ELECTRONIC STATES
AND
OPTICAL TRANSITIONS IN SOLIDS

by
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PREFACE

THE aim of this book is to give a self-contained account of the theoretical foundations and of the basic data relating to the electronic energy levels and wave functions in solids.

Our original idea, when Dr. B. R. Pamplin invited us to write a monograph as the theoretical counterpart of the book by Greenaway and Harbeke on optical properties, was to review the band structure of crystals, emphasizing the role of symmetry. The reasons why crystals with the same number of valence electrons per unit cell and the same symmetry have similar energy band properties began to be understood in the early sixties. As more sophisticated band structure calculations became available in an increasing variety of materials, simple criteria to determine the sequence of the energy levels maintained their usefulness, and their validity was confirmed. It turns out that the full symmetry of the space group is the essential feature in determining the structure of the electronic levels; the available electrons then fill the frame and this accounts for the basic properties of the material.

As in atomic physics, the most precise and direct analysis of the electronic structure is provided by the optical excitation spectrum and it seemed that a band structure monograph without an account of the interaction of electrons with the electromagnetic field would be lifeless. This prompted us to expand our scope to interband transitions and to exciton states, keeping the symmetry determined properties as our guidelines.

Impurity states and the effect of external perturbations were then considered, as further probes for the band structure, as well as for their intrinsic interest. We tried here to emphasize the connection between states of the perfect lattice and states of the perturbed lattice and found again the symmetry arguments extremely useful.

As a final result, what was originally intended as a monograph developed into a textbook. Though its domain is not as extended as that of the classical textbooks in the theory of solids (those of Seitz, Slater, Kittel, and Ziman for instance) it is nevertheless sufficiently wide to be used in advanced courses. This book is self-contained and does not require outside references for comprehension. The pedagogical novelty may be the frequent use of group theoretical arguments, but we found from experience that one quickly learns to master group theory as a simple algebra without perhaps having to understand all its subtleties; this we tried to teach from the beginning. No previous knowledge is implied except for the basic quantum mechanical foundations as are taught in undergraduate courses. Information on elementary crystallography and descriptive facts about solids can be of help, but are not essential.

A problem we had to face was how to move in the wide forests of the literature. We could have refrained from all quotations except to books, monographs, and to some review articles, but we are aware that many readers are interested to learn more on some specific topics and like to find a guide to original papers. We decided then

to refer to some articles, and by necessity we mentioned only some of those we are most familiar with because of our specific research interests at one time or another. We do not claim to have been fair or accurate and we must apologize to our colleagues on this account.

The final manuscript was completed at the École Polytechnique Fédérale of Lausanne, where one of us (Franco Bassani) was invited to lecture on this subject within the post-graduate programme of Swiss Western Universities (CICP). The list of friends and colleagues who helped us is too long to quote here. We are grateful to all of them. Acknowledgements are due to Dr. R. A. Ballinger for his pains in correcting an earlier version of the manuscript and for his constructive criticisms and suggestions.

Before closing, we owe special thanks to Professor F. Seitz who encouraged us in this field; we consider ourselves very fortunate to have been at the University of Illinois in the early years of our professional life.

Lausanne 1973

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CHAPTER 1

USE OF SYMMETRY IN QUANTUM MECHANICS

THE fundamental problem of quantum mechanics is to solve the Schrödinger equation or the Dirac equation, to determine energy levels and eigenfunctions. Except for some standard problems (such as the harmonic oscillator, hydrogenic atoms, and so on) the solutions of an eigenvalue problem cannot be obtained exactly; in general, rather laborious approximation procedures are required. The symmetry properties of the Hamiltonian operator can be used in these cases to simplify the problem and to obtain the symmetry properties of the exact solutions. In particular, the group theoretical study of an operator's symmetry properties makes it possible to classify its eigenstates, to determine essential degeneracies, to derive selection rules, and to reduce the order of the secular determinants which must be diagonalized in order to compute approximate eigenvalues. Though all group theoretical results are contained in the basic equations of quantum mechanics, in practice group theory is an essential tool for the quantum mechanical study of atoms, molecules, and crystals.

