Elements of Group Theory for Physicists

SECOND EDITION

A W Joshi

A HALSTED PRESS BOOK

BY THE SAME AUTHOR

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Elements of Group Theory for Physicists

THIRD EDITION

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To MADHUBALA
and MANJARI

That is infinite, this is infinite; from that infinity emanates this infinity. Taking away this infinity from that infinity, infinity still remains behind.

Ishavasya Upanishad

Preface to the Third Edition

Several small changes and modifications have been made in bringing out this edition. These have been prompted by the feedback received from students during my courses and by the suggestions received from several teachers.

It has been found that determination of the character tables even of simple groups is a hurdle most students find difficult to cross. Therefore Chapter 3 of this edition contains a flow-chart explaining step by step the method of determining the character table of a group, along with a parallel-running example illustrating the procedure in full details. An Appendix on mappings and functions has also been added. Temptation to add material of advanced nature has been resisted.

Thanks are due to several readers for helpful suggestions.

Simla, March 1982 A.W. Joshi

Preface to the Second Edition

It gives me great pleasure to bring out this second edition. It was very gratifying to see that the first edition of this work was generally liked by physicists. I have continued to give courses on group theory during this period and the response from students has been very encouraging.

Many little changes have been made here and there in this edition in an attempt to improve the treatment and presentation. Sections 1.1, 1.2, 1.6, 2.4, 4.1 and 4.2 have been considerably rewritten. A section on Lorentz group has been added in Chapter 4.

I am grateful to Dr. R. Vasudevan, now in the Department of Mathematics, Regional Engineering College, Thiruchirapalli, for useful discussions clarifying many mathematical subtleties, to Dr. Bipin Kumar Agarwal, Department of Physics, University of Allahabad, and to Dr. Tulsi Dass, Department of Physics, Indian Institute of Technology, Kanpur, for fruitful correspondence. I am thankful to a number of reviewers and readers who took great pains to go through the first edition and made suggestions for its improvement.

A.W. JOSHI

Meerut, October 1976

Preface to the First Edition

One main reason has prompted me to write this book—there is hardly any self-contained book at present on group theory for physicists at an introductory level. It is my own experience that in my student days, I had to refer to over half a dozen books to obtain a rudimentary knowledge of group theory and representation theory. At the introductory level, it is desirable that a beginner should be able to get most (preferably all) of the relevant material in a single book which can then serve as a textbook for a course on group theory for the graduate student in physics. It is with this aim that I have tried to collect diverse material such as vector spaces, Hilbert spaces, operators. direct product of matrices, topological groups, connectedness and compactness, etc. These are pure mathematical topics and a physics student would invariably have to go to the mathematics department to master these concepts.

Having included such relevant topics which are *sine qua non* for understanding every step in the applications of group theory in physics in general, some of the most important and illustrative applications in quantum mechanics, atomic physics and solid state physics have been taken up. For example, the general applications in quantum mechanics include symmetry and degeneracy, good quantum numbers, matrix element theorem, level splitting and selection rules, dynamical symmetry, time-reversal symmetry, etc. In atomic physics, the applications of group theory to selection rules, Zeeman effect, addition of angular momenta, irreducible tensor operators and the Wigner-Eckart theorem have been treated. The crystal field splitting of atomic leveis, Brillouin zones and the electronic structure of crystals are discussed as exemplary applications in solid state physics.

It has been one of my major aims to keep the book at an introductory level. I have often sacrificed rigour in favour of clarity. Attempt

has been made to make sure that the student grasps the fundamental principles throughly at every stage of his progress. Having grasped these, the student is left to himself to develop his knowledge in any desired direction. For example, Chapter 4 on continuous groups provides, I presume, a fairly sound base for elementary particle physics. But only the basic principles of $SU(2)$ and $SU(3)$ are discussed and I have stopped as soon as we really approach elementary particle physics.

Although a few special topics have been dealt with in the appendices, I am aware that a large number of applications of group theory are still left out. One could think of the role of symmetry in molecular vibrations, various physical properties of crystals, crystal field theory, lattice dynamics, higher symmetry schemes for elementary particles, and numerous other applications. However, I believe, only a specialist is likely to refer to these topics; the purpose of the beginner should be well served by this book in its present form.

At present, very few Indian universities have courses in group theory for M.Sc. (physics) students. It is my sincere hope that the easy availability of an elementary book such as this would accelerate the process of inclusion of group theory in the M.Sc. (physics) syllabi by more and more universities. While giving courses based on the material of this book for the last three years, I have tried to appreciate the difficulties of the students and have modified the presentation of the material accordingly to remove the obstacles. I hope this book will be equally useful to teachers and students.

A large number of problems has been provided at the end of every chapter. These serve a twofold purpose. Firstly, they enable the student to test his understanding, providing at the same time a better and firm grasp of the principles involved. Secondly, some of the problems can also be looked upon as extensions of the material treated in the respective chapters. The results of such problems have quite often been used in succeeding chapters.

I am thankful to the referees of this book for making valuable suggestions for improving the manuscript. I am very grateful to Mr. Sudarshan Kumar Bahl for help in proofreading. I shall be glad to receive any comments and suggestions from the readers.

A.W. JOSHI

Meerut, August 1973

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ELEMENTS OF GROUP THEORY FOR PHYSICISTS

CHAPTER 1

Abstract Group Theory

The concept of groups had its origin more than 150 years ago, in the beginning of the nineteenth century. The early development of the theory of groups was due to the famous mathematicians Gauss, Cauchy, Abel, Hamilton, Galois, Sylvester, Cayley, and many others.[1] However, till the advent of modern quantum mechanics in 1925, it did not find much use in physics. The advantages of group theory in physics were soon recognized and the new tool was put to use in the calculations of the atomic structures and spectra by, to name only a few, H.A. Bethe, E.P. Wigner and others. Group theory has now become indispensable in most branches of physics and physical chemistry.

Although a mathematician is generally more interested in the formal development of abstract group theory, a physicist finds the representation theory of groups of direct use in quantum physics and other branches of physics. In this chapter, we shall discuss only those aspects of abstract group theory which will be needed for understanding the representation theory; this will be taken up in Chapter 3 for finite groups and in Chapter 4 for continuous groups.

1.1 What is a Group?

Consider the set I of all integers, $I = \{\ldots, -3, -2, -1, 0, 1, 2, \ldots\}$, and consider the following four properties of this set: (a) The sum of any two elements of the set I is again an integer and hence belongs

[1] Bell (1965).

to the set I. (b) The set contains an element 0, called *zero*, which has the property that for any element $m \in I$, $m+0=0+m=m$. (c) For every element m of I, there exists a unique element n also belonging to I, such that $m+n=n+m=0$; evidently, $n=-m$. (d) If m, n and p are any three elements of I, $m+(n+p)=(m+n)+p$; this means that the law of addition is associative.

Consider another set, the set $U(n)$ of all unitary matrices of order n, where n is a fixed finite positive integer. This set has the following four properties: (a) If U and V are any two unitary matrices of order n, their product UV is again a unitary matrix of order n and hence belongs to the set $U(n)$. (b) The set contains the unit matrix I which has the property $UI=IU=U$ for every $U \in U(n)$. (c) If U is an element of $U(n)$, there exists a unique element V also in $U(n)$ such that $UV=VU=I$. (d) If U, V and W are any three elements of the set, $U(VW)=(UV)W$.

It will be noticed that the four properties satisfied by the above two sets are very much similar in nature. In fact, these properties define a *group* and both the sets discussed above are examples of a group.

Abstractly, a group is a set of *distinct* elements, $G \equiv \{E, A, B, C, D, \ldots\}$, endowed with a law of composition (such as addition, multiplication, matrix multiplication, etc.), such that the following properties are satisfied:

(a) The composition of any two elements A and B of G under the given law results in an element which also belongs to G. Thus,

$$A \circ B \in G, \quad B \circ A \in G, \tag{1.1}$$

where we have denoted the composition of two elements of G by the symbol $\circ$. Symbolically,

$$A \circ B \in G \; \forall \; A, B \in G.$$

This property is known as the *closure* property of the group and the set is said to be closed under the given law of composition.

(b) There exists an identity element $E \in G$ such that for all $A \in G$,

$$E \circ A = A \circ E = A. \tag{1.2}$$

Symbolically,

$$\exists \, E \in G \ni E \circ A = A \circ E = A \; \forall \; A \in G.$$

E is known as the *identity element* of G.

(c) For any element $A \in G$, there exists a unique element $B \in G$ such that

$$A \circ B = B \circ A = E. \tag{1.3}$$

Symbolically,

$$\forall \; A \in G \exists \, B \in G \ni A \circ B = B \circ A = E.$$

B is called the *inverse* of A, and vice versa.

(d) The law of composition of the group elements is *associative*, i.e., for any $A, B, C \in G$,

$$A \circ (B \circ C) = (A \circ B) \circ C. \tag{1.4}$$

Symbolically,

$$A \circ (B \circ C) = (A \circ B) \circ C \;\forall\; A, B, C \in G.$$

The number of elements in a group is called its *order*. A group containing a finite number of elements is called a *finite group*; a group containing an infinite number of elements is called an *infinite group*. An infinite group may further be either discrete or continuous: if the number of the elements in a group is denumerably infinite (such as the number of all integers), the group is *discrete*; if the number of the elements in a group is nondenumerably infinite (such as the number of all real numbers), the group is *continuous*.

Some more examples of a group are:

(i) The group of order two consisting of the real numbers 1, —1, with ordinary multiplication as the law of composition.

(ii) The group of order four consisting of the complex numbers $1, i, -1, -i$ (where $i^2 = -1$), under multiplication.

(iii) The discrete infinite group of all real integers discussed above. The law of composition is addition and the identity element is 0.

(iv) The set of all real numbers under addition. This is a continuous group with 0 as the identity element. The inverse of a number b is its negative $-b$.

(v) The set of all positive (zero excluded) real numbers under multiplication. The identity element is 1 and the inverse of x is its reciprocal $1/x$.

(vi) The single point set containing just the unity is a group of order one under multiplication.

(vii) The set of the two matrices $\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$ and $\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}$ under matrix multiplication.

(viii) The set of all nonsingular square matrices of order n (n a positive integer) under matrix multiplication.

(ix) If k is a positive integer, the set $(0, 1, 2, \ldots, k-1)$ of k integers is a group under[2] addition modulo (k). The identity element is zero and the inverse of an element r is $k-r$.

[2]A number n modulo (k) is defined as the remainder obtained on dividing n by k. Thus, 10 modulo (6) $=4$, 3 modulo (3) $=0$, etc. Let $k=6$ in Example (ix); then $3+4=1$, $5+1=0$, etc.

(x) If p is a prime number greater than 1, the set $(1, 2, \ldots, p-1)$ of $p-1$ integers is a group under multiplication[3] modulo (p). The identity element is 1 and the inverse of an element r is $(sp+1)/r$ where s is the smallest positive integer which makes $sp+1$ an integral multiple of r in the ordinary sense.

(xi) The set of all matrices of order $m \times n$ under matrix addition. The identity element is the null matrix of order $m \times n$ and the inverse of an element A is its negative $-A$.

In the above examples, we come across two basic laws of composition—addition and multiplication—each referring to scalars and matrices. When the law of composition of a group is addition, the inverse of an element is called the *additive inverse*; when it is multiplication, the inverse is called the *multiplicative inverse*. Thus, if x is a number, $-x$ is its additive inverse and $1/x$ the multiplicative inverse provided $x \neq 0$. If A is a matrix, $-A$ is its additive inverse and A^{-1} the multiplicative inverse provided A is nonsingular. Similarly, in the case of a group of numbers, 0 is the *additive identity* and 1 the *multiplicative identity*; in the case of a group of matrices, the null matrix (of appropriate order) is the additive identity while the unit matrix (of appropriate order) is the multiplicative identity.

Hereafter, the symbol $\circ$ will be dropped and, for example, AB will be written for $A \circ B$. Similarly, we shall often replace the word 'composition' by 'multiplication' or 'product' of group elements.

The product of the group elements is not necessarily commutative, i.e., in general, $AB \neq BA$. If all the elements of a group commute with each other, it is said to be an *abelian group*. Such groups have important consequences as will be seen later. All the groups considered above, except the group $U(n)$ of all unitary matrices of order n and the group of all nonsingular matrices of order n, are abelian groups.

1.1.1 Group of transformations. The groups of particular interest to a physicist are the groups of transformations[4] of physical systems. A transformation which leaves a physical system invariant is called a *symmetry transformation* of the system. Thus any rotation of a circle about an axis passing through its centre and perpendicular to the plane of the circle is a symmetry transformation for it. A permutation of two identical atoms in a molecule is a symmetry transformation for the molecule.

[3]See footnote 2. In this Example, if $p=7$, then $3.4=5$, $2.5=3$, etc.; the inverse of 4 is 2, since $4.2=1$.

[4]Such as rotations, reflections, permutations, translations, etc.

We shall now show that the set of all symmetry transformations of a system is a group. First we observe that if we perform two symmetry transformations of the system successively, the system remains invariant. Thus the composition of any two symmetry transformations of the system is again a symmetry transformation of the system, i.e., the set considered is closed under the law of successive transformations. We can define an identity transformation which leaves the system unchanged; and this obviously belongs to the set. Given a symmetry transformation, we see that there exists an inverse transformation which also belongs to the set. Finally, the successive transformation of the system obeys the associative law. This proves that the set considered is a group.

The group of all symmetry transformations of a system is called the *group of symmetry* of the system.

1.1.2 The group of symmetry of a square. Suppose we have a square cut out in a piece of cardboard as shown in Fig. (1.1). Let us label the various points of the square as shown in the figure: the corners by a, b, c, d; the centres of the edges by e, f, g, h; and the centre of the square by o. The points marked 1, 2,..., 8 are fixed on the paper (they are not marked on the square). Now suppose we

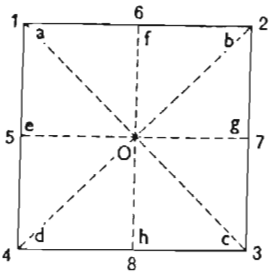


FIGURE 1.1 The axes and the planes of symmetry of a square

rotate the square through a right angle about a line perpendicular to the square and passing through o. But for the labeling $a, b, \ldots, h$, we would not notice any change in the square. Consider all such symmetry transformations of the square (such as rotating or reflecting it, without bending or stretching) which leave the position of the boundaries of the square unchanged but give a distinct labeling of the marked points $a, b, \ldots, h$. Before listing all such transformations, it would be proper to say a few words about the notation we shall be using.

If a rotation through an angle $2\pi/n$ (n a positive integer) about some axis leaves the system invariant, the axis is known as an *n-fold symmetry axis* of the system and the corresponding operation is denoted by C_n. Its integral powers, which will also be symmetry transformations of the system, will be denoted by C_n^k; this represents k successive operations of C_n on the system, or a rotation of $2\pi k/n$ about the axis. A reflection in a plane will be denoted by m or σ with a subscript specifying the plane of reflection. The identity transformation will be denoted by E.

While enumerating all the symmetry transformations of a square, which are listed in Table (1.1), we shall use the shorthand notation 'reflection in a line' to mean 'reflection in a plane perpendicular to the square passing through the line'.

It can be seen that the operations listed in Table (1.1) exhaust the symmetry transformations of a square, i.e., there is no other transformation which leaves the square in the same position and yet gives a distinct labeling for the points $a, b, \ldots, h$. One may think of inversion through the centre o; but it can be readily verified that it is identical to C_4^2.

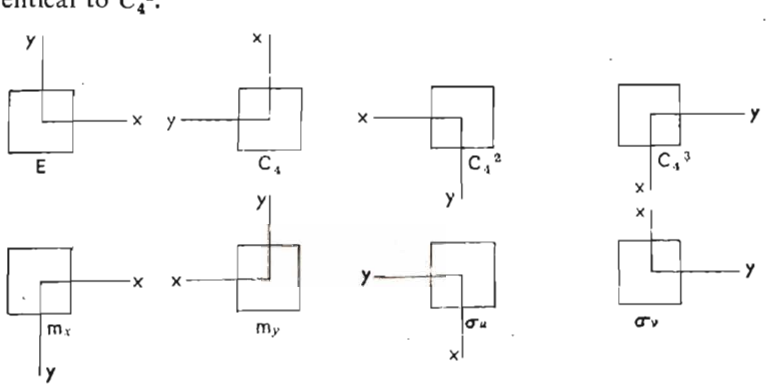
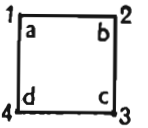
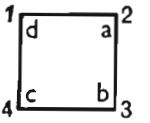
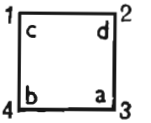
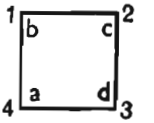
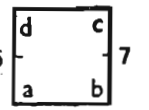
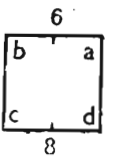
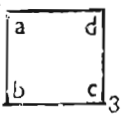
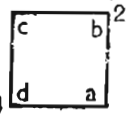


FIGURE 1.2 The equivalance of the transformations of a square with those of a cartesian coordinate system

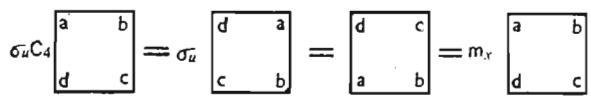
It is interesting to note that these eight transformations correspond to the eight different ways in which we can choose a cartesian coordinate system with axes parallel to the edges of the square. These are shown in Fig. (1.2). We either consider that the coordinate system is held fixed while the square is transformed, which is known as the *active viewpoint*, or that the square is held fixed while the coordinate system is transformed, which is known as the *passive viewpoint*. It should be noted that a transformation in the active viewpoint is

TABLE 1.1 SYMMETRY TRANSFORMATIONS OF A SQUARE

Symbol	*Operation*	*Result*
E	The identity.	
C_4	A clockwise rotation through 90° about an axis normal to the square and passing through o.	
C_4^2	A rotation through 180° about the above axis.	
C_4^3	A clockwise rotation through 270° about the same axis.	
m_x	Reflection in the line 5–7.	
m_y	Reflection in the line 6–8.	
σ_u	Reflection in the line 1–3.	
σ_v	Reflection in the line 2–4.	

equivalent to the inverse transformation in the passive viewpoint. Thus, if in the active viewpoint, we define C_4 as a clockwise rotation of the square, in the passive viewpoint, C_4 would mean an anticlockwise rotation of the coordinate system. This convention will be used throughout this book and is illustrated explicitly in Fig. (1.2).

