed point $P'(x_1', x_2', x_3')$ of E_3. This transformation can be expressed by the three equations:

$$\begin{cases} x_1' = \alpha_{11}x_1 + \alpha_{12}x_2 + \alpha_{13}x_3 + t_1 \\ x_2' = \alpha_{21}x_1 + \alpha_{22}x_2 + \alpha_{23}x_3 + t_2 \\ x_3' = \alpha_{31}x_1 + \alpha_{32}x_2 + \alpha_{33}x_3 + t_3 \end{cases} \tag{1}$$

the coordinates adopted in this chapter being Cartesian, unless otherwise stated.

If we put $\boldsymbol{r} = \boldsymbol{OP}$ and $\boldsymbol{r}' = \boldsymbol{OP}'$, the Eqs. (1) are equivalent to the vectorial equation:

$$\boldsymbol{r}' = \alpha \cdot \boldsymbol{r} + \boldsymbol{t} = (\alpha, \boldsymbol{t})\boldsymbol{r} = S \cdot \boldsymbol{r} \tag{2}$$

where $S = (\alpha, \boldsymbol{t})$, α is a square 3×3 *regular* matrix, and $\boldsymbol{t}$ is a vector translation. The operator $S = (\alpha, \boldsymbol{t})$ is associated with the linear transformation which converts $\boldsymbol{r}$ into $\boldsymbol{r}'$. It is evident that the ensemble of operators S forms an infinite group.

Properties of the Group of Operators.

(a) $E = (I, \boldsymbol{O})$ is the unit operator, where I is the unit 3×3 matrix.

(b) The composition law: consider two linear transformations:

$$\boldsymbol{r}_1 = S_1\boldsymbol{r} = (\alpha_1, \boldsymbol{t}_1)\boldsymbol{r} = \alpha_1\boldsymbol{r} + \boldsymbol{t}_1$$

$$\boldsymbol{r}_2 = S_2\boldsymbol{r}_1 = (\alpha_2, \boldsymbol{t}_2)\boldsymbol{r}_1 = \alpha_2\boldsymbol{r}_1 + \boldsymbol{t}_2$$

Then:

$$\boldsymbol{r}_2 = S_2S_1\boldsymbol{r} = \alpha_2[\alpha_1\boldsymbol{r} + \boldsymbol{t}_1] + \boldsymbol{t}_2 = \alpha_2\alpha_1\boldsymbol{r} + \alpha_2\boldsymbol{t}_1 + \boldsymbol{t}_2$$

from which:

$$S_2S_1 = (\alpha_2\alpha_1, \alpha_2\boldsymbol{t}_1 + \boldsymbol{t}_2) \tag{3}$$

Particular case: the powers of S:

$$S^2 = (\alpha, \boldsymbol{t})(\alpha, \boldsymbol{t}) = (\alpha^2, \alpha\boldsymbol{t} + t) = (\alpha^2, (\alpha + 1)\boldsymbol{t})$$

$$S^3 = (\alpha^3, (\alpha^2 + \alpha + 1)\boldsymbol{t}) \tag{4}$$

$$S^n = (\alpha^n, (\alpha^{n-1} + \alpha^{n-2} + \ldots + 1)\boldsymbol{t})$$

(c) The inverse of S.

If $S^{-1} = (\beta, \boldsymbol{\tau})$, then:

$$SS^{-1} = (\alpha, \boldsymbol{t})(\beta, \boldsymbol{\tau}) = (I, \boldsymbol{O}) = E$$

from which:

$$\alpha\beta = 1 \qquad \text{and} \qquad 0 = \alpha\boldsymbol{\tau} + \boldsymbol{t}$$

Finally, if $S = (\alpha, \boldsymbol{t})$, its inverse is:

$$S^{-1} = (\alpha^{-1}, -\alpha^{-1}\boldsymbol{t})$$

Theorem. *The subgroup of translations is an invariant subgroup of the linear group.*

Let $\Gamma = (I, \boldsymbol{t})$ be a translation operator; it suffices to show that if $S = (\alpha, \boldsymbol{\tau})$, we have:

$$\Gamma_1 = S^{-1}\Gamma S$$

Γ_1 also being a translation operator.

Then:

$$\Gamma \cdot S = (I, \boldsymbol{t})(\alpha, \boldsymbol{\tau}) = (\alpha, \boldsymbol{\tau} + \boldsymbol{t})$$

$$S^{-1}\Gamma S = (\alpha^{-1}, -\alpha^{-1}\boldsymbol{\tau})(\alpha, \boldsymbol{\tau} + \boldsymbol{t})$$

from which:

$$\Gamma_1 = (I, \alpha^{-1}\boldsymbol{\tau} + \alpha^{-1}\boldsymbol{t} - \alpha^{-1}\boldsymbol{\tau}) = (I, \alpha^{-1}\boldsymbol{t}) \tag{5}$$

2. THE SYMMETRY GROUPS OF THE SPACE E_3

The ensemble of linear transformations which leaves invariant the distance between two points in E_3 forms a symmetry subgroup of E_3. In Cartesian coordinates, it is well known that the matrix α is *real* and *orthogonal*; that is:

$$S = (\alpha, \boldsymbol{t}) \qquad \text{with} \qquad \tilde{\alpha} = \alpha^{-1}$$

Further, any real orthogonal matrix can be transformed into:

$$\alpha' = \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & \cos\varphi & \sin\varphi \\ 0 & -\sin\varphi & \cos\varphi \end{pmatrix} \tag{6}$$

through the use of another real, orthogonal matrix (geometrically, we accomplish the transformation of orthonormal reference frames such that the axis Ox_3 of the new frame is parallel to the axis of rotation associated with α). The matrices α and α' are equivalent, so that their traces are equal:

$$\text{trace } \alpha = \text{trace } \alpha' = \pm 1 + 2\cos\varphi \tag{7}$$

and similarly, their determinants are equal:

$$\det \alpha = \det \alpha' = \pm 1$$

If $\det \alpha = +1$, the matrix is associated with a *proper* rotation; if $\det \alpha = -1$, the rotation is *improper*. Note that the inversion is an improper rotation for which $\varphi = \pi$ (the geometry of these operations is discussed in [7]).

If we use oblique coordinates to represent the symmetry group of E_3, the corresponding matrices β are non-orthogonal, since they are obtained from the matrices α by a non-orthogonal transforming matrix. But the matrices β are equivalent to the matrices α and we always have:

$$\text{trace } \beta = \text{trace } \alpha \qquad \text{and} \qquad \det \beta = \det \alpha = \pm 1 \tag{8}$$

Evidently, the subgroup of translations is, in this case, again an invariant subgroup of the symmetry group of E_3.

Remark. The subgroup of translations and the subgroup of proper rotations form the displacement group of E_3. Let us recall that the ensemble of improper rotations does not form a group.

3. THE INFINITE SPACE GROUP OF A CRYSTAL LATTICE

1. **Definition.** An ideal crystalline lattice consists of the infinite ensemble of points P in E_3 such that $\boldsymbol{r}_n = \boldsymbol{OP}$, where:

$$\boldsymbol{r}_n = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \tag{9}$$

The origin O is any arbitrary lattice point; $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ are three non-coplanar vectors forming the basis; n_1, n_2, n_3 are integers (positive, negative, or zero).

2. The ensemble of symmetry operations of E_3 which transforms the lattice into itself constitutes the infinite space group associated with the crystal lattice.

If $S = (\alpha, \boldsymbol{t})$ represents an operation of G, we must have:

$$\boldsymbol{r}'_n = S\boldsymbol{r}_n = n'_1\boldsymbol{a}_1 + n'_2\boldsymbol{a}_2 + n'_3\boldsymbol{a}_3 \tag{10}$$

the n'_i again being integers.

3. The ensemble of operations of G represented by $\Gamma = (I, \boldsymbol{r}_n)$ forms the subgroup of *primitive translations* of G.

We now state the following fundamental theorem:

The subgroup of primitive translations of G is an invariant subgroup.

Let $\Gamma = (I, \boldsymbol{r}_n)$ be a primitive translation; the transformation of Γ by an operation of G represented by $S = (\alpha, \boldsymbol{t})$ is a primitive translation $\Gamma' = (I, \boldsymbol{r}'_n)$. Equation (5) permits us to write:

$$\Gamma' = (I, \boldsymbol{r}'_n) = (I, \alpha^{-1}\boldsymbol{r}_n) = (\alpha^{-1}, -\alpha^{-1}\boldsymbol{t})(I, \boldsymbol{r}_n)(\alpha, \boldsymbol{t}) \quad (11)$$

This theorem imposes severe restrictions on the matrices α and the translation vectors $\boldsymbol{t}$ of the operators S. In the space E_3, there exists only a finite number (230) of possible space groups.

4. Restrictions on the Matrices α. For the moment, let us go to an oblique coordinate system determined by the three non-coplanar vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$. In rectangular coordinates, the matrix α represents a given rotation; in oblique coordinates, the same rotation is specified by a matrix β, equivalent to α. Using (10):

$$\boldsymbol{r}'_n = \beta \boldsymbol{r}_n \qquad \text{with} \qquad \begin{aligned} \boldsymbol{r}_n &= n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \\ \boldsymbol{r}'_n &= n'_1\boldsymbol{a}_1 + n'_2\boldsymbol{a}_2 + n'_3\boldsymbol{a}_3 \end{aligned} \quad (12)$$

The vectorial equation, (12) is equivalent to:

$$\begin{aligned} n'_1 &= \beta_{11}n_1 + \beta_{12}n_2 + \beta_{13}n_3 \\ n'_2 &= \beta_{21}n_1 + \beta_{22}n_2 + \beta_{23}n_3 \\ n'_3 &= \beta_{31}n_1 + \beta_{22}n_2 + \beta_{33}n_3 \end{aligned}$$

Since the n_i and the n'_i are whole numbers, then the β_{ij} must be likewise. The trace of the matrix β, and consequently that of α, are integers, and in accordance with Eq. (7):

$$\pm 1 + 2\cos\varphi = \text{an integer}$$

which means that the axes of rotation can only be of order $n = 1, 2, 3, 4, 6$. Similar considerations show that these axes must lie along the directions of the lattice-vectors (See [10], Chap. 2, Sec. 2).

5. Restrictions on the Translations t. Since the matrices α are orthogonal and since $\varphi = 2\pi/n$ (n being a whole number), there always exists an integer m such that $\alpha^m = 1$. It is easy to verify that $m = n$ for matrices associated with proper rotations or with improper rotations when n is even, while $m = 2n$ for an improper rotation with n odd.*

Consider, then, an operator $S(\alpha, \boldsymbol{t})$ of G. It can be expressed:

$$S^m = [\alpha^m, (\alpha^{m-1} + \alpha^{m-2} + \ldots + I)\boldsymbol{t}]$$

or:

$$S^m = (I, \{\alpha\}\boldsymbol{t}) \qquad \text{where} \qquad \{\alpha\} = \alpha^{m-1} + \alpha^{m-2} + \ldots + I$$

Then $\{\alpha\}\boldsymbol{t}$ must be a primitive lattice translation, which imposes restrictions on the possible vectors $\boldsymbol{t}$. Let us put:

$$\boldsymbol{t} = \boldsymbol{v}(\alpha) + \boldsymbol{r}_n$$

where the vector $\boldsymbol{v}(\alpha)$ represents a *non-primitive translation* associated with the matrix:

$$\boldsymbol{v}(\alpha) = v_1\boldsymbol{a}_1 + v_2\boldsymbol{a}_2 + v_3\boldsymbol{a}_3 \qquad 0 \leqslant v_i < 1 \qquad i = 1, 2, 3$$

Since $\{\alpha\}\boldsymbol{t}$ must be a primitive translation, this results in $\{\alpha\}\boldsymbol{v}(\alpha)$ also being a primitive translation, thus imposing conditions on the vector $\boldsymbol{v}(\alpha)$. We shall not consider these in detail; they lead to the study of the 230 possible crystalline space groups ([10], Chap. 2, Sec. 6).

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* In considering Eq. (6), we find that the eigenvalues of α' are ± 1, $e^{i\phi}$, and $e^{-i\phi}$. Hence, the diagonal matrix $\Lambda = (\pm 1, e^{i\phi}, e^{-i\phi})$ is equivalent to the matrix α'. Now $\Lambda^m = 1$ if $(\pm 1)^m = 1$ and $(e^{i\phi})^m = 1$, and α'^m will be equivalent to the unit matrix Λ^m, and will be a unit matrix itself, since:

$$\alpha'^{m}_{ij} = \sum_{lk} (P^{-1})_{il}\delta_{lk}(P)_{kj} = \sum_{l} (P^{-1})_{il}P_{lj} = (I)_{ij}$$

6. Concept of a Factor Group. Consider $S = (\alpha, \boldsymbol{t}) = [\alpha, \boldsymbol{v}(\alpha) + \boldsymbol{r}_n]$ and put $\alpha \boldsymbol{r}'_n = \boldsymbol{r}_n$. We can write:

$$S = [\alpha, \boldsymbol{v}(\alpha)] \cdot (I, \boldsymbol{r}'_n) = (I, \boldsymbol{r}_n) \cdot [\alpha, \boldsymbol{v}(\alpha)]$$

Since the subgroup of translations is an invariant subgroup of G, we can consider the group as the product of the translation subgroup Γ and the factor group G/Γ. Here, the factor group has elements $[\alpha, \boldsymbol{v}(\alpha)]$. The operations of the factor group will correspond to screw axes and glide planes in the crystal $[\Gamma]$.

7. Concept of a Point Group. The elements $(\alpha, \boldsymbol{O})$ form a point group which is simply isomorphic to the factor group with elements $[\alpha, \boldsymbol{v}(\alpha)]$. We have:

$$(\alpha_1, \boldsymbol{O})(\alpha_2, \boldsymbol{O}) = (\alpha_1 \alpha_2, \boldsymbol{O})$$

The number of point groups with axes of rotation of order 1, 2, 3, 4, or 6 is obviously finite. It can be demonstrated that there are 32 of these groups (See Ref. [10], Chap. 2, Sec. 4). We refer the reader to specialized works for their description, the notation used, and the character tables [9].

8. The Bravais Lattices. Let us recall again that the subgroup of primitive translations $(I, \boldsymbol{r}_n)$ is an invariant subgroup of the space group G. Thus, if α is the matrix associated with the operation S of G, and $\boldsymbol{r}_n$ is a primitive translation, then $\alpha \boldsymbol{r}_n$ is also a possible primitive translation. Further, given a point group with elements $(\alpha, 0)$, restrictions will be imposed on the primitive translations associated with the point group. It has been shown (Bravais) that there exist only 14 possible lattices, customarily grouped into 7 systems.

Remark. There are 73 space groups for which the factor group $[\alpha, \boldsymbol{v}(\alpha)]$ is identical to the point group $(\alpha, \boldsymbol{O})$. These groups, called symmomorphic, do not have any non-primitive (or fractional) translations. The remaining 157 space groups have non-zero vectors $\boldsymbol{v}(\alpha)$.

4. THE BORN CYCLIC CONDITIONS

Space groups are, in fact, infinite groups and the fundamental theorems of Sec. 4, Chap. 2 cannot be applied. Let us impose the cyclic conditions of Born and assume that every crystal is cyclic. Let:

$$\boldsymbol{r}_n = n_1\boldsymbol{a}_1 + n_2\boldsymbol{a}_2 + n_3\boldsymbol{a}_3 \tag{13}$$

the numbers n_1, n_2, n_3 being integers such that:

$$0 \leqslant n_1 < N_1 \qquad 0 \leqslant n_2 < N_2 \qquad 0 \leqslant n_3 < N_3 \tag{14}$$

where N_1, N_2, N_3 are generally very large whole numbers. The crystalline lattice includes then only the $N = N_1N_2N_3$ distinct translations. The space group associated with the crystal is now *finite*; the hypothesis (14) means that the translation $N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2 + N_3\boldsymbol{a}_3$ is equivalent to the identity translation $(I, \boldsymbol{O})$. The finite group Γ of primitive translations should then satisfy:

$$(I, \boldsymbol{a}_1)^{N_1} = (I, \boldsymbol{a}_2)^{N_2} = (I, \boldsymbol{a}_3)^{N_3} = (I, \boldsymbol{O}) \tag{15a}$$

We note in addition that every function $f(\boldsymbol{r})$ associated with the lattice points of the crystal will also satisfy the Born boundary conditions. That is:

$$f(\boldsymbol{r} + \boldsymbol{A}) = f(\boldsymbol{r}) \tag{15b}$$

if:

$$\boldsymbol{A} = N_1\boldsymbol{a}_1 + N_2\boldsymbol{a}_2 + N_3\boldsymbol{a}_3$$

5. IRREDUCIBLE REPRESENTATIONS OF THE FINITE GROUP OF TRANSLATIONS. THE RECIPROCAL LATTICE

The group Γ of translations is the direct product of three groups whose elements are $(I, \boldsymbol{a}_i)$ and its powers, $(i = 1, 2, 3)$, since the translations $n_i\boldsymbol{a}_i$ commute among themselves. We then assume that the irreducible representations of Γ are the product of the irreducible representations of the constituent

groups. The group $(I, \boldsymbol{a}_1)^{n_1}$, $0 \leqslant n_1 < N_1$ is abelian, so that every representation is one-dimensional.