In this chapter we wish to present elements of group theory which are required for classifying electronic states and which are useful in computing them. We will give only the basic elements emphasizing the operational point of view, and will refer to some of the standard books on group theory for demonstrating most of the results. The purpose is not that of adding to the excellent existing literature on group theory, but rather of providing non-experts with a working knowledge of it. We believe that this chapter will also be useful to people who already know some group theory but have not applied it extensively to problems of solid state physics.

1-1 Groups and their properties[1]

A group is an ensemble $\mathcal{G}$ of elements among which a multiplication operation is defined which associates a third element with any ordered pair and which satisfies the following requirements:

(i) The product of any two elements in $\mathcal{G}$ is also an element of $\mathcal{G}$.

(ii) The associative law of multiplication holds for any three elements R_i, R_j, R_l of $\mathcal{G}$.

$$R_i(R_jR_l) = (R_iR_j)\,R_l.$$

(iii) There is in $\mathcal{G}$ only one identity or unit element E such that

$$ER_i = R_iE = R_i$$

for any R_i of $\mathcal{G}$.

(iv) Every element R_i of $\mathscr{G}$ has a unique inverse R_i^{-1} which is a member of the ensemble and satisfies:

$$R_i R_i^{-1} = R_i^{-1} R_i = E.$$

The number of elements in the group is called the *order* of the group. For our purposes we will mainly consider finite order groups, i.e. groups containing a finite number of elements.

If the products are commutative so that

$$R_i R_j = R_j R_i$$

for any element R_i, R_j of $\mathscr{G}$, the group is said to be commutative or *abelian*.

A group constituted from the sequence of elements $R, R^2, \ldots, R^n = E$ is said to form a *cyclic group* of order n generated by R. We note that all cyclic groups are also abelian.

Two groups $\mathscr{G}(R)$ and $\mathscr{G}(R')$ are said to be *isomorphic* when it is possible to establish a one-to-one correspondence between their elements so that $R_i R_j = R_l$ implies $R_i' R_j' = R_l'$, and vice versa.

Any subset of elements within a group $\mathscr{G}$, which in itself forms a group, is called a *subgroup* of $\mathscr{G}$.

It is useful at this point to introduce the notion of *complex* as a collection $\mathscr{A} = A_1, A_2, \ldots, A_n$ of elements in a group. In a complex, a given element may appear more than once. We define as *product* $\mathscr{A} \cdot \mathscr{B}$ *of two complexes* $\mathscr{A} = A_1, A_2, \ldots, A_n$ and $\mathscr{B} = B_1, B_2, \ldots, B_m$ the complex containing the set of elements

$$A_1B_1, A_2B_1, \ldots, A_nB_1; \ldots; A_1B_m, A_2B_m, \ldots, A_nB_m.$$

The elements of the complex $\mathscr{A} \cdot \mathscr{B}$ are thus obtained when all the elements of $\mathscr{A}$ are multiplied on the right by all the elements of $\mathscr{B}$.

We define as *inner product* $(\mathscr{A} \cdot \mathscr{B})$ *of two complexes* the complex obtained by listing *only once* the distinct elements of the complex $\mathscr{A} \cdot \mathscr{B}$.

Two elements R_i and R_j of a group $\mathscr{G}(R)$ are said to be *conjugate* if we can find an element X in $\mathscr{G}$ so that

$$R_i = X^{-1} R_j X.$$

The ensemble of all mutually conjugate elements of a group constitute a *class* of the group. The elements of a group can be separated into classes by considering for every element R_i all its conjugate elements $X^{-1}R_iX$, obtained by letting X range over all the elements of the group. The distinct elements so obtained form a class. We note that the identity E always forms a class by itself. If a group is abelian, the number of classes is equal to the number of elements in the group.

Let $\mathscr{C}_i$ and $\mathscr{C}_j$ indicate two classes of a group and $\mathscr{C}_i \cdot \mathscr{C}_j$ the complex obtained by multiplying all the elements of $\mathscr{C}_i$ by all the elements of $\mathscr{C}_j$. It can be proved[1] that the product of two classes is composed of a number of classes in the group. Thus we can write

$$\mathscr{C}_i \cdot \mathscr{C}_j = \sum_s c_{ijs} \mathscr{C}_s, \tag{1-1}$$

where c_{ijs} are integer numbers (including zero).