It can be readily verified that the set of the eight transformations listed in Table (1.1) is a group which is the group of symmetry of a square. Thus, consider the operation of C_4 followed by that of σ_u on the square. This can be found as follows:



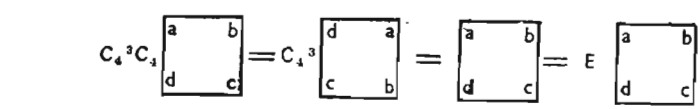
(1.5)

In the operator notation, we can write this as

$$\sigma_u C_4 = m_x, \tag{1.6}$$

meaning thereby that the operations of $\sigma_u C_4$ and of m_x on the square or in fact, on any system, give the same result.

The inverse of an operator is that operator which nullifies the effect of the first. Thus, consider the successive operation $C_4^3 C_4$ on the square:



(1.7)

The same result would be obtained if we operate by C_4 and C_4^3 in the reverse order. Thus, by (1.3), C_4 is the inverse of C_4^3 and vice versa. In the operator notation, we may write this as

$$(C_4)^{-1} = C_4^3 \text{ or } C_4 C_4^3 = C_4^3 C_4 = E. \tag{1.8}$$

It is left as an exercise to verify that each of the eight symmetry transformations has an inverse which is just one of these eight transformations.

Finally, the transformations obey the associative law. Hence the set of the symmetry transformations of a square is a group. This symmetry group of a square of order eight is denoted by C_{4v} in crystallography[5].

[5]The crystallographic point groups are dealt with in Chapter 7. If instead of the reflections, we consider rotations through π about the four lines of Fig. (1.1), we have the group D_4 which is also the symmetry group of a square and has the eight elements (E, C_4, C_4^2, C_4^3, C_{57}, C_{68}, C_{13}, C_{24}) where C_{57} denotes a twofold rotation about the line 5–7, etc. See Chapter 7 for more details.

1.2 The Multiplication Table

Let us consider the following operations

$$C_4\ m_x = \sigma_u,\ \sigma_u\ C_4^3 = i m_y,$$
$$\sigma_u\ \sigma_v = C_4^2, \text{ and so on.}$$

All such products of the group elements can be represented by a table, known as the *group multiplication table*. It is shown in Table (1.2) for the symmetry group of a square, C_{4v}. Note that in a successive operation such as $ABC\ldots$, the order of operation is *from right to left*. Thus, in the product $C_4 m_x$, m_x is the *first operation* and C_4 the *second operation*. The entry for $C_4 m_x$ would therefore be found in Table (1.2) in the column corresponding to m_x and the row corresponding to C_4.

TABLE 1.2 THE MULTIPLICATION TABLE FOR THE GROUP C_{4v}

SECOND OPERATION	*FIRST OPERATION*							
	E	C_4	C_4^2	C_4^3	m_x	m_y	σ_u	σ_v
E	E	C_4	C_4^2	C_4^3	m_x	m_y	σ_u	σ_v
C_4^3	C_4^3	E	C_4	C_4^2	σ_v	σ_u	m_x	m_y
C_4^2	C_4^2	C_4^3	E	C_4	m_y	m_x	σ_v	σ_u
C_4	C_4	C_4^2	C_4^3	E	σ_u	σ_v	m_y	m_x
m_x	m_x	σ_v	m_y	σ_u	E	C_4^2	C_4^3	C_4
m_y	m_y	σ_u	m_x	σ_v	C_4^2	E	C_4	C_4^3
σ_u	σ_u	m_x	σ_v	m_y	C_4	C_4^3	E	C_4^2
σ_v	σ_v	m_y	σ_u	m_x	C_4^3	C_4	C_4^2	E

The ordering of the rows and the columns in writing down the multiplication table of a group is immaterial. We have chosen a different ordering for the rows and for the columns: the ordering is such that an element in the first column (second operation) is the inverse of the corresponding element in the first row (first operation). If the multiplication table is written in this way, the principal diagonal contains only the identity element E. The advantage of this arrangement will be clear in Section 3.7.

1.2.1 The rearrangement theorem. It will be noticed from the multiplication Table (1.2) that each element of the group occurs once and only once in each column. This is known as the *rearrangement*

theorem. The arrangement of elements in a row (column) is different from that in every other row (column).

To prove this theorem, we first show that no element can occur more than once in a row or a column. For, suppose an element D occurs twice in a column corresponding to the element A. This means that there exist two elements, say B and C, such that

$$BA=D \text{ and } CA=D.$$

Multiplying from the right by A^{-1}, we get

$$B=DA^{-1},\ C=DA^{-1},$$

showing that $B=C$, which is contrary to the hypothesis that the group elements are distinct. The same line of argument can be used to show that no element can occur more than once in a row.

The second part is now easy to prove: since no element can occur more than once in a row or in a column and since the number of places to be filled in each row or each column is equal to the order of the group, each element must occur once and only once in each row and in each column. This completes the proof.

An important consequence of this theorem is that if f is any function of the group elements, then

$$\sum_{A\in G} f(A)=\sum_{A\in G} f(AB), \tag{1.9}$$

where B is an element of the finite group G and the sum runs over all the group elements.

1.2.2 Generators of a finite group. It is possible to generate all the elements of a group by starting from a certain set of elements which are subject to some relations. Consider the smallest set of elements whose powers and products generate all the elements of the group. The elements of this set are called the *generators of the group*. We shall restrict ourselves here to finite groups only and illustrate by means of two examples.

EXAMPLE 1. We wish to generate a group starting from an element A subject only to the relation $A^n=E$ such that n is the smallest positive integer satisfying this relation.

Since A is an element of the group, all its integral powers must also be in the group. Thus, we generate new elements $A^2, A^3, \ldots,$ of the group and the process stops at $A^n=E$. The higher powers of A do not give us new elements because $A^{n+k}=A^k$. The desired group is thus $(A, A^2, A^3, \ldots, A^{n-1}, A^n=E)$, whose order is n.

EXAMPLE 2. We wish to generate a group from two elements A and B subject only to the relations $A^2=B^3=(AB)^2=E$.

The group must contain the elements E, A, B and B^2, since $A^2=E$ and $B^3=E$. But then it must also contain all the products of A, B and B^2 among themselves. Hence we get two new elements of the group, AB and BA. It can be shown that A and B do not commute, since if they do, then from the relation $(AB)^2=E$, we have

$$E=ABAB=A^2B^2=B^2,$$

which is not true. Therefore AB and BA are distinct elements. We have thus generated the six elements of the group E, A, B, B^2, AB, BA.

It can now be shown that this set is a group, i.e., it is closed under multiplication. Suppose we wish to show that the product $(AB)B=AB^2$ belongs to this set. From the relation $(AB)^2=E$, we have $(AB)^{-1}=AB$ or $B^{-1}A^{-1}=AB$ or $AB=B^{-1}A$ since $A^2=E$. But from $B^3=E$, we have $B^{-1}=B^2$. Hence $AB=B^2A$. Using this, we find that

$$(AB)B=B^2AB=B^2B^2A=BA,$$

which indeed belongs to the set. Similarly, it can be verified that the inverse of each element of the set also belongs to the set. Hence the desired group is (E, A, B, B^2, AB, BA), whose order is six.

The generators of a group are not unique; they can be chosen in a variety of ways. Thus, for example, the group of order six of Example 2 above may be generated by any one of the following sets of generators: (A, B), (A, B^2), (A, AB), (B, AB), etc. See Problem (1.25)

1.3 Conjugate Elements and Classes

Consider a relation such as

$$A^{-1}BA=C, \tag{1.10}$$

where A, B and C are elements of a group. When such a relation exists between two elements B and C, they are said to be *conjugate elements*. The operation is called a *similarity transformation* of B by A. It is clear that

$$ACA^{-1}=B. \tag{1.11}$$

It is not difficult to find such relationships among the elements of the group C_{4v}. Thus,

$$C_4^{-1}m_xC_4=m_y, \tag{1.12}$$

showing that m_x and m_y are conjugate to each other.

It is a simple exercise to show that if B is conjugate to C and B is also conjugate to D, then C and D are conjugate elements; or B, C and D are all conjugate to each other.

It immediately follows that we can split a group into sets such that all the elements of a set are conjugate to each other but no two elements belonging to different sets are conjugate to each other. In fact, such sets of elements are called the *conjugacy classes* or simply the *classes* of a group. The identity element E always constitutes a class by itself in any group, since, for any element A of the group, $A^{-1}EA=E$. It is left as an exercise to show that the classes of C_{4v} are

$$(E),\ (C_4,\ C_4^3),\ (C_4^2),\ (m_x,\ m_y),\ (\sigma_u,\ \sigma_v). \tag{1.13}$$

In case we are dealing with groups of transformations consisting of rotations, reflections and inversion of a physical system, there are some simple rules which allow the determination of the classes of a group without having to perform explicit calculations for all the elements. These are:

(i) Rotations through angles of different magnitudes must belong to different classes. Thus C_4 and C_4^2 of C_{4v} belong to different classes (see Problem 1.17).

(ii) Rotations through an angle in the clockwise and in the anticlockwise sense about an axis belong to a class if and only if there exists a transformation in the group which reverses the direction of the axis or which changes the sense of a cartesian coordinate system (i.e., takes a right-handed system into a left-handed one or vice versa). Thus, C_4 and C_4^3 of C_{4v} belong to the same class because a reflection (such as m_x or σ_u) changes the sense of the coordinate system.

(iii) Rotations through the same angle about two different axes or reflections in two distinct planes belong to the same class if and only if the two axes or the two planes can be brought into each other by some element of the group. Thus, m_x and m_y belong to the same class since the line 5–7 of Fig. (1.1) can be brought into the line 6–8 by the application of C_4; σ_u and m_x do not belong to the same class since there is no operation in C_{4v} which can bring the line 1–3 into the line 5–7.

These simple criteria are very useful in obtaining the classes of the molecular and the crystallogarphic point groups simply by inspection.

1.3.1 Multiplication of classes. We now define the product of two classes as follows. Let $C_i=(A_1, A_2, \ldots, A_m)$ and $C_j=(B_1, B_2, \ldots, B_n)$ be two classes (same or distinct) of a group containing m and n elements, respectively. We define their product as a set containing all the elements obtained by taking the products of each element of C_i with every element of C_j. We keep each element as many times as it occurs in the product. Thus,

$$C_i C_j=(A_1B_1, A_1B_2, \ldots, A_lB_k, \ldots, A_mB_n). \tag{1.14}$$

We can easily show that the set $C_i C_j$ consists of complete classes. It would be enough to show that if an element A_lB_k belongs to the set $C_i C_j$, then any element conjugate to A_lB_k also belongs to the set. Consider an element conjugate to A_lB_k with respect to some element X of the group G:

$$\begin{aligned} X^{-1}(A_lB_k)X&=(X^{-1}A_lX)\,(X^{-1}B_kX) \\ &=A_rB_s, \text{ say,} \end{aligned} \tag{1.15}$$

where, by the definition of a class, A_r belongs to C_i and B_s belongs to C_j. Hence A_rB_s belongs to the set C_iC_j.

We can then express the product of two classes of a group as a sum of complete classes of the group:

$$C_i C_j=\sum_k a_{ijk}\, C_k, \tag{1.16}$$

where a_{ijk} are nonnegative integers giving the number of times the class C_k is contained in the product $C_i C_j$, and the sum is over all the classes of the group.

1.4 Subgroups

A set H is said to be a *subgroup* of a group G if H is itself a group under the same law of composition as that of G and if all the elements of H are also in G.

As an example, consider the four elements (E, C_4, C_4^2, C_4^3) of C_{4v}. It is easy to see that this set satisfies all the axioms defining a group; hence it is a subgroup of C_{4v}. Some more examples of the subgroups of C_{4v} are (E, C_4^2, m_x, m_y), (E, σ_u), etc.

Every group G has two trivial subgroups—the identity element and the group G itself. A subgroup H of G is called a *proper subgroup* if $H\neq G$, i.e., if G has more elements than H.

If we work out the classes of the two subgroups (E, C_4, C_4^2, C_4^3) and (E, C_4^2, m_x, m_y), we find that in both of these groups every element constitutes a class by itself (see Problem 1.12). The

elements C_4 and C_4^3 *do not belong to the same class* in the group (E, C_4, C_4^2, C_4^3) because there is no operation in this group which changes the sense of the coordinate system. Similarly, m_x and m_y do not belong to the same class in the group (E, C_4^2, m_x, m_y) because there is no operation in this group which can take the x axis into the y axis. It is therefore important to note that *elements belonging to a class in a larger group may not belong to a class in a smaller subgroup.*

1.4.1 Cyclic groups. If A is an element of a group G, all integral powers of A such as $A^2, A^3, \ldots$, must also be in G. If G is a finite group there must exist a finite positive integer n such that

$$A^n = E, \tag{1.17}$$

the identity element. The smallest positive (nonzero) integer satisfying (1.17) is called the *order of the element A.*

The group $(A, A^2, A^3, \ldots, A^n \equiv E)$, which we have already discussed in Example 1 of Section 1.2.2, has the property that each of its elements is some power of one particular element. Such groups are called *cyclic groups. A group generated by a single element is a cyclic group.* Clearly, cyclic groups are abelian, while the converse is not necessarily true.

1.4.2 Cosets. Consider a subgroup $H = (H_1 \equiv E, H_2, \ldots, H_h)$ of order h of a group G which is of order g. Let X be any element of G. Construct all the products such as XE, XH_2, etc., and denote the set of these elements by[6]

$$XH = (XE, XH_2, XH_3, \ldots, XH_h). \tag{1.18}$$

Now there arise two cases—X may be in the subgroup H or X may not be in H. If X is a member of H, the set XH must be identical to the group H by the definition of a group. In the set XH, we only have a rearrangement of the elements of H. We may denote this by writing

$$XH = H \quad \text{if} \quad X \in H. \tag{1.19}$$

On the other hand, if X does not belong to H, it can be shown that no element of the set XH belongs to H. This we do by starting from a contrary assumption. Thus, suppose that XH_i for some value of i $(1 \leq i \leq h)$ belongs to H. Now since H is a group, H_i^{-1} also belongs to H. Hence it follows that $(XH_i)\, H_i^{-1} = X$ is in H,

[6]This is the multiplication of a set by an element. We have previously discussed the product of two sets in Section 1.3.1.

contrary to the hypothesis that X is not a member of H. This proves that H and XH have no common element. We say that H and XH are *disjoint sets* and express it, in the set theoretic notation, by saying that the intersection of H and XH is the null set ϕ:

$$H \cap (XH)=\phi. \tag{1.20}$$

The set XH is called the *left coset* of H in G with respect to X. Similarly, we can define the *right coset* of H in G with respect to X as the set of elements

$$HX=(EX, H_2X, H_3X, \ldots, H_hX), \tag{1.21}$$

which will also be disjoint to H if X is not in H. All the elements of the left coset and the right coset must of course belong to the bigger group G since X as well as H_i belong to G.

1.4.3 A theorem on subgroups. We are almost half-way through to prove an important theorem: *If a group H of order h is a subgroup of a group G of order g, then g is an integral multiple of h.*

To prove this, let $H=(E, H_2, H_3, \ldots, H_h)$ be the subgroup of G. As before, form the left coset of H with respect to an element $X \in G$ which does not belong to H. All the elements XH_i $(1 \leq i \leq h)$ belong to G but none of them is a member of H, as already shown above. Thus, we have h new elements of the group G. We have so far generated the following $2h$ members of G:

$$H \cup XH=(E, H_2, H_3, \ldots, H_h, X, XH_2, \ldots, XH_h). \tag{1.22}$$

If this does not exhaust the group G, then pick up an element Y from the remaining elements of G such that Y belongs neither to H nor to XH. Again, forming the left coset YH, we see by the previous argument that all the elements YH must belong to G, but that no element of YH can belong to H. That is, the sets H and YH are disjoint. We now prove that the sets YH and XH are also disjoint. For, if an element YH_i were to be identical to an element, say, XH_j $(1 \leq i, j \leq h)$, then we have

$$YH_i=XH_j,$$

or

$$Y=XH_j\,H_i^{-1} \equiv XH_k, \text{ say,} \tag{1.23}$$

with $1 \leq k \leq h$, showing that Y belongs to XH, contrary to the hypothesis. Thus we have a set of h new elements of G, making altogether the $3h$ elements

$$H \cup XH \cup YH$$
$$=(E, H_2, \ldots, H_h, X, XH_2, \ldots, XH_h, Y, YH_2, \ldots, YH_h). \tag{1.24}$$

If this still does not exhaust the group G, then we pick up one of the remaining elements of G and continue the process. Every time we generate h *new* elements, they must all belong to G and hence the order of G must be an integral multiple of h.

The integer g/h is called the *index* of the subgroup H in G.

If an element A of a finite group G is of order n, we have seen that the set $(A, A^2, \ldots, A^n \equiv E)$ is a subgroup of G. Hence it follows that *the order of every element of a finite group must be an integral divisor of the order of the group.*

1.4.4 Normal subgroups and factor groups. If the left and the right cosets of a subgroup H with respect to *all* the elements $X \in G$ are the same, then H is called a *normal subgroup* or an *invariant subgroup* of G. This condition can be written as

$$XH = HX,$$

or

$$X^{-1}HX = H \text{ for all } X \in G. \tag{1.25}$$

We can also express this condition alternatively by requiring that every element of XH be equal to some element of HX, or

$$XH_i = H_j X,$$

which gives

$$X^{-1}H_j X = H_i. \tag{1.26}$$

But this is just the conjugation relation between the elements H_i and H_j and shows that if an element H_i belongs to a normal subgroup H of G, then all the elements conjugate to H_i also belong to H. This is often expressed by saying that *a normal subgroup consists of complete classes of the bigger group*. The converse also holds, i.e., if a subgroup H consists of complete classes of G, then H is a normal subgroup of G (see Problem 1.26). This may therefore be taken as an alternative definition of a normal subgroup. For example, (E, C_4^2, m_x, m_y) is a normal subgroup of C_{4v} whereas (E, m_x) is not.

We now introduce another important concept, that of a factor group. We shall illustrate this first by an example and then follow with a general discussion.

Consider a normal subgroup of C_{4v}, say $K_1 = (E, C_4^2)$, and form all its distinct cosets with respect to various elements of C_{4v}. There are four such distinct cosets including K_1:

$$K_1 = (E, C_4^2), \quad K_2 = (C_4, C_4^3),$$
$$K_3 = (m_x, m_y), \quad K_4 = (\sigma_u, \sigma_v). \tag{1.27}$$

We can make this set of cosets a group if we define the product of two cosets as follows: The multiplication of two cosets is a set

obtained by multiplying each element of the first coset with every element of the other, *repeated elements being taken only once.*[7] In general, the product of two cosets will depend on the order of multiplication. Thus, we consider

$$K_2K_3=(C_4, C_4^3)\,(m_x, m_y)$$
$$=(\sigma_u, \sigma_v, \sigma_u, \sigma_v)\rightarrow(\sigma_u, \sigma_v)=K_4. \tag{1.28}$$

It can then be seen that the set $K\equiv(K_1, K_2, K_3, K_4)$ is closed under coset multiplication defined above. Similarly, it can be verified that this set also satisfies all the other requirements for being a group. Hence it follows that the set K, where each coset K_i is considered an 'element' on a higher plane of abstraction, is a group under the given law of composition. This group K is called the *factor group* of G with respect to the normal subgroup K_1.