We shall use the relation $(I, \boldsymbol{a}_1)^{N_1} = (I, \boldsymbol{O})$; if $D[(I, \boldsymbol{a}_1)] = c$ is the representation value associated with $(I, \boldsymbol{a}_1)$, then $c^{N_1} = 1$, from which:

$$c = \exp(2\pi i p_1/N_1), \qquad p_1 = 0, 1, 2, \ldots, (N_1 - 1)$$

The representation value associated with the element $(I, n_1\boldsymbol{a}_1)$ will then be:

$$D[(I, n_1\boldsymbol{a}_1)] = \exp\left(2\pi i \frac{n_1 p_1}{N_1}\right)$$

and the value for the general element $(I, \boldsymbol{r}_n)$ will be:

$$D[(I, \boldsymbol{r}_n)] = \exp\left[2\pi i \left(\frac{n_1 p_1}{N_1} + \frac{n_2 p_2}{N_2} + \frac{n_3 p_3}{N_3}\right)\right] \tag{16}$$

Let us introduce a vector $\boldsymbol{k}$ defined by:

$$\boldsymbol{k} = k_1\boldsymbol{b}_1 + k_2\boldsymbol{b}_2 + k_3\boldsymbol{b}_3 \tag{17}$$

the vectors $\boldsymbol{b}_i$ $(i = 1, 2, 3)$ being related to the basis vectors $\boldsymbol{a}_i$ by the equations:

$$\boldsymbol{a}_i \cdot \boldsymbol{b}_j = \delta_{ij} \qquad (i, j = 1, 2, 3) \tag{18}$$

and the numbers k_i being equal to:

$$p_i/N_i, \qquad p_i = 0, 1, 2, \ldots, (N_i - 1)$$

Equation (16) can be simplified as follows:

$$D[(I, \boldsymbol{r}_n)] = \exp(2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_n) \tag{19}$$

We have thus found $N = N_1N_2N_2$ irreducible representations of the finite group of primitive translations of a cyclic crystal.

Definition. *The three non-coplanar vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, $\boldsymbol{b}_3$ define the basis vectors of the reciprocal lattice of a given crystal lattice.*

Study of the reciprocal lattice. The solution of Eqs. (18) permits us to express the vectors $\boldsymbol{b}_i$ in terms of the vectors $\boldsymbol{a}_j$ as follows:

$$\boldsymbol{b}_1 = \frac{\boldsymbol{a}_2 \times \boldsymbol{a}_3}{V_a}, \qquad \boldsymbol{b}_2 = \frac{\boldsymbol{a}_3 \times \boldsymbol{a}_1}{V_a}, \qquad \boldsymbol{b}_3 = \frac{\boldsymbol{a}_1 \times \boldsymbol{a}_2}{V_a} \tag{20}$$

where $V_a = [\boldsymbol{a}_1\, \boldsymbol{a}_2\, \boldsymbol{a}_3]$ is the fundamental volume of the crystal lattice. Similarly, we can introduce the corresponding quantity V_b for the reciprocal lattice and it is easy to show that $V_b = [\boldsymbol{b}_1\, \boldsymbol{b}_2\, \boldsymbol{b}_3] = 1/V_a$.

The ends of the vectors $\boldsymbol{k}$ defined by Eqs. (17) and (18) lie in the interior of the fundamental volume V_b or on its surface. Let us consider a vector $\boldsymbol{K}$ whose endpoint falls outside the volume V_b. We can put:

$$\boldsymbol{K} = \boldsymbol{k} + \boldsymbol{K}_q, \qquad \boldsymbol{K}_q = q_1\boldsymbol{b}_1 + q_2\boldsymbol{b}_2 + q_3\boldsymbol{b}_3 \tag{21}$$

the numbers q_i being integers and the end of the vector $\boldsymbol{k}$ lying within volume V_b. From (21):

$$\boldsymbol{K}\cdot\boldsymbol{r}_n = \boldsymbol{k}\cdot\boldsymbol{r}_n + \boldsymbol{K}_q\cdot\boldsymbol{r}_n$$

so that:

$$\boldsymbol{K}_q\cdot\boldsymbol{r}_n = \left(\sum_i q_i\boldsymbol{b}_i\right)\cdot\left(\sum_j n_j\boldsymbol{a}_j\right) = \sum_{ij} q_i r_j \delta_{ij} = \sum_i q_i r_i$$

Since $\Sigma\, q_i r_i$ is a whole number, the two scalars $\boldsymbol{K}\cdot\boldsymbol{r}_n$ and $\boldsymbol{k}\cdot\boldsymbol{r}_n$ differ by an integer. The representations $\exp(2\pi i\boldsymbol{k}\cdot\boldsymbol{r}_n)$ and $\exp(2\pi i\boldsymbol{K}\cdot\boldsymbol{r}_n)$ of the finite group of translations are, therefore, identical and there are *only* N irreducible representations of the group.

As a consequence of the Born cyclic conditions, we are led naturally to the concept of reciprocal space and to the introduction of the finite number N of vectors $\boldsymbol{k}$.

6. UNIT CELLS

Definition. *A unit cell is the smallest volume of a crystal lattice which will generate this lattice through the use of the primitive translations.*

For example, the parallelopiped formed by the basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ constitute a unit cell. The unit cell can be chosen in a

number of ways. The parallelopiped just defined above is simple but it has the fault that it does not remain invariant under the operations of the point group which leave the lattice invariant. We can demonstrate, however, that the first Brillouin zone is a unit cell remaining invariant with respect to the point group of the lattice. The first Brillouin zone is constructed as follows [15]: choose an arbitrary lattice point O and construct the planes which bisect the lines joining O with the other lattice points. The smallest polyhedron which can be constructed in this way delineates the first Brillouin zone, and it can be shown that the volume of this zone is always $V_a = [\boldsymbol{a}_1\, \boldsymbol{a}_2\, \boldsymbol{a}_3]$.

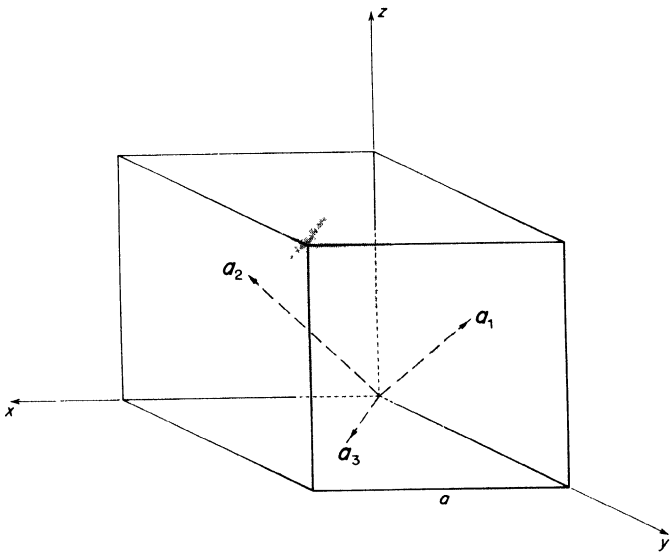

FIG. 2

In the same way, we can construct the first Brillouin zone of the reciprocal lattice; it is of prime importance for what follows. It contains the ends of the N vectors $\boldsymbol{k}$ (which are said to be

reduced) occurring in the N irreducible representations of the finite group Γ of primitive lattice translations.

Example. The crystal lattice of diamond, germanium, and silicon is face-centered cubic. If a is the length of an edge of the cube, the basis vectors (Fig. 2) can be taken as:

$$\boldsymbol{a}_1 = (0, \tfrac{1}{2}a, \tfrac{1}{2}a), \qquad \boldsymbol{a}_2 = (\tfrac{1}{2}a, 0, \tfrac{1}{2}a), \qquad \boldsymbol{a}_3 = (\tfrac{1}{2}a, \tfrac{1}{2}a, 0)$$

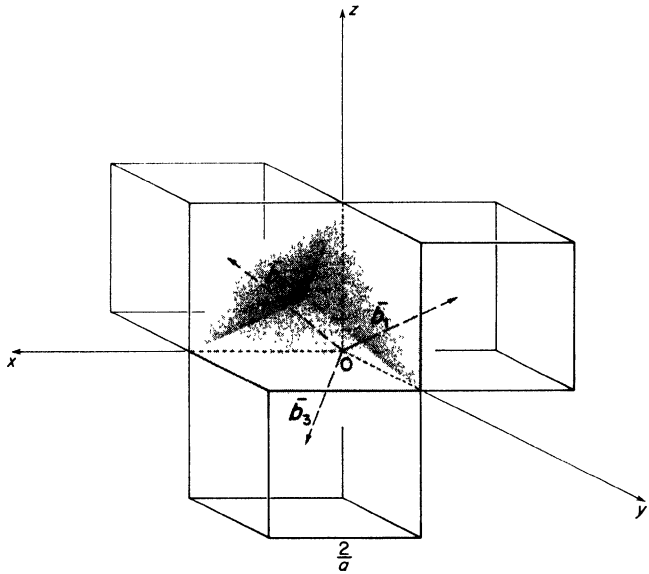

FIG. 3

where the coordinate axes are parallel to the edges of the cube.

The basis vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$, $\boldsymbol{b}_3$ of the reciprocal lattice corresponding to the vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$, $\boldsymbol{a}_3$ will have components (Fig. 3):

$$\boldsymbol{b}_1 = (-1/a, 1/a, 1/a)$$
$$\boldsymbol{b}_2 = (1/a, -1/a, 1/a)$$
$$\boldsymbol{b}_3 = (1/a, 1/a, -1/a)$$

In Figs. 2 and 3, we have indicated the unit cells as being constructed from the basis vectors. Figure 4 represents the first

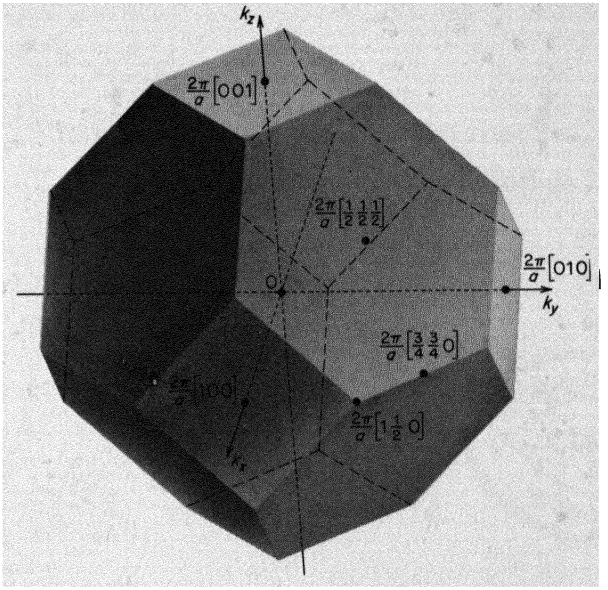

FIG. 4

Brillouin zone of the reciprocal lattice and gives the coordinates of some representative $\boldsymbol{k}$ vectors.

4

The variational approximation method in quantum mechanics

1. INTRODUCTION

Consider the Schroedinger equation:

$$H\psi = E\psi$$

as applied to an electron in a system (an atom, molecule, or crystal), where H is the Hamiltonian operator $-\nabla^2 + V(\boldsymbol{r})$, the Laplacian ∇^2 being written in reduced coordinates to eliminate the factor $h^2/8\pi^2 m$, and $V(\boldsymbol{r})$ is the potential energy of interaction for the electrons and nuclei of the system.

The solutions ψ_i of this equation, which are eigenfunctions of the operator H, form a complete orthonormal system in a domain D of configuration space, and the energy levels E_i are the corresponding eigenvalues.

Let us recall that in quantum mechanics, we restrict ourselves to functions which are said to belong to class Q; that is, func-

tions of the configuration variables which are well-behaved, piecewise continuous, and such that:

$$\int_D \psi^* \psi d\tau$$

is finite.

We shall consider here an approximate method for the solution of the Schroedinger equation known as the Ritz variational method.

2. FUNDAMENTAL THEOREMS

Theorem I. If φ is a function of class Q, and normalized, satisfying the same conditions at the limits as the functions ψ_i, and if E_0 is the smallest eigenvalue of H, then:

$$\int_D \varphi^* H \varphi d\tau \geqslant E_0$$

Let us consider the integral:

$$I = \int_D \varphi^*(H - E_0)\varphi d\tau$$

$$= \int_D \varphi^* H \varphi d\tau - E_0 \int_D \varphi^* \varphi d\tau = \int_D \varphi^* H \varphi d\tau - E_0$$

From the conditions imposed on φ, we know that it can be expanded in a series in terms of the ψ_i as follows:

$$\varphi = \sum_{i=0}^{\infty} c_i \psi_i$$

The integral I then becomes:

$$I = \int_D \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* c_j \psi_i^* (H - E_0)\psi_j d\tau$$

Since:

$$H\psi_j = E_j \psi_j$$

we then have:

$$I = \int_D \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* c_j \psi_i^* \psi_j (E_j - E_0) d\tau$$

$$= \sum_{i=0}^{\infty} \sum_{j=0}^{\infty} c_i^* c_j (E_j - E_0)\delta_{ij}$$

and finally:

$$I = \sum_{i=0}^{\infty} c_i^* c_i (E_i - E_0)$$

The integral I is positive or zero since $c_i^* c_i > 0$ and $E_i \geqq E_0$. Then I will be zero if $\varphi = \psi_0$.

The eigenvalue E_0 is the *absolute* minimum of the integral $\int_D \varphi^* H \varphi d\tau$ when the normalized functions φ satisfy the same conditions as the eigenfunctions of H.

Theorem II. If φ is of class Q and normalized, and is *orthogonal* to ψ_0, and if E_0, E_1 are the first two eigenvalues of H ($E_1 > E_0$), then:

$$\int_D \varphi^* H \varphi d\tau \geqq E_1$$

The proof is similar to the above; but since φ is orthogonal to ψ_0, then the coefficient c_0 in the expansion for φ is zero, and:

$$\varphi = \sum_{i=1}^{\infty} c_i \psi_i$$

This time we consider the integral:

$$J = \int_D \varphi^* (H - E_1)\varphi d\tau$$

which becomes:

$$J = \sum_{i=1}^{\infty} c_i^* c_i (E_i - E_1)$$

The integral J is positive or zero; it is zero when $\varphi = \psi_1$.

The eigenvalue E_1 is the *absolute* minimum of the integral $\int_D \varphi^* H \varphi d\tau$ when the normalized functions φ satisfy the same conditions at the limits as the functions ψ_i.

Theorem III. If φ is a function of class Q, and normalized, and is *orthogonal* to the eigenfunctions $\psi_0, \psi_1, \ldots, \psi_{n-1}$ of H, satisfy-

ing the same conditions at the limits as the functions ψ_i, then:

$$\int_D \varphi^* H \varphi d\tau \geqslant E_n$$

where E_n is the $(n+1)$st eigenvalue of H, these eigenvalues being arranged in increasing order. The proof is exactly analogous to the preceding ones, and the integral $\int_D \varphi^* H \varphi d\tau$ has for an absolute minimum the eigenvalue E_n, if the functions φ satisfy the conditions of Theorem III.

Conclusion. We can determine E_n and ψ_n in solving the following variational problem:

$$\int_D \varphi^* H \varphi d\tau = \text{an absolute minimum}$$

while holding the functions φ to the following supplementary conditions:

$$\int_D \varphi^* \varphi d\tau = 1 \quad \text{and} \quad \int_D \varphi^* \psi_j d\tau = 0, \quad j = 0, 1, \ldots, (n-1)$$

3. THE VARIATIONAL PROBLEM

We shall show that we can obtain the eigenvalues E_n and the corresponding eigenfunctions ψ_i by starting with the same variational problem, but by trying to determine the extrema of the integrals in the preceding section. We pose the following problem:

What conditions must a normalized function of class Q fulfill to render an extremum the integral $\int_D \varphi^* H \varphi d\tau$?

For every variation $\delta\phi$, we must have:

$$\delta \int_D \varphi^* H \varphi d\tau - \lambda \cdot \delta \int \varphi^* \varphi d\tau = 0$$

or:

$$\int_D \delta\varphi^*(H - \lambda)\varphi d\tau + \int_D \varphi^*(H - \lambda)\delta\varphi d\tau = 0 \qquad (1)$$

Then H is a hermitian operator:

$$\int_D \varphi^* H \delta\varphi d\tau = \int_D \delta\varphi H^* \varphi^* d\tau$$

and (1) becomes:

$$\int_D \delta\varphi^*(H - \lambda)\varphi d\tau + \int_D \delta\varphi(H^* - \lambda)\varphi^* d\tau = 0$$

Taking $\delta\phi$ real, $\delta\phi = \delta\phi^*$, then:

$$\int_D \delta\varphi[(H - \lambda)\varphi + (H^* - \lambda)\varphi^*]d\tau = 0$$

Taking $\delta\varphi$ imaginary, $\delta\varphi = -\delta\varphi^*$, and:

$$\int_D \delta\varphi[(H - \lambda)\varphi + (H^* - \lambda)\varphi^*]d\tau = 0$$

In both cases, the term in brackets must vanish, and:

$$(H - \lambda)\varphi = 0, \qquad (H^* - \lambda)\varphi^* = 0$$

The integral $\int_D \varphi^* H \varphi d\tau$ will be an extremum if φ is an eigenfunction of H, λ being the corresponding eigenvalue.

4. THE RITZ METHOD

This consists of choosing at random n functions f_i of class Q, satisfying the same conditions at the limits as the eigenfunctions of H, and of determining the coefficients c_i such that:

$$\varphi = \sum_{i=1}^{n} c_i f_i, \qquad \lambda = \frac{\int_D \varphi^* H \varphi d\tau}{\int_D \varphi^* \varphi d\tau}$$

λ being made an extremum (the denominator is necessary, since

φ is not normalized). The functions f_i will be called *competitive functions.** Let us put:

$$H_{ij} = \int_D f_i^* H f_j d\tau, \qquad S_{ij} = \int_D f_i^* f_j d\tau \tag{2}$$

we then have:

$$\lambda \sum_{i,j=1}^{n} c_i^* c_j S_{ij} = \sum_{i,j=1}^{n} c_i^* c_j H_{ij} \tag{3}$$

and λ will be an extremum if $\partial\lambda/\partial c_i = 0$, $\partial\lambda/\partial c_i^* = 0$ for $c = 1, 2, \ldots, n$. Let us differentiate (3) with respect to c_i^*:

$$\frac{\partial\lambda}{\partial c_i^*} \sum_{ij} c_i^* c_j S_{ij} + \lambda \sum_j c_j S_{ij} = \sum_{ij} c_j H_{ij}$$

and using $\partial\lambda/\partial c_i^* = 0$ shows that:

$$\sum_{j=1}^{n} (H_{ij} - \lambda \cdot S_{ij}) c_j = 0 \qquad i = 1, 2, \ldots, n \tag{4}$$

The differentiation with respect to c_i gives the conjugates of Eq. (4).