Let $\mathscr{S} = E, S_2, S_3, \ldots$, be a subgroup of a group $\mathscr{G}$. We call *right coset* $\mathscr{S} \cdot X$ the set of elements $EX, S_2X, S_3X, \ldots$, obtained by multiplying all the elements of the subgroup $\mathscr{S}$ by an element X of the group $\mathscr{G}$. In a similar way we define the set of ele-

ments XE, XS_2, XS_3, ..., as being the *left coset* $X \cdot \mathcal{S}$. Two right (or left) cosets of a subgroup $\mathcal{S}$ are either identical or have no elements in common. A subgroup and all its *distinct* right (or left) cosets contain all the elements of the group once and only once. From this it follows that the order of a subgroup is a divisor of the order of the group.

If a subgroup $\mathcal{S}$ of a group $\mathcal{G}$ consists of complete classes of $\mathcal{G}$ it is called an *invariant or a normal subgroup*. An invariant subgroup is characterized by the fact that its right and left cosets are identical. An invariant subgroup $\mathcal{S}$ and its distinct cosets considered as entities in themselves, constitute a group when the multiplication operation is defined as the *inner product* among the above complexes. Such a group is called *factor group* of the normal subgroup.

Let $\mathcal{G}_1(R)$ and $\mathcal{G}_2(S)$ be two groups in which all the elements of the first group commute with all the elements of the second, and the groups have in common only the identity E. It can be shown that all possible elements RS constitute a group $\mathcal{G}_1 \times \mathcal{G}_2$ called the *direct product* of $\mathcal{G}_1$ and $\mathcal{G}_2$. The order of the direct product of two groups is equal to the product of the order of the two composing groups.

Illustrative examples

As an example of how the definitions and results so far described may be applied, we consider the group of transformations which leave the figure of a cube coincident with its original position. The symmetry group of a cube [1] (called O_h) is very important in crystal physics, and throughout this book we will often refer to this group to illustrate operational applications of general results of group theory. With the aid of Fig. 1-1

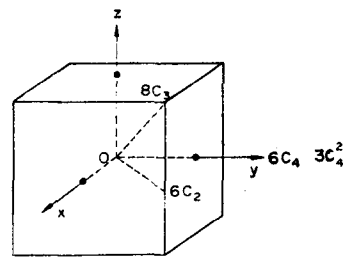

FIG. 1-1. The symmetry elements of a cube.

it is possible to determine the symmetry operations for the cubic group O_h. There are a total of 48 symmetry operations, namely:

The identity (E).
The rotations by π about the axes $x, y, z(3C_4^2)$.
The rotations by $\pm\pi/2$ about the axes $x, y, z(6C_4)$.
The rotations by π about the bisectrices in the planes xy, yz, $xz(6C_2)$.
The rotations by $\pm 2\pi/3$ about the four diagonals of the cube $(8C_3)$.
The combination of the inversion (I) with the above 24 symmetry operations.

The symbols E, I, and C_n have been used to indicate the identity, the spatial inversion through the centre and a rotation by $2\pi/n$ respectively. In Table 1-1 all the 48 symmetry operations of the group O_h are listed, using crystallographic notations and co-

ordinate transformations. The mathematical description of the symmetry operations by means of coordinate transformation is particularly convenient for obtaining rapidly the product of two (or more) elements in the group and analysing the group structure in that way.

TABLE 1-1. Symmetry operations of cubic group O_h. The notations for the 48 operations of the group are given in columns 2 and 5. For example, $I\delta_{2y\bar{z}}$ indicates a rotation by $2\pi/2$ about the axis whose director cosines on the x, y, z axis are in the ratio $0:1:\bar{1}$, followed by the inversion. Notations for the classes are given in columns 1 and 4; columns 3 and 6 indicate the coordinate transformations