Quite generally, if H is a normal subgroup of G, the set of all the distinct cosets of H in G, together with the coset multiplication defined above, is called the *factor group* or the *quotient group* of G with respect to H and is denoted by

$$K=G/H. \tag{1.29}$$

If g is the order of G and h that of H, then it is easy to see that the order of K is g/h, the index of H in G.

1.5 Direct Product of Groups

The direct product of two groups $H=(H_1\equiv E, H_2, H_3, \ldots, H_h)$ of order h and $K=(K_1\equiv E, K_2, K_3, \ldots, K_k)$ of order k is defined as a group G of order $g=hk$ consisting of elements obtained by taking the products of each element of H with every element of K, provided (i) that H and K have no common element except the identity E and (ii) that each element of H commutes with every element of K. The direct-product group is denoted by

$$G=H\otimes K=(E, EK_2, EK_3, \ldots, EK_k, H_2K_2, \ldots,$$
$$H_2K_k, \ldots, H_hK_k). \tag{1.30}$$

Clearly, both H and K are normal subgroups of G. The subgroups of C_{4v} afford a simple example of this concept. Thus,

$$(E, m_x)\otimes(E, m_y)=(E, C_4^2, m_x, m_y). \tag{1.31}$$

Taking the direct product of groups provides the simplest method of enlarging a group. This concept finds its immediate use in the study of symmetry of physical systems such as atoms, molecules,

[7]Note that this is different from the class multiplication defined earlier.

crystals, nuclei and elementary particles. To take an example, suppose G is a group of symmetry (of a system) consisting of proper rotations only. Suppose we later discover that the inversion, J, is also a symmetry transformation of the system. The inversion operator J along with the identity E constitutes a group of order 2, (E, J). Since the inversion commutes with all the rotations, we can take the direct product of G with (E, J) to obtain a bigger symmetry group for the system which is now $G \otimes (E, J)$. Although it is not possible in reality to tell whether we have found all the symmetries of a given system, it is naturally desirable to know as many of them as possible. We shall discuss this concept in more detail when we come to the applications of group theory to quantum mechanics in Chapters 5 and 6.

1.6 Isomorphism and Homomorphism

A group multiplication table, such as that shown in Table (1.2) for the group of a square, characterizes the group completely and contains all the information about the analytical structure of the group. All groups having similar multiplication tables have the same structure—they are said to be *isomorphic* to each other.

Mathematically, there is an *isomorphism* between two groups $G=\{E, A, B, C, \ldots\}$ and $G'=\{E', A', B', C', \ldots\}$, both of the same order g, if there exists a one-to-one correspondence between the elements of G and G'. In other words, if the one-to-one correspondence is denoted by $A \leftrightarrow A'$, $B \leftrightarrow B'$, $C \leftrightarrow C'$, etc., then a multiplication such as $AB=C$ in the group G implies that $A'B'=C'$ in the group G'. The multiplication table of G' can thus be obtained from that of G simply by replacing the elements of G by the corresponding elements of G'. It should be noted that the identity element of one group corresponds to the identity element of the other group under isomorphic mapping.

As an example, it can be seen that the group $\{1, i, -1, -i\}$ of numbers is isomorphic to the group $\{E, C_4, C_4^2, C_4^3\}$ of rotations under the mapping

$$1 \leftrightarrow E,\ i \leftrightarrow C_4, -1 \leftrightarrow C_4^2, -i \leftrightarrow C_4^3.$$

Thus, for example, the product $(-1)\ (-i)=i$ in one group corresponds to the product $C_4^2\ C_4^3=C_4$ in the other. We shall come across many other examples of isomorphism later.

Very often we come across a many-to-one correspondence or mapping from one group to another (or one set to another, in

general). We say that there is a *homomorphism* from a group G_1 to another G_2 if to each element A in G_1 there corresponds a unique element $\phi(A)$ of G_2 such that $\phi(AB)=\phi(A)\,\phi(B)$. The mapping ϕ must be defined for all elements of G_1. The element $\phi(A)$ of G_2 is called the *image* or *map* of the element A of G_1 under the homomorphism. Although each element A of G_1 is mapped onto a unique element $\phi(A)$ of G_2, several elements of G_1 may be mapped onto the same element in G_2. Thus it may happen that $\phi(A)=\phi(B)$ even if $A\neq B$. If n elements of G_1 are mapped onto each element of G_2, we say that there is an n-to-1 mapping or homomorphism from G_1 to G_2. It is evident that if $n=1$, the mapping reduces to isomorphism.

Let us develop a slightly different notation to make the concepts more clear. Let $G=\{E, A, B, C, \ldots\}$ be a group of order g and let $G'=\{E_1, E_2, \ldots, E_n, A_1, A_2, \ldots, A_n, \ldots\}$ be a group of order ng (note that only one element, say E_1, is the identity of G'). Suppose that it is possible to split the group G' into g sets (E_l), (A_l), etc., each containing n elements such that the elements of G' can be mapped onto the elements of G according to the scheme

$$E_1, E_2, \ldots, E_n \rightarrow E;$$
$$A_1, A_2, \ldots, A_n \rightarrow A; \text{ etc.} \qquad (1.32)$$

Then the group G' is said to be *homomorphic* to G if the mapping is such that the product

$$A_l B_j = C_k, \quad 1 \leqslant k \leqslant n, \qquad (1.33)$$

in G' implies $AB = C$ in G, and vice versa, where C is the image in G of the elements $C_1, C_2 \ldots, C_n$ of G'. We say that there is an n-to-1 *homomorphism* or mapping from G' to G.

Again the subgroups of C_{4v} provide a simple example of homomorphism. Thus, the group (E, C_4^2, m_x, m_y) is homomorphic to the group (E, m_x) with the following two-to-one mapping:

$$E, C_4^2 \rightarrow E; \; m_x, m_y \rightarrow m_x. \qquad (1.34)$$

1.6.1 The set (E_l) is a normal subgroup of G'. It can be shown quite generally that the set (E_l) of G', whose elements $E_1, E_2, \ldots, E_n$ are mapped onto the identity element E of G, is a normal subgroup of G'. To prove this, we first show that the set (E_l) is a group. In the group G, we have $EE=E$; therefore, by the definition of homomorphism, the product of any two elements E_l and E_j of G' must belong to the same set (E_l). Thus, the set (E_l) is closed under multiplication. Now we must show that the identity element, which we denote by E' for a moment, belongs to the set (E_l). Suppose E' belongs to

some other set of G', say, $E' \in (A_i)$; then for any element $B_k \in G'$, we must have $E'B_k = B_k$. By homomorphism, we must then have $AB = B$ in G, which is possible only if $A = E$, i.e., only if $E' \in (E_i)$. It is now almost trivial to show that if $E_j \in (E_i)$, then E_j^{-1} also belongs to the set (E_i). Thus we have proved that (E_i) is a group.

To prove the second part, that (E_i) is a normal subgroup of G', we consider its left and right cosets with any other element, say $A_l \in G'$, i.e., we consider $A_l(E_j)$ and $(E_j)A_l$. Because $EA = AE = A$ in G, any product element such as E_jA_l or A_lE_j of G' must belong to the set (A_i). Moreover, the products of A_l with all the n elements E_j of the set (E_j) exhaust the set (A_i). To put it briefly, every element of (A_l) must occur once and only once in the product $A_l(E_j)$; the same will clearly be true for $(E_j)A_l$. Thus, we have

$$A_l(E_j) = (A_i),$$
$$(E_j)A_l = (A_i), \tag{1.35}$$

showing that (E_i) is a normal subgroup of G'.

The set (E_i) of G' which is mapped onto E of G is called the *kernel of homomorphism*. The above theorem can therefore be stated briefly by saying that *the kernel of homomorphism from G' to G is a normal subgroup of G'*.

The identity element furnishes a trivial example of homomorphism. There is a homomorphism from any group G onto the group of order one containing only the identity element, which, in turn, is a normal subgroup of any group.

1.7 Permutation Groups

These groups are of considerable importance in the quantum mechanics of identical particles. Consider a system of n identical objects. If we interchange any two or more of these objects, the resulting configuration is indistinguishable from the original one. We can consider each interchange as a transformation of the system and then all such possible transformations form a group under which the system is invariant. Since there are altogether $n!$ permutations on n objects, the group has order $n!$. It is known as the *permutation group* of n objects or the *symmetric group* of degree n and is usually denoted by S_n.

Taking a specific example of three identical objects, we see that there are six possible permutations which may be denoted as:

$$E=\begin{pmatrix}1&2&3\\1&2&3\end{pmatrix},\quad A=\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix},\quad B=\begin{pmatrix}1&2&3\\3&1&2\end{pmatrix},$$
$$C=\begin{pmatrix}1&2&3\\2&1&3\end{pmatrix},\quad D=\begin{pmatrix}1&2&3\\3&2&1\end{pmatrix},\quad F=\begin{pmatrix}1&2&3\\1&3&2\end{pmatrix}. \tag{1.36}$$

The labels 1, 2 and 3 refer to the positions of the three objects rather than to the objects themselves.[8] The system itself has six possible 'states' which may be denoted by

$$\psi_1=(1\ 2\ 3),\quad \psi_2=(2\ 3\ 1),\quad \psi_3=(3\ 1\ 2),$$
$$\psi_4=(2\ 1\ 3),\quad \psi_5=(3\ 2\ 1),\quad \psi_6=(1\ 3\ 2). \tag{1.37}$$

The six operators of (1.36) then act on any of the above six states and their operations are to be interpreted as follows. The operation of A, for example, on any state ψ_i means that the object in position 2 is to be put in position 1, that in position 3 to be put in position 2, and that in position 1 to be brought to position 3. Thus,

$$A\psi_1=\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix}(1\ 2\ 3)=(2\ 3\ 1)=\psi_2; \tag{1.38a}$$

$$C\psi_2=\begin{pmatrix}1&2&3\\2&1&3\end{pmatrix}(2\ 3\ 1)=(3\ 2\ 1)=\psi_5. \tag{1.38b}$$

It can be readily shown that the set of the six permutations of (1.36) is a group. The successive operation of two permutations on a state can be easily worked out. Thus, operating on (1.38b) from the left, say, by A, we find

$$A(C\psi_2)=\begin{pmatrix}1&2&3\\2&3&1\end{pmatrix}(3\ 2\ 1)=(2\ 1\ 3)=\psi_4. \tag{1.39}$$

But we also have

$$F\psi_2=\begin{pmatrix}1&2&3\\1&3&2\end{pmatrix}(2\ 3\ 1)=(2\ 1\ 3)=\psi_4. \tag{1.40}$$

Thus, we have

$$AC\psi_2=F\psi_2. \tag{1.41}$$

It will be seen that if we start from any other state, the result is the same, i.e.,

$$AC\psi_i=F\psi_i,\quad 1\leq i\leq 6. \tag{1.42}$$

Therefore, in the operator notation, we can write

$$AC=F. \tag{1.43}$$

It is left as an exercise in Problem (1.19) to work out the multiplication table of S_3.

[8] In quantum mechanics it is futile to try to label identical particles!

Coming back to the general case of n identical objects, we see that each permutation of these objects can be expressed as the successive interchange or transposition of two objects taken at a time. We define a *transposition* (mk) on n identical objects as the operation in which the objects in the positions m and k are to be interchanged leaving all the other objects where they are. It can then be verified that the symmetric group S_n of degree n (n finite) can be generated by the $n-1$ transpositions (12), (13),..., $(1n)$.

As an example, a set of generators of S_3 are the two transpositions (12) and (13). All the elements of S_3 can be written as suitable products of these generators. Thus, $B=(13)(12)$, $F=(13)(12)(13)$, $C=(12)$, etc., where, as per the convention, the order of operation is from right to left.

If a permutation consists of an even number of transpositions, it is called an *even permutation*; if it consists of an odd number of transpositions, it is called an *odd permutation*. Thus, the operators E, A and B of (1.36) are even permutations, while C, D and F are odd permutations.

The product of two even or of two odd permutations is an even permutation, whereas the product of an even permutation with an odd permutation is an odd permutation. It then immediately follows that the set of all even permutations among the group S_n is a subgroup.[9] This is known as the *alternating group* of degree n and is usually denoted by A_n. Its order is clearly $n!/2$. Thus, the alternating group of degree 3 is $A_3=(E, A, B)$, where the elements have been defined in (1.36).

Some more discussion of the permutation group and its classes is given in Section 6.1.3.

1.8 Distinct Groups of a Given Order

We have already mentioned that isomorphic groups have identical analytical structures. A number of isomorphic groups may stand for altogether different physical situations, but it is sufficient to study only one of them mathematically. The elements of a number of isomorphic groups may be matrices or permutations or coordinate transformations; it suffices to study a group which is isomorphic to all of these and its elements need not have any

[9] A similar result does not hold for the set of all odd permutations. Why?

'meaning' and may be treated in the abstract sense. Notice that the whole theory is based on the four fundamental group axioms which are quite independent of any particular interpretation given to the group elements. This part of the theory is therefore called *abstract group theory*. We may 'put in' any interpretation for the group elements demanded by the physical situation at hand and 'take out' the corresponding results.

It is therefore desirable to enumerate the distinct (nonisomorphic) groups of a given order n. It is particularly easy to do so for small values of n. We list below the possible structures of groups of orders upto $n=6$.

(i) $n=1$. There is only one distinct structure: a group having only the identity element E.

(ii) $n=2$. Again, there is only one distinct structure: a group (E, A), where, because the group is of order two, A^2 must equal E. Any group of order 2 must be isomorphic to (E, A). Examples are (E, m_x), (E, σ_u), $(1, -1)$, etc.

(iii) $n=3$. This case also has only one structure: a group generated by an element A of order 3, i.e., $(A, A^2, A^3 \equiv E)$.

(iv) $n=4$. This is the lowest order for which there are two nonisomorphic groups. If we denote the group by (E, A, B, C), then the two possible structures are discussed below.

As discussed at the end of Section 1.4.3, the elements A, B and C can be of order 2 or 4. If any one element, say A, is of order 4, it follows that the remaining three elements must be equal to the powers of A and we get the structure

$$A^2=B,\ A^3=C,\ A^4=E. \tag{1.44}$$

This gives us the cyclic group of order 4, $(A, A^2, A^3, A^4 \equiv E)$.

In the second case, when no element is of order 4, it follows that all the elements (excluding the identity) are of order 2; hence

$$A^2=B^2=C^2=E. \tag{1.45}$$

The result of Problem (1.11) then shows that the group must be abelian. Now consider the product AB; the two possibilities are $AB=E$ and $AB=C$. But $AB=E$ implies that B is the inverse of A, whereas, from (1.45), we see that A is its own inverse. In other words, $AB=E$ would imply $B=A$; therefore the only possibility is $AB=C$.

The two nonisomorphic structures are then

(a) a cyclic group of order 4, $(A, A^2, A^3, A^4 \equiv E)$;

(b) a noncyclic abelian group of order 4, (E, A, B, C) with

the structure $A^2=B^2=C^2=E$, $AB=C$, $BC=A$, $CA=B$. This is the lowest order noncyclic group.

Any group of order 4 must be isomorphic to one of these two groups.

(v) $n=5$. Only one distinct structure is possible in this case: the cyclic group of order 5, $(A, A^2, A^3, A^4, A^5\equiv E)$.

(vi) $n=6$. There are again two distinct (nonisomorphic) groups. We shall prove only a part of this statement to illustrate the argument involved.

Let us denote the group by (E, A, B, C, D, F). As before, we note that the orders of all the elements except E must be 2, 3 or 6. If the order of any one elements is 6, it follow that we have a cyclic group of order 6, $(A, A^2, A^3, A^4, A^5, A^6\equiv E)$. Therefore, to find the second possible structure we exclude this case.

Now we shall show that not all the elements A, B, C, D and F can be of order 2. For if they are, then by Problem (1.11), the group is abelian. Then consider any two elements, say A and B with $A^2=B^2=E$, and let $AB=BA=C$. It is clear that the set (E, A, B, C) of four elements is a subgroup of order 4. But this is not possible, because it violates the fundamental theorem on subgroups that the order of a subgroup must be an integral divisor of the order of the group. Hence we conclude that at least one element is of order 3.

The remaining part of the proof is left to the reader. The two resulting structures are:

(a) a cyclic group $(A, A^2, A^3, A^4, A^5, A^6\equiv E)$;

(b) a noncyclic group (E, A, B, C, D, F) which is also nonabelian and has the structure $A^3=B^3=E$, $C^2=D^2=F^2=E$, $B=A^2$, $AC=F$, $CA=D$, $BC=D$, etc. This is the lowest order nonabelian group and is isomorphic to S_3.

It is not easy, although possible in principle, to go on in this way to higher values of n. The number of nonisomorphic groups would increase, in general, with increasing n. However, two comments are worthy of note:

(i) For every finite value of n, there is always a cyclic group generated by an element of order n, i. e., $(A, A^2, A^3, \ldots, A^n\equiv E)$.

(ii) If the order n of a group is a prime number, there is only one possible structure, i. e., the cyclic group of order n.

We conclude this chapter with one solved example.

EXAMPLE. Prove that a set of a group G is a system of generators of

G *if and only if* no proper subgroup of G exists which contains all the elements of the set S.

Choose a subset of the group G such that S is a system of generators of G. To begin with, let us assume that there exists a proper subgroup H of G such that $S \subseteq H \subseteq G$. Since H is a group and S is contained in H, the powers and products of the elements of S give elements belonging to the group H alone, not G, which contradicts the assumption that S is a system of generators of G. Hence, *if S is a system of generators of G, there exists no proper subgroup of G which contains S.*

Now, assume that there exists no proper subgroup of G which contains S. Let us generate a group by taking all powers and products of the elements of S. Suppose this gives rise to the group K; evidently, $K \subseteq G$. But, by assumption, G contains no proper subgroup which contains S. Hence it follows that $K = G$, showing that S is a system of generators of G. Thus *if no proper subgroup of G exists which contains S, then S is a system of generators of G.*

The desired result follows immediately on combining the above two results.