The system of n linear, homogeneous equations with the c_i as the unknowns will have non-zero solutions only if:

$$\det |H_{ij} - \lambda S_{ij}| = 0 \tag{5}$$

The smallest root E_0' of the secular Eq. (5) will be an approximation to the smallest eigenvalue E_0 of the Schroedinger equation, this approximation improving as the functions f_i approach the n correct eigenfunctions corresponding to the first n eigenvalues $E_0, \ldots, E_n$. The other roots of (5) approximate the eigenvalues $E_1, \ldots, E_n$.

Fundamental Remark. Let us suppose that for a given system, we know the n lowest eigenvalues $E_0, \ldots, E_{n-1}$ and the corresponding n eigenfunctions $\psi_0, \ldots, \psi_{n-1}$, and that we wish to know the eigenvalues E_n, E_{n+1}. *It is then obligatory* to take as

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* *Translator's Note:* Although this is an unusual use of the word "competitive," there does not seem to be a more suitable English term.

the competitive functions f_i those functions which are *orthogonal* to the functions $\psi_0, \ldots, \psi_{n-1}$ in order that $\varphi = \Sigma\, c_i f_i$ be orthogonal to the functions $\psi_0, \ldots, \psi_{n-1}$. Thanks to this essential precaution, Theorem III applies and the variational method yields an approximation to the eigenvalues $E_n, E_{n+1}, \ldots$.

5

Theory of groups and the Schroedinger equation

1. SYMMETRY PROPERTIES OF THE EIGENFUNCTIONS

Let us consider a system S which is invariant under the operations of a group G. The group G is then the symmetry group of system S.

Let ψ_i be the eigenfunctions associated with the energy states E_i of the system; they are solutions of the Schroedinger equation:

$$H\psi_i = E_i\psi_i \tag{1}$$

We shall now consider the effect of an element L of G on the eigenfunctions ψ_i.

Definition of the Operator P_L [23]. The operator P_L associated with an element L of G is an operator such that:

$$P_L f(\boldsymbol{r}) = f(L^{-1}\boldsymbol{r}) \tag{2}$$

where $\boldsymbol{r} = \boldsymbol{OP}$ marks the position of a point P of the system with respect to an origin O and $f(\boldsymbol{r})$ is an arbitrary function of $\boldsymbol{r}$.

The ensemble of operators P_L constitutes a group which is

isomorphic to the symmetry group G. Consider now the operator P_{Lb} associated with the element Lb of G. By definition (2), we have:

$$P_{Lb}f(\boldsymbol{r}) = f(Lb^{-1}\boldsymbol{r}) \equiv g(\boldsymbol{r}) \tag{3}$$

Applying the operator P_{La} associated with La of G to $g(\boldsymbol{r})$ gives:

$$P_{La}P_{Lb}f(\boldsymbol{r}) = P_{La}g(\boldsymbol{r}) = g(La^{-1}\boldsymbol{r}) = g(\boldsymbol{r}')$$

where we have put:

$$\boldsymbol{r}' = La^{-1}\boldsymbol{r}$$

Thus, from (3):

$$g(\boldsymbol{r}') = f(Lb^{-1}\boldsymbol{r}') = f(Lb^{-1}La^{-1}\boldsymbol{r})$$

and finally:

$$P_{La}P_{Lb}f(\boldsymbol{r}) = f(Lb^{-1}La^{-1}\boldsymbol{r}) = f[(La\cdot Lb)^{-1}\boldsymbol{r}]$$

which is equivalent to:

$$P_{La}\cdot P_{Lb} = P_{La\cdot Lb}$$

Fundamental Property of the Hamiltonian H. Every element L of G leaves invariant the Hamiltonian H of the system S, since the operator ∇^2 and the potential $V(\boldsymbol{r})$, both completely symmetric with respect to the elements L of G, are invariant. This idea is a generalization of the well-known property of a molecule having a symmetry group G: its kinetic and potential energies are invariant with respect to G.

Let us apply to the two sides of Eq. (1) the operator P_L:

$$P_L(H\psi_i) = P_L(E_i\psi_i)$$

Since H is invariant with respect to the elements L, this becomes:

$$P_LH\psi_i = HP_L\psi_i = E_i\cdot P_L\psi_i$$

from which we obtain the fundamental theorem:

Theorem. *The operators P_L and H commute and the function $P_L\psi_i$ is a solution of the Schroedinger equation corresponding to the eigenvalue E_i.*

Corollaries.

1. If the eigenvalue E_i is nondegenerate, we must have:

$$P_L\psi_i = a\psi_i, \qquad a \text{ being a constant}$$

If the functions are normalized, a reduces to ± 1.

2. Suppose now that the eigenvalue E_i is ν-fold degenerate; there then exist ν linearly independent eigenfunctions $\psi_1^i, \psi_2^i, \ldots, \psi_\nu^i$ associated with E_i. Every function $P_{La}\psi_n^i$ $(n = 1, 2, \ldots, \nu)$, being an eigenfunction associated with E_i, is a linear combination of functions $\psi_1^i, \ldots, \psi_\nu^i$, and can be expressed:

$$P_{La}\psi_n^i = \sum_{m=1}^{\nu} a_{mn}^i \psi_m^i \tag{5}$$

Now consider another operator P_{Lb} of the group G:

$$P_{Lb}\psi_n^i = \sum_{m=1}^{\nu} b_{mn}^i \psi_m^i \tag{6}$$

Apply the operator P_{La} to the function $P_{Lb}\psi_n^i$:

$$P_{La}P_{Lb}\psi_n^i = \sum_{m=1}^{\nu} b_{mn}^i \cdot P_{La}\psi_m^i = \sum_{m=1}^{\nu} b_{mn}^i \sum_{l=1}^{\nu} a_{lm}^i \psi_l^i$$

$$= \sum_{l=1}^{\nu} c_{ln}^i \psi_l^i$$

and using:

$$c_{ln}^i = \sum_{m=1}^{\nu} a_{lm}^i \cdot b_{mn}^i$$

proves the following theorem:

Theorem. *The matrices (a_{ij}^i), (b_{ij}^i), (c_{ij}^i) associated with the elements La, Lb, Lc of G form a representation of order ν of the symmetry group G, while the eigenfunctions $\psi_1^i, \psi_2^i, \ldots, \psi_\nu^i$ form a basis for this representation.*

(*Note.* If the functions ψ_n^i are normalized, the representation is unitary.)

If no accidental degeneracy exists—that is, a degeneracy produced by the particular initial conditions imposed on the problem—the ensemble of functions ψ_n^i forms a basis for *an irreducible representation* of G. In fact, every eigenfunction associated with the eigenvalue E_i is a linear combination of *all* the functions ψ_n^i and there does not exist an invariant subspace of the ν-dimensional space defined by the basis of the ψ_n^i.

2. SOLUTION OF THE SCHROEDINGER EQUATION BY THE RITZ METHOD

In the preceding chapter, we studied the principle of the Ritz method: one chooses initially n competitive functions f_i; by invoking an extremum principle, one shows that an approximation to the energy levels is given by the secular equation:

$$\det |K_{ij}| = \det |H_{ij} - \lambda S_{ij}| = 0$$

with:

$$H_{ij} = \int_D f_i^* H f_j d\tau, \qquad S_{ij} = \int_D f_i^* f_j d\tau$$

If we wish a small error in our approximation, it is necessary to choose a large number of competitive functions, and the resulting high-order secular determinant is difficult to expand. The use of group theory permits the factorization of such a determinant.

Assume that we can find n competitive functions forming the basis for a *completely reducible representation* Γ of the symmetry group G of the system. Decomposing the representation Γ into its irreducible representations, let:

$$\Gamma = c_1\Gamma^1 + c_2\Gamma^2 + \ldots + c_\rho\Gamma^\rho$$

We distinguish two cases:

Case I. Assume that all irreducible representations, for example, Γ^{α} and Γ^{β}, appear *once only* in Γ, and that their respective degrees of degeneracy are d_{α} and d_{β}. We shall have d_{α} competitive functions, designated $f_k^{(\alpha)}$ $(k = 1, 2, \ldots, d_{\alpha})$, associated with the irreducible representation Γ^{α} and d_b functions $f_l^{(\beta)}$, $(l = 1, 2, \ldots, d_{\beta})$, associated with Γ^{β}.

Let us then evaluate the integral:

$$S_{kl}^{(\alpha\beta)} = \int_D f_k^{*(\alpha)} f_l^{(\beta)} d\tau$$

This integral can only be zero or invariant for every operation L of the group G; in the latter case:

$$L \cdot S_{kl}^{(\alpha\beta)} = S_{kl}^{(\alpha\beta)} \tag{8}$$

Let us form $L \cdot S_{kl}^{(\alpha\beta)}$. If we designate the terms of the matrix corresponding to L in the representation Γ^{α} by $D_{km}^{(\alpha)}(L)$, then we have:

$$L \cdot f_k^{*(\alpha)} = \sum_{m=1}^{d_{\alpha}} D_{km}^{*(\alpha)}(L) f_m^{*(\alpha)}$$

and:

$$L \cdot f_m^{(\beta)} = \sum_{n=1}^{\beta} D_{ln}^{(\beta)}(L) f_n^{(\beta)}$$

Equation (8) becomes:

$$L \cdot S_{kl}^{\alpha\beta} = \int_D \sum_{m=1}^{d_{\alpha}} D_{km}^{*\alpha}(L) f_m^{*\alpha} \cdot \sum_{n=1}^{d_{\beta}} D_{ln}^{\beta} f_n^{\beta} d\tau = \int_D f_k^{*\alpha} f_l^{\beta} d\tau$$

in which we have omitted the superscript parentheses for simplicity. Removing the constant terms from the integral results in:

$$\int_D f_k^{*\alpha} f_l^{\beta} \cdot d\tau = \sum_{m=1,n=1}^{d_{\alpha}, d_{\beta}} D_{km}^{*\alpha}(L) \cdot D_{ln}^{\beta}(L) \int_D f_m^{*\alpha} f_n^{\beta} d\tau \tag{9}$$

Writing Eqs. (9) for all the elements L of G and summing:

$$\int_D f_k^{*\alpha} f_l^{\beta} d\tau = \frac{1}{g} \sum_{m,n} \left(\sum_L D_{km}^{*\alpha}(L) D_{ln}^{\beta}(L) \right) \int_D f_m^{*\alpha} f_n^{\beta} d\tau \qquad (10)$$

where g is the order of the group G, considered here to be *finite*.

Let us now apply to the righthand side of (10) the fundamental relation (22) of Chap. 2:

$$\int_D f_k^{*\alpha} f_l^{\beta} d\tau = \frac{1}{d_\alpha} \delta_{\alpha\beta} \cdot \delta_{kl} \sum_{m,n} \delta_{mn} \int_D f_m^{*\alpha} f_n^{\beta} d\tau \qquad (11)$$

where Eq. (11) expresses the orthogonality property of the competitive functions.

Theorem. *The competitive functions forming a basis for a completely reducible representation* Γ *of the finite group* G *associated with the system* S *are orthogonal.*

In Eq. (11):

(a) if $\alpha \neq \beta$ $\quad S_{kl}^{\alpha\beta} = 0$

(b) if $\alpha = \beta$, $k \neq 1$ $\quad S_{kl}^{\alpha\alpha} = 0$

(c) finally if $\alpha = \beta$, $k = l$, we have

$$\int_D f_k^{*\alpha} f_k^{\alpha} d\tau = \frac{1}{d_\alpha} \sum_m \int_D f_m^{*\alpha} f_m^{\alpha} d\tau \qquad (12)$$

Formula (12) is true for $k = 1, 2, \ldots, d_\alpha$. Then the integrals $S_{kk}^{\alpha\alpha}$ are all equal, for $k = 1, 2, \ldots, d_\alpha$.

The Hamiltonian operator H is totally symmetric under all of the group operations, and the conditions found for the integrals $S_{kl}^{\alpha\beta}$ apply without change to the integrals $H_{kl}^{\alpha\beta}$. Then the only non-zero terms in the determinant $|H_{ij} - \lambda S_{ij}|$ will be the diagonal terms. Further, the d_γ terms belonging to the irreducible representation Γ^γ of degeneracy d_γ are all equal.

Example. Suppose we have:

$$\Gamma = \Gamma^1 + \Gamma^2 + \Gamma^3$$

Γ^1 being nondegenerate, Γ^2 being two-fold degenerate and Γ^3 being three-fold degenerate. A basis for Γ will consist of six

competitive functions: f^1; f_1^2, f_2^2; and f_1^3, f_2^3, f_3^3. The secular matrix will have the following appearance:

	f^1	f_1^2	f_2^2	f_1^3	f_2^3	f_3^3
f^{*1}	K^{11}					
f_1^{*2}		K_{11}^{22}				
f_2^{*2}			K_{22}^{22}			
f_1^{*3}				K_{11}^{33}		
f_2^{*3}					K_{22}^{33}	
f_3^{*3}						K_{33}^{33}

The only non-zero terms are those shown; further $K_{11}^{22} = K_{22}^{22}$, $K_{11}^{33} = K_{22}^{33} = K_{33}^{33}$. In such a problem, three energy levels appear: a nondegenerate, a doubly-degenerate, and a triply-degenerate.

Case II. Let us consider now the more complex case where, for example, the irreducible representation Γ^α appears more than once in the completely reduced representation Γ. For simplicity, we shall assume that Γ^α appears twice. There then exist two ensembles of functions, denoted $f_1', f_2', \ldots, f_{d_\alpha}'$ and $f_1'', f_2'', \ldots, f_{d_\alpha}''$, associated with the irreducible representation Γ^α. In order to obtain the maximum factorization of the secular determinant, the two ensembles f' and f'' should be chosen so that the functions in them *transform in the same manner* for every operation L of the group G. We can then verify, for example, that:

$$\int_D f_1^{*\prime\alpha} f_2^{\prime\prime\alpha} d\tau = 0$$

The demonstration that this integral vanishes, used in the first case, also applies here, for if:

$$f_1^{\prime\alpha} \xrightarrow[L]{} \sum_j D_{1j}^{\alpha}(L) f_j^{\prime\alpha}$$

we then have:

$$f_2^{\prime\prime\alpha} \xrightarrow[L]{} \sum_j D_{2l}^{\alpha}(L) f_l^{\prime\prime\alpha}$$

Let us again consider an example for clarity: consider the representation $\Gamma = 2\Gamma^1 + 3\Gamma^2$, Γ^1 being nondegenerate and Γ^2 doubly-degenerate. A basis of the representation Γ will consist of eight functions:

$$f'^1 f''^1, \qquad f_1'^2 f_2'^2, \qquad f_1''^2 f_2''^2, \qquad f_1'''^2 f_2'''^2$$

The secular determinant then has the following form:

	f'^1	f''^1	f'^2	f''^2	f'''^2	f'^2	f''^2	f'''^2
$f^{*\prime 1}$								
$f^{*\prime\prime 1}$								
$f^{*\prime 2}$			$K_{11}^{2'2'}$	$K_{11}^{2'2''}$	$K_{11}^{2'2'''}$			
$f^{*\prime\prime 2}$			$K_{11}^{2''2'}$	$K_{11}^{2''2''}$	$K_{11}^{2''2'''}$			
$f^{*\prime\prime\prime 2}$			$K_{11}^{2'''2'}$	$K_{11}^{2'''2''}$	$K_{11}^{2'''2'''}$			
$f^{*\prime 2}$						$K_{11}^{2'2'}$	$K_{11}^{2'2''}$	$K_{11}^{2'2'''}$
$f^{*\prime\prime 2}$						$K_{11}^{2''2'}$	$K_{11}^{2''2''}$	$K_{11}^{2''2'''}$
$f^{*\prime\prime\prime 2}$						$K_{11}^{2'''2'}$	$K_{11}^{2'''2''}$	$K_{11}^{2'''2'''}$

and it has been factored into a second-order determinant and two *identical* third-order ones.

Before stating the fundamental theorem on the factorization of the secular determinant, we should be in a position to define correctly the symmetric competitive functions.

Definition. The *symmetric competitive functions* form a basis for a completely reduced unitary representation of the group G. If there are *several* ensembles of competitive functions belonging to the *same* irreducible representation, *all* these ensembles must be transformed in the *same* manner by *every* operation of the group G.

The following theorem constitutes the conclusion of our present study:

Theorem. *If symmetric competitive functions are used, the secular equation is automatically factorized. There will be d_γ equal factors corresponding to each irreducible representation Γ^γ of degeneracy d_γ. The degree of a factor is the number of times the corresponding irreducible representation appears in the completely reduced representation.*

In practice, we cannot set up a procedure which will give us initially the symmetric competitive functions. However, it is easy to find those functions which are simply a basis for an arbitrary representation of the group G. Then, the tricky problem which remains to be solved is two-fold:

(a) It is necessary to find linear combinations of the preceding functions which are symmetric competitive functions, and

(b) The transformation which takes us from the initial competitive functions to the symmetric ones is unitary. The determinant which is to be factorized will be transformed by this unitary transformation from the determinant in-

volving the original competitive functions. Sometimes this last step is long and tedious.

3. DETERMINATION OF THE COMPETITIVE SYMMETRIC FUNCTIONS [2]

Let us take n competitive symmetric functions W_r $(r = 1, 2, \ldots, n)$ forming a basis for a representation Γ' of order n of the group G. It is necessary to first know the structure of the completely reduced representation Γ equivalent to the representation Γ'. Thus, we will know the distribution of the symmetric functions to be determined.

1. Characters of the Representation Γ (or Γ'). The n functions W_r transform among themselves via the operations L of the group G. By establishing an array of these transformations (an example will be given in Chap. 7), we can easily find the character $\chi_L^{\Gamma'}$ of each class of G in the representation Γ' (or Γ).

2. Composition of the Representation Γ. If we have established a character table for the irreducible representations of the group G, by applying Eq. (32) of Chap. 2:

$$n_\gamma = 1/g \cdot \sum_j g_j \chi_j^\Gamma \chi_j^{*\gamma}$$

we can find the irreducible representations Γ^γ constituting Γ and the number of times each one occurs. For example, if a triply-degenerate irreducible representation Γ^3 appears twice in Γ, we know that we must construct two ensembles of three symmetric functions associated with Γ^3.