Class	Symmetry operation	Coordinate transformation	Class	Symmetry operation	Coordinate transformation
E	E	$x\ y\ z$	I	I	$\bar{x}\ \bar{y}\ \bar{z}$
C_4^2	δ_{2z}	$\bar{x}\ \bar{y}\ z$	IC_4^2	$I\delta_{2z}$	$x\ y\ \bar{z}$
	δ_{2x}	$x\ \bar{y}\ \bar{z}$		$I\delta_{2x}$	$\bar{x}\ y\ z$
	δ_{2y}	$\bar{x}\ y\ \bar{z}$		$I\delta_{2y}$	$x\ \bar{y}\ z$
C_4	δ_{4z}^{-1}	$\bar{y}\ x\ z$	IC_4	$I\delta_{4z}^{-1}$	$y\ \bar{x}\ \bar{z}$
	δ_{4z}	$y\ \bar{x}\ z$		$I\delta_{4z}$	$\bar{y}\ x\ \bar{z}$
	δ_{4x}^{-1}	$x\ \bar{z}\ y$		$I\delta_{4x}^{-1}$	$\bar{x}\ z\ \bar{y}$
	δ_{4x}	$x\ z\ \bar{y}$		$I\delta_{4x}$	$\bar{x}\ \bar{z}\ y$
	δ_{4y}^{-1}	$z\ y\ \bar{x}$		$I\delta_{4y}^{-1}$	$\bar{z}\ \bar{y}\ x$
	δ_{4y}	$\bar{z}\ y\ x$		$I\delta_{4y}$	$z\ \bar{y}\ \bar{x}$
C_2	δ_{2xy}	$y\ x\ \bar{z}$	IC_2	$I\delta_{2xy}$	$\bar{y}\ \bar{x}\ z$
	δ_{2xz}	$z\ \bar{y}\ x$		$I\delta_{2xz}$	$\bar{z}\ y\ \bar{x}$
	δ_{2yz}	$\bar{x}\ z\ y$		$I\delta_{2yz}$	$x\ \bar{z}\ \bar{y}$
	$\delta_{2x\bar{y}}$	$\bar{y}\ \bar{x}\ \bar{z}$		$I\delta_{2x\bar{y}}$	$y\ x\ z$
	$\delta_{2\bar{x}z}$	$\bar{z}\ \bar{y}\ \bar{x}$		$I\delta_{2\bar{x}z}$	$z\ y\ x$
	$\delta_{2y\bar{z}}$	$\bar{x}\ \bar{z}\ \bar{y}$		$I\delta_{2y\bar{z}}$	$x\ z\ y$
C_3	δ_{3xyz}^{-1}	$z\ x\ y$	IC_3	$I\delta_{3xyz}^{-1}$	$\bar{z}\ \bar{x}\ \bar{y}$
	δ_{3xyz}	$y\ z\ x$		$I\delta_{3xyz}$	$\bar{y}\ \bar{z}\ \bar{x}$
	$\delta_{3x\bar{y}z}^{-1}$	$z\ \bar{x}\ \bar{y}$		$I\delta_{3x\bar{y}z}^{-1}$	$\bar{z}\ x\ y$
	$\delta_{3x\bar{y}z}$	$\bar{y}\ \bar{z}\ x$		$I\delta_{3x\bar{y}z}$	$y\ z\ \bar{x}$
	$\delta_{3x\bar{y}\bar{z}}^{-1}$	$\bar{z}\ \bar{x}\ y$		$I\delta_{3x\bar{y}\bar{z}}^{-1}$	$z\ x\ \bar{y}$
	$\delta_{3x\bar{y}\bar{z}}$	$\bar{y}\ z\ \bar{x}$		$I\delta_{3\bar{x}\bar{y}\bar{z}}$	$y\ \bar{z}\ x$
	δ_{3xyz}^{-1}	$\bar{z}\ x\ \bar{y}$		$I\delta_{3xyz}^{-1}$	$z\ \bar{x}\ y$
	$\delta_{3xy\bar{z}}$	$y\ \bar{z}\ \bar{x}$		$I\delta_{3xy\bar{z}}$	$\bar{y}\ z\ x$

Now we would like to show how to separate the 48 elements of O_h into classes. We note that the identity E forms a class by itself. The inversion I commutes with all the elements of O_h and thus constitutes a class by itself. The elements $(\delta_{2x}, \delta_{2y}, \delta_{2z})$ form a class because we have

$$X^{-1}\delta_{2x}X = \delta_{2x}, \quad \text{or} \quad \delta_{2y}, \quad \text{or} \quad \delta_{2z},$$

depending on the choice of the element X of O_h. In a similar way one can divide all the elements of the group into classes. We find that the elements of O_h are divided into 10 classes (which we can denote as $\mathscr{C}_1, \mathscr{C}_2, \ldots, \mathscr{C}_{10}$ following the order of Table 1-1).