PROBLEMS ON CHAPTER 1

(1.1) Show that the following sets are groups under the given laws of composition and classify them according to their properties:

(i) the set of all rational numbers[10] under addition;
(ii) the set of all nonzero rational numbers under scalar multiplication;
(iii) the set of all complex numbers under addition;
(iv) the set of all nonzero complex numbers under scalar multiplication;
(v) the set of the eight matrices

$$\left\{\begin{bmatrix}1&0\\0&1\end{bmatrix}, \begin{bmatrix}0&1\\-1&0\end{bmatrix}, \begin{bmatrix}-1&0\\0&-1\end{bmatrix}, \begin{bmatrix}0&-1\\1&0\end{bmatrix}, \begin{bmatrix}1&0\\0&-1\end{bmatrix}, \begin{bmatrix}-1&0\\0&1\end{bmatrix}, \begin{bmatrix}0&-1\\-1&0\end{bmatrix}, \begin{bmatrix}0&1\\1&0\end{bmatrix}\right\}$$

under matrix multiplication;

(vi) the set of all unitary matrices of order n under matrix multiplication;
(vii) the set of all even integers under addition;
(viii) the set of all complex numbers of unit magnitude under scalar multiplication.

(1.2) Show that the following sets are not groups under the given laws of composition. Which of the group axioms do they fail to satisfy?

(i) The set of *all* real numbers under multiplication;

[10] A *rational number* is one which can be expressed as the ratio of two integers, p/q. A real number which cannot be expressed as the ratio of two integers (such as $\sqrt{2}$) is called an *irrational number*.

(ii) the set of all nonnegative real numbers under addition;
(iii) the set of all odd integers under (a) multiplication, (b) addition;
(iv) the set $(1, 2, \ldots, p-1)$ of $p-1$ integers under multiplication modulo (p) where p is not a prime number.

(1.3) (a) Do the three matrices

$$E=\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&1&0\\0&0&0&1\end{bmatrix},\quad A=\begin{bmatrix}0&0&0&1\\1&0&0&0\\0&1&0&0\\0&0&1&0\end{bmatrix},\quad B=\begin{bmatrix}0&0&1&0\\0&0&0&1\\1&0&0&0\\0&1&0&0\end{bmatrix}$$

form a group (under matrix multiplication)? Add a minimum number of matrices to this set to make it a group. Find these necessary additional matrices and write down the multiplication table and classes. Is this group isomorphic to (E, C_4, C_4^2, C_4^3) or to (E, C_4^2, m_x, m_y), or to both?

(b) To the group obtained in the above problem, one more matrix is added:

$$\begin{bmatrix}0&0&0&1\\0&0&1&0\\0&1&0&0\\1&0&0&0\end{bmatrix}.$$

Again, add to this set of matrices a minimum number of matrices to make it a group. Show that the resulting group has order eight and that it is isomorphic to C_{4v}. (This fact will be used in Section (3.9)

(1.4) Show that the n n-th roots of unity, i.e., $\exp(i2\pi k/n)$ for $1 \leq k \leq n$, form a cyclic group of order n under scalar multiplication. Show that if m is an integral divisor of n, then the said group has a subgroup of order m.

(1.5) Construct the group multiplication tables for the groups of Example (ix) of Section 1.1 for $k=4$ and 5, and for those of Example (x) for $p=5$ and 7.

(1.6) Write down the multiplication table for the group of the eight matrices of Problem 1.1 (v). Obtain the classes and all the subgroups. Which of them are normal subgroups? Show that this group is isomorphic to the group C_{4v} treated in this chapter by finding a suitable one-to-one correspondence.

(1.7) Generate the matrix group two of whose elements are

$$\begin{bmatrix}0&1\\-1&0\end{bmatrix} \text{ and } \begin{bmatrix}0&i\\i&0\end{bmatrix}.$$

Show that the group is of order 8 and has 5 classes, but is not isomorphic to C_{4v}. (Hint: Show that the matrix group generated here has six elements of order 4 whereas C_{4v} has only two such elements. The multiplication tables can therefore not be identical.) (This shows that *two groups of the same order having the same number of classes are not necessarily isomorphic.*)

(1.8) Obtain the products of the various classes of the group C_{4v} and express them as sums of classes in accordance with Eq. (1.16).

(1.9) Generate a group from two elements A and B subject only to the relations $A^2=B^k=(AB)^2=E$, where k is a finite integer greater than 1, and find out its order. (Such groups are known as the *dihedral groups* and are denoted by D_k.)

(1.10) What are the generators of the groups C_{4v} and S_3? What are the generators of the matrix group of Problem 1.1 (v)?

(1.11) Show that a group in which each element except the identity is of order 2 is abelian.

(1.12) Show that an element of a group G constitutes a class by itself *if and only if* it commutes with all the elements of G. Hence show that in an abelian group every element is a class.

(1.13) Let H be a subgroup of a group G and let S be an arbitrary subset of G.

(i) Let $C(S\,;\,H)$ be the set of elements of H each of which commutes with every element of S, i.e.,

$$C(S\,;\,H)=(X \in H \mid XA=AX \;\forall\; A \in S).$$

Show that $C(S\,;\,H)$ is a group. (This group is known as the *centralizer* of S in H.)

(ii) Let $N(S\,;\,H)$ be the set of elements of H such that for all $X \in H$, $X^{-1}SX=S$, i.e.,

$$N(S\,;\,H)=(X \in H \mid X^{-1}SX=S).$$

Show that $N(S\,;\,H)$ is a group. (This group is known as the *normalizer* of S in H).

(1.14) Show that the group generated by two commuting elements A and B such that $A^2=B^3=E$ is cyclic. What is its order?

(1.15) Let H be a subgroup of G and let XH be a coset of H which is disjoint to H. Let Y be an element of G belonging neither to H nor to XH. Show that the set YXH need not be disjoint to *both* H and XH. (Hint: Show that if YXH were disjoint to both H and XH, then in the proof of the theorem in Section 1.4.3, we would arrive at the erroneous result that the integer g/h must be an integral power of 2.)

(1.16) Show that every subgroup of index 2 is a normal subgroup.

(1.17) Show that all the elements belonging to a class of a group have the same order. Show, by giving a contrary example, that the converse is not necessarily true.

(1.18) Let C_i be a class of a group and let C_i^* be the set of elements which are the inverses of those of C_i. Show that C_i^* is also a class. (The class C_i^* is usually called the *inverse of the class* C_i.)

(1.19) Construct the multiplication table of the symmetric group S_3 and obtain its classes.

(1.20) Show that the symmetric group S_n of degree n is homomorphic to the symmetric group S_2 of degree 2.

(1.21) Construct the symmetry group of an equilateral triangle (this group is denoted by C_{3v} in crystallography). Write down its multiplication table, classes, subgroups and normal subgroups. Show that C_{3v} is isomorphic to S_3.

(1.22) Construct the alternating group of degree 4, A_4. Write down its multiplication table and obtain its classes.[11]

(1.23) If $G=H \otimes K$, show that

(i) both H and K are normal subgroups of G;

(ii) the factor group G/H is isomorphic to K;

[11]See Falicov (1967), p. 14.

(iii) G is homomorphic to both H and K;
(iv) the number of classes in G is equal to the product of the numbers of classes in H and K.

(1.24) Show that the group C_{4v} is homomorphic to the group $(1, -1)$ under multiplication. Also show that this 4-to-1 homomorphic mapping can be established in three distinct ways.

(1.25) Given that $A^2=B^3=(AB)^2=E$, generate groups starting from the elements (i) (A, AB), (ii) (B^2, BA). Show that in both the cases, you get the same group as that obtained in Example 2 of Section 1.2.2.

(1.26) If a subgroup H of a bigger group G consists of complete classes of G, show that H is a normal subgroup of G, that is, the left and the right cosets of H with respect to any element of G are the same.

(1.27) Consider the symmetric group S_4 of degree 4 with generators (12), (13) and (14). In the notation of the text, this means that $(12)=\begin{pmatrix}1&2&3&4\\2&1&3&4\end{pmatrix}$, etc.

(a) Express the two permutations

$$A=\begin{pmatrix}1&2&3&4\\4&3&2&1\end{pmatrix} \text{ and } B=\begin{pmatrix}1&2&3&4\\3&1&4&2\end{pmatrix}$$

as products of the generators.

(b) What is the order of each of the two elements A and B? Find the number of transpositions in each of these elements.

(c) Obtain both the products AB and BA of these two elements.

(d) Obtain the inverse of each of the two elements.

(1.28) Find the subgroup of the symmetric group S_4 which leaves the polynomial $x_1x_2+x_3+x_4$ invariant. (Such a group is called the group of the given polynomial.)

(1.29) Find the group of the polynomial $x_1x_2+x_3x_4$ and verify that it contains as a subgroup the group obtained in Problem (1.28).

(1.30) Prove that the group of all positive numbers under multiplication is isomorphic to the group of all real numbers under addition. (Hint: The isomorphic mapping is set up by taking logarithms.)

(1.31) Let G denote a cyclic group of order 12 generated by an element A and let H be a subgroup generated by the element A^3. Find all the cosets of H in G and obtain the multiplication table for the factor group G/H.

(1.32) Consider the set of the following six functions:

$$f_1(x)=x, \quad f_2(x)=1-x, \quad f_3(x)=x/(x-1),$$
$$f_4(x)=1/x, \quad f_5(x)=1/(1-x), \quad f_6(x)=(x-1)/x.$$

Let the operation of composition of two functions be defined as the substitution of a function into another (that is, 'function of a function'). Thus for example,

$$(f_5f_3)(x)=f_5(f_3(x))=f_5(x/(x-1))=1/(1-x/(x-1))$$
$$=1-x\equiv f_2(x),$$

so that $f_5f_3=f_2$, etc. Show that the set is a group under this law of composition. Show that

$$(f_5)^{-1}=f_6, \text{ and } (f_i)^{-1}=f_i \text{ for } i=2, 3, 4.$$

Finally, show that the group is isomorphic to S_3 or C_{3v}.

(1.33) Determine the symmetry groups of a regular pentagon and a regular hexagon. Also find their classes.

Bibliography for Chapter 1

Albert (1956), Chapter 1; Alexandroff (1959); Dixon (1967); Falicov (1967); Hall (1968); Hamermesh (1964); Jansen and Boon (1967); Margenau and Murphy (1966), Chapter 15; Meijèr and Bauer (1962); Schenkman (1965); Tinkham (1964); Wigner (1959).

CHAPTER 2

Hilbert Spaces and Operators

It is an axiom of quantum mechanics that to every physical observable, there corresponds a hermitian operator and that the set of all eigenfunctions of a hermitian operator is a complete set. The Hilbert space of the operator is the set of all linear combinations of the eigenfunctions. Each state of the system is represented by a vector of the Hilbert space on which the operator acts. We then proceed to expand 'any' function as a linear combination of all the eigenfunctions. Sometimes this can be dangerous and misleading unless we know that the function under consideration belongs to the Hilbert space and the conditions under which such an expansion is possible. In this chapter, we shall develop the concepts of Hilbert spaces and operators and prepare the ground for the applications of group theory in quantum mechanics. In most respects, this chapter is independent of the first one. None the less, these two chapters will form the basis of all the remaining chapters.

2.1 Vector Spaces and Hilbert Spaces

In this section, we shall introduce the idea of Hilbert spaces. Some of their important properties will be described in the next section. We are very familiar with the ordinary three-dimensional vector algebra. To a mathematician, however, the familiar three-dimensional space is just a particular example of the generalized concept of a vector space of arbitrary dimensions. This purely abstract concept of n-dimensional spaces (n a finite real positive

integer or infinite) indeed becomes essential in many problems in modern physics and mathematics.

Before we begin, it will not be out of place to define in brief a field. Let F be a set of elements $(a, b, c, d, \ldots)$ and suppose that two binary operations are defined for the elements of F: an operation denoted by $+$ (called *addition*) and an operation denoted by $.$ (called *multiplication*). Then F is a *field* if

(i) F is an abelian group under addition, with an identity element denoted by 0 and called *zero*, and

(ii) the set of the nonzero elements of F also is an abelian group under multiplication. The identity element of this group is denoted by 1 and is called the *unity*.

We shall quote only three examples of a field to which we shall frequently refer:

(a) The set of all real numbers, commonly denoted by R;

(b) The set of all complex numbers, commonly denoted by C;

(c) The set of all rational numbers, commonly denoted by Q.

Loosely speaking, the fields are the number systems of mathematics. An example of a finite field is given in Problem 2.12.

The elements of a field are called *scalars*.

We shall now define a vector space and the subsequent subsections will be steps towards defining a Hilbert space.

2.1.1 Vector space. A set L of elements $u, v, w, \ldots$ is called a *vector space*[1] over a field F if the following two conditions are fulfilled:

(a) An operation of addition is defined in L, which we denote by $+$, such that L is an abelian group under addition. The identity element of this group will be denoted by **0**.

(b) Any scalar of the field F and any element of L can be combined by an operation called *scalar multiplication* to give an element of L such that for every $u, v \in L$ and $a, b \in F$, we have

$$\begin{aligned} a(u+v) &= au+av \in L, \\ (a+b)u &= au+bu \in L, \\ a(bu) &= (a.b)u, \\ 1u &= u,\ 0u = \mathbf{0}. \end{aligned} \tag{2.1}$$

Note here that 0 is an element of the field F, whereas **0** is the 'null' element of L.

[1]The names *vector space*, *linear vector space* and *linear space* are all synonimous.

The elements of a vector space are called *vectors*. The 'multiplication' of two elements of a vector space is not necessarily defined.[2]

Henceforth, we shall not distinguish between the two zeros 0 and **0**.

Examples of a vector space are:

(i) The familiar three-dimensional space of position vectors over the field of real numbers. In the sophisticated mathematical language, this should now be described as 'the set of all position vectors together with the operations of ordinary vector addition and multiplication of a scalar by a vector'.

(ii) The set of all n-tuplets of numbers such as $u \equiv (u_1, u_2, u_3, \ldots, u_n)$ over a field to which the scalars u_i belong. Thus, the set of all n-tuplets of complex numbers is a vector space over C; the set of all n-tuplets of real numbers is a vector space over R; the set of all n-tuplets of rational numbers is a vector space over Q. Two elements u and $w \equiv (w_1, w_2, \ldots, w_n)$ of this set are said to be equal if and only if $u_i = w_i$ for all $1 \leq i \leq n$. We denote this by writing $u = w$. The addition of two vectors u and $v \equiv (v_1, v_2, \ldots, v_n)$ of this space and scalar multiplication are defined by

$$\begin{aligned} (u_1, u_2, \ldots, u_n) + (v_1, v_2, \ldots, v_n) &= (u_1 + v_1, u_2 + v_2, \ldots, u_n + v_n), \\ c(u_1, u_2, \ldots, u_n) &= (cu_1, cu_2, \ldots, cu_n). \end{aligned} \tag{2.2}$$

Moreover, if $u_i = 0$ for $1 \leq i \leq n$, we say that $u = 0$.

Example (i) above is clearly a special case of the example at hand—it is the set of all triplets of real numbers.

(iii) The set of all real numbers.

(iv) The set of all complex numbers.

(v) The set of all rational numbers.

In the last three examples above the scalars and the vectors are the same. If a vector space is defined over the field of real numbers, it is called a *real vector space*; a vector space defined over the field of complex numbers is called a *complex vector space*.

2.1.2 Inner product space. A vector space L defined over a field F, where F refers to the field of complex numbers or of real numbers, is further called an *inner product space* if its elements satisfy one more condition:

(c) With every pair of elements $u, v \in L$, there is associated a unique number belonging to the field F—denoted by (u, v) and

[2] If the composition of two elements of a vector space is defined and also belongs to the space (with a few more conditions on the product), we have an *algebra*.

called the *inner product* or the *scalar product* of u and v—for which the following properties hold.

$$(u, v)=(v, u)^*,$$
$$(au, bv)=a^*b\,(u, v), \tag{2.3}$$
$$(w, au+bv)=a(w, u)+b(w, v),$$

where the asterisk denotes the complex conjugate.

The linear space of all n-tuplets of complex numbers becomes an inner product space if we define the scalar product of two elements u and v as the complex number given by

$$(u, v)=\sum_{i=1}^{n} u_i^* v_i. \tag{2.4}$$

The ordinary three-dimensional space of position vectors is also an inner product space with the familiar rule for taking the scalar product of two vectors. The vector spaces mentioned as examples after (2.2) are all, in fact, inner product spaces with suitable rules for taking the inner product.

Taking the inner product of an element with itself, we find, from (2.4)

$$(u, u)=\sum_{i=1}^{n} |u_i|^2, \tag{2.5}$$

where $|\ |$ denotes the absolute magnitude of the number enclosed. We introduce the notation

$$\|u\|^2 \equiv (u, u). \tag{2.6}$$

and the nonnegative square root of this real number, denoted by $\|u\|$, is called the *norm* of the vector u. Clearly, in the familiar language, this corresponds to the *length* of a vector. It is easy to see that the norm has the following properties:

(i) $\|u\| \geqslant 0$, and $\|u\|=0$ if and only if $u=0$;
(ii) $\|u+v\| \leq \|u\|+\|v\|$; this is the usual triangular inequality;
(iii) $\|au\|=|a|\,\|u\|$.

Before we go a step further and define a Hilbert space, we must consider what a Cauchy sequence is.

2.1.3 Cauchy sequence. If with each positive integer n we can associate a number c_n (in general, complex), then these numbers $c_1, c_2, c_3, \ldots, c_n, \ldots$ are said to form an infinite sequence or, simply, a *sequence*.

A sequence $c_1, c_2, \ldots, c_n, \ldots$ is said *to converge to* a number c, or *to be convergent with* the limit c, if for every real positive number

ϵ, however small, there exists a positive (finite) integer N such that for every integer $n>N$,

$$| c_n - c | < \epsilon. \tag{2.7}$$

The number c is called the *limit* of the sequence.

A sequence $c_1, c_2, \ldots$ is said to be a *Cauchy sequence* if for every real positive number ϵ, however small, we can find a finite positive integer N such that for any two integers $n>N$ and $m>N$,

$$| c_n - c_m | < \epsilon. \tag{2.8}$$

Examples of convergent, and therefore Cauchy, sequences are:

(i) the sequence of the real numbers whose terms are $c_n=2+5/n$, i.e.,

7, 9/2, 11/3, 13/4, 3, 17/6,..., $(2n+5)/n$,..., with the limit $c=2$;

(ii) 1, 1/2, 1/3,..., $1/n$,..., with the limit $c=0$;

(iii) 1.9, 1.99, 1.999, 1.9999,..., with the limit 2.0;

(iv) the sequence of the complex numbers whose terms are $c_n=(5n+3)/4n+i\,(2n-8)/3n$ with the limit $c=5/4+i\,2/3$.

The following sequences are divergent:

(i) the sequence of numbers whose terms are $c_n=p^n$ for $p>1$,

(ii) the sequence of positive integers, 1, 2, 3, 4,..., n,... .