3. Fundamental Formula. Let ρ be the number of irreducible representations of the group G $(\alpha = 1, 2, \ldots, \rho)$, let Γ^α be one of these representations, let a_α be the number of times the representation Γ^α appears in Γ, and let d_α be the dimension of Γ^α.

Let f^{α}_{pm} be a symmetric competitive function belonging to the representation Γ^{α}:

$$1 \leqslant \alpha \leqslant \rho, \qquad 1 \leqslant p \leqslant a_{\alpha}, \qquad 1 \leqslant m \leqslant d_{\alpha}$$

Since the symmetric functions f^{α}_{pm} are obtained by a non-singular linear transformation of the functions W_r, then, conversely, every function W_r is a linear combination of the functions f^{α}_{pm} and we can write:

$$W_r = \sum_{\alpha=1}^{\rho} \sum_{p=1}^{a_{\alpha}} \sum_{m=1}^{d_{\alpha}} b_{\alpha pm} f^{\alpha}_{pm} \tag{13}$$

We now apply the operator P_{Ls} associated with the element Ls of G to W_r. By (13), P_{Ls} operates on the function f^{α}_{pm} and since it is a *symmetric* function belonging to the irreducible representation Γ^{α}, we must necessarily have:

$$P_{Ls} f^{\alpha}_{pm} = \sum_{n=1}^{d_{\alpha}} D^{\alpha}_{nm}(Ls) f^{\alpha}_{pn} \tag{14}$$

From this, we can write:

$$P_{Ls} W_r = \sum_{\alpha} \sum_{p} \sum_{w} b_{\alpha pm} \sum_{n=1}^{d_{\alpha}} D^{\alpha}_{nm}(Ls) f^{\alpha}_{pn} \tag{15}$$

Multiply both sides of (15) by:

$$\chi^{*}_{\beta}(Ls) = \sum_{t=1}^{d_{\beta}} D^{*\beta}_{tt}(Ls)$$

and sum over all the elements Ls of group G:

$$\sum_{s=1}^{g} \chi^{*}_{\beta}(Ls) \cdot P_{ls} W_r$$

$$= \sum_{\alpha} \sum_{p} \sum_{m} b_{\alpha pm} \cdot \sum_{n=1}^{d_{\alpha}} \sum_{j=1}^{d_{\beta}} \sum_{s=1}^{g} D^{*\beta}_{tt}(Ls) D^{\alpha}_{nm} f^{\alpha}_{pn} \tag{16}$$

Writing the orthogonality relation, Eq. (22) of Chap. 2, in the form:

$$\sum_{s=1}^{g} D^{\alpha}_{mn}(Ls) \sqrt{\frac{d_{\alpha}}{g}} \cdot D^{*\beta}_{m'n'}(Ls) \sqrt{\frac{d_{\beta}}{g}} = \delta_{\alpha\beta} \delta_{mm'} \delta_{nn'}$$

we can transform (16) as follows:

$$\sum_{s=1}^{g} \chi_\beta^*(Ls) P_{Ls} W_r = \sum_{p=1}^{a_\beta} \sum_{m=1}^{d_\beta} b_{\beta pm} \frac{g}{d_\beta} \sum_{n=1}^{d_\alpha} \sum_{t=1}^{d_\beta} \delta_{tn} \delta_{tm} f_{pn}^{\beta}$$

by noting that:

$$\sum_{\alpha=1}^{\rho} b_{\alpha pm} \frac{\delta_{\alpha\beta}}{\sqrt{d_\alpha d_\beta}} f_{pn}^{\alpha} = b_{\beta pm} \frac{1}{d_\beta} f_{pn}^{\beta}$$

We then have:

$$\sum_{s=1}^{g} \chi_\beta^*(Ls) P_{Ls} W_r = \sum_{p=1}^{a_\beta} \sum_{m=1}^{d_\beta} b_{\beta pm} \frac{g}{d_\beta} \sum_{t=1}^{d_\beta} \delta_{tm} f_{pt}^{\beta}$$

or:

$$\sum_{s=1}^{g} \chi_\beta^*(Ls) P_{Ls} W_r = \sum_{p=1}^{a_\beta} \sum_{t=1}^{d_\beta} \frac{g}{d_\beta} b_{\beta pt} f_{pt}^{\beta} \tag{17}$$

and this is the desired fundamental formula.

4. Discussion.

(a) If the representation Γ^β is nondegenerate, and if it appears only once in Γ, then $a_\beta = 1$ and Eq. (17) becomes:

$$\sum_{s=1}^{g} \chi_\beta^*(Ls) \cdot P_{Ls} W_r = g \cdot b_{\beta 11} \cdot f_{11}^{\beta} \tag{17a}$$

Then, to a constant factor, we have obtained the symmetric function associated with Γ^β.

(b) If the representation Γ^β is d_β-fold degenerate, and if $a_\beta = 1$, Eq. (17) gives:

$$\sum_{s=1}^{g} \chi_\beta^*(Ls) \cdot P_{Ls} W_r = c_1 f_{11}^{\beta} + c_2 f_{12}^{\beta} + \ldots + c_{d_\beta} f_{1d_\beta}^{\beta} \tag{17b}$$

and we have obtained a linear combination of symmetric functions belonging to Γ^β. In applying the formula to the d_β functions W_r, we would obtain d_β linear combinations of the d_β symmetric functions f_{1t}^{β}.

(c) If the representation Γ^β is degenerate and if $a_\beta > 1$, it is necessary to use (17) as it stands. The determination of

the symmetric functions is then very tedious and there are no general rules to follow; it is necessary to be guided to some extent by intuition.

Remark. The symmetric functions associated with the degenerate, irreducible representation Γ^β must be mutually orthogonal. It is not a certainty that Eq. (17) will lead to orthogonal functions in the case of degeneracy. It is necessary to check this point, and if it is not the case, to search for linear combinations which are orthogonal.

These calculations appear extremely involved at first sight, but we can rely on the following: the irreducible representations Γ^β in the cases generally encountered in practice are, at the most, triply-degenerate and appear once or twice in the completely reduced representation Γ. Chapter 7 will be devoted to these calculations for a particular example.

4. APPLICATION TO CRYSTALS

1. Consider a *cyclic* crystal for which the *finite* space group is G. We know that all the irreducible representations of the subgroup of translations of G are one-dimensional and of the form $\exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)$, where $\boldsymbol{k}$ is a vector in the first Brillouin zone such that:

$$\begin{gathered}\boldsymbol{k} = p_1/N_1\cdot\boldsymbol{b}_1 + p_2/N_2\cdot\boldsymbol{b}_2 + p_3/N_3\cdot\boldsymbol{b}_3 \\ p_i = 0, 1, \ldots, (N_i - 1)\end{gathered} \tag{18}$$

Every eigenfunction of the crystal must be a function of a vector $\boldsymbol{k}$ satisfying the equality (18). In addition, it must satisfy:

$$(I, \boldsymbol{r}_n)\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)\psi_{\boldsymbol{k}}(\boldsymbol{r})$$

which is equivalent to:

$$\psi_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{r}_n) = \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)\psi_{\boldsymbol{k}}(\boldsymbol{r}) \tag{19}$$

Every reduced vector $\boldsymbol{k}$ corresponds to an ensemble of solutions of the Schroedinger equation given by:

$$H\psi_{\boldsymbol{k}}(\boldsymbol{r}) = E_{\boldsymbol{k}}\psi_{\boldsymbol{k}}(\boldsymbol{r}) \tag{20}$$

To each solution $\psi_{i,\boldsymbol{k}}$ associated with the vector $\boldsymbol{k}$ there corresponds an energy level $E_{i,\boldsymbol{k}}$. If we can solve the set of equations (20) for every reduced vector $\boldsymbol{k}$, we will be able to construct the electronic energy level diagram giving energy as a function of $\boldsymbol{k}$.

2. We are going to study the effect of the subgroup of translations on the eigenfunctions of the crystal, and it is therefore necessary to examine how these eigenfunctions are transformed by elements of the factor group G/Γ. Let us apply the operator P_L associated with the element $L = (\alpha, \boldsymbol{v}_\alpha)$ to both sides of Eq. (19):

$$P_L\psi_{\boldsymbol{k}}(\boldsymbol{r} + \boldsymbol{r}_n) = P_L \exp(2\pi i\boldsymbol{k}\cdot\boldsymbol{r}_n)P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}) \tag{21}$$

We then have:

$$P_L \exp(2\pi i\boldsymbol{k}\cdot\boldsymbol{r}_n) = \exp(2\pi i\boldsymbol{k}\cdot L^{-1}\boldsymbol{r}_n)$$

Evaluating $L^{-1}\boldsymbol{r}_n$ by Sec. 1, Chap. 3:

$$L^{-1}\boldsymbol{r}_n = \alpha^{-1}\boldsymbol{r}_n - \alpha^{-1}\boldsymbol{v}_\alpha = \alpha^{-1}(\boldsymbol{r}_n - \boldsymbol{v}_\alpha)$$

since:

$$\boldsymbol{k}\cdot L^{-1}\boldsymbol{r}_n = \boldsymbol{k}\cdot\alpha^{-1}(\boldsymbol{r}_n - \boldsymbol{v}_\alpha) = \alpha\boldsymbol{k}\cdot(\boldsymbol{r}_n - \boldsymbol{v}_\alpha)$$

the last equality resulting from the orthogonality of the matrix α^{-1}. In fact, it is easy to show that:

$$\boldsymbol{U}\cdot O\boldsymbol{V} = (O^{-1}\boldsymbol{U})\cdot\boldsymbol{V}$$

if $\boldsymbol{U}$ and $\boldsymbol{V}$ are two arbitrary vectors in the space where the orthogonal matrix O operates, for:

$$\boldsymbol{U}\cdot O\boldsymbol{V} = \sum_i U_i(OV)_i = \sum_{ik} U_i O_{ik} V_k$$

$$(O^{-1}\boldsymbol{U})\cdot\boldsymbol{V} = \sum_k (O^{-1}U)_k V_k = \sum_{ik} (O^{-1})_{ki} U_i V_k$$

Thus, the matrix O is orthogonal:

$$O_{ik} = (O^{-1})_{ki}$$

Equation (21) now becomes:

$$P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{r}_n) = \exp(-2\pi i\alpha\boldsymbol{k}\cdot\boldsymbol{v}_\alpha)\cdot\exp(2\pi i\alpha\boldsymbol{k}\cdot\boldsymbol{r}_n)P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}) \tag{22}$$

This fundamental relation merits further examination:

(a) If $\alpha\boldsymbol{k}\cdot\boldsymbol{v}_\alpha$ is a whole number (positive, negative, or zero), Eq. (22) reduces to:

$$P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}+\boldsymbol{r}_n) = \exp(2\pi i\alpha\boldsymbol{k}\cdot\boldsymbol{r}_n)P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}) \tag{23}$$

In this case, by Eq. (19), we can write:

$$P_L\psi_{\boldsymbol{k}}(\boldsymbol{r}) = \psi_{\alpha\boldsymbol{k}}(\boldsymbol{r}) \tag{24}$$

If $\boldsymbol{v}(\alpha)$ is identically zero, Eq. (24) always applies. This is the case of the 73 space groups for which the factor group reduces to $(\alpha, 0)$.

(b) In the general case, only Eq. (22) applies, but it often happens that $\exp(-2\pi i\alpha_{\boldsymbol{k}}\cdot\boldsymbol{v}_\alpha)$ takes on the simple values $+1, -1, +i, -i$ (groups of the cubic system).

3. The Group $C(k)$ of the Vector k.

Definition. *The group of the vector $\boldsymbol{k}$ is the ensemble of symmetric operations of the group G which transforms the vector k into either itself or an equivalent vector of the reciprocal lattice.*

Evidently, this group is a subgroup of G. If we are looking for the energy levels E_k associated with the vector $\boldsymbol{k}$, we must solve Eq. (20) and find the eigenfunctions localized by the $\boldsymbol{k}$ vector under consideration. We can then work with the group $C(\boldsymbol{k})$ of the vector $\boldsymbol{k}$ rather than with the entire symmetry group G of the crystal. In fact, only this group transforms the functions $\psi_{\boldsymbol{k}}$ into functions of the same vector $\boldsymbol{k}$ [to within a factor of $\exp(-2\pi i\alpha\boldsymbol{k}\cdot\boldsymbol{v}_\alpha)$].

It is not necessary to consider the group $C(\boldsymbol{k})$ in its entirety; it suffices to deal with the factor group of $C(\boldsymbol{k})$, because an

invariant subgroup of $C(\boldsymbol{k})$ is a subgroup of the invariant subgroup of translations Γ of G. Thus, we may apply all the theory developed in Secs. 1, 2, and 3 of this chapter to the symmetry group $C(\boldsymbol{k})$ in determining the energy levels associated with the vector $\boldsymbol{k}$. Evidently the competitive functions will be functions of the vector $\boldsymbol{k}$ and will satisfy Eq. (19).

4. A Consideration of Particular k Vectors. For an arbitrary vector $\boldsymbol{k}$ in the reduced zone, the group $C(\boldsymbol{k})$ reduces to the identity, and group theory is no longer of any help. However, there are certain points and lines of high symmetry for which the group $C(\boldsymbol{k})$ contains many elements and group theory may be applied in factorizing the secular determinant. In particular, the point $\boldsymbol{k} = (0, 0, 0)$ at the center of the reduced zone is of special interest: the factor group of $C(\boldsymbol{k})$ is then the same as the factor group of the crystal.

Example. For diamond, germanium, and silicon, the factor group is the group O_h^7 of 48 elements, and the reduced zone is a truncated octahedron (see Fig. 4). For the central point $\boldsymbol{k} = (1/a)\ (0, 0, 0)$, the factor group of $C(\boldsymbol{k})$ is the group O_h^7. Other points of high symmetry will be all points on the axes Ox, Oy, Oz, the centers of the hexagonal faces, etc. The corresponding factor groups of $C(\boldsymbol{k})$ will be subgroups of O_h^7.

6

The approximation method of orthogonalized plane waves

1. PLANE WAVE EIGENFUNCTIONS

1. Consider the Schroedinger equation as applied to a cyclic crystal:

$$[-\nabla^2(\boldsymbol{r}) + V(\boldsymbol{r})]\psi_{\boldsymbol{k}} = E_{\boldsymbol{k}}\psi_{\boldsymbol{k}} \tag{1}$$

where $V(\boldsymbol{r})$ is the potential at a point in the crystal defined by the vector $\boldsymbol{r}$ and is due to the interaction between the electrons and nuclei of the system. If $\boldsymbol{r}_n$ is a primitive lattice translation, then:

$$V(\boldsymbol{r} + \boldsymbol{r}_n) = V(\boldsymbol{r}) \tag{2}$$

We shall assume that $V(\boldsymbol{r})$, which is an invariant periodic function for every primitive lattice translation, can be developed in a triple Fourier series (See Ref. [15], Chaps. 7 and 8):

$$V = \sum_{\boldsymbol{l}} V_{\boldsymbol{l}} \exp(2\pi i \boldsymbol{l}\cdot\boldsymbol{r}) \tag{3}$$

the vector $\boldsymbol{l}$ being a reciprocal lattice vector such that:

$$\boldsymbol{l} = l_1\boldsymbol{b}_1 + l_2\boldsymbol{b}_2 + l_3\boldsymbol{b}_3$$

and the l_i are integers.

2. Consider first the "empty" lattice, so that $V(\boldsymbol{r}) = 0$. Physically, this case corresponds to "free" electrons; that is, electrons having no interaction among themselves or with the nuclei. Let us then look for solutions of Eq. (2) associated with a given $\boldsymbol{k}$ vector and having the form:

$$\psi_{\boldsymbol{k}+\boldsymbol{h}} = A \exp\left[2\pi i(\boldsymbol{k} + \boldsymbol{h})\boldsymbol{r}\right]$$

with (4)

$$E_{\boldsymbol{k}+\boldsymbol{h}} = 4\pi^2(\boldsymbol{k} + \boldsymbol{h})^2$$

these solutions representing the spatial part of a progressive plane wave. For brevity, we shall call them plane waves. Equation (3) shows that the potential $V(\boldsymbol{r})$ has been expanded as a series of plane waves: $\exp(2\pi i\boldsymbol{l}\cdot\boldsymbol{r})$.