As an example of multiplication among classes, we give

$$\mathscr{C}_2 \cdot \mathscr{C}_2 = (\delta_{2x}, \delta_{2y}, \delta_{2z})(\delta_{2x}, \delta_{2y}, \delta_{2z})$$

$$= E, \delta_{2z}, \delta_{2y}, \delta_{2z}, E, \delta_{2x}, \delta_{2y}, \delta_{2x}, E = 3E + 2(\delta_{2x}, \delta_{2y}, \delta_{2z}).$$

Thus

$$\mathscr{C}_2 \cdot \mathscr{C}_2 = 3\mathscr{C}_1 + 2\mathscr{C}_2.$$

Similarly

$$\mathscr{C}_2 \cdot \mathscr{C}_3 = \mathscr{C}_3 + 2\mathscr{C}_4,$$

and so forth.

We will now give examples of subgroups of O_h. If we consider the rotations only, we obtain a subgroup O composed of the 24 operations listed on the left part of Table 1-1. The subgroup O is an invariant subgroup of O_h because it consists of complete classes of O_h. It can be verified immediately that another invariant subgroup T_d of order 24 exists and is formed by the classes E, C_4^2, IC_4, IC_2, C_3 of Table 1-1. The symmetry operations of O_h that interchange x, y, z among themselves constitute a subgroup (called C_{3v}). If we add the inversion to the symmetry operations of group C_{3v} we obtain a group called D_{3d} containing a double number of elements. The rotations $(E, \delta_{4x}, \delta_{2x}, \delta_{4x}^{-1})$ about the x axis constitute a subgroup called C_4; this is a cyclic group generated by δ_{4x}. The subgroup of the elements that change x into itself is C_{4v}. The subgroup of the elements that change x into $-x$ or x is called D_{4h}. The elements E and I constitute a subgroup of O_h that is designated by C_i. We notice that the group O_h can be considered as the direct product of the subgroup O and C_i: $O_h = O \times C_i$. In a similar way we have $D_{3d} = C_{3v} \times C_i$; $D_{4h} = C_{4v} \times C_i$. The subdivision into classes of the above mentioned groups is different for each one of them, even when a number of operations are common to different groups. We leave to the reader the simple exercise of obtaining the classes of all the above-mentioned groups.

1-2 Group representations

In this section we give an outline of the mathematical properties of the representations of groups; this is preliminary to the classification of the electronic states which will be developed in the following section. The basic theorems are stated and working examples are given. For a more detailed discussion of the theory of representations we refer to the standard books on group theory.[1,2]

1-2a *Definitions and basic theorems*

By a *representation* of a group we mean a collection of square non-singular matrices associated with the elements of a group and obeying the group multiplication rules. If we indicate with $\mathbf{D}(R)$ the matrix that corresponds to the operation R, in a given representation D, from

$$R_i R_j = R_l$$

it follows

$$\mathbf{D}(R_i) \cdot \mathbf{D}(R_j) = \mathbf{D}(R_l),$$

where the multiplication operation among matrices is defined by the usual row by column multiplication rule. In particular, from $E\,E = E$ it follows $\mathbf{D}(E) \cdot \mathbf{D}(E) = \mathbf{D}(E)$

and then $\mathbf{D}(E) = 1$. In any representation the unit matrix is assigned to the identity element E. If all the matrices of a representation are different the representation is said to be *faithful*. If some of the matrices of a representation are equal, the representation is said to be *unfaithful*. If we assign the identity matrix to all the elements of a group, we obtain an unfaithful representation called the *identical representation*. The number of rows (or columns) of the matrices of a representation is called the *dimension* of the representation.