Although, in the above discussion, we have defined a sequence with reference to numbers (real or complex), it should be clear that we can easily extend the idea to sequences of arbitrary entities provided they are all of the same nature. Thus, we may speak of a sequence of vectors in a two- or a three-dimensional space, a sequence of n-tuplets in their vector space, etc. Of course, in each case we must suitably interpret the quantities $|c_n-c|$ and $|c_n-c_m|$ while studying their convergence. This will be illustrated with reference to a sequence of n-tuplets because all the other examples follow as special cases of this one.

Consider a sequence of elements in the vector space of all n-tuplets (real or complex) whose terms are denoted by $u^{(1)}, u^{(2)}, \ldots, u^{(k)}, \ldots$, where

$$u^{(k)} \equiv (u_1{}^{(k)}, u_2{}^{(k)}, \ldots, u_n{}^{(k)}). \tag{2.9}$$

We say that this is a Cauchy sequence if for every positive number ϵ there exists a positive integer N such that for any two integers $k>N$ and $m>N$,

$$| u^{(k)} - u^{(m)} | < \epsilon \tag{2.10}$$

in the sense that

$$| u_i{}^{(k)} - u_i{}^{(m)} | < \epsilon \text{ for } 1 \leq i \leq n.$$

Similarly, the sequence is said to converge to a limit $u \equiv (u_1, u_2, \ldots, u_n)$ if for every real positive number ϵ, we can find a positive integer N such that for all integers $m > N$,

$$| u^{(m)} - u | < \epsilon \tag{2.11}$$

in the sense that

$$| u_i^{(m)} - u_i | < \epsilon \text{ for } 1 \leq i \leq n.$$

2.1.4 Hilbert space. We are now ready to define a Hilbert space. We shall restrict ourselves to the field of real or complex numbers. Consider an inner product space L. If every Cauchy sequence of elements belonging to L has a limit which also belongs to L, the space L is said to be *complete*. A complete inner product space is called a *Hilbert space*.

Examples of Hilbert spaces, as well as contrary examples, are easy to construct. All the inner product spaces discussed above, except the vector space of all n-tuplets of rational numbers (which includes, as a special case for $n=1$, the set of all rational numbers), are also Hilbert spaces. The space of all rational numbers is not complete because we can construct a Cauchy sequence in this space whose limit is an irrational number, which does not belong to this space. For example, the sequence of the successive approximations to the square root of 2, i.e., 1.414, 1.4142, 1.41421, 1.414213, . . ., is a Cauchy sequence whose limit $\sqrt{2}$ does not belong to the set of rational numbers. A similar argument shows that the set of all n-tuplets of rational numbers is not a Hilbert space.

2.2 Coordinate Geometry and Vector Algebra in a New Notation

In what follows, we shall treat Hilbert spaces in general. We shall denote a Hilbert space of n-dimensions (the dimensionality is defined below) by L_n. Although drawing pictures or diagrams for the sake of understanding an argument should not be encouraged in modern pure physics and mathematics, it may be advisable to take some specific examples with $n=2$ or $n=3$ to make the ideas clear. Some important concepts and properties are enumerated below.

(i) In the ordinary three-dimensional space of position vectors, we need a set of three axes, and any point in this space can then be located by means of three coordinates measured along the three axes. Similarly, in an n-dimensional vector space, we would need a set of n 'independent' vectors $r_1, r_2, \ldots, r_n$ to 'span' the whole space.

Two vectors r_i and r_j of L_n are said to be *linearly independent* of each other if one is not a constant multiple of the other, i.e., it is impossible to find a scalar c such that $r_i = cr_j$. In the familiar language, this means that r_i and r_j are not 'parallel' vectors. In general, m vectors of L_n are said to be *a set of linearly independent vectors* if and only if the equation

$$\sum_{i=1}^{m} a_i r_i = 0 \tag{2.12}$$

is satisfied only when all the scalars $a_i = 0$ for $1 \leq i \leq m$. In other words, the m vectors are linearly independent if it is impossible to construct the null element of the space by a linear combination of the vectors with at least one nonzero coefficient. Or again, the set of m vectors is linearly independent if none of them can be expressed as a linear combination of the remaining $m-1$ vectors. A simple test for the linear independence of a set of vectors is to construct the determinant of their scalar products with each other as

$$\Gamma = \begin{vmatrix} (r_1, r_1) & (r_1, r_2) & \ldots (r_1, r_m) \\ (r_2, r_1) & (r_2, r_2) & \ldots (r_2, r_m) \\ \cdot & & \\ \cdot & & \\ \cdot & & \\ (r_m, r_1) & (r_m, r_2) & \ldots (r_m, r_m) \end{vmatrix},$$

known as the Gram determinant. If $\Gamma = 0$, it follows that one of the vectors can be expressed as a linear combination of the remaining $m-1$ vectors, so that the vectors are linearly dependent; if $\Gamma \neq 0$, the vectors are linearly independent.

(ii) In an n-dimensional complete vector space, or Hilbert space, L_n, a set of n linearly independent vectors is called a *complete set in* L_n. If the number of vectors chosen is less than n, they are called an *incomplete set in* L_n; clearly they are not enough to span the full space. On the other hand, if more than n vectors are chosen in L_n, they form an *overcomplete* or *redundant set in* L_n. They cannot all be linearly independent and it is possible to find at least two nonvanishing scalars a_i such that

$$\sum_{i=1}^{m} a_i r_i = 0, \; m > n. \tag{2.13}$$

(iii) The dimension of a vector space is the maximum number of linearly independent vectors in the space or the minimum number of vectors required to span the space. In other words, the dimension is the number of linearly independent vectors which are both *necessary*

and sufficient to span the full space. Thus, in the ordinary three-dimensional space of position vectors, we can find at most three linearly independent vectors; three is also the minimum number of linearly independent vectors required to span the space.

A set of n linearly independent vectors in an n-dimensional vector space is called a *basis*, and the vectors are called the *basis vectors*. Clearly, the choice of the basis vectors is not unique; they can be chosen in an infinite number of ways.

(iv) Any vector u in L_n can now be expanded in terms of a complete set of basis vectors r_i, i.e.,

$$u=\sum_{i=1}^{n} u_i r_i, \tag{2.14}$$

where u_i is the *component* of u along r_i. We say that the space L_n can be *fully spanned by the basis vectors*. This result holds only if $\{r_i\}$ is a complete set. The scalars u_i are also called the *Fourier coefficients* of u and (2.14) is called the *Fourier expansion of u*.

(v) We choose a unit for the norm of the vectors in the space L_n (in the familiar language, a unit for the 'length' of the vectors). A vector of unit norm is called a *unit vector* or *normalized vector*. Rather than choosing the basis vectors r_i of arbitrary norm, we then choose a basis consisting of the unit vectors $e_1, e_2, \ldots, e_n$ in L_n.

(vi) So far, we have not assumed any relationship among the basis vectors except their linear independence. But now, for the sake of convenience and to make our algebra simpler, we will choose a complete set of orthogonal basis vectors, without loss of generality. In the ordinary three-dimensional space, this means that we choose cartesian coordinate axes rather than oblique ones. If e_i are the orthonormal basis vectors, we have

$$(e_i, e_j)=\delta_{ij}, \tag{2.15}$$

where δ_{ij} is the Kronecker delta given by

$$\delta_{ij}=\begin{cases}1 & \text{if } i=j,\\ 0 & \text{if } i\neq j.\end{cases} \tag{2.16}$$

(vii) The scalar product of two vectors

$$u=\sum_{i=1}^{n} u_i e_i \quad \text{and} \quad v=\sum_{i=1}^{n} v_i e_i \tag{2.17a}$$

is then easily found to be

$$(u, v)=(v, u)^*=\sum_{i=1}^{n} u_i^* v_i. \tag{2.17b}$$

Also $$\|u\|^2 \equiv (u, u) = \sum_{i=1}^{n} |u_i|^2. \tag{2.17c}$$

(viii) A linear transformation in the space L_n can be defined by an operator T such that T acting on a vector $u \in L_n$ gives a vector v, also belonging to L_n. The operation is denoted by

$$Tu = v. \tag{2.18}$$

When this happens, that is, when $Tu \in L_n$ for all $u \in L_n$, the space L_n is said to be *closed* under the action of T.

Note that this is the active view point of transformations discussed in Section 1.1.2.

If the vector Tu is unique for all $u \in L_n$ and if the inverse transformation is also uniquely defined, T is said to be a *one-to-one mapping of the space L_n onto itself.*

We shall be mainly concerned with transformations which preserve the Euclidean properties of the space L_n, such as the norms of the vectors and the scalar product of two vectors. Rotations, reflections and inversion are obvious examples of such transformations.

(ix) In the passive view point, we can define transformations of the basis vectors e_i (keeping everything else fixed) resulting in a new set of basis vectors e_i' as follows:

$$e_i \to e_i' = Te_i = \sum_{j=1}^{n} e_j T_{ji}, \quad 1 \leq i \leq n, \tag{2.19}$$

where T_{ji} is a scalar denoting the component of e_i' along e_j. Transformations which take one orthonormal set of basis vectors into another orthonormal set are called *unitary transformations*; the operators associated with them are called *unitary operators*[3]. It can be seen that this definition amounts to preserving the norms and the scalar products of vectors.

(x) Eq. (2.19) is in fact a set of n linear equations which can be written explicitly as

$$\begin{aligned} T(e_1, e_2, \ldots, e_n) &= (e_1', e_2', \ldots, e_n') \\ &= (e_1, e_2, \ldots, e_n) \begin{bmatrix} T_{11} & T_{12} & \ldots & T_{1n} \\ T_{21} & T_{22} & \ldots & T_{2n} \\ \cdot & & & \\ \cdot & & & \\ T_{n1} & T_{n2} & \ldots & T_{nn} \end{bmatrix}. \end{aligned} \tag{2.20}$$

[3] If the vectors of the space L_n are real, i.e., if L_n is defined over the field of real numbers, these reduce to *orthogonal transformations* and *orthogonal operators*, respectively.

The square matrix[4] $[T_{ij}] \equiv T$ of order n on the right hand side is called *a representation of the operator T in the basis (e_i)*.

(xi) Consider a vector e_i' of (2.19). If we take its scalar product with any of the original basis vectors, say e_k, we get

$$(e_k, e_i') = (e_k, Te_i) = (e_k, \sum_{j=1}^{n} e_j T_{ji}),$$

or
$$(e_k, Te_i) = T_{ki} \tag{2.21}$$

by using (2.15). We call this *the matrix element of the operator T between the basis vectors e_k and e_i*. It means that if the operator T is applied on e_i, the resulting vector has a projection T_{ki} along the vector e_k.

(xii) The scalar product of any two vectors u and Tv of L_n, where u and v are the vectors of (2.17a), is given by[5]

$$\begin{aligned}(u, Tv) &= (\sum_k u_k e_k, \quad T \sum_i v_i e_i) \\ &= (\sum_k u_k e_k, \quad \sum_{i,j} v_i e_j T_{ji}) \\ &= \sum_{i,j,k} u_k^* v_i T_{ji} (e_k, e_j) \\ &= \sum_{i,k} u_k^* v_i T_{ki}. \end{aligned} \tag{2.22}$$

(xiii) Since, by assumption, the transformed basis vectors e_i' are each of unit length and orthogonal to each other, we have

$$(e_i', e_j') = \delta_{ij}. \tag{2.23}$$

It immediately follows that the matrix T has the following properties (see Problem 2.2):

$$\left.\begin{aligned} \sum_{i=1}^{n} T_{ij}^* T_{ik} &= \delta_{jk} \qquad (2.24a) \\ \sum_{i=1}^{n} T_{ji}^* T_{ki} &= \delta_{jk}, \qquad (2.24b) \end{aligned}\right\} \quad 1 \leq j, k \leq n;$$

$$|\det T| = 1. \tag{2.24c}$$

These are the well-known conditions for a *unitary matrix*. It is

[4] The matrix $T \equiv [T_{ij}]$ should not be confused with the operator T appearing on the left hand side of (2.20). We shall often use the same symbol for an operator and a matrix representing it.

[5] Although u and v are not elements of a complete set of basis vectors and there is no apparent matrix for T here, (u, Tv) is called the 'matrix element' of T between u and v in quantum mechanics.

often said that all the rows (columns) of a unitary matrix are orthogonal to each other and normalized, which is just what Eqs. (2.24) tell. In the matrix notation, (2.24) can be written concisely as

$$T^\dagger = T^{-1} \quad \text{or} \quad TT^\dagger = T^\dagger T = E, \tag{2.25}$$

where E is the unit matrix of order n and $T^\dagger$ denotes the hermitian conjugate of T.

(xiv) The scalar product of two vectors in L_n is invariant under a unitary transformation: Let u and v be any two vectors of L_n and T be a unitary operator, then

$$(Tu, Tv) = (u, v). \tag{2.26}$$

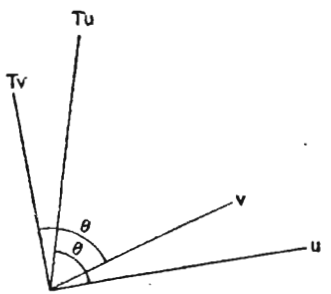


FIGURE 2.1 The scalar product of two vectors is invariant under a unitary transformation

Leaving the proof of (2.26) to Problem (2.3), we show the simple physical interpretation of this result in a two-dimensional space. In Fig (2.1), we have shown the four vectors u, v, Tu and Tv, assuming that T is an anticlockwise rotation through an angle θ about an axis normal to the plane of the paper. The validity of (2.26) for the particular case considered in this figure should be obvious.

(xv) An important operator is the projection operator. This is an operator which, when it operates on a vector $u \in L_n$, gives the projection of u along a given basis vector. It can be written in the form

$$P_i \equiv e_i\,(e_i,\ \ ), \tag{2.27}$$

where the notation means that the scalar product is to be taken with the vector on which P_i operates. Thus, if u is the vector of (2.17a), then

$$\begin{aligned} P_i u &= e_i\,(e_i, u) \\ &= u_i e_i \\ &= \text{the projection of } u \text{ along } e_i. \end{aligned} \tag{2.28}$$

It should be noted that P_i is not a unitary operator.

If we apply the operator P_i once more on the resulting vector u_ie_i of (2.28), clearly, the result is the same vector u_ie_i again, i.e.,

$$P_i(P_iu)=P_i(u_ie_i)=u_ie_i\equiv P_i(u). \tag{2.29}$$

Since this is true for all $u\in L_n$, we can write in the operator notation,

$$P_i^2=P_i, \tag{2.30}$$

which is an important property of projection operators. In fact, any operator P, acting on a Hilbert space L_n, for which $P^2=P$, (i.e., $P^2u=Pu\ \forall\ u\in L_n$) is called a projection operator. It can be readily verified that

$$\sum_{i=1}^{n} P_i=E, \tag{2.31}$$

where E is the identity operator.

(xvi) We now introduce the concept of the direct sum of two or more spaces. Consider a vector space L_n of n dimensions with a coordinate system $(e_1, e_2, \ldots, e_n)$, and a vector space L_m of m dimensions with the basis vectors $(i_1, i_2, \ldots, i_m)$. Provided that the two spaces have no common vector except the null vector, the *direct-sum space* L_t is the vector space defined by the $t=m+n$ basis vectors $(e_1, e_2, \ldots, e_n, i_1, i_2, \ldots, i_m)$. These may be relabeled by the t vectors $(k_1, k_2, \ldots, k_t)$. If L_n and L_m are complete spaces, so is L_t, and any vector u in L_t can be expanded as

$$u=\sum_{i=1}^{t} u_ik_i, \tag{2.32}$$

where u_i are scalars.

As a simple example, consider a two-dimensional vector space (a plane) with the basis vectors (x, y) and a one-dimensional vector space (a line) with the basis vector (z), which does not lie in the plane (x, y). If the null element is common to both the spaces, the direct-sum space is the three-dimensional vector space with the basis vectors (x, y, z).

(xvii) Finally, we consider the direct product (also known as the Kronecker product) of two vector spaces. Consider, again, the two spaces L_n and L_m defined above. The *direct-product space* is a space L_p of dimensions $p=nm$ defined by the p basis vectors $(e_1i_1, e_1i_2, \ldots, e_1i_m, e_2i_1, \ldots, e_ni_m)$. At the first thought, e_ji_k seems to be a tensor rather than a vector; but it can be seen, without much difficulty, that we can identify it with a vector in the p-dimensional space. If we

make this identification and denote the resulting basis vectors by the new labels $(l_1, l_2, \ldots, l_p)$, then, as before, they form a complete set in L_p if L_n and L_m are complete spaces. Any vector $v \in L_p$ can then be expressed as

$$v = \sum_{j=1}^{p} v_j \, l_j. \tag{2.33}$$

2.3 Function Spaces

Consider the set of all continuous, 'square integrable' functions $f, g, h, \ldots$), each of which is a function of one independent variable x on the interval $[a, b]$. We define the equality of two functions as follows: Two functions f and g are said to be equal on $[a, b]$, denoted by writing $f=g$, if and only if $f(x)=g(x)$ for all values of x on the interval $[a, b]$.

Referring to the definition of vector spaces in Section (2.1.1), we then see that the set of functions considered above is a vector space over a field F if we define the addition of two functions and scalar multiplication by

$$(f+g)(x) = f(x)+g(x), \tag{2.34a}$$

$$(cf)(x) = cf(x). \tag{2.34b}$$

Eq. (2.34a) is called the operation of *pointwise addition* of two functions. If the functions of the set considered are real, we have a vector space over the field of real numbers; if they are complex, we have a vector space over the field of complex numbers. The identity in either case is a function which is identically zero for all values of x on $[a, b]$ and the inverse of a function f is the function $-f$ with the property $(-f)(x) = -f(x)$ (i.e., the value of the function $-f$ at a point x is the negative of the value of f at x).

As a concrete example, consider the set $\{ f_e(x) \}$ of all continuous, square integrable, even, periodic functions of x of period $2l$. We shall allow, in general, complex functions to be included in the set. The sum of two functions of this set is also a continuous, square integrable, even periodic function of period $2l$, and hence belongs to the set. In fact, it is easy to verify that the set is an abelian group under the rule of pointwise addition. Moreover, scalar multiplication by complex numbers as defined in (2.34b) satisfies the conditions (2.1). Hence it follows that the set $\{ f_e(x) \}$ is a vector space, which we shall denote by L_e.

A vector space whose elements are functions is also called a *function space.*

All the concepts developed in Sections (2.1) and (2.2) can then be applied to function spaces, because, as emphasized in Section 1.8 in connection with groups, the mathematical definition of a vector space is quite independent of the exact nature of its elements. This gives us considerable freedom in handling different vector spaces by the same abstract methods.