3. Let us now consider the potential $V(\boldsymbol{r})$ as a perturbation term to the Laplacian $\nabla^2(\boldsymbol{r})$ of Eq. (1), and we seek a solution of (1) of the form:

$$\psi = \sum_{\boldsymbol{h}} c_{\boldsymbol{h}} f_{\boldsymbol{h}}$$

Since the plane waves are solutions of the zero-th approximation equation and the potential $V(\boldsymbol{r})$ is developable in a series of plane waves, it is natural to choose these plane waves as the competitive functions $f_{\boldsymbol{h}}$. We put:

$$f_{\boldsymbol{h}} = \exp\left[2\pi i(\boldsymbol{k} + \boldsymbol{h})\cdot\boldsymbol{r}\right] \tag{5}$$

$$\boldsymbol{h} = h_1\boldsymbol{b}_1 + h_2\boldsymbol{b}_2 + h_3\boldsymbol{b}_3$$

where the h_i are whole numbers. It is evident that the functions $f_{\boldsymbol{h}}$ satisfy the Born cyclic conditions, that they are functions of the vector $\boldsymbol{k}$, and that they also satisfy Eq. (19) of the preceding chapter:

$$f_{\boldsymbol{h}}(\boldsymbol{r} + \boldsymbol{r}_n) = \exp(2\pi i\boldsymbol{k}\cdot\boldsymbol{r}_n)\cdot f_{\boldsymbol{h}}(\boldsymbol{r})$$

4. This accomplished, the energy levels will be approximated by the roots of the secular equation (see Chap. 4):

$$\det\left|H_{\boldsymbol{h}\boldsymbol{h}'} - ES_{\boldsymbol{h}\boldsymbol{h}'}\right| = 0 \tag{6}$$

with:

$$H_{hh'} = \int_D f_h^* H f_{h'} d\tau, \qquad S_{hh'} = \int_D f_h^* \cdot f_{h'} d\tau$$

the domain of integration D being that portion of the crystal assumed as cyclic. It is possible to convert the determinant (6) into a more tractable form, for:

$$\int_D [-f_h^* \nabla^2 f_{h'}] d\tau = -\int_D \operatorname{div} (f_h^* \operatorname{grad} f_{h'}) d\tau + \int_D \operatorname{grad} f_h^* \cdot \operatorname{grad} f_{h'} d\tau$$

By the Born cyclic conditions, the first integral on the right is zero (the equivalent surface integral vanishes), and there remains:

$$\int_D (-f_h^* \cdot f_{h'}) d\tau = 4\pi^2 (\boldsymbol{k} + \boldsymbol{h})(\boldsymbol{k} + \boldsymbol{h}') \int_D \exp [2\pi i (\boldsymbol{h}' - \boldsymbol{h}) \cdot \boldsymbol{r}] d\tau$$

Using the Fourier expansion (3) of $V(\boldsymbol{r})$, the term $H_{hh'}$ becomes:

$$H_{hh'} = 4\pi^2 (\boldsymbol{k} + \boldsymbol{h})(\boldsymbol{k} + \boldsymbol{h}') \int_D \exp [2\pi i (\boldsymbol{h}' - \boldsymbol{h}) \cdot \boldsymbol{r}] d\tau + \int_D \sum_l V_l \exp [2\pi i (\boldsymbol{h}' - \boldsymbol{h} + \boldsymbol{l}) \cdot \boldsymbol{r}] d\tau$$

From the cyclic conditions, the first integral vanishes except for $\boldsymbol{h} = \boldsymbol{h}'$ (its value is then D) while the second vanishes except for $\boldsymbol{l} = \boldsymbol{h} - \boldsymbol{h}'$ (and its value is then $DV_{h-h'}$). Hence:

$$H_{hh'} = \mathrm{D}[4\pi^2 (\boldsymbol{k} + \boldsymbol{h})^2 \delta_{hh'} + V_{h-h'}]$$

and in the same way:

$$S_{hh'} = \int_D f_h^* f_{h'} d\tau = D\delta_{hh'}$$

where the functions f_h are orthogonal over the domain D. The secular equation is then:

$$\det |\{4\pi^2 (\boldsymbol{h} + \boldsymbol{k})^2 - E\} \delta_{hh'} + V_{h-h'}| = 0 \qquad (7)$$

For a crystal with symmetry group G and for reduced vectors $\boldsymbol{k}$ of high symmetry, this equation can be factored, permitting

numerical solutions. In the following chapter, we shall return to this problem, which is the core of this monograph. For the moment, let us consider the rapidity of the convergence of the series $\sum_{h} c_h f_h$. In simple cases, the secular equation (7) can be solved by using a moderate number of plane waves. Unfortunately, it has been found that the smallest root of the secular equation corresponds to a valence band energy such that if a *complete* ensemble of plane waves is used, the smallest root must give the energy of the innermost "core" electrons [19]. It is then necessary to have a large number of plane waves to represent the wave function with precision. This we can understand, since this function varies rapidly in the vicinity of the nuclei and it is necessary to set up a constructive interference among waves for which the vector $\boldsymbol{k} + \boldsymbol{h}$ is large (small wavelength); this question should be examined in a little more detail.

2. CONSTRUCTION OF BLOCH FUNCTIONS FOR A CRYSTAL [17]

1. The electronic energy levels of an isolated atom are discrete. Imagine the N atoms constituting a crystal to be infinitely separated from one another. We will have N Schroedinger equations, all alike, and the levels will remain discrete, but N-fold degenerate. Let the N atoms now approach one another, forming the real crystal. The potential $V(\boldsymbol{r})$ inside the crystal is not the same as the potential $\mathcal{U}(\boldsymbol{r})$ of the individual atoms, for the electron waves are introduced and the degeneracy is lifted: the energy *bands* appear. But in the vicinity of each atom, we may assume that the atomic wave is practically unperturbed; it corresponds to a "core" electron. Obviously, this approximation does not hold for the valence electrons.

2. Guided by these considerations, we show that the Bloch functions for a reduced vector $\boldsymbol{k}$ corresponding to the core electrons are given by:

$$\Phi_k^i = \sum_{r_n} \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)\cdot u_i(\boldsymbol{r}-\boldsymbol{r}_n)$$

$u_i(\boldsymbol{r})$ being an eigenfunction associated with a core electron of the isolated atom. These Bloch functions will be solutions of the Schroedinger equation for the crystal to a high degree of approximation. One cannot say as much for the Bloch functions associated with the valence electrons.

3. THE METHOD OF ORTHOGONALIZED PLANE WAVES [18], [19], [20]

Let us use the Ritz method for finding the wave functions of the crystal associated with the valence and conduction energy levels. We will again look for a development in a series of plane waves for a given value of $\boldsymbol{k}$, but since we want the valence and conduction states, and not the core states, *it is necessary to take orthogonalized plane waves* as Bloch core functions. We shall apply here the fundamental remark given at the end of Chap. 4, thus avoiding the extremely tedious calculations associated with the use of a simple plane wave development.

We shall orthogonalize the Bloch function plane waves by the Schmitt process. Let:

$$X_i = \exp(2\pi i \boldsymbol{k}_i\cdot\boldsymbol{r}) - \Sigma\mu_{ij}\Phi_j^k(\boldsymbol{r}), \qquad \boldsymbol{k}_i = \boldsymbol{k} + \boldsymbol{h} \tag{8}$$

and determine the coefficients μ_{ij} in such a manner that:

$$\int_D X_i^*\cdot\Phi_i^k d\tau = 0, \qquad \Phi_j^k(\boldsymbol{r}) = \sum_{r_n} \exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)\cdot u_j(\boldsymbol{r}-\boldsymbol{r}_n) \tag{9}$$

Next, let:

$$\int_D X_i^*\Phi_j^k d\tau = A - B$$

with:

$$A = \sum_{r_n}\int_D \exp(-2\pi i \boldsymbol{k}_i\cdot\boldsymbol{r})\exp(2\pi i \boldsymbol{k}\cdot\boldsymbol{r}_n)\cdot u_j(\boldsymbol{r}-\boldsymbol{r}_n)d\tau$$

$$B = \int_D \sum_l \mu_{il}^*\Phi_l^{*k}(\boldsymbol{r})\Phi_j^k(\boldsymbol{r})d\tau$$

Evaluating A first:

$$A = \int_D \sum_{r_n} \exp\left[-2\pi i(\boldsymbol{k}_i \cdot \boldsymbol{r} - \boldsymbol{k} \cdot \boldsymbol{r}_n)\right] \cdot u_j(\boldsymbol{r} - \boldsymbol{r}_n) d\tau$$

$$= \int_D \sum_{r_n} \exp\left[-2\pi i \boldsymbol{k}_i \cdot (\boldsymbol{r} - \boldsymbol{r}_n)\right] \cdot u_j(\boldsymbol{r} - \boldsymbol{r}_n) d\tau$$

Since:

$$\boldsymbol{k} \cdot \boldsymbol{r} - \boldsymbol{k} \cdot \boldsymbol{r}_n = \boldsymbol{k}_i(\boldsymbol{r} - \boldsymbol{r}_n) + \boldsymbol{h} \cdot \boldsymbol{r}_n$$

the scalar product $\boldsymbol{h} \cdot \boldsymbol{r}_n$ is an integer. Finally:

$$A = N \int_D \exp\left(-2\pi i \boldsymbol{k}_i \cdot \boldsymbol{r}\right) \cdot u_j(\boldsymbol{r}) d\tau$$

Next, we evaluate B:

$$B = \sum_{r_{n_i} \neq r_{n1}} \exp\left[2\pi i \boldsymbol{k} \cdot (\boldsymbol{r}_{n1} - \boldsymbol{r}_n)\right] \cdot \mu_{il}^* \int_D u_l^*(\boldsymbol{r} - \boldsymbol{r}_n) u_j(\boldsymbol{r} - \boldsymbol{r}_{n1}) d\tau$$

Putting:

$$\boldsymbol{r}_n - \boldsymbol{r}_{n1} = \boldsymbol{r}_{n2}$$

noting that:

$$\Sigma\, \boldsymbol{r}_n \boldsymbol{r}_{n1} = N\, \Sigma \boldsymbol{r}_{n2}$$

and making the change in variable:

$$\boldsymbol{r} - \boldsymbol{r}_{n1} = \boldsymbol{r}'$$

gives:

$$B = N \sum_{l, r_{n2}} \exp\left(-2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_{n2}\right) \cdot \mu_{il}^* \int_D u_l^*(\boldsymbol{r}' - \boldsymbol{r}_{n2}) u_j(\boldsymbol{r}') d\tau$$

the domain of integration D being also translated by an amount r_{n1}.

Consider now the integral:

$$\int_D u_l^*(\boldsymbol{r}' - \boldsymbol{r}_{n2}) u_j(\boldsymbol{r}') d\tau$$

This represents the overlap of wave functions on different atoms. To a first approximation, we assume the overlap is negligible and replace the integral by the term $\delta_{lj}\delta \boldsymbol{r}_{n2,0}$. Then:

$$B = N \sum_{l, r_{n2}} \exp\left(-2\pi i \boldsymbol{k} \cdot \boldsymbol{r}_{n2}\right) \cdot \mu_{il}^* \delta_{lj} \delta \boldsymbol{r}_{n2,0} = N \mu_{ij}^*$$

Requiring that $A = B$ for orthogonality, we have:

$$\mu_{ij}^* = \int_D \exp(-2\pi i \boldsymbol{k}_i \cdot \boldsymbol{r}) u_j(\boldsymbol{r}) d\tau$$

$$\mu_{ij} = \int_D \exp(2\pi i \boldsymbol{k}_i \cdot \boldsymbol{r}) u_j(\boldsymbol{r}) d\tau$$

From a given value of the reduced vector $\boldsymbol{k}$, we can thus determine a series of plane waves $X_i(\boldsymbol{r})$. Putting:

$$\psi = \sum_i \beta_i X_i \qquad \text{and} \qquad D_{ij} = \int X_i^*(H - E) X_j d\tau$$

the Ritz method leads to the secular determinant:

$$\det |D_{ij}| = 0$$

from which we obtain the eigenvalues of E for a given value of $\boldsymbol{k}$. The convergence of the series of plane waves is sufficient for our purpose, as has been shown by Herman [21].

In this work, we shall not set down in full detail the calculations described above. This is a long and tedious job and has, in particular, been carried out by Herman and Woodruff for the diamond lattice.

7

The method of factorizing secular determinants

[using the diamond lattices as an example]

1. INTRODUCTION

In this chapter, we shall apply the methods previously described to a particular example: the calculation of electronic levels at $\boldsymbol{k} = 0$ (the center point of the Brillouin zone) for diamond, germanium or silicon crystals. We shall not follow these calculations through to the final answer, but merely show for a precise example how the use of the symmetry group G of the crystal aids in factorizing the secular determinant. If we wish to find the valence and conduction band energy levels, the competitive functions must be orthogonal plane waves.

The essential procedures of this chapter come from the work of F. Herman [22] and T. O. Woodruff [23], who have carried the calculations through to the final, numerical steps, making use of orthogonal plane waves.

2. LATTICE AND SPACE GROUP OF THE DIAMOND TYPE

In a diamond-type crystal, each atom is located with respect to its four nearest neighbors in an identical manner (principle of tetravalence). The diamond lattice is complex; its *basis lattice* is face-centered cubic. If a is the side of the cube, one generally adopts as *fundamental vectors* the following three vectors:

$$\boldsymbol{a}_1(0, \tfrac{1}{2}a, \tfrac{1}{2}a), \qquad \boldsymbol{a}_2(\tfrac{1}{2}a, 0, \tfrac{1}{2}a), \qquad \boldsymbol{a}_3(\tfrac{1}{2}a, \tfrac{1}{2}a, 0)$$

the coordinates being rectangular and parallel to the cube edge, while the origin O is at a corner. But here, the atoms are not at the corners of the unit cell. Each unit cell contains two atoms located by *two interior vectors*.

$$\boldsymbol{d}_1 = \tfrac{1}{8}a(1, 1, 1), \qquad \boldsymbol{d}_2 = -\tfrac{1}{8}a(1, 1, 1)$$

The origin O is halfway between the two atoms and will be designated as "*the standard origin*" (see Fig. 5).

The associated space group evidently divides the cubic system into centered lattices. The factor group $(\alpha, \boldsymbol{v}_\alpha)$ is the group O_h^7. It is isomorphic to the complete cubic symmetry group O_h with 48 elements. The vector $\boldsymbol{v}_\alpha$ when it exists is such that:

$$\boldsymbol{v}_\alpha = \tfrac{1}{4}(\boldsymbol{a}_1 + \boldsymbol{a}_2 + \boldsymbol{a}_3) = \tfrac{1}{4}a(1, 1, 1)$$

Of these 48 operations of the factor group O_h^7, the first 24 are *simple* (they consist of pure rotations or of rotations plus the inversion) and the other 24 are *complex* (besides rotations and the inversion they incorporate a *fractional translation* $\boldsymbol{v}_\alpha$). The nth complex operation is derived from the nth simple one by multiplying from the left by $(\sim, v)$, where $\sim$ is the symbol for the inversion.

Table I describes these 48 operations; it is taken from the thesis of Woodruff and the symbols are those of Seitz:

δ_{4i}, δ_{4i}^{-1} $(i = x, y, z)$: rotations of 90° around the axes Ox, Oy, Oz.

$$\delta_{2i} = (\delta_{4i})^2; \; i = x, y, z.$$

δ_{3s}, δ_{3s}^{-1} ($s = xyz, \bar{x}yz, x\bar{y}z, xy\bar{z}$): rotations of 120° about the diagonals of the cube of side a ($\bar{x}$ is used to indicate $-x$).

δ_{2p} ($p = xy, yz, zx, \bar{x}y, \bar{y}z, \bar{z}x$): rotations of 180° around axes bisecting two coordinate axes.

$\sim$ the inversion:

$$\nu_{4i} = \sim \cdot \delta_{4i}, \qquad \rho_i = \sim \cdot \delta_{2i}$$

$$\nu_{6s} = \sim \cdot \delta_{3s}, \qquad \rho_p = \sim \cdot \delta_{2p}$$

$$\boldsymbol{v} = \tfrac{1}{4}a(1, 1, 1)$$

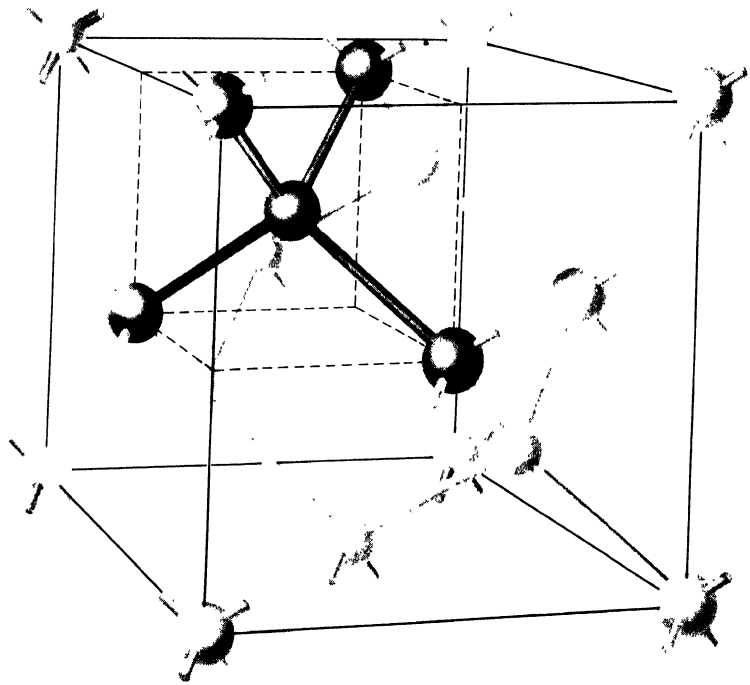

FIG. 5

TABLE I ELEMENTS OF THE FACTOR GROUP O_h^7

s	Class	Operation L	$L^{-1}\mathbf{r}$ Origin at Center	$L^{-1}\mathbf{r}$ Standard Origin		
1	E	$(I, 0)$	$x\ y\ z$	x	y	z
2	C_4^2	$(\delta_{2z}, 0)$	$\bar{x}\ \bar{y}\ z$	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	z
3		$(\delta_{2x}, 0)$	$x\ \bar{y}\ \bar{z}$	x	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
4		$(\delta_{2y}, 0)$	$\bar{x}\ y\ \bar{z}$	$\bar{x} - \frac{1}{4}a$	y	$\bar{z} - \frac{1}{4}a$
5	JC_4	$(\sigma_{4z}^{-1}, 0)$	$y\ \bar{x}\ \bar{z}$	y	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$
6		$(\sigma_{4z}, 0)$	$\bar{y}\ x\ \bar{z}$	$\bar{y} - \frac{1}{4}a$	x	$\bar{z} - \frac{1}{4}a$
7		$(\sigma_{4x}^{-1}, 0)$	$\bar{x}\ z\ \bar{y}$	$\bar{x} - \frac{1}{4}a$	z	$\bar{y} - \frac{1}{4}a$
8		$(\sigma_{4x}, 0)$	$\bar{x}\ \bar{z}\ y$	$\bar{x} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	y
9		$(\sigma_{4y}^{-1}, 0)$	$\bar{z}\ \bar{y}\ x$	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$	x
10		$(\sigma_{4y}, 0)$	$z\ \bar{y}\ \bar{x}$	z	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$
11	JC_2	$(\rho_{xy}, 0)$	$\bar{y}\ \bar{x}\ z$	$\bar{y} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	z
12		$(\rho_{xz}, 0)$	$\bar{z}\ y\ \bar{x}$	$\bar{z} - \frac{1}{4}a$	y	$\bar{x} - \frac{1}{4}a$
13		$(\rho_{yz}, 0)$	$x\ \bar{z}\ \bar{y}$	x	$\bar{z} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
14		$(\rho_{x\bar{y}}, 0)$	$y\ x\ z$	y	x	z
15		$(\rho_{x\bar{z}}, 0)$	$z\ y\ x$	z	y	x
16		$(\rho_{y\bar{z}}, 0)$	$x\ z\ y$	x	z	y
17	C_3	$(\delta_{3xyz}^{-1}, 0)$	$z\ x\ y$	z	x	y
18		$(\delta_{3xyz}, 0)$	$y\ z\ x$	y	z	x
19		$(\delta_{3x\bar{y}z}^{-1}, 0)$	$z\ \bar{x}\ \bar{y}$	z	$\bar{x} - \frac{1}{4}a$	$\bar{y} - \frac{1}{4}a$
20		$(\delta_{3x\bar{y}z}, 0)$	$\bar{y}\ \bar{z}\ x$	$\bar{y} - \frac{1}{4}a$	$\bar{z} - \frac{1}{4}a$	x
21		$(\delta_{3x\bar{y}\bar{z}}^{-1}, 0)$	$\bar{z}\ \bar{x}\ y$	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$	y
22		$(\delta_{3xy\bar{z}}, 0)$	$\bar{y}\ z\ \bar{x}$	$\bar{y} - \frac{1}{4}a$	z	$\bar{x} - \frac{1}{4}a$
23		$(\delta_{3xy\bar{z}}^{-1}, 0)$	$\bar{z}\ x\ \bar{y}$	$\bar{z} - \frac{1}{4}a$	x	$\bar{y} - \frac{1}{4}a$
24		$(\delta_{3xy\bar{z}}, 0)$	$y\ \bar{z}\ \bar{x}$	y	$\bar{z} - \frac{1}{4}a$	$\bar{x} - \frac{1}{4}a$