Given a representation D of a group $\mathcal{G}(R)$ and a nonsingular matrix $\mathbf{S}$, the ensemble of matrices $\mathbf{S}^{-1} \cdot \mathbf{D}(R) \cdot \mathbf{S} = \mathbf{D}'(R)$ constitutes a representation D' of the group $\mathcal{G}(R)$. We say that the two representations D and D' are connected by a *similarity transformation*, defined by the matrix $\mathbf{S}$. Two representations are *equivalent* if they are related one to the other by a similarity transformation. We recall at this point that any two matrices connected by a similarity transformation have the same *trace* (sum of diagonal elements). Two representations are *inequivalent* if it is impossible to find a similarity transformation that connects one of them to the other. As will be shown clearly in the following Section 1-3, only inequivalent representations are different from a physical point of view, and therefore we need to consider only one among all the infinite equivalent representations.

A representation D is said to be *reducible* if it is equivalent to a representation having the block form

$$\begin{pmatrix} \mathbf{D}^{(1)}(R) & \mathbf{O} \\ \mathbf{O} & \mathbf{D}^{(2)}(R) \end{pmatrix}$$

where $\mathbf{D}^{(1)}(R)$ and $\mathbf{D}^{(2)}(R)$ are square matrices and $\mathbf{O}$ represents a block of zeros. It is easily verified that the matrices $\mathbf{D}^{(1)}(R)$ (or $\mathbf{D}^{(2)}(R)$) constitute a representation $D^{(1)}$ (or $D^{(2)}$) of the group $\mathcal{G}(R)$. The representation D is said to be reducible in the representations $D^{(1)}$ and $D^{(2)}$,

$$D = D^{(1)} + D^{(2)}.$$

A representation is called *irreducible* if it is impossible to reduce all the matrices representing the elements of the group to block form by a similarity transformation. We note that a reducible representation can always be decomposed by an appropriate similarity transformation into a number of irreducible representations. In what follows it will be important to establish how a reducible representation can be decomposed into irreducible representations, to determine whether or not two representations are equivalent, and to find all the inequivalent, irreducible representations. These results can be derived as a consequence of some fundamental properties of the representations of a group whose proofs can be found in classical books on group theory.[2] Here we report the basic theorems in order to emphasize the implied consequences and to derive operational procedures.

First we mention a lemma which applies both to reducible and irreducible representations of a group and allows the use of only those representations with unitary matrices:*

Any representation is equivalent to a representation with unitary matrices.

* We recall that a matrix $\mathbf{U}$ is said to be unitary if $\mathbf{U}^{+}\mathbf{U} = \mathbf{1}$, where $\mathbf{U}^{+}$ indicates the conjugate of the transpose of $\mathbf{U}$. The elements of a unitary matrix satisfy the equations $\sum U_{ij}^{*} U_{il} = \delta_{jl}$, i.e. columns (or rows) of unitary matrices are orthonormals.

Next we consider two theorems which are appropriate to irreducible representations with unitary matrices.

SCHUR'S LEMMA: *Any matrix which commutes with all the matrices of an irreducible representation must be a constant matrix (i.e. a matrix of the form $c\delta_{lk}$, where c is a constant and δ_{lk} the Kronecker symbol).*

We point out as an immediate application that if an element commutes with all the other elements of the group it forms a class by itself, and the matrix that represents this element commutes with all matrix representatives. Thus in any irreducible representation such an element of the group must be represented by a constant matrix.

THE ORTHOGONALITY THEOREM: *The non-equivalent, irreducible, and unitary representations of a group satisfy the relation*

$$\sum_R D^{(\alpha)}(R)^*_{mn} D^{(\alpha')}(R)_{m'n'} = \frac{h}{l_\alpha} \delta_{\alpha\alpha'} \delta_{mm'} \delta_{nn'}, \tag{1-2}$$

where R runs over all the elements of the group, h is the order of the group, and l_α is the dimension of the representation $D^{(\alpha)}$.