Thus, a function space can be made an inner product space if we associate with any two functions a scalar such that the conditions (2.3) are satisfied. This can be easily done if we define the inner product of two functions f and g by

$$(f, g) \equiv \int_a^b f^*(x)\, g(x)\, dx, \tag{2.35}$$

where the integral is over the range $[a, b]$ of x on which the functions of the space are defined. The norm $\|f\|$ of a function f is given by[6]

$$\|f\|^2 \equiv (f, f) = \int_a^b |f(x)|^2\, dx. \tag{2.36}$$

A Cauchy sequence of functions is defined as follows: A sequence $f_1, f_2, \ldots, f_n, \ldots$ of functions of one variable x is said to be a Cauchy sequence *on* $[a, b]$ if for every real positive number ϵ, we can find a positive integer N such that for all integers $n > N$ and $m > N$,

$$\|f_n - f_m\| < \epsilon \tag{2.37}$$

in the sense that

$$\int_a^b |f_n(x) - f_m(x)|^2\, dx < \epsilon.$$

In a similar way (cf. Section 2.1.3), we can define a convergent sequence and its limit. The definition of a Hilbert space of functions follows immediately.

A set of n functions $f_1, f_2, \ldots, f_n$ of a vector space is said to be a set of linearly independent functions *on* $[a, b]$ if and only if the equation

$$\sum_{i=1}^{n} a_i f_i(x) = 0 \tag{2.38}$$

for all x *on* $[a, b]$ implies that all the scalars $a_i = 0$ for $1 \leq i \leq n$.

Coming back to the vector space L_e of all continuous square integrable even periodic functions of period $2l$, we see that any func-

[6] If the norm of a function is finite, the function is said to be *square integrable.*

tion of this space can be expanded in the well-known Fourier cosine series

$$f(x)=\sum_{n=0}^{\infty} a(n)\,(1/\sqrt{l}\,)\cos(n\pi x/l). \tag{2.39}$$

The infinite set of functions $(1/\sqrt{l})\cos(n\pi x/l)$ for $0\leq n<\infty$ clearly serves as an orthonormal basis in this space, for the functions of this set satisfy the relations

$$\frac{1}{l}\int_{-l}^{l}\cos(n\pi x/l)\cos(m\pi x/l)\,dx=\delta_{mn}. \tag{2.40}$$

Thus the vector space under consideration is denumerably infinite dimensional.

2.3.1 The dual space. For each function f in the space L_e, we have a set of coefficients $a(n)$ for $0\leq n<\infty$ as in (2.39). These can be obtained very easily by Fourier inversion of (2.39), which gives

$$a(n)=\int_{-l}^{l} f(x)\,(1/\sqrt{l})\cos(n\pi x/l)\,dx. \tag{2.41a}$$

These Fourier coefficients are unique, i.e., if we have another function $g\in L_e$ whose Fourier coefficients are

$$b(n)=\int_{-l}^{l} g(x)\,(1/\sqrt{l})\cos(n\pi x/l)dx, \tag{2.41b}$$

then $a(n)=b(n)$ for all $0\leq n<\infty$ if and only if $f=g$ on $[-l, l]$.

Now we may treat a as a function of the discrete variable n. It is easy to see that the function corresponding to $f+g$ would be $a+b$, and that corresponding to $-f$ would be $-a$. In fact, it can be readily verified that the set of functions $(a, b, \ldots)$ is a vector space which is defined over the same field as the space L_e. This is known as the *dual space* of L_e and its vectors have a one-to-one correspondence with the vectors of L_e. It therefore follows that the dual space is also denumerably infinite dimensional.

It should be clear that this is similar to the space of all n-tuplets where n is now denumerably infinite. The scalar product of two functions in this space is

$$(a, b)=\sum_{n=0}^{\infty} a^*(n)\,b(n). \tag{2.42a}$$

By using Eqs. (2.41) in (2.42a), we find

$$(a, b)=\int_{-l}^{l} f^*(x)\,g(x)\,dx=(f, g). \tag{2.42b}$$

In the above equation, we have an important property of the Fourier transforms that the scalar product of f and g is the same as that of their transforms a and b.

2.3.2 Direct sum of function spaces. Consider the set $\{f_o(x)\}$ of all continuous square integrable *odd* periodic functions of period $2l$, that is, the set of functions satisfying the relations

$$f_o(x+2l)=f_o(x)$$
$$f_o(-x)=-f_o(x). \tag{2.43}$$

Once again, it can be verified that this set is a vector space[7] which we denote by L_o. Any function $\phi(x)$ of L_o can be expanded in the well-known Fourier sine series

$$\phi(x) = \sum_{n=1}^{\infty} \alpha(n)\,(1/\sqrt{l})\,\sin(n\pi x/l). \tag{2.44}$$

The infinite set of functions $(1/\sqrt{l})\sin(n\pi x/l)$ for $1\leq n<\infty$ can be chosen as the orthonormal basis functions in this space, because

$$\frac{1}{l}\int_{-l}^{l} \sin(n\pi x/l)\,\sin(m\pi x/l)\,dx=\delta_{mn}. \tag{2.45}$$

We can now take the direct sum of the two function spaces L_e and L_o since they have no common element except the function which is identically zero. We then have a space of *all* periodic functions with period $2l$, The Fourier expansion for a function of this space is

$$f(x) = \sum_{n=0}^{\infty} a(n)\;(1/\sqrt{l})\;\cos(n\pi x/l)+\sum_{n=1}^{\infty}\alpha(n)\,(1/\sqrt{l})\,\sin(n\pi x/l). \tag{2.46}$$

The basis functions of this space chosen in (2.46) are clearly orthonormal since, in addition to (2.40) and (2.45), they satisfy

$$\frac{1}{l}\int_{-l}^{l} \cos(n\pi x/l)\,\sin(m\pi x/l)\,dx=0 \;\forall\; n,\; m. \tag{2.47}$$

The spaces L_e, L_o and their direct-sum space are all denumerably infinite dimensional. The dual space of L_o is the set all functions $(\alpha, \beta, \ldots)$, each element of which is the Fourier transform of an element of L_o.

It is a fairly easy matter to extend the concepts of this section to functions of more than one variables.

[7] The function which is identically zero for all values of x is even as well as odd in x. It is therefore common to, and is the 'zero' element of, both the spaces $\{f_e(x)\}$ and $\{f_o(x)\}$.

2.4 Operators

In this section, we shall use the symbols $\phi_n(x)$ for the orthonormal basis functions of a Hilbert space L of functions,[8] which may be finite or infinite dimensional.

An operator T is said to be defined on the space L if the action of T on any function $f \in L$ results in a function which also belongs to L. Thus,

$$Tf(x)=g(x) \text{ where } g \in L. \tag{2.48}$$

To know the action of an operator on any function of L, it is enough to know its effect on the basis functions of L. Thus, when an operator T acts on a basis function $\phi_n(x)$, the result is some function of L, say $\phi_n'(x)$, which can be expanded in a linear combination of the original basis functions:

$$T\,\phi_n(x)=\phi_n'(x)=\sum_m \phi_m(x)T_{mn},\ n, m=1, 2, \ldots . \tag{2.49}$$

This represents a system of linear equations, one for each value of n. Written out in an expanded form, this becomes

$$\begin{aligned}(\phi_1', \phi_2', \ldots, \phi_n', \ldots)&=T\,(\phi_1, \phi_2, \ldots, \phi_n, \ldots)\\ =(\phi_1, \phi_2, \ldots, \phi_n \ldots)&\begin{bmatrix} T_{11} & T_{12}\ldots T_{1n}\ldots \\ T_{21} & T_{22}\ldots T_{2n}\ldots \\ \cdot & \\ \cdot & \\ T_{n1} & T_{n2}\ldots T_{nn}\ldots \\ \cdot & \\ \cdot & \end{bmatrix}\end{aligned} \tag{2.50}$$

The matrix $[T_{ij}]$ is the representation of the operator T with the basis $\{\phi_n\}$. It can be seen in analogy with (2.21) that a matrix element of T is given by

$$\begin{aligned}T_{mn}=(\phi_m, \phi_n')&=(\phi_m, T\phi_n)\\ &=\mathcal{S}\phi_m^*(x)\ T\phi_n(x),\end{aligned} \tag{2.51}$$

where $\mathcal{S}$ denotes summation over the discrete variables and integration over the continuous variables of the set x on which ϕ's depend (see footnote 8).

If we introduce the following notation for row vectors

$$\begin{aligned}\Phi&\equiv(\phi_1, \phi_2, \ldots, \phi_n, \ldots),\\ \Phi'&\equiv(\phi_1', \phi_2', \ldots, \phi_n', \ldots),\end{aligned} \tag{2.52}$$

[8] Here, x stands for the set of variables on which the functions of L may depend.

then (2.49) can be simply written in the matrix notation as

$$\Phi' = \Phi T. \tag{2.53}$$

2.4.1 Special operators. We shall consider some special operators in this subsection. An operator T is said to be a *linear operator* if for every f and g in L,

$$T(cf+dg) = cTf+dTg, \tag{2.54}$$

where c and d are any scalars of the field over which L is defined. On the other hand, T is called an *antilinear operator* if

$$T(cf+dg) = c^*Tf+d^*Tg \quad \forall\ f, g \in L. \tag{2.55}$$

An obvious example of such an operator is the operator for complex conjugation. If we denote it by K, it is defined by

$$Kf = f^*,\ K(cf) = c^*\ Kf = c^*\ f^*. \tag{2.56}$$

If two operators A and B satisfy the relation

$$(f,\ Ag) = (Bf,\ g) \quad \forall\ f, g \in L, \tag{2.57}$$

A is said to be the *hermitian conjugate* of B, and vice versa, which is expressed by writing

$$A = B^\dagger, \quad A^\dagger = B. \tag{2.58}$$

Let

$$f = \sum_n a_n\phi_n, \quad g = \sum_n b_n\phi_n. \tag{2.59}$$

Then, on using the orthogonality of ϕ_n, (2.57) becomes

$$\sum_{n,\,m} a_n^* b_m A_{nm} = \sum_{n,\,m} a_n^* b_m B_{mn}^*. \tag{2.60}$$

Since this must be true for all f and g in L, i.e., for all scalars a_n and b_n, it follows that

$$A_{nm} = B_{mn}^*. \tag{2.61}$$

If the scalars of the space L are real numbers, (2.58) and (2.61) reduce to

$$A = \widetilde{B},\ \widetilde{A} = B,\ A_{nm} = B_{mn}, \tag{2.62}$$

and A is said to be the *transpose* of B, and vice versa.

If an operator T is its own hermitian conjugate (adjoint), it is said to be *hermitian* or *self-adjoint*. From (2.57), we see that T is hermitian if and only if

$$(f,\ Tg) = (Tf,\ g) \quad \forall\ f, g \in L. \tag{2.63}$$

With (2.59), this reduces to

$$T_{nm} = T_{mn}^*. \tag{2.64}$$

This is just the definition of a hermitian matrix—that is, a matrix which equals its own hermitian conjugate—and is written as

$$T=T^{\dagger}=(\tilde{T})^{*}=\tilde{T}^{*}. \tag{2.65}$$

Thus a hermitian operator is represented by a hermitian matrix in a linear vector space.

T is said to be a unitary operator if

$$TT^{\dagger}=T^{\dagger}T=E, \tag{2.66}$$

where E is the identity operator. It can be readily seen that if T is unitary, then

$$(Tf,\ Tg)=(f,\ g)\ \forall\ f,\ g\in L. \tag{2.67}$$

If the scalars of the space are real numbers, (2.66) reduces to

$$T\tilde{T}=\tilde{T}T=E, \tag{2.68}$$

in which case T is said to be an *orthogonal operator.*

2.4.2 The eigenvalue problem. We have already discussed the operation of an operator T on a basis function, which is

$$T\phi_n=\sum_m \phi_m T_{mn}. \tag{2.49}$$

The choice of the set of basis functions $\{\phi_n\}$ is not unique, and, as such, we would like to choose that set of orthonormal basis functions $\{\psi_n\}$ in L which simplifies Eq. (2.49) as much as possible. Clearly, the simplest nontrivial case arises when the only nonvanishing term on the right-hand side is the n-th term, in which case we have

$$T\psi_n=T_{nn}\psi_n\equiv t_n\psi_n, \tag{2.69}$$

which defines the scalars t_n. A nonzero vector ψ_n satisfying (2.69) is called an *eigenvector* or an *eigenfunction* of T corresponding to the *eigenvalue* t_n. The problem of obtaining the eigenvalues and the eigenfunctions of an operator (acting on a Hilbert space) is usually referred to as the *eigenvalue problem*, and (2.69) is often called the *eigenvalue equation.*

The eigenvalues need not all be distinct, that is, two or more eigenvectors may correspond to the same eigenvalue; in this case, such eigenvectors are said to be *degenerate.* The *multiplicity* of an eigenvalue is defined as the number of linearly independent eigenvectors which have the same eigenvalue under consideration.

It is proper to ask whether each operator has eigenvalues and eigenvectors. If the vector space L is defined over the field of real numbers, every operator acting on L does not necessarily possess

eigenvalues and eigenvectors. Thus, consider the operation of a rotation through 90° on a two-dimensional vector space of (real) position vectors. This operator has no eigenvectors since there is no nonzero vector in this space which transforms into a real multiple of itself.

However, if L is a vector space over the field of complex numbers, every operator on L has eigenvectors. If we count each eigenvalue as many times as it occurs, then the number of eigenvalues is precisely equal to the dimension of the space L.

The set of the eigenvalues of an operator is called its *spectrum.*

2.4.3 Diagonalization. We see from (2.69) that if we choose the set $\{\psi_n\}$ as the basis in the space L, rather than the original set $\{\phi_n\}$, then the matrix representing the operator T is diagonal, i.e.,

$$T_d = \begin{bmatrix} t_1 & & & \\ & t_2 & & 0 \\ & & \ddots & \\ & 0 & & t_n \\ & & & & \ddots \end{bmatrix} \tag{2.70}$$

The eigenvalues t_n are the solutions of the N-th order equation

$$\det(T - tE) = 0. \tag{2.71}$$

As we have said, N may be infinite, as is indeed the case in most physical problems. We are then faced with the problem of solving an infinite determinant. However, we are usually interested only in a few lowest eigenvalues in the spectrum of the operator and we can suitably reduce the determinant to a new determinant of a finite order N with small error if the subspace is properly chosen.

Once the eigenvalues are determined in this way, the eigenfunctions can be easily obtained. For this, we express an eigenfunction ψ_n corresponding to the eigenvalue t_n as a linear combination of the original basis functions:

$$\psi_n = \sum_{m=1}^{N} \phi_m U_{mn}. \tag{2.72}$$

If both the sets $\{\psi_n\}$ and $\{\phi_n\}$ are orthonormal, U will be a unitary matrix. Let us express ψ_n in the row vector notation as $\psi_n = (U_{1n}, U_{2n}, \ldots, U_{Nn})$. The eigenvalue Eq. (2.69) then becomes

$$T\psi_n \equiv (U_{1n}, U_{2n}, \ldots, U_{Nn}) \begin{bmatrix} T_{11} & T_{21} & \ldots & T_{N1} \\ T_{12} & T_{22} & \ldots & T_{N2} \\ \cdot & & & \\ \cdot & & & \\ T_{1N} & T_{2N} & \ldots & T_{NN} \end{bmatrix}$$

$$= t_n (U_{1n}, U_{2n}, \ldots, U_{Nn}). \tag{2.73a}$$

where we have used (2.69) in the last step. Note that the matrix of transformation which appears in (2.73a) is the transpose of that appearing in (2.49). This is because in (2.49), T acts on the basis vectors ϕ_n (the passive viewpoint), while in (2.73a), it acts on vectors of the space leaving the basis vectors unchanged (the active viewpoint).

Writing the m-th column of (2.73a), we have

$$\sum_{k=1}^{N} U_{kn} T_{mk} = t_n U_{mn}, \tag{2.73b}$$

where $1 \leq n \leq N$. This is a system of N linear equations for the N unknowns U_{mn} ($1 \leq m \leq N$, fixed n). However, these equations are not all independent due to the condition (2.71). If the eigenvalue t_n is k-fold degenerate, it can be shown that the matrix $(T - t_n E)$ has rank $N-k$ and hence only $N-k$ equations from (2.73) are independent. This means that we can determine at most $N-k$ components U_{mn} (fixed n). The general method is then to fix arbitrarily, say, the first k components and to obtain the remaining $N-k$ components in terms of them.[9] Thus there is a considerable arbitrariness which results from the fact that any linear combination of the degenerate eigenfunctions is also an eigenfunction with the same eigenvalue. We may conveniently choose any k orthonormal functions in this k-dimensional subspace of the full space.

Having obtained in this way a set of N orthonormal eigenfunctions, we can show that the representation of T with the basis $\{\psi_n\}$ is a diagonal matrix. We write Eqs. (2.49) and (2.72) in the matrix notation as

$$T\Phi = \Phi[T], \tag{2.74a}$$

$$\Psi = \Phi U, \tag{2.74b}$$

where Φ and Ψ stand for the row vectors

$$\Phi = (\phi_1, \phi_2, \ldots, \phi_N),$$

$$\Psi = (\psi_1, \psi_2, \ldots, \psi_N),$$

[9] Joshi (1984), Section 8; Kreyszig (1972), Section 6.9.

and we have distinguished between the operator T and the matrix $[T]$. From (2.72), it is clear that the n-th column of the matrix U just contains the components of the eigenfunction ψ_n, i.e.,

$$U=\begin{bmatrix} U_{11} & U_{12} & \dots & U_{1n} & \dots & U_{N1} \\ U_{21} & U_{22} & \dots & U_{2n} & \dots & U_{2N} \\ \cdot & & & & & \\ \cdot & & & & & \\ \cdot & & & & & \\ U_{N1} & U_{N2} & \dots & U_{Nn} & \dots & U_{NN} \end{bmatrix} \tag{2.75}$$

Multiplying (2.74a) from the right by U, we get

$$T\,\Phi\,U=\Phi\,U\,U^{-1}\,[T]\,U.$$

or

$$T\Psi=\Psi\,(U^{-1}\,[T]\,U). \tag{2.76}$$

Thus, the matrix $U^{-1}\,[T]\,U$ is the representation of the operator T with the basis $\{\psi_n\}$. Now it can be readily verified that, by the construction of U as in (2.75), we have

$$U^{-1}\,[T]\,U=T_d.$$

This can be seen by taking the (l, n) element of the left-hand side of the above equation, which gives

$$\sum_{m,k}[U^{-1}]_{lm}\,T_{mk}\,U_{kn}=\sum_{m}[U^{-1}]_{lm}\,U_{mn}\,t_n \text{ [by (2.73b)]}$$

$$=t_n\,\delta_{ln},$$

which is just the (l, n) element of T_d. Eq. (2.76) then finally gives us

$$T\Psi=\Psi\,T_d. \tag{2.77}$$

which is the desired result. This process is called the *diagonalization* of an operator.[10]

2.4.4 The spectral Theory of operators. We shall restrict ourselves to the case when the Hilbert space of the operator T is finite dimensional. Moreover, we shall consider T to be a hermitian operator or a unitary oparator.[11]

Let L_n be the n-dimensional $(0<n<\infty)$ Hilbert space of T. We assume that L_n is defined over the field of complex numbers, so that T has exactly n eigenvalues. Let $t_1, t_2, \dots, t_m$ be the *distinct*

[10]See also Joshi (1984), pp. 95-97

[11]The discussion of this subsection is, in fact, valid for a more general class of operators known as normal operators. An operator T is *normal* if it commutes with its own hermitian conjugate, that is, if $TT^{\dagger}=T^{\dagger}T$. Hermitian and unitary operators are clearly normal operators.

eigenvalues of T, so that $m \leq n$. If the eigenvalue t_l is k_l-fold degenerate, there are k_l linearly independent eigenvectors of T in L_n which have the same eigenvalue t_l. These eigenvectors constitute the basis for a k_l-dimensional subspace M_l of L_n; M_l is called the *eigenspace* of T corresponding to the eigenvalue t_l. Any vector of M_l is an eigenvector of T with the eigenvalue t_l.