TABLE I (*cont'd*)

s	Class	Operation L	$L^{-1}\boldsymbol{r}$ Origin at Center			$L^{-1}\boldsymbol{r}$ Standard Origin		
25	J	$(\sim, v)$	$\bar{x}+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$\bar{x}$	$\bar{y}$	$\bar{z}$
26	JC_4^2	(ρ_z, v)	$x+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{z}$
27		(ρ_x, v)	$\bar{x}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{x}$	$y+\frac{1}{4}a$	$z+\frac{1}{4}a$
28		(ρ_y, v)	$x+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{y}$	$z+\frac{1}{4}a$
29	C_4	(δ_{4z}^{-1}, v)	$\bar{y}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{y}$	$x+\frac{1}{4}a$	$z+\frac{1}{4}a$
30		(δ_{4z}, v)	$y+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{x}$	$z+\frac{1}{4}a$
31		(δ_{4x}^{-1}, v)	$x+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{z}$	$y+\frac{1}{4}a$
32		(δ_{4x}, v)	$x+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{y}$
33		(δ_{4y}^{-1}, v)	$z+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{x}$
34		(δ_{4y}, v)	$\bar{z}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{z}$	$y+\frac{1}{4}a$	$x+\frac{1}{4}a$
35	C_2	(δ_{2xy}, v)	$y+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{z}$
36		(δ_{2xz}, v)	$z+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{y}$	$x+\frac{1}{4}a$
37		(δ_{2yz}, v)	$\bar{x}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{x}$	$z+\frac{1}{4}a$	$y+\frac{1}{4}a$
38		$(\delta_{2x\bar{y}}, v)$	$\bar{y}+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$\bar{y}$	$\bar{x}$	$\bar{z}$
39		$(\delta_{2x\bar{z}}, v)$	$\bar{z}+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$\bar{z}$	$\bar{y}$	$\bar{x}$
40		$(\delta_{2y\bar{z}}, v)$	$\bar{x}+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$\bar{x}$	$\bar{z}$	$\bar{y}$
41	JC_3	(σ_{6xyz}^{-1}, v)	$\bar{z}+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$\bar{z}$	$\bar{x}$	$\bar{y}$
42		(σ_{6xyz}, v)	$\bar{y}+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$\bar{y}$	$\bar{z}$	$\bar{x}$
43		$(\sigma_{6x\bar{y}z}^{-1}, v)$	$\bar{z}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{z}$	$x+\frac{1}{4}a$	$y+\frac{1}{4}a$
44		$(\sigma_{6x\bar{y}\bar{z}}, v)$	$y+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{x}$
45		$(\sigma_{6x\bar{y}\bar{z}}^{-1}, v)$	$z+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{y}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{y}$
46		$(\sigma_{6x\bar{y}\bar{z}}, v)$	$y+\frac{1}{4}a$	$\bar{z}+\frac{1}{4}a$	$x+\frac{1}{4}a$	$y+\frac{1}{4}a$	$\bar{z}$	$x+\frac{1}{4}a$
47		$(\sigma_{6xy\bar{z}}^{-1}, v)$	$z+\frac{1}{4}a$	$\bar{x}+\frac{1}{4}a$	$y+\frac{1}{4}a$	$z+\frac{1}{4}a$	$\bar{x}$	$y+\frac{1}{4}a$
48		$(\sigma_{6xy\bar{z}}, v)$	$\bar{y}+\frac{1}{4}a$	$z+\frac{1}{4}a$	$x+\frac{1}{4}a$	$\bar{y}$	$z+\frac{1}{4}a$	$x+\frac{1}{4}a$

Legend for Table I:

(a) $\bar{x}$, $\bar{y}$, $\bar{z}$, for example (or $-x$, $-y$, $-z$) denotes the coordinates of a point P' transformed from $P(x, y, z)$ by the operator $L_2 = (\delta_{2z}, 0)$.

(b) In the first 24 *simple* operations, $\boldsymbol{v}_\alpha = 0$, if we take an atom as the origin (origin at the center), whereas the 24 *composite* operations contain the fractional translation $\boldsymbol{v}_\alpha = (a/4)(1, 1, 1)$.

(c) For the standard origin 0, some of the simple operations involve translations of the form $(a/4, 0, a/4)$.

(d) In the discussion of this chapter, we shall use only the standard origin, since this gives the simplest possible definition of the reciprocal lattice, in terms of which $\boldsymbol{k}$ and $\boldsymbol{h}$ are expressed. To avoid confusion, we shall use $\boldsymbol{w}$ to designate coordinates with respect to the standard origin.

Example. For the operation L_5:

$$L^{-1}\boldsymbol{r} = (\alpha, \boldsymbol{v}_\alpha) = (\alpha, 0)$$

with:

$$\alpha = \begin{pmatrix} xyz \\ y\bar{x}\bar{z} \end{pmatrix}$$

but with respect to the standard origin:

$$L^{-1}\boldsymbol{r} = (\alpha, \boldsymbol{w}_\alpha) \quad \text{with} \quad \alpha = \begin{pmatrix} xyz \\ y\bar{x}\bar{z} \end{pmatrix} \text{ and } \boldsymbol{w}_\alpha = (0, -\tfrac{1}{4}a, -\tfrac{1}{4}a)$$

The first Brillouin Zone of diamond is shown in Fig. 4, Chap. 3. The center point $\boldsymbol{k} = (1/a)\ (0, 0, 0)$ is invariant for every operation of the group O_h, so that here the group $C(\boldsymbol{k})$ of the vector $\boldsymbol{k}$ is identical to the factor group O_h^7.

Remark. The existence of fractional translations $\mathbf{v}_\alpha$ introduces unavoidable complications into our problem. The distinction

between the 73 symmomorphic space groups and the 157 others is a fundamental physical condition.

3. PLANE WAVES AS COMPETITIVE FUNCTIONS

Let us choose plane waves as competitive functions, and since the vector $\boldsymbol{k}$ is zero, they will have the form:

$$W_r = \exp\left(2\pi i \frac{\boldsymbol{h}}{a} \cdot \boldsymbol{r}\right)$$

We set up a table (Table II) of those waves arranged by increasing values of the scalar $\boldsymbol{h}^2$. The symbol (h_1, h_2, h_3) symbolizes the plane wave:

$$\exp\left[2\pi \frac{i}{a}(h_1 x + h_2 y + h_3 z)\right]$$

with:

$$h^2 = (h_1)^2 + (h_2)^2 + (h_3)^2$$

The symbol $\langle h_1\, h_2\, h_3\rangle$ represents an ensemble of waves (h_1, h_2, h_3) where the numbers h_i are fixed, but can be permuted among themselves or have their signs reversed, so that they all belong to the same scalar value h^2. For example, $\langle 1\ 1\ 1\rangle$ represents the ensemble of 8 waves:

$$(1\ 1\ 1),\ (1\ \bar{1}\ \bar{1}),\ (\bar{1}\ 1\ \bar{1}),\ (\bar{1}\ \bar{1}\ 1),\ (\bar{1}\ \bar{1}\ \bar{1}),\ (\bar{1}\ 1\ 1),\ (1\ \bar{1}\ 1),\ (1\ 1\ \bar{1})$$

with:

$$(h)^2 = 1^2 + 1^2 + 1^2 = 3$$

The physical significance of h^2 is simple: for a plane wave solution to the Schroedinger equation for the "empty" lattice, h^2 is the energy, to within a factor of $4\pi^2$ [see Eq. (4), Chap. 6].

In Table II, (left-hand side), we have indicated the scalar energy h^2 and the degeneracy N for each ensemble $\langle h_1\, h_2\, h_2\rangle$.

TABLE II

h	$(h)^2$	N	h	$(h)^2$	N
⟨000⟩	0	0	⟨000⟩	0	1
⟨100⟩	1	6			
⟨110⟩	2	12			
⟨111⟩	3	8	⟨111⟩	3	8
⟨200⟩	4	6	⟨200⟩	4	6
⟨210⟩	5	18			
⟨211⟩	6	24			
⟨220⟩	8	12	⟨220⟩	8	12
⟨221⟩	9	24			
⟨300⟩	9	6			
⟨310⟩	10	18			
⟨311⟩	11	24	⟨311⟩	11	24
⟨222⟩	12	8	⟨222⟩	12	8
⟨321⟩	14	18			
⟨400⟩	16	6	⟨400⟩	16	6
⟨322⟩	17	24			
⟨410⟩	17	18			
⟨330⟩	18	12			
⟨331⟩	19	24			

We shall now proceed by successive approximations; as a first approximation, we shall use the 6 competitive functions ⟨100⟩; for the second approximation, we use the $6 + 12 = 18$ plane waves ⟨100⟩ and ⟨110⟩; progressively, to improve the precision, we add higher energy waves. It is necessary, however, to note the following: every ensemble $\langle h_1\, h_2\, h_3 \rangle$ must be a *complete basis* of the representation of the factor group O_h^7 (see Sec. 2 of Chap. 5). We shall see that in the case of diamond, this does not always turn out to be the case. It is then necessary to examine in detail the effects of the elements of the group O_h^7 on the plane waves under consideration.

4. TRANSFORMATION OF THE PLANE WAVES BY THE ELEMENTS OF THE GROUP O_h^7

Let $W_i = \exp[(2\pi i/a)\boldsymbol{h}\cdot\boldsymbol{r}]$ be a plane wave belonging to the vector $\boldsymbol{h}$, and let an operator P_L, in which $L = (\alpha, \boldsymbol{w}_\alpha)$ act on W_i (where we are using $\boldsymbol{w}_\alpha$ in conjunction with the standard origin, as explained in connection with Table I). Since:

$$P_L f(\boldsymbol{r}) = f(L^{-1}\boldsymbol{r})$$

and:

$$L^{-1} = (\alpha^{-1}, -\alpha^{-1}\boldsymbol{w}_\alpha)$$

we have:

$$P_L W_i = \exp\left[2\pi\frac{i}{a}\boldsymbol{h}\cdot(\alpha^{-1}\boldsymbol{r} - \alpha^{-1}\boldsymbol{w}_\alpha)\right]$$

$$P_L W_i = \exp\left[2\pi\frac{i}{a}\boldsymbol{h}\cdot\alpha^{-1}(\boldsymbol{r} - \boldsymbol{w}_\alpha)\right]$$

Now the matrix is orthogonal, so that:

$$P_L W_i = \exp\left(2\pi\frac{i}{a}\alpha\boldsymbol{h}\cdot\boldsymbol{r}\right)\exp\left(-2\pi\frac{i}{a}\alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha\right)$$

from which:

$$P_L W_i = \exp\left(-2\pi\frac{i}{a}\alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha\right)W_j$$

$$\text{with} \qquad W_j = \exp\left(2\pi\frac{i}{a}\alpha\boldsymbol{h}\cdot\boldsymbol{r}\right) \tag{1}$$

Thus, to within a factor of $\exp(-2\pi i a^{-1}\alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha)$, a wave W_i is transformed by P_L into a *unique wave* W_j. In the case of the group O_h^7, the possible values of the coefficient $A = \exp(-2\pi i\alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha)$ are simple and small in number; Table I shows that A must be ± 1 or $\pm i$.

Let us try to determine those wave ensembles $\langle h_1\, h_2\, h_3\rangle$ of Table II which give *only* the coefficients $A = \pm 1$, and in addition, $\pm i$. The fractional translations possible for group O_h^7, using the *standard origin*, are of the type:

$$(-\tfrac{1}{4}a, -\tfrac{1}{4}a, 0), \quad (-\tfrac{1}{4}a, 0, -\tfrac{1}{4}a), \quad (-\tfrac{1}{4}a, -\tfrac{1}{4}a, 0)$$
$$(\tfrac{1}{4}a, \tfrac{1}{4}a, 0), \quad (\tfrac{1}{4}a, 0, \tfrac{1}{4}a), \quad (\tfrac{1}{4}a, \tfrac{1}{4}a, 0)$$

It is apparent that the ensembles $\langle 100\rangle$, $\langle 110\rangle$, $\langle 210\rangle$, $\langle 211\rangle$, $\langle 221\rangle$, $\langle 300\rangle$, $\langle 310\rangle$, $\langle 321\rangle$, $\langle 322\rangle$, $\langle 410\rangle$, $\langle 330\rangle$, etc., lead to possible factors $A = \pm i$, while the remaining ones of Table II lead *only* to $A = \pm 1$.

Example: Consider the wave (100). Then, by Table I, the operator $L = (\sigma_{4z}, 0)$ converts every point $P(x, y, z)$ into $P'[y, (\bar{x} - a/4), (\bar{z} - a/4)]$, so that the wave (100) becomes the wave $(0\bar{1}0)$ and $\alpha(\boldsymbol{h}/a)\cdot\boldsymbol{w}_\alpha = (1/a)(0, \bar{1}, 0)(0, -a/4, -a, 4) = 1/4$, thus giving $\exp(2\pi i\alpha\boldsymbol{h}/a\cdot\boldsymbol{w}_\alpha) = e^{i\pi/2} = +i$.

Consider now the ensemble of 6 waves $\langle 100\rangle$; they are transformed by the operators P_L of the group O_h^7 not only among themselves (ignoring sign changes) but also into waves of the form $i\cdot(100)$.

Thus we have the fundamental fact that the ensemble of waves $\langle 100\rangle$ is not a *complete basis* for a representation of the group O_h^7, because it is necessary to add waves which differ from the (100) waves by a factor of $i = \exp(i\pi/2)$. This is not permitted, since the crystal potential $V(\boldsymbol{r})$ is developed only in terms of the real waves and not the imaginary ones. Only those ensembles $\langle 111\rangle$, $\langle 200\rangle$, $\langle 220\rangle$, etc., found in the righthand half of Table II produce complete bases of representation of the group O_h^7. Thus, the presence of the vector $\boldsymbol{v}_\alpha$ in the factor group O_h^7 eliminates certain ensembles of plane waves. For the case of the 73 symmomorphic groups, these restrictions do not occur.

5. IRREDUCIBLE REPRESENTATIONS FOR THE REPRESENTATIONS BY PLANE WAVES

1. The ensemble of waves $\langle 111\rangle$ forms a representation Γ' of order 8 of the group O_h^7. Let us determine the composition of

the completely reduced representation Γ equivalent to Γ'. It is necessary to know the character in the representation Γ' of each element in the group. Applying Eq. (1) to the 8 waves $\langle 111 \rangle$ and using for P_L the 48 operators of O_h^7 referred to the standard origin, gives us Table III.

TABLE III

	r in W_r							
s in P_{Ls}	1	2	3	4	5	6	7	8
1	1	2	3	4	5	6	7	8
2	−4	3	2	−1	−8	7	6	−5
3	−2	−1	4	3	−6	−5	8	7
4	−3	4	−1	2	−7	8	−5	6
5	−3	−1	4	2	−7	−5	8	6
6	−2	4	−1	3	−6	8	−5	7
7	−4	3	−1	2	−8	7	−5	6
8	−3	4	2	−1	−7	8	6	−5
9	−2	3	4	−1	−6	7	8	−5
10	−4	−1	2	3	−8	−5	6	7
11	−4	2	3	−1	−8	6	7	−5
12	−3	2	−1	4	−7	6	−5	8
13	−2	−1	3	4	−6	−5	7	8
14	1	3	2	4	5	7	6	8
15	1	4	3	2	5	8	7	6
16	1	2	4	3	5	6	8	7
17	1	4	2	3	5	8	6	7
18	1	3	4	2	5	7	8	6
19	−4	−1	3	2	−8	−5	7	6
20	−2	4	3	−1	−6	8	7	−5
21	−3	2	4	−1	−7	6	8	−5
22	−4	2	−1	3	−8	6	−5	7
23	−2	3	−1	4	−6	7	−5	8
24	−3	−1	2	4	−7	−5	6	8

TABLE III (*cont'd*)

s in P_{Ls}	r in W_r							
	1	2	3	4	5	6	7	8
25	5	6	7	8	1	2	3	4
26	−8	7	6	−5	−4	3	2	−1
27	−6	−5	8	7	−2	−1	4	3
28	−7	8	−5	6	−3	4	−1	2
29	−7	−5	8	6	−3	−1	4	2
30	−6	8	−5	7	−2	4	−1	3
31	−8	7	−5	6	−4	3	−1	2
32	−7	8	6	−5	−3	4	2	−1
33	−6	7	8	−5	−2	3	4	−1
34	−8	−5	6	7	−4	−1	2	3
35	−8	6	7	−5	−4	2	3	−1
36	−7	6	−5	8	−3	2	−1	4
37	−6	−5	7	8	−2	−1	3	4
38	5	7	6	8	1	3	2	4
39	5	8	7	6	1	4	3	2
40	5	6	8	7	1	2	4	3
41	5	8	6	7	1	4	2	3
42	5	7	8	6	1	3	4	2
43	−8	−5	7	6	−4	−1	3	2
44	−6	8	7	−5	−2	4	3	−1
45	−7	6	8	−5	−3	2	4	−1
46	−8	6	−5	7	−4	2	−1	3
47	−6	7	−5	8	−2	3	−1	4
48	−7	−5	6	8	−3	−1	2	4

To simplify our discussion, we use the notation of Woodruff:

$W_1 = (1\ 1\ 1)$, $W_2 = (1\ \bar{1}\ \bar{1})$, $W_3 = (\bar{1}\ 1\ \bar{1})$, $W_4 = (\bar{1}\ \bar{1}\ 1)$

$W_5 = (\bar{1}\ \bar{1}\ \bar{1})$, $W_6 = (\bar{1}\ 1\ 1)$, $W_7 = (1\ \bar{1}\ 1)$, $W_8 = (1\ 1\ \bar{1})$

This table shows us that:

(a) $\chi_E^\Gamma = 8$, since the identity does not change any of the waves.