The orthogonality theorem and its consequences are fundamental in group representation theory. To demonstrate a first important consequence we can observe that the matrix elements $D^{(\alpha)}(R)_{mn}$, when R runs over the h elements of a group, constitute a number $\sum_\alpha l_\alpha^2$ of independent and mutually orthogonal vectors. Since in any h-dimensional space there can exist at most h-orthogonal vectors, it follows that $\sum_\alpha l_\alpha^2 \leqq h$. Actually it can be proved[2] that *the sum of the squares of the dimensions of the irreducible representations is equal to the order of the group*; i.e.

$$\sum_\alpha l_\alpha^2 = h. \tag{1-3}$$

A second important consequence follows from (1-2) when applied to the traces $\chi^{(\alpha)}(R)$ of the matrices $D^{\alpha}(R)$:

$$\chi^{(\alpha)}(R) = \sum_{m=1}^{l_\alpha} D^{(\alpha)}(R)_{mm}. \tag{1-4}$$

The traces $\chi^{(\alpha)}(R)$ satisfy the orthogonality relation

$$\sum_R \chi^{(\alpha)}(R)^* \chi^{(\alpha')}(R) = h\delta_{\alpha\alpha'}. \tag{1-5a}$$

The set of numbers $\chi^{(\alpha)}(R)$, when R runs over the h elements of the group, is called the *character* of the representation $D^{(\alpha)}(R)$. We note explicitly that the character $\chi(E)$ of the identity element equals the dimension of the representation. Performing a similarity transformation does not change the trace of a matrix, so that representations that are equivalent have the same character. The specification of a representation by means of complete matrices presents a high degree of arbitrariness (due to the fact that all matrix representations related to each other through a similarity transformation are equivalent). Instead, the specification of a representation by means of the character is unique for any of the equivalent representations. Only non-equivalent representations have different characters. We also note that, for the same reason, all the elements which belong to the same class have the same character, and we can therefore rewrite (1-5a) as

$$\sum_{\mathscr{C}_i} \chi^{(\alpha)}(\mathscr{C}_i)^* \chi^{(\alpha')}(\mathscr{C}_i)\, n_i = h\delta_{\alpha\alpha'} \tag{1-5b}$$

where the sum now runs over the classes and n_i is the number of elements of the class $\mathscr{C}_i$. From (1-5b) the following theorem[1,2] is obtained: *The number of irreducible representations of a group is equal to the number of classes in the group.*

The orthogonality relation (1-5a) provides a simple method of decomposing a reducible representation into irreducible representations. A reducible representation D can always be decomposed in the form

$$D = \sum_{\alpha} n_\alpha D^{(\alpha)}, \tag{1-6a}$$

where n_α indicates the number of times the irreducible representation $D^{(\alpha)}$ is contained in D. To determine n_α we note that the character $\chi(R)$ of D can be expressed in the form

$$\chi(R) = \sum_{\alpha} n_\alpha \chi^{(\alpha)}(R), \tag{1-6b}$$

where $\chi^{(\alpha)}(R)$ is the character of the irreducible representation $D^{(\alpha)}$. Multiplying (1-6b) by $\chi^{(\alpha')}(R)^*$ summing on R, and using (1-5a),

$$n_\alpha = \frac{1}{h} \sum_{R} \chi^{(\alpha)}(R)^* \chi(R). \tag{1-7}$$

1-2b *Rules for constructing the character table of a group*

It is convenient to display in table form the characters of the irreducible representations of a group. Such a table gives less information than a complete set of matrices would, but it is sufficient for classifying the electronic states and allows us to derive an explicit set of unitary matrices, as will be explained in Section 1-3. From the results described above a number of practical rules can be given which are sufficient for constructing the character table of finite symmetry groups.

1. The number of irreducible representations equals the number of classes in the group.
2. The sum of the squares of the dimensions l_α of the irreducible representations is equal to the number of elements in the group

$$\sum_{\alpha} l_\alpha^2 = h.$$

3. The characters of the irreducible representations must be mutually orthogonal and normalized to the order of the group

$$\sum_{R} \chi^{(\alpha)}(R)^* \chi^{(\alpha')}(R) = h\delta_{\alpha\alpha'}.$$

4. Every group admits the one-dimensional identical representation in which each element in the group is represented by the number 1. The orthogonality relation between characters then shows that for any irreducible representation, except the identical representation, $\sum_{R} \chi^{(\alpha)}(R)$ is zero.
5. The characters of the irreducible representations satisfy the relation[1]

$$\sum_{\alpha} \chi^{(\alpha)}(\mathscr{C}_i)^* \chi^{(\alpha)}(\mathscr{C}_j) = \frac{h}{n_i} \delta_{ij},$$