We thus have the eigenspaces $M_1, M_2, \ldots, M_l, \ldots, M_m$, corresponding to the eigenvalues $t_1, t_2, \ldots, t_l, \ldots, t_m$, respectively. If T is a hermitian or a unitary operator, then these subspaces are pairwise orthogonal;[12] two spaces are said to be *orthogonal* if every vector of one space is orthogonal to every vector of the other. In our case, this is denoted by writing $M_i \perp M_j$ if $i \neq j$.

Any vector $u \in L_n$ can now be expressed uniquely in the form

$$u = u_1 + u_2 + \ldots + u_m, \tag{2.78}$$

where u_l is in M_l. The u_l's are therefore pairwise orthogonal. The operation of T on u then gives

$$\begin{aligned} Tu &= Tu_1 + Tu_2 + \ldots + Tu_m \\ &= t_1u_1 + t_2u_2 + \ldots + t_mu_m. \end{aligned} \tag{2.79}$$

This then determines uniquely the action of T on any vector of the Hilbert space L_n. To express the above result in a more convenient form, we define the m projection operators P_l on the eigenspaces M_l, such that the action of P_l on u gives the projection of u on M_l, or

$$P_l u = u_l. \tag{2.80}$$

Eq. (2.79) then becomes

$$Tu = t_1P_1u + t_2P_2u + \ldots + t_mP_mu \quad \forall \; u \in L_n,$$

so that we can write

$$T = t_1P_1 + t_2P_2 + \ldots + t_mP_m. \tag{2.81}$$

This expression is known as the *spectral resolution* of T. For every hermitian or unitary operator acting on a finite-dimensional Hilbert space, the spectral resolution exists and is unique.

The concepts developed in this section are closely related to, and find useful applications in, the eigenvalue problem in physics, because in quantum mechanics, we are concerned with the eigenvalues and the eigenfunctions of hermitian operators.

[12] In this subsection, we shall state the important results of the spectral theory without proofs. For proofs, the reader is referred to Simmons (1963).

2.5 Direct Sum and Direct Product of Matrices

We now digress a little in this section and consider two important operations with matrices which are not normally treated in elementary books on matrix algebra. These are the direct sum and the direct product (also known as the *outer product* or the *Kronecker product*) of matrices.

2.5.1 Direct sum of matrices. The *direct sum of two square matrices* $A \equiv [A_{ij}]$ of order m and $B \equiv [B_{ij}]$ of order n is a square matrix C of order $m+n$ defined by

$$C = A \oplus B = \begin{bmatrix} A & 0 \\ 0 & B \end{bmatrix} = \begin{bmatrix} A_{11} & \dots & A_{1m} & & & \\ \vdots & & \vdots & & \mathbf{0}_1 & \\ A_{m1} & \dots & A_{mm} & & & \\ & & & B_{11} & \dots & B_{1n} \\ & \mathbf{0}_2 & & \vdots & & \vdots \\ & & & B_{n1} & \dots & B_{nn} \end{bmatrix}, \quad (2.82)$$

where $\mathbf{0}_1$ and $\mathbf{0}_2$ are null matrices of order $m \times n$ and $n \times m$, respectively. Here the symbol $\oplus$ stands for the direct sum. This idea can be easily extended to more than two matrices. For example, the direct sum of

$$A = a, \quad B = \begin{bmatrix} b & c \\ d & e \end{bmatrix}, \quad \text{and} \quad C = \begin{bmatrix} f & g & h \\ i & j & k \\ l & m & n \end{bmatrix}$$

is a matrix of order six given by

$$D = A \oplus B \oplus C = \left[\begin{array}{c|cc|ccc} a & 0 & 0 & 0 & 0 & 0 \\ \hline 0 & b & c & 0 & 0 & 0 \\ 0 & d & e & 0 & 0 & 0 \\ \hline 0 & 0 & 0 & f & g & h \\ 0 & 0 & 0 & i & j & k \\ 0 & 0 & 0 & l & m & n \end{array}\right]. \quad (2.83)$$

Such a matrix, which has nonvanishing elements in square blocks along the main diagonal and zeros elsewhere, is said to be in the *block-diagonalized form*. It has the important properties:

$$\det D=(\det A)\,(\det B)\,(\det C), \tag{2.84a}$$

$$\text{trace } D=\text{trace } A+\text{trace } B+\text{trace } C, \tag{2.84b}$$

$$D^{-1}=A^{-1}\oplus B^{-1}\oplus C^{-1}, \tag{2.84c}$$

which should be clear from (2.83). Also, if A_1 and A_2 are square matrices of the same order, say n, and B_1 and B_2 are square matrices of the same order, say m, then[13]

$$(A_1\oplus B_1)\,(A_2\oplus B_2)=(A_1A_2)\oplus(B_1B_2). \tag{2.84d}$$

2.5.2 Direct product of matrices. The *direct product* of two matrices $A\equiv[A_{lm}]$ of order $L\times M$ and $B\equiv[B]_{pq}$ of order $P\times Q$ is a matrix C of order $I\times J$ where $I=LP$ and $J=MQ$. It can be written as

$$C=A\otimes B=\begin{bmatrix} A_{11}B & A_{12}B & \dots & A_{1M}B \\ A_{21}B & A_{22}B & \dots & A_{2M}B \\ \vdots & & & \\ A_{L1}B & A_{L2}B & \dots & A_{LM}B \end{bmatrix}, \tag{2.85}$$

where an 'element' $A_{lm}B$ stands for a matrix of order $P\times Q$ given by

$$A_{lm}B=\begin{bmatrix} A_{lm}B_{11} & A_{lm}B_{12} & \dots & A_{lm}B_{1Q} \\ A_{lm}B_{21} & A_{lm}B_{22} & \dots & A_{lm}B_{2Q} \\ \cdot & & & \\ \cdot & & & \\ A_{lm}B_{P1} & A_{lm}B_{P2} & \dots & A_{lm}B_{PQ} \end{bmatrix}. \tag{2.86}$$

To obtain an element of C in terms of the elements of A and B, we use the notation $C\equiv[C_{lp,\,mq}]$ where a row of C is denoted by a dual symbol (lp) and a column of C by a dual symbol (mq), such that

$$C_{lp,\,mq}=A_{lm}\,B_{pq}. \tag{2.87}$$

We may relabel the rows and the columns of C by two new indices i and j $(1\le i\le I,\ 1\le j\le J)$ so that

$$C\equiv[C_{ij}]=[C_{lp,\,mq}]. \tag{2.88}$$

This rather complicated notation can be made clear by an example. The direct product of

$$A=\begin{matrix}\\(1)\\(2)\end{matrix}\begin{matrix}\begin{matrix}(1)&(2)&(3)\end{matrix}\\\begin{bmatrix} a & b & c \\ d & e & f \end{bmatrix}\end{matrix}, \qquad B=\begin{matrix}(1)\\(2)\\(3)\end{matrix}\begin{matrix}\begin{matrix}(1)&(2)\end{matrix}\\\begin{bmatrix} h & r \\ k & s \\ l & t \end{bmatrix}\end{matrix}$$

[13]For proofs of various results mentioned in this and the following subsections, see Joshi (1984), Section 13.

is the 6×6 matrix

$$C=A\otimes B=\begin{array}{c} \\ (11)\\(12)\\(13)\\(21)\\(22)\\(23)\end{array}\begin{array}{c}\begin{array}{cccccc}(11)&(12)&(21)&(22)&(31)&(32)\end{array}\\ \begin{bmatrix} ah & ar & bh & br & ch & cr\\ ak & as & bk & bs & ck & cs\\ al & at & bl & bt & cl & ct\\ dh & dr & eh & er & fh & fr\\ dk & ds & ek & es & fk & fs\\ dl & dt & el & et & fl & ft\end{bmatrix}\end{array}. \tag{2.89}$$

Note that *the rows and the columns of the matrix C are labeled by different schemes.* Thus, while the third row of C is labeled as the (13) row, the third column is labeled as the (21) column. An element of C is, for example,

$$C_{21,\,31}=fh=A_{23}B_{11},$$

which is consistent with (2.87). We now relabel the rows and the columns by identifying each dual symbol with one number, separately for the rows and for the columns. We then have the matrix $[C_{ij}]\equiv[C_{lp,\,mq}]$ with $(lp)\to i$, $(mq)\to j$ and $1\leq i,j\leq 6$. Thus, in the above example, $C_{21,\,31}\equiv C_{45}$.

In the general case, the identification of the dual symbol with the single running index can be made by letting $i=(l-1)\,P+p$ and $j=(m-1)\,Q+q$; thus,

$$C_{lp,\,mq}\equiv C_{ij}=C_{(l-1)P+p,\,(m-1)\,Q+q}.$$

The concept can once again be extended to the direct product of more than two matrices. There is no restriction on the order of the matrices whose direct product is to be taken.

If A_1, A_2, B_1 and B_2 are any matrices whose dimensions are such that the ordinary matrix products A_1A_2 and B_1B_2 are defined, then the direct product has the important property

$$(A_1\otimes B_1)\,(A_2\otimes B_2)=(A_1A_2)\otimes(B_1B_2). \tag{2.90a}$$

Further, if F is the direct product of a number of square matrices $A, B, C, \ldots$, that is, $F = A\otimes B\otimes C\otimes\ldots$, then

$$\text{trace } F=(\text{trace } A)\,(\text{trace } B)\,(\text{trace } C)\ldots. \tag{2.90b}$$

The operation of the direct product of matrices is associative, so that

$$A\otimes(B\otimes C)=(A\otimes B)\otimes C\equiv A\otimes B\otimes C. \tag{2.91}$$

The operation is also distributive with respect to matrix addition. Thus,

$$A\otimes(C+D)=A\otimes C+A\otimes D. \tag{2.92}$$

Moreover, from (2.90a), we have

$$(AB)\otimes(AB)\otimes(AB)=(AB)\otimes((A\otimes A)(B\otimes B))$$
$$=(A\otimes A\otimes A)(B\otimes B\otimes B). \quad (2.93)$$

Generalizing the above equation, we have

$$(AB)^{[k]}=(A)^{[k]}(B)^{[k]}, \quad (2.94)$$

where

$$A^{[k]}=A\otimes A\otimes A\otimes \ldots \otimes A \ (k \text{ times}). \quad (2.95)$$

Finally, if A and B are square matrices with eigenvalues and eigenvectors λ_i, x_i and μ_j, y_j, respectively, the eigenvalues of $A\otimes B$ are $\lambda_i\mu_j$ and its eigenvectors are $x_i\otimes y_j$. That is, if $Ax_i=\lambda_i x_i$ and $By_j=\mu_j y_j$, then

$$(A\otimes B)(x_i\otimes y_j)=\lambda_i\mu_j(x_i\otimes y_j). \quad (2.96)$$

The proof follows directly from (2.90a).

We shall find these concepts very useful in the next chapter.

PROBLEMS ON CHAPTER 2

(2.1) Show that the following sets are vector spaces. Also indicate how you would choose a basis in each space. What is the dimension of each space? Which is the field over which each vector space is defined?

(i) The set of all vectors denoting the possible velocities of a free particle in classical mechanics.

(ii) The set of all vectors denoting the possible wave vectors of a free particle in classical or quantum mechanics (note that this is usually referred to as the **k**-space).

(iii) The set of all continuous square integrable solutions of an n-th order ordinary linear homogeneous differential equation.

(iv) The set of all continuous square integrable functions which depend on a set of variables.

(v) The set of all real square matrices of order n.

(vi) The set of all complex square matrices of order n.

(2.2) Prove Eq. (2.24).

(2.3) Prove Eq. (2.26). [Hint: Use (2.24).]

(2.4) State whether the following statements are true or false and explain your answer:

(i) If all the vectors of a set are pairwise orthogonal, it necessarily follows that it is an orthogonal set.

(ii) If all the vectors of a set are pairwise independent of each other, it necessarily follows that it is a set of linearly independent vectors.

(2.5) Consider the projection operators P defined in (2.28). Show that $P_iP_j=0$ if $i\neq j$. (This is expressed by saying that the ***projection operators are pairwise orthogonal.***)

(2.6) Show that the eigenvalues of a hermitian operator are real and that those of a unitary operator have absolute magnitude equal to unity.

(2.7) Show that the functions $P_0(x)=1$ and $P_1(x)=x$ are orthogonal on the interval $-1\leq x\leq 1$. Find scalars a' and b' such that $P_2(x)=1+a'x+b'x^2$ is orthogonal to both $P_0(x)$ and $P_1(x)$ on the same interval. In this way, generate polynomials $P_n(x)=1+ax+bx^2+\ldots+gx^n$ such that $P_n(x)$ is orthogonal to each $P_m(x)$, $0\leq m\leq n-1$, on the interval $[-1, 1]$. [Note that these are the Legendre polynomials, apart from constant factors.]

(2.8) Obtain the eigenvalues and the eigenvectors of the following matrices:

(i) $\begin{bmatrix} 1/2 & 0 & -3\sqrt{3}/2 \\ 0 & 1 & 0 \\ -3\sqrt{3}/2 & 0 & -5/2 \end{bmatrix}$, (ii) $\begin{bmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{bmatrix}$.

(2.9) Obtain the direct sum and the direct product of the following matrices:

(i) $\begin{bmatrix} 2 & 5 & 9 \\ 1 & 4 & 7 \\ 3 & 3 & 3 \end{bmatrix}$ and $\begin{bmatrix} 6 & 4 \\ 2 & 7 \end{bmatrix}$.

(ii) $\begin{bmatrix} 10 & 3 & -5 \\ -9 & 2 & 5 \\ 0 & 5 & -1 \end{bmatrix}$ and $\begin{bmatrix} 3 & 9 & 0 \\ 5 & -7 & 8 \\ 4 & 2 & -2 \end{bmatrix}$.

(2.10) Obtain the direct product of the two matrices:

$$\begin{bmatrix} -2 & 3 & 4 \\ 8 & 7 & -6 \end{bmatrix} \text{ and } \begin{bmatrix} 9 \\ 6 \\ 3 \end{bmatrix}.$$

(2.11) In Problem (2.9) verify Eqs. (2.84a), (2.84b), (2.84c) and (2.90b).

(2.12) Let p be a prime number and consider the set of the p integers $(0, 1, 2, \ldots, p-1)$. Show that this set is a field with addition mod (p) and multiplication mod (p) as the two binary operations. (A finite field is called a *Galois field*.)

(2.13) If $T(A)$ is the matrix representing an operator T in the vector space L_a and $T(B)$ that representing T in the vector space L_b, show that the matrix representing T in the vector space $L_a \otimes L_b$ is $T(A) \otimes T(B)$.

Bibliography for Chapter 2

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CHAPTER 3

Representation Theory of Finite Groups

In the first chapter, we discussed some elementary notions of groups in terms of the abstract concepts of elements and sets. In Chapter 2, we treated operators acting on their Hilbert spaces and studied their properties which are relevant to quantum physics. In physics, we are interested in groups of transformations which act on suitable Hilbert spaces of physical systems, each vector of the Hilbert space characterizing a 'state' of the system. In Section 2.2, we have introduced the concept of a matrix representing an operator in a Hilbert space. It is therefore natural to combine these two concepts and to obtain matrices representing all the elements of a group. The study of such matrices comes under the representation theory of groups. In this chapter, we shall consider finite groups only, although most of the results either hold good as they are or can be easily modified to the case of infinite groups. Continuous groups and their representations are dealt with in the next chapter.

3.1 Introduction

3.1.1 Definition. Let $G=\{E, A, B, C, \ldots\}$ be a finite group of order g with E as the identity element. Let $T=\{T(E), T(A), T(B), \ldots\}$ be a collection of nonsingular square matrices, all of the same order, having the property

$$T(A)\,T(B)=T(AB), \tag{3.1a}$$

that is, if $AB=C$ in the group G, then

$$T(A)\,T(B)=T(C), \tag{3.1b}$$

then the collection T of matrices is said to be *a representation of the group G*. The order of the matrices of T is called the *dimension of the representation*.

Let L_n be an n-dimensional vector space on which the operators of G act. Let $\{\phi_i\}$ be an orthonormal basis in L_n. The operation of an element $A \in G$ on a basis vector is then given by [see (2.19) and (2.20)]

$$A\,\phi_i = \sum_{j=1}^{n} \phi_j\, T_{ji}(A), \tag{3.2}$$

where $T(A)$ is the matrix representing A with the basis $\{\phi_i\}$. An element of the matrix $T(A)$ could then be, in analogy with (2.21), given by

$$T_{ji}(A)=(\phi_j,\ A\phi_i). \tag{3.3}$$

We could similarly obtain matrices corresponding to all the elements of G (with the same basis $\{\phi_i\}$). It is then obvious that these matrices generate a representation of G, for, on the one hand,

$$AB\,\phi_i = A \sum_{j=1}^{n} \phi_j T_{ji}(B) = \sum_{k,j=1}^{n} \phi_k\, T_{kj}\,(A)\, T_{ji}\,(B),$$

while, on the other hand,

$$AB\,\phi_i = \sum_{k=1}^{n} \phi_k\, T_{ki}\,(AB).$$

Since the above two operations must give the same result, we have

$$\sum_{j=1}^{n} T_{kj}\,(A)\, T_{ji}\,(B) = T_{ki}\,(AB) \quad \forall \quad 1 \leq i, k \leq n;$$

or

$$T(A)\,T(B)=T(AB),$$

which is just (3.1a).