(b) $\chi^{\Gamma_2}_{C_4} = 0$, since the operation L_2, for example, changes all the waves.

(c) For the same reasons:

$$\chi^{\Gamma}_{JC_4} = \chi^{\Gamma}_{J} = \chi^{\Gamma_2}_{JC_4} = \chi^{\Gamma}_{C_4} = \chi^{\Gamma}_{C_2} = \chi^{\Gamma}_{JC_3} = 0$$

(d) $\chi^{\Gamma}_{JC_2} = 4$, for the operation L_{11}, for example, does not affect W_2, W_3, W_6, and W_7.

(e) Finally, $\chi^{\Gamma}_{C_3} = 2$.

Now the character table for the irreducible representations of the group O_h^7, is as follows:

TABLE IV CHARACTERS OF THE IRREDUCIBLE REPRESENTATIONS OF THE GROUP O_h^7

	Γ_1	Γ_2'	Γ_{25}'	Γ_{15}	Γ_{12}'	Γ_{12}	Γ_{25}	Γ_{15}'	Γ_1'	Γ_2'
(1) E	1	1	3	3	2	2	3	3	1	1
(3) C_4^2	1	1	−1	−1	2	2	−1	−1	1	1
(6) JC_4	1	1	−1	−1	0	0	1	1	−1	−1
(6) JC_2	1	1	1	1	0	0	−1	−1	−1	−1
(8) C_3	1	1	0	0	−1	−1	0	0	1	1
(1) J	1	−1	3	−3	−2	2	−3	3	−1	1
(3) JC_4^2	1	−1	−1	1	−2	2	1	−1	−1	1
(6) C_4	1	−1	−1	1	0	0	−1	1	1	−1
(6) C_2	1	−1	1	−1	0	0	1	−1	1	−1
(8) JC_3	1	−1	0	0	1	−1	0	0	−1	1

Using Eq. (32) of Chap. 2:

$$n_\gamma = \frac{1}{g} \cdot \sum_j g_j \chi_j^{\Gamma} \chi_j^{*\gamma}$$

(where the characters in the present case are real), we obtain:

$$n_\gamma = \frac{1}{48}\left[8\chi_E^\gamma + 24\chi_{C_2}^\gamma + 16\chi_{C_3}^\gamma\right]$$

where:

$$n_{\Gamma_1} = 1, \qquad n_{\Gamma'_2} = 1, \qquad n_{\Gamma'_{25}} = 1, \qquad n_{\Gamma_{15}} = 1$$

and the other n_γ are zero. Hence, the completely reducible representation Γ, of order 8, contains two nondegenerate irreducible representations Γ and Γ'_2 and two triply-degenerate irreducible representations Γ'_{25} and Γ_{15}. We would expect that the eighth-order secular determinant would yield 8 first-order determinants if we had used "symmetric" competitive functions [see Eq. (7) of Chap. 6].

Since the three determinants associated with the triply-degenerate irreducible representation are equal, we obtain four distinct energy values: two nondegenerate and two triply-degenerate. In the case of an "empty" crystal, the level $E_{O+\mathbf{h}} = 4\pi^2 h^2$ is eight-fold degenerate; the crystal field considered as a perturbation has dissociated it into four distinct levels, two of which are now triply-degenerate.

Note. Table III is not strictly necessary to find the characters χ_J^Γ. It suffices to consider, as we have already seen, one element per class. Nevertheless, we have given the entire table, since it

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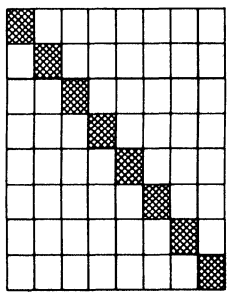

is used to find the symmetric combinations of plane waves which effectively factorize the secular determinant.

2. The ensemble of six waves $\langle 200 \rangle$ forms a basis for a representation of order 6 of the factor group. In putting:

$$W_1 = (200), \quad W_2 = (020), \quad W_3 = (002)$$
$$W_4 = (\bar{2}00), \quad W_5 = (0\bar{2}0), \quad W_6 = (00\bar{2})$$

we form Table V analogous to Table III:

TABLE V

s in P_{Ls}	r in W_r					
	1	2	3	4	5	6
1	1	2	3	4	5	6
2	−4	−5	3	−1	−2	6
3	1	−5	−6	4	−2	−3
4	−4	2	−6	−1	5	−3
5	2	−4	−6	5	−1	−3
6	−5	1	−6	−2	4	−3
7	−4	3	−5	−1	6	−2
8	−4	−6	2	−1	−3	5
9	−6	−5	1	−3	−2	4
10	3	−5	−4	6	−2	−1
11	−5	−4	3	−2	−1	6
12	−6	2	−4	−3	5	−1
13	1	−6	−5	4	−3	−2
14	2	1	3	5	4	6
15	3	2	1	6	5	4
16	1	3	2	4	6	5
17	3	1	2	6	4	5
18	2	3	1	5	6	4
19	3	−4	−5	6	−1	−2
20	−5	−6	1	−2	−3	4
21	−6	−4	2	−3	−1	5
22	−5	3	−4	−2	6	−1
23	−6	1	−5	−3	4	−2
24	2	−6	−4	5	−3	−1

TABLE V (*cont'd*)

s in P_{L_s}	r in W_r					
	1	2	3	4	5	6
25	4	5	6	1	2	3
26	−1	−2	6	−4	−5	3
27	4	−2	−3	1	−5	−6
28	−1	5	−3	−4	2	−6
29	5	−1	−3	2	−4	−6
30	−2	4	−3	−5	1	−6
31	−1	6	−2	−4	3	−5
32	−1	−3	5	−4	−6	2
33	−3	−2	4	−6	−5	1
34	6	−2	−1	3	−5	−4
35	−2	−1	6	−5	−4	3
36	−3	5	−1	−6	2	−4
37	4	−3	−2	1	−6	−5
38	5	4	6	2	1	3
39	6	5	4	3	2	1
40	4	6	5	1	3	2
41	6	4	5	3	1	2
42	5	6	4	2	3	1
43	6	−1	−2	3	−4	−5
44	−2	−3	4	−5	−6	1
45	−3	−1	5	−6	−4	2
46	−2	6	−1	−5	3	−4
47	−3	4	−2	−6	1	−5
48	5	−3	−1	2	−6	−4

The table shows that:

$\chi_E^\Gamma = 6, \qquad \chi_{C_4^2}^\Gamma = 2, \qquad \chi_{JC_2}^\Gamma = 2, \qquad \chi_{JC_4^2}^\Gamma = 4, \qquad \chi_{C_4}^\Gamma = -2$

the other characters being zero. Then Eq. (32) of Chap. 2 gives:

$$n_\gamma = \frac{1}{48}\left[6\chi_E^\gamma + 6\chi_{C_4^2}^\gamma + 12\chi_{JC_2}^\gamma - 12\chi_{JC_4^2}^\Gamma - 12\chi_{C_4}^\gamma\right]$$

from which·

$$n_{\Gamma'_2} = 1, \qquad n_{\Gamma'_{25}} = 1, \qquad n_{\Gamma'_{12}} = 1$$

Thus, the ensemble of 14 waves ⟨111⟩ and ⟨200⟩ forms a basis of a representation equivalent to a completely reduced representation Γ such that:

$$\Gamma = \Gamma_1 + 2\Gamma'_2 + 2\Gamma'_{25} + \Gamma_{15} + \Gamma'_{12}$$

The secular determinant, using the symmetric plane wave combinations, will factorize into:

1 determinant of order 1

1 determinant of order 2

3 equal determinants of order 2

3 equal determinants of order 1

2 equal determinants of order 1

3. There should be no difficulty in studying in the same manner the wave ensembles ⟨220⟩, ⟨311⟩, etc. The results are collected in the following table taken from Herman:

TABLE VI

h	$(h)^2$	N	Irreducible Representations									
			Γ_1	Γ'_2	Γ'_{25}	Γ_{15}	Γ'_{12}	Γ_{12}	Γ_{25}	Γ'_{15}	Γ'_1	Γ_2
⟨111⟩	3	8	1	1	1	1						
⟨200⟩	4	6		1	1		1					
⟨220⟩	8	12	1		1	1		1	1			
⟨311⟩	11	24	1	1	2	2	1	1	1	1		
⟨222⟩	12	8	1	1	1	1						
Total...		58	4	4	6	5	2	2	2	1		

Considering these waves as competitive functions, we finally arrive at a determinant of order 58, and the use of symmetric waves factorizes it as follows:

1 determinant of order 4

1 determinant of order 4

3 equal determinants of order 6

3 equal determinants of order 5

2 equal determinants of order 2

2 equal determinants of order 2

3 equal determinants of order 2

3 equal determinants of order 1

6. DETERMINATION OF SYMMETRIC COMBINATIONS OF PLANE WAVES (SCPW)

To effectively factorize the secular determinant, it is necessary to use a basis formed of *symmetric* linear combinations of the competitive functions. We shall call these *symmetric combinations of plane waves*, abbreviated as SCPW.

1. Let us first consider the SCPW associated with the ensemble of waves $\langle 111 \rangle$. We then need a SCPW belonging to Γ_1, one belonging to Γ_2^1, three for Γ_{25} and three for Γ_{15}. We shall use Eq. (17) of Chap. 5 to find these combinations.

(a) Γ_1 is nondegenerate and appears only once, so that

$$\sum_{s=1}^{48} \chi_{\Gamma_1}(Ls) \cdot P_{Ls} W_r = \mathfrak{N} \cdot f_{11}^1 \tag{2}$$

where $\mathfrak{N}$ is a constant factor. We choose $W_r = W_1$ and note that $\chi_{\Gamma_1}(Ls) = 1$ for all 48 terms. Thus, it suffices to sum all the waves of the first column in Table III:

$$f^1_{11} = \begin{array}{cccccc} 1 & -4 & -2 & -3 & -3 & -2 \\ -4 & -3 & -2 & -4 & -4 & -3 \\ -2 & +1 & +1 & +1 & +1 & +1 \\ -4 & -2 & -3 & -4 & -2 & -3 \\ 5 & -8 & -6 & -7 & -7 & -6 \\ -8 & -7 & -6 & -8 & -8 & -7 \\ -6 & +5 & +5 & +5 & +5 & +5 \\ -8 & -6 & -7 & -8 & -6 & -7 \end{array}$$

In this sum, we have written 1, 2, . . . for W_1, W_2, ... Hence:

$$f^1_{11} = (1 - 2 - 3 - 4 + 5 - 6 - 7 - 8) \qquad (6 \text{ times})$$

and if we normalize:

$$f^1_{11} = \frac{1}{\sqrt{8}}(1 - 2 - 3 - 4 + 5 - 6 - 7 - 8) \qquad (3)$$

Remark. Since there is only one SCPW associated with Γ_1, Eq. (2) applies to any of the waves of the ensemble $\langle 111 \rangle$, and they all lead to (3).

(b) Γ'_2 is nondegenerate and appears only once. Then Eq. (2) becomes:

$$\sum_{s=1}^{48} \chi_{\Gamma'_2}(Ls) P_{Ls} W_r = \mathfrak{N} \cdot f^2_{11}$$

The procedure is the same as above and we note that for the first 24 terms:

$$\chi_{\Gamma'_2}(Ls) = 1$$

while for the second 24:

$$\chi_{\Gamma'_2}(Ls) = -1$$

giving:

$$f^2_{11} = \frac{1}{\sqrt{8}}(1 - 2 - 3 - 4 - 5 + 6 + 7 + 8) \qquad (4)$$

(c) Γ'_{25} is triply-degenerate but appears only once. We then use Eq. (17b) of Chap. 5, and in applying $\sum_{s=1}^{48} \chi_{\Gamma'_{25}}(Ls)P_{Ls}$ successively to W_1, W_2, W_2, and W_4, obtain four combinations Q_1, Q_2, Q_2, Q_4 of the SCPW:

$$f^3_{11}, \qquad f^3_{12}, \qquad f^3_{13}$$

We notice that $Q_1 = Q_2 + Q_3 + Q_4$ and that Q_2, Q_3, Q_4 form three linearly independent combinations. Unfortunately, Q_2, Q_3, and Q_4 are not mutually orthogonal and cannot be taken as SCPW. However, the combinations $Q_1 - Q_4$, $Q_1 - Q_3$, and $Q_1 - Q_2$ are mutually orthogonal and, neglecting normalization factors, are the same as f^3_{11}, f^3_{12}, f^3_{13}. Hence, we find that:

$$\begin{aligned} f^3_{11} &= \frac{1}{\sqrt{8}}(1 + 2 + 3 - 4 + 5 + 6 + 7 - 8) \\ f^3_{12} &= \frac{1}{\sqrt{8}}(1 + 2 - 3 + 4 + 5 + 6 - 7 + 8) \\ f^3_{13} &= \frac{1}{\sqrt{8}}(1 - 2 + 3 + 4 + 5 - 6 + 7 + 8) \end{aligned} \tag{5}$$

Note. The operation $\sum_{s=1}^{48} \chi_{\Gamma'_{25}}(Ls)P_{Ls}$ applied to W_5, W_6, W_7, W_8 would have led to the same Q_i.

(d) An analogous argument (with several long, tedious calculations) leads us to the three SCPW for the representation Γ_{15}, which are:

$$\begin{aligned} f^4_{11} &= \frac{1}{\sqrt{8}}(1 + 2 + 3 - 4 - 5 - 6 - 7 + 8) \\ f^4_{12} &= \frac{1}{\sqrt{8}}(1 + 2 - 3 + 4 - 5 - 6 + 7 - 8) \\ f^4_{13} &= \frac{1}{\sqrt{8}}(1 - 2 + 3 + 4 - 5 + 6 - 7 - 8) \end{aligned} \tag{6}$$

In this transformation, we have gone from the orthonormal basis of the waves ⟨111⟩ to a new orthonormal basis composed of SCPW f_{ij}, using the following orthogonal matrix P:

	W_1	W_2	W_3	W_4	W_5	W_6	W_7	W_8
f_{11}^1	1	−1	−1	−1	1	−1	−1	−1
.	.	.	.	.	.	.	.	.
f_{11}^2	1	−1	−1	−1	−1	1	1	1
.	.	.	.	.	.	.	.	.
f_{11}^3	1	1	1	−1	1	1	1	−1
$P = f_{12}^3$	1	1	−1	1	1	1	−1	1
f_{13}^3	1	−1	1	1	1	−1	1	1
.	.	.	.	.	.	.	.	.
f_{11}^4	1	1	1	−1	−1	−1	−1	1
f_{12}^4	1	1	−1	1	−1	−1	1	−1
f_{13}^4	1	−1	1	1	−1	1	−1	−1

2. Now we shall consider the SCPW associated with the ⟨200⟩ waves. The same considerations as above again apply, but now we are concerned with the irreducible representations Γ_2' and Γ_{25}', which appear twice in the representations formed by the ⟨111⟩ and ⟨200⟩ waves. Hence, we shall have two ensembles of SCPW and both must transform in the same manner for every operation of the group O_h^7 (see Sec. 2, Chap. 5).

In order to satisfy this requirement, we use an elegant method indicated by Woodruff. Let us find all the representative matrices in Γ_{25}' for the operations Ls. To do this, we make use of the SCPW associated with the wave ensemble ⟨100⟩ and belonging to the irreducible representation Γ_{25}'. To simplify the nota-

tion, write f_1, f_2, f_2 for $f^3_1, f^3_{12}, f^3_{13}$. Let us find, for example, the matrix belonging to the operation L_2:

$$P_{L2}f_1 = \frac{1}{\sqrt{8}} P_{L2}(1 + 2 + 3 - 4 + 5 + 6 + 7 - 8)$$

With the help of Table III, this becomes:

$$P_{L2}f_1 = \frac{1}{\sqrt{8}} (-4 + 3 + 2 + 1 - 8 + 7 + 6 + 5) = f_1$$

Similarly:

$$P_{L2}f_2 = -f_2, \qquad P_{L2}f_3 = -f_3$$

and:

$$D^{\Gamma'25}_{ij}(L_2) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Thus, we can establish Table VII with 48 matrices representing the 48 operations of O^7_h belonging to the representation Γ'_{25}:

Let us now find the three SCPW belonging to Γ'_{25} and associated with the waves $\langle 200 \rangle$, using the notation:

$$W_1 = (200), \qquad W_2 = (020), \qquad W_3 = (002)$$
$$W_4 = (\bar{2}00), \qquad W_5 = (0\bar{2}0), \qquad W_6 = (00\bar{2})$$

The irreducible representations appear only once in the representation due to the wave ensemble $\langle 200 \rangle$ and it is possible to write:

$$W_r = \sum_{\alpha=1}^{\rho} \sum_{j=1}^{d_\alpha} b_{\alpha j} f^\alpha_j$$

by considering W_r as a function F [Eq. (4) of the appendix] to which we apply Eq. (5) of the same appendix. That is:

$$\sum_L D^{*\Gamma'_\alpha}_{ll'}(L) P_L W_r = \lambda \cdot f^\alpha_l \tag{8}$$

the coefficient λ being zero. This is the eventuality which occurs when we apply formula (8) for the case $l = 1$, $r = 1, 2, 4, 5$ and use Tables 6 and 7, so that:

TABLE VII MATRICES REPRESENTING Γ'_{25}

$D(1) = \begin{matrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{matrix}$	$D(9) = \begin{matrix} 0 & 0 & -1 \\ 0 & -1 & 0 \\ 1 & 0 & 0 \end{matrix}$	$D(17) = \begin{matrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$
$D(2) = \begin{matrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{matrix}$	$D(10) = \begin{matrix} 0 & 0 & 1 \\ 0 & -1 & 0 \\ -1 & 0 & 0 \end{matrix}$	$D(18) = \begin{matrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{matrix}$
$D(3) = \begin{matrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{matrix}$	$D(11) = \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{matrix}$	$D(19) = \begin{matrix} 0 & 0 & 1 \\ -1 & 0 & 0 \\ 0 & -1 & 0 \end{matrix}$
$D(4) = \begin{matrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{matrix}$	$D(12) = \begin{matrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 0 \end{matrix}$	$D(20) = \begin{matrix} 0 & -1 & 0 \\ 0 & 0 & -1 \\ 1 & 0 & 0 \end{matrix}$
$D(5) = \begin{matrix} -1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{matrix}$	$D(13) = \begin{matrix} 0 & -1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{matrix}$	$D(21) = \begin{matrix} 0 & 0 & -1 \\ 1 & 0 & 0 \\ 0 & -1 & 0 \end{matrix}$
$D(6) = \begin{matrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & 1 & 0 \end{matrix}$	$D(14) = \begin{matrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{matrix}$	$D(22) = \begin{matrix} 0 & 1 & 0 \\ 0 & 0 & -1 \\ -1 & 0 & 0 \end{matrix}$
$D(7) = \begin{matrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & -1 \end{matrix}$	$D(15) = \begin{matrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{matrix}$	$D(23) = \begin{matrix} 0 & 0 & -1 \\ -1 & 0 & 0 \\ 0 & 1 & 0 \end{matrix}$
$D(8) = \begin{matrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{matrix}$	$D(16) = \begin{matrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{matrix}$	$D(24) = \begin{matrix} 0 & -1 & 0 \\ 0 & 0 & 1 \\ -1 & 0 & 0 \end{matrix}$
$D(n + 24) = D(n)$	$n = 1, 2, \ldots, 24$	

$$\sum_{s=1}^{48} D_{11}^{\Gamma'_{25}}(Ls) P_{Ls} W_r = 0$$

But when $l = 1$, $r = 3, 6$, we have:

$$\sum_{s=1}^{48} D_{11}^{\Gamma'_{25}}(Ls) P_{Ls} W_r = 4W_3 + 4W_6$$

and we have thus determined a SCPW:

$$f_{11}^3 = \frac{1}{\sqrt{2}} (W_3 + W_6)$$

Equation (8) for $l = 2$ and 3 leads to the two other SCPW of Γ'_{25} associated with the ensemble $\langle 200 \rangle$:

$$f_{12}^3 = \frac{1}{\sqrt{2}} (W_2 + W_5)$$

$$f_{13}^3 = \frac{1}{\sqrt{2}} (W_1 + W_4)$$

Hence, we are sure of having constructed two ensembles of SCPW for the representation Γ'_{25} which transform in the same manner for all operations of O_h^7. There remains the analogous job of doing the same thing for Γ'_2.

7. THE SECULAR DETERMINANT

1. Returning to Eq. (7) of Chap. 6 (for which $\boldsymbol{k} = 0$):

$$\det D = \det \left| \left(4\pi^2 \frac{h^2}{a^2} - E \right) \delta_{hh'} + V_{h-h'} \right| = 0 \qquad (9)$$

In order not to present too much detail, we shall consider only the 8 functions $\langle 111 \rangle$ as competitive functions. We then obtain Table VIII, where $\beta = 3 \cdot 4\pi^2/a^2$.

To factorize this determinant, we take as basis functions the 8 SCPW associated with the $\langle 111 \rangle$ ensemble. If we transform D by using the matrix P of (7):

TABLE VIII THE DETERMINANT D

	(111)	$(1\bar{1}\bar{1})$	$(\bar{1}1\bar{1})$	$(\bar{1}\bar{1}1)$	$(\bar{1}\bar{1}\bar{1})$	$(\bar{1}11)$	$(1\bar{1}1)$	$(11\bar{1})$
(111)*	V_{000} $+\beta-E$	$V_{0\bar{2}\bar{2}}$	$V_{\bar{2}0\bar{2}}$	$V_{\bar{2}\bar{2}0}$	$V_{\bar{2}\bar{2}\bar{2}}$	$V_{\bar{2}00}$	$V_{0\bar{2}0}$	$V_{00\bar{2}}$
$(1\bar{1}\bar{1})$*	V_{022}	V_{000} $+\beta-E$	$V_{\bar{2}20}$	$V_{\bar{2}02}$	$V_{\bar{2}00}$	$V_{\bar{2}\bar{2}2}$	V_{002}	V_{020}
$(\bar{1}1\bar{1})$*	V_{202}	$V_{2\bar{2}0}$	V_{000} $+\beta-E$	$V_{0\bar{2}2}$	$V_{0\bar{2}0}$	V_{002}	$V_{2\bar{2}2}$	V_{200}
$(\bar{1}\bar{1}1)$*	V_{220}	$V_{20\bar{2}}$	$V_{02\bar{2}}$	V_{000} $+\beta-E$	$V_{00\bar{2}}$	V_{020}	V_{200}	$V_{22\bar{2}}$
$(\bar{1}\bar{1}\bar{1})$*	V_{222}	V_{200}	V_{020}	V_{002}	V_{000} $+\beta-E$	V_{022}	V_{202}	V_{220}
$(\bar{1}11)$*	V_{200}	$V_{22\bar{2}}$	$V_{00\bar{2}}$	$V_{0\bar{2}0}$	$V_{0\bar{2}\bar{2}}$	V_{000} $+\beta-E$	$V_{2\bar{2}0}$	$V_{20\bar{2}}$
$(1\bar{1}1)$*	V_{020}	$V_{00\bar{2}}$	$V_{\bar{2}2\bar{2}}$	$V_{\bar{2}00}$	$V_{\bar{2}0\bar{2}}$	$V_{\bar{2}20}$	V_{000} $+\beta-E$	$V_{02\bar{2}}$
$(11\bar{1})$*	V_{002}	$V_{0\bar{2}0}$	$V_{\bar{2}00}$	$V_{\bar{2}\bar{2}2}$	$V_{\bar{2}\bar{2}0}$	$V_{\bar{2}02}$	V_{022}	V_{000} $+\beta-E$

$$\bar{D} = PDP^{-1} \tag{10}$$

then the determinant of $\bar{D}$ will be automatically factorized.

2. Previously, we have precisely expressed the symmetry properties of $V(\boldsymbol{r})$. These symmetries permit a reduction in the number of different terms $V_{\boldsymbol{h}-\boldsymbol{h}'}$. That is:

$$V(\boldsymbol{r}) = \sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(2\pi \frac{1}{a} \boldsymbol{h}\cdot\boldsymbol{r}\right)$$

and we operate on both sides of this equation with the operator P_L. Since $V(\boldsymbol{r})$ is invariant under the operations of the group O_h, we have

$$P_L V(\boldsymbol{r}) = P_L \left[\sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(2\pi \frac{1}{a} \boldsymbol{h}\cdot\boldsymbol{r}\right)\right] = V(\boldsymbol{r})$$

so that:

$$P_L \left(\sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(2\pi \frac{i}{a} \boldsymbol{h}\cdot\boldsymbol{r}\right)\right] = \sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left[2\pi \frac{i}{a} \boldsymbol{h}\cdot(L^{-1}\boldsymbol{r})\right]$$

Evaluating the scalar $\boldsymbol{h}\cdot(L^{-1}\boldsymbol{r})$ gives:

$$\begin{aligned} \boldsymbol{h}\cdot(L^{-1}\boldsymbol{r}) &= \boldsymbol{h}\cdot(\alpha^{-1}\boldsymbol{r} - \alpha^{-1}\boldsymbol{w}_\alpha\cdot\boldsymbol{r}) \\ &= \boldsymbol{h}\cdot\alpha^{-1}(\boldsymbol{r} - \boldsymbol{w}_\alpha) = \alpha\boldsymbol{h}\cdot(\boldsymbol{r} - \boldsymbol{w}_\alpha) \end{aligned}$$

and:

$$P_L V(\boldsymbol{r}) = \sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(-2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha\right) \cdot \exp\left(2\pi i \alpha\boldsymbol{h}\cdot\boldsymbol{r}\right) = V(\boldsymbol{r})$$

Finally, whatever $\boldsymbol{r}$ is:

$$\sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(2\pi \frac{i}{a} \boldsymbol{h}\cdot\boldsymbol{r}\right)$$

$$= \sum_{\boldsymbol{h}} V_{\boldsymbol{h}} \exp\left(-2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha\right) \exp\left(2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{r}\right)$$

from which:

$$V_{\alpha\boldsymbol{h}} = V_{\boldsymbol{h}} \exp\left(-2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{w}_\alpha\right) \tag{11}$$

Expression (11) shows that the coefficients $V_{\boldsymbol{h}}$ are not all independent.

(a) Now consider the 12 coefficients V_{220}, V_{202}, V_{022}, ... The operation L_{14} of Table I transforms 202 into 022 and $\boldsymbol{w}_{14} = 0$. Then $V_{022} = V_{202}$. The operation L_3 transforms 022 into $0\bar{2}\bar{2}$ and

$$\exp\left(-2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{w}_3\right) = 1$$

so that $V_{022} = V_{0\bar{2}\bar{2}}$. The operation L_{28} transforms 022 into $0\bar{2}2$, but in this case

$$\exp\left(-2\pi \frac{i}{a} \alpha\boldsymbol{h}\cdot\boldsymbol{w}_{28}\right) = -1 \qquad \text{and} \qquad V_{022} = -V_{0\bar{2}2}$$

and $V_{022} = -V_{0\bar{2}2}$.

Thus, we gradually obtain the following relations connecting the 12 coefficients:

$$\begin{cases} V_{220} = V_{202} = V_{022} \\ V_{\bar{2}\bar{2}0} = V_{\bar{2}0\bar{2}} = V_{0\bar{2}\bar{2}} \\ V_{\bar{2}20} = V_{\bar{2}02} = V_{0\bar{2}2} \\ V_{2\bar{2}0} = V_{20\bar{2}} = V_{02\bar{2}} \\ V_{220} = V_{\bar{2}\bar{2}0} = -V_{\bar{2}20} = -V_{2\bar{2}0} \end{cases}$$

(b) In the same way, Eq. (11) also gives:

$$V_{200} = V_{020} = V_{002} = -V_{\bar{2}00} = -V_{0\bar{2}0} = -V_{00\bar{2}}$$

and

$$V_{222} = V_{2\bar{2}\bar{2}} = V_{\bar{2}2\bar{2}} = V_{\bar{2}\bar{2}2} = V_{\bar{2}\bar{2}\bar{2}} = V_{\bar{2}22} = V_{2\bar{2}2} = V_{22\bar{2}}$$

Hence, the determinant of Table VIII is converted into the one of Table IX.

3. We have now arrived at the final point of our considerations: given the matrix D, how to find the equivalent matrix $\overline{D} = PDP^{-1}$. Let us note that since P is orthogonal, its inverse is the same as its transpose. We also know in the present case that only the diagonal terms are zero and that:

$$\overline{D}_{33} = \overline{D}_{44} = \overline{D}_{55}, \qquad \overline{D}_{66} = \overline{D}_{77} = \overline{D}_{88}$$

It suffices then to find $\overline{D}_{11}$, $\overline{D}_{22}$, $\overline{D}_{33}$, and $\overline{D}_{66}$. For example:

$$\overline{D}_{11} = \sum_{k,j} P_{1k} D_{kj} (P^{-1})_{j1}$$

The calculation is long, but not difficult, since all the elements of P and P^{-1} are ± 1. The results are:

$$\overline{D}_{11} = V_{000} + \beta - E - 3V_{220} + V_{222}$$

$$\overline{D}_{22} = V_{000} + \beta - E - 3V_{220} - V_{222}$$

$$\overline{D}_{33} = V_{000} + \beta - E + V_{220} + V_{222}$$

$$\overline{D}_{66} = V_{000} + \beta - E + V_{220} - V_{222}$$

TABLE IX THE DETERMINANT $\bar{D}$

	(111)	(1$\bar{1}\bar{1}$)	($\bar{1}$1$\bar{1}$)	($\bar{1}\bar{1}$1)	($\bar{1}\bar{1}\bar{1}$)	($\bar{1}$11)	(1$\bar{1}$1)	(11$\bar{1}$)
(111)*	V_{000} $+\beta-E$	V_{220}	V_{220}	V_{220}	V_{222}	$-V_{200}$	$-V_{200}$	$-V_{200}$
(1$\bar{1}\bar{1}$)*	V_{220}	V_{000} $+\beta-E$	$-V_{220}$	$-V_{220}$	$-V_{200}$	V_{222}	V_{200}	V_{200}
($\bar{1}$1$\bar{1}$)*	V_{220}	$-V_{220}$	V_{000} $+\beta-E$	$-V_{220}$	$-V_{200}$	V_{200}	V_{222}	V_{200}
($\bar{1}\bar{1}$1)*	V_{220}	$-V_{220}$	$-V_{220}$	V_{000} $+\beta-E$	$-V_{200}$	V_{200}	V_{200}	V_{222}
($\bar{1}\bar{1}\bar{1}$)*	V_{222}	V_{200}	V_{200}	V_{200}	V_{000} $+\beta-E$	V_{220}	V_{220}	V_{220}
($\bar{1}$11)*	V_{200}	V_{222}	$-V_{200}$	$-V_{200}$	V_{220}	V_{000} $+\beta-E$	$-V_{220}$	$-V_{220}$
(1$\bar{1}$1)*	V_{200}	$-V_{200}$	V_{222}	$-V_{200}$	V_{220}	$-V_{220}$	V_{000} $+\beta-E$	$-V_{220}$
(11$\bar{1}$)*	V_{200}	$-V_{200}$	$-V_{200}$	V_{222}	V_{220}	$-V_{220}$	$-V_{220}$	V_{000} $+\beta-E$

By way of verification, we can calculate some of the $\bar{D}_{ij}$ $(i \neq j)$ and verify that they vanish. The four energy values are given by the equations:

$$\bar{D}_{11} = 0, \qquad \bar{D}_{22} = 0, \qquad \bar{D}_{33} = 0, \qquad \bar{D}_{66} = 0$$

8. CONCLUSION

We have demonstrated the factorization of a secular determinant using the diamond lattice as an example. We have factorized here an 8th-order determinant; by including the SCPW associated with the ensemble of plane waves $\langle 200 \rangle$, we could have done a 14th-order determinant, although this would be much more involved.

In this chapter, we chose the central point $\boldsymbol{k} = 0$ of the Brillouin zone. The same reasoning can be extended to points of high symmetry in the reduced zone [21], [22]. However, the group $C(\boldsymbol{k})$ will then be only a subgroup of the factor group O_h^7.

To obtain numerical results, a knowledge of the coefficients $V_{\boldsymbol{h}}$ is necessary. Their calculation is beyond our present scope and we refer the reader to items [21], [22], and [23] of the bibliography.

Appendix

Let Γ^{α} be the irreducible representation of dimension d_{α} of a finite group of operators P_L and let the d_{α} functions f_j $(j = 1, 2, \ldots, d_{\alpha})$ form a basis of this representation. The operator P_L transforms the function f_j^{α} into a linear combination of functions f_i^{α}, the coefficients of which are the terms of the representative matrix $D_{ij}^{\alpha}(L)$:

$$P \cdot f_j^{\alpha} = \sum_{i=1}^{d_{\alpha}} D_{ij}^{\alpha}(L) f_i^{\alpha} \tag{1}$$

Let us form:

$$\sum_{L} D_{im}^{*\beta}(L) P_L f_j^{\alpha} = \sum_{L} \sum_{i} D_{ij}^{\alpha}(L) D_{im}^{*\beta}(L) f_i^{\alpha}$$

Applying the fundamental formula, Eq. (22) of Chap. 2, this becomes:

$$\sum_{L} D_{im}^{*\beta}(L) P_L f_j^{\alpha} = \sum_{i} \frac{g}{d_{\alpha}} \cdot \delta_{\alpha\beta}\delta_{il}\delta_{jm} f_i^{\alpha} = \frac{g}{d_{\alpha}} \delta_{\alpha\beta}\delta_{jm} f_l^{\alpha} \tag{2}$$

In particular, we can show that:

$$\sum_{L} D_{ll}^{*\alpha}(L) P_L f_i^{\alpha} = \frac{g}{d_{\alpha}} \cdot f_i^{\alpha} \tag{3}$$

Consider now a function F which is a linear combination of the function f_L^{α}. Let:

$$F = \sum_{\alpha=1}^{\rho} \sum_{j=1}^{d_\alpha} b_{\alpha j} f_j^{\alpha} \tag{4}$$

Applying P_L to the function F and forming

$$\sum_L D_{ii}^{*\alpha}(L) P_L F$$

we have:

$$\sum_L D_{ii}^{*\alpha}(L) P_L F = \sum_{\alpha'} \sum_{j'} \sum_L D_{ii}^{*\alpha}(L) b_{\alpha' j'} P_L f_{j'}^{\alpha'}$$

$$= \sum_{\alpha'} \sum_{j'} b_{\alpha' j'} \sum_L D_{ii}^{*\alpha}(L) P_L f_{j'}^{\alpha'}$$

By (2):

$$\sum_L D_{ii}^{*\alpha}(L) P_L F = \sum_{\alpha'} \sum_{j'} b_{\alpha' j'} \cdot \frac{g}{d_\alpha} \cdot \delta_{\alpha\alpha'} \delta_{j' l} f_i^{\alpha'}$$

from which:

$$\sum_L D_{ii}^{*\alpha}(L) P_L F = b_{\alpha l} \cdot \frac{g}{d_\alpha} \cdot f_i^{\alpha}$$

or:

$$\sum_L D_{ii}^{*\alpha}(L) P_L F = \lambda \cdot f_i^{\alpha}$$

where λ may take on zero as a value.

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