One may be tempted to jump to the conclusion that T is a group under matrix multiplication. However, one must be careful here because the matrices of T need not all be distinct. If each distinct matrix of T is taken only once, the resulting set is certainly a group under matrix multiplication. Hereafter, whenever we refer to the 'group' T, we shall really mean the set of the distinct matrices of T.

If all the matrices of T are distinct, there is clearly a one-to-one correspondence between the elements of G and the matrices of

T. In this case, the groups G and T are isomorphic to each other and the representation generated by the matrices of T is called a *faithful representation* of G. On the other hand, if the matrices of T are not all distinct, there exists only a homomorphism from G to T and such a representation is called an *unfaithful representation* of G.

The simplest representation of a group is obtained when we associate unity[1] with every element of the group. Thus, in our example of the group C_{4v} (cf. Section 1.1.2), we would have the correspondence

Element	:	E	C_4	C_4^2	C_4^3	m_x	m_y	σ_u	σ_v
Representation	:	1	1	1	1	1	1	1	1.

The set (1, 1, ..., 1) does indeed form a representation of any group in general. For example, the product of two elements, say, $C_4 m_x = \sigma_u$ in the above case, corresponds to $1 \times 1 = 1$ in the considered representation. This is known as the *identity representation*.

The identity representation is clearly an unfaithful representation of any group. The set of the eight matrices of Problem 1.1(v) is a faithful representation of C_{4v}, because, as shown in Problem (1.6), it is isomorphic to C_{4v}. Every group has at least one faithful representation, the proof of which is left to Problem (3.14).

3.1.2 Some properties of representations of a group. We note that the identity element E of G has the property that $EA = AE = A$ for all elements $A \in G$. In terms of the matrices of a representation, this implies that

$$T(E)T(A) = T(A)T(E) = T(A). \tag{3.4}$$

We see that this matrix equation is satisfied only if $T(E) = E$, the unit matrix.[2] Thus, in any representation, the identity element of the group must be represented by the unit matrix of the appropriate order.

On taking A^{-1} for B in (3.1a), we see that

$$T(A)\,T(A^{-1}) = T(AA^{-1}) = T(E) = E,$$

or

$$T(A^{-1}) = [T(A)]^{-1}. \tag{3.5}$$

This is to say that the matrix representing the inverse of an element is equal to the inverse of the matrix representing the element.

[1] A constant number is a special case of a matrix—it is a square matrix of order one.

[2] In accordance with our convention, we shall use the same symbol E to denote the identity operator and the unit matrix.

Suppose we have two representations of a group G given by

$$T_1=\{T_1(E),\ T_1(A),\ldots\},$$
$$T_2=\{T_2(E),\ T_2(A),\ldots\}.$$

If there exists a nonsingular matrix S such that

$$T_1(A)=S^{-1}\ T_2(A)\ S,\quad T_1(B)=S^{-1}\ T_2(B)S,\ \text{etc.},\tag{3.6}$$

for all the elements of the group G, then T_1 and T_2 are said to be *equivalent representations* of G. This means that the matrices of the first set can be obtained from those of the second set by a similarity transformation of the coordinate vectors of the vector space in which both the representations are defined. We express this by writing in short

$$T_1=S^{-1}\ T_2S.\tag{3.7}$$

If two representations of a group are not equivalent to each other, they are said to be *inequivalent* or *distinct* representations.

3.2 Invariant Subspaces and Reducible Representations

It is evident that the vector space L_n which is used to generate a representation of the group G has the following property: For every element A of G and every vector $\phi\in L_n$, $A\phi$ also belongs to L_n. We say that the vector space L_n is *closed under the transformations of* G or, simply *closed under* G. It means that the operation of any element of G on any vector of L_n does not take us outside L_n.

A vector space L_m is said to be a subspace of another vector space L_n if every vector of L_m is also contained in L_n. L_m is called a *proper subspace* of L_n if the vectors of L_m do not exhaust the space L_n. Thus L_n is also a subspace of itself, but, of course, not proper.

The vector space L_n, which is closed under G, may possess a proper subspace L_m which is also invariant under G. In such a case, L_m is said to be *an invariant subspace of* L_n *under* G, and the space L_n is said to be *reducible under* G.

3.2.1 Reducibility of a representation. Let, as before, $\{T(E), T(A), T(B),\ldots\}$ be a representation of G in L_n. We now state that if L_n has an invariant subspace L_m $(m<n)$ under G, then in a suitable basis the matrices of the representation have the form

$$T(A)=\left[\begin{array}{c|c} D^{(1)}(A) & 0 \\ \hline X(A) & D^{(2)}(A) \end{array}\right],\tag{3.8}$$

where $D^{(1)}(A)$ and $D^{(2)}(A)$ are square matrices of order m and $n-m$

respectively, $X(A)$ is of order $(n-m)\times m$ and 0 is a null matrix of order $m\times(n-m)$. To show this, we use the row vector notation for the vectors:

$$\phi_i=(0\ 0\ 0\ldots 1_i\ 0\ldots 0), \tag{3.9}$$

which means that the i-th column has unity and all the other elements are zero. The labeling of the n basis vectors may conveniently be chosen in such a way that the first m basis vectors are in L_m. The operation of $A\in G$ on a basis vector ϕ_μ $(1\leq\mu\leq m)$ is then given by

$$A\phi_\mu=(0\,0\ldots 1_\mu\,0\ldots 0)\left[\begin{array}{c|c} T_{11}\ldots T_{1m} & T_{1,m+1}\ldots T_{1n} \\ \vdots & \vdots \\ T_{m1}\ldots T_{mm} & T_{m,m+1}\ldots T_{mn} \\ \hline T_{m+1,1}\ldots & \ldots\ldots\quad T_{m+1,n} \\ \vdots & \vdots \\ T_{n1}\ldots T_{nm} & T_{n,m+1}\ldots T_{nn} \end{array}\right]$$

$$=(T_{\mu 1}\ T_{\mu 2}\ldots T_{\mu m}T_{\mu,m+1}\ldots T_{\mu n}), \tag{3.10}$$

where we have written T_{ij} for $T_{ij}(A)$ for the sake of brevity. Now, since L_m is itself invariant under G, the transformed vector $A\phi_\mu$ also belongs to L_m; hence its components along the basis vectors ϕ_{m+1}, $\phi_{m+2},\ldots,\phi_n$ must be zero, i.e.,

$$T_{\mu k}(A)=0,\ m+1\leq k\leq n. \tag{3.11}$$

However, μ is arbitrary, and letting it run from 1 to m, we see that all the elements in the rectangular block of order $m\times(n-m)$ at the top right corner of $T(A)$ must be zero. Hence $T(A)$ has the form shown in (3.8).

Let us consider the product of two elements of the group G, say, $AB=C$. In terms of the matrices of the representation considered above, we have $T(A)\ T(B)=T(C)$, or

$$T(C)=\left[\begin{array}{c|c} D^{(1)}(A) & 0 \\ \hline X(A) & D^{(2)}(A) \end{array}\right]\left[\begin{array}{c|c} D^{(1)}(B) & 0 \\ \hline X(B) & D^{(2)}(B) \end{array}\right]$$

$$=\left[\begin{array}{c|c} D^{(1)}(A)\,D^{(1)}(B) & 0 \\ \hline X(A)\,D^{(1)}(B)+D^{(2)}(A)\,X(B) & D^{(2)}(A)\,D^{(2)}(B) \end{array}\right]. \tag{3.12}$$

But $T(C)$ must itself be of the form

$$T(C)=\left[\begin{array}{c|c} D^{(1)}(C) & 0 \\ \hline X(C) & D^{(2)}(C) \end{array}\right]$$

therefore, we have

$$D^{(1)}(A)\,D^{(1)}(B)=D^{(1)}(C), \tag{3.13}$$

$$D^{(2)}(A)\,D^{(2)}(B)=D^{(2)}(C),$$

and

$$X(A)\,D^{(1)}(B)+D^{(2)}(A)\,X(B)=X(C). \tag{3.14}$$

From (3.13), it is clear that the two sets of matrices $D^{(1)}=\{D^{(1)}(E), D^{(1)}(A), \ldots\}$ and $D^{(2)}=\{D^{(2)}(E), D^{(2)}(A), \ldots\}$ also give us two new representations of dimensions m and $n-m$ respectively for the group G. It is also clear that the basis vectors $\{\phi_1, \phi_2, \ldots, \phi_m\}$ are the basis for the representation $D^{(1)}$ and the remaining $n-m$ basis vector $\{\phi_{m+1}, \ldots, \phi_n\}$ for $D^{(2)}$.

In this case, T is said to be a *reducible representation.* Thus, we see that *the reducibility of a representation is connected with the existence of a proper invariant subspace of the full space.*

We shall denote the $n-m \equiv p$-dimensional vector space defined by the basis vectors $\{\phi_{m+1}, \ldots, \phi_n\}$ by L_p.

3.2.2 A theorem on representations. We shall now show that any representation T of a finite group, whose matrices may be non-unitary, is equivalent (through a similarity transformation) to a representation by unitary matrices. For this purpose, we define a hermitian matrix

$$H=\sum_{A\in G} T(A)\,T^{\dagger}(A), \tag{3.15}$$

where the summation is over all the elements of the group G. We invoke a theorem from matrix algebra that a hermitian matrix can be fully diagonalized by a unitary transformation. If U is the necessary transformation, then

$$U^{-1}HU=H_d, \tag{3.16}$$

where H_d is a diagonal matrix whose diagonal elements are the (real) eigenvalues of H. Using (3.15) in (3.16), we have

$$\begin{aligned} H_d &= U^{-1}\sum_{A\in G} T(A)\,T^{\dagger}(A)\,U \\ &= \sum_{A\in G} U^{-1}T(A)\,UU^{-1}T^{\dagger}(A)\,U \\ &= \sum_{A\in G} T'(A)\,T'^{\dagger}(A), \end{aligned} \tag{3.17}$$

where $T'(A)=U^{-1}T(A)\,U$. Taking the k-th diagonal element of (3.17), we get

$$[H_d]_{kk}\equiv d_k=\sum_{A\in G}\sum_{j} T_{kj}'(A)\,T_{jk}'^{\dagger}(A)$$

$$= \sum_{A\in G} \sum_{j} T_{kj}'(A)\, T_{kj}'^{*}(A)$$

$$= \sum_{A\in G} \sum_{j} |\, T_{kj}'(A)\,|^2. \tag{3.18}$$

Since each term in this summation is nonnegative, we have $d_k \geq 0$. But d_k can be zero if and only if $T_{kj}'(A)=0$ for all values of j and for all the elements $A\in G$. This would give a vanishing determinant for all the matrices of the representation, a case which we have excluded. Hence $d_k>0$, that is, d_k must be positive.[3]

As a consequence, it is also clear that H_d is a nonsingular matrix. We can therefore obtain any power of the matrix H_d simply by taking the corresponding power of all the diagonal elements of H_d, i.e.,

$$[(H_d)^p]_{kk}=(d_k)^p. \tag{3.19}$$

where p is any real number, positive or negative.

The required similarity transformation matrix which converts the nonunitary matrices $T(A)$ into unitary matrices $\Gamma(A)$ is then seen to be

$$V=UH_d^{1/2}, \tag{3.20}$$

giving

$$\Gamma(A)=V^{-1}\,T(A)\,V \tag{3.21}$$

$$=H_d^{-1/2}\,U^{-1}\,T(A)\,UH_d^{1/2}$$

$$=H_d^{-1/2}\,T'(A)\,H_d^{1/2}. \tag{3.22}$$

To verify that the matrices $\Gamma(A)$ are indeed unitary, we note that

$$\Gamma'(A)\,\Gamma\dagger(A)=[H_d^{-1/2}\,T'(A)\,H_d^{1/2}]\,[H_d^{1/2}\,T'\dagger(A)\,H_d^{-1/2}]$$

$$=H_d^{-1/2}\,T'(A)\,H_d\,T'\dagger(A)\,H_d^{-1/2}$$

$$=H^{-}{}_d^{1/2}\,T'(A)\sum_{B\in G} T'(B)\,T'\dagger(B)\,T'\dagger(A)\,H_d^{-1/2} \text{ by (3.17)}$$

$$=H_d^{-1/2}\sum_{B\in G} T'(AB)\,T'\dagger(AB)\,H_d^{-1/2}$$

$$=H_d^{-1/2}\,H_d\,H_d^{-1/2} \text{ by (1.9)}$$

$$=E,$$

which shows that $\Gamma(A)$ is a unitary matrix.

If the elements of the group G are unitary operators, the similarity transformation of the representation T to the representation Γ has a simple physical meaning—it implies going over from an

[3] A matrix all of whose eigenvalues are positive is called a *positive definite matrix.*

oblique system of coordinate axes to an orthonormal one. The nonunitary nature of the matrices $T(A)$, etc., indicates that the basis vectors of L_n, chosen as the basis for the representation T, are not orthonormal, whereas the representation Γ by unitary matrices shows that the basis vectors for the representation Γ are orthonormal. We have achieved this transformation from the oblique coordinate system, say $\Phi=(\phi_1, \phi_2, \ldots, \phi_n)$, to the orthonormal coordinate system, say $\Psi=(\psi_1, \psi_2, \ldots, \psi_n)$, by means of the matrix V of (3.20) so that $\Psi=\Phi V$. In this light, what we have said in this theorem is really very simple and almost trivial: It is possible to choose an orthonormal set of basis vectors in any finite dimensional vector space, which is obviously true! The difficulty in extending this theorem to infinite-dimensional representations or to the representations of infinite groups is regarding the convergence of the various sums encountered in its proof. The theorem may none the less be proved to hold for certain classes of infinite groups known as compact groups which will be treated in the next chapter.

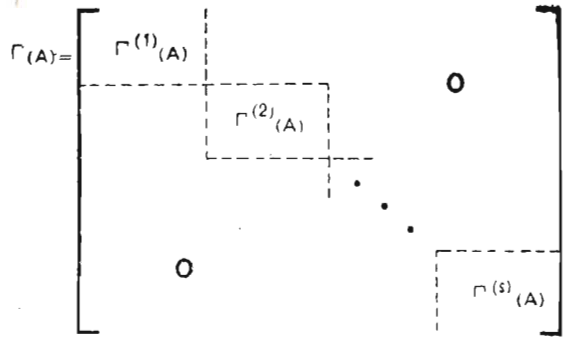
Owing to this theorem, hereafter, we need to consider representations by unitary matrices only. This no doubt affords a great simplification.

3.2.3 Irreducible representations. If the representation T considered above is reducible, the representation $\Gamma=\{\Gamma(E), \Gamma(A), \ldots\}$, defined by (3.21), is also reducible, since they are defined in the same space and are equivalent. Moreover, since the matrices of Γ are unitary, they must have the form

$$\Gamma(A)=\left[\begin{array}{c|c} S^{(1)}(A) & 0 \\ \hline 0 & S^{(2)}(A) \end{array}\right], \text{ etc.,} \qquad (3.23)$$

where we have the two representations by unitary matrices $S^{(1)}=\{S^{(1)}(E), S^{(1)}(A), \ldots\}$ and $S^{(2)}=\{S^{(2)}(E), S^{(2)}(A), \ldots\}$ which are defined in the spaces L_m and L_p and hence are equivalent to $D^{(1)}$ and $D^{(2)}$ respectively.

It may be possible that the representations $S^{(1)}$ and $S^{(2)}$ are further reducible, i.e., the spaces L_m and L_p may contain further invariant (proper) subspaces within them. This process can be carried on until we can find no unitary transformation which reduces *all* the matrices of a representation further. Thus, the final form of the matrices of the representation Γ may look like



, etc., (3.24)

with all the matrices of Γ *having the same reduced structure.* When such a complete reduction of a representation is achieved, the component representations $\Gamma^{(1)}$, $\Gamma^{(2)}$,..., $\Gamma^{(s)}$ are called the *irreducible representations* of the group G and the representation Γ is said to be *fully reduced.*

It may be noted that an irreducible representation may occur more than once in the reduction of a reducible representation Γ. The matrices of the representation Γ are just the direct sum of the matrices of the component irreducible representations and this may be denoted by

$$\begin{aligned}\Gamma &= a_1\,\Gamma^{(1)} \oplus a_2\,\Gamma^{(2)} \oplus \ldots \oplus a_c\,\Gamma^{(c)} \\ &= \sum_i a_i\,\Gamma^{(i)},\end{aligned} \tag{3.25}$$

where, in the last step, the symbol for summation is to be understood in the sense of direct sum.

At first sight, it may appear from (3.24) that the number of distinct irreducible representations of a group is very large and unlimited. However, for finite groups, this is not the case, because the irreducible representations of a group satisfy various conditions which limit their number and which are, at the same time, very useful in the applications of the theory of groups to physical problems. In the next few sections we take up the study of such properties of the irreducible representations. As an example, the irreducible representations of C_{4v} are discussed in Section 3.6.

3.3 The Schur's Lemmas and the Orthogonality Theorem

There are two theorems of fundamental importance which go by the name of Schur's lemmas and which are extremely useful for the study of the irreducible representations of a group. They also lead to the orthogonality theorem of the irreducible representations and we shall now consider them. It is assumed that the space in which the representations are defined is a complex vector space.

3.3.1 Schur's lemma 1. *If $\Gamma^{(l)}$ is an irreducible representation of a group G and if a matrix P commutes with all the matrices of $\Gamma^{(l)}$, then P must be a constant matrix, that is, $P=cE$ where c is a scalar.*

We shall prove this lemma by two methods.

First proof: Let A be any element of the group G; then it is given that

$$\Gamma^{(l)}(A)P=P\,\Gamma^{(l)}(A) \text{ for all } A\in G. \tag{3.26}$$

If the dimension of $\Gamma^{(l)}$ is n, P is a square matrix of order n. Since it has been remarked in Section 3.2.2 that the matrices of a representation can be taken to be unitary, it follows that each of the matrices $\Gamma(A)$, $\Gamma(B)$, etc., possesses a complete set of n eigenvectors. Since P commutes with $\Gamma(A)$, etc., it follows that P also has[4] n linearly independent eigenvectors. Let x_j be the eigenvectors of P with the eigenvalues c_j. Then we have

$$Px_j=c_j x_j. \tag{3.27}$$

Multiplying both sides from the left by $\Gamma^{(l)}(A)$, we get

$$\Gamma^{(l)}(A)Px_j=\Gamma^{(l)}(A)\,c_j\,x_j,$$

or

$$P\Gamma^{(l)}(A)\,x_j=c_j\,\Gamma^{(l)}(A)\,x_j, \tag{3.28}$$

by using (3.26). This means that $\Gamma^{(l)}(A)x_j$, for all $A\in G$, are eigenvectors of P with the same eigenvalue c_j. Let there be m such independent eigenvectors of P having the same eigenvalue c_j. But the eigenvectors belonging to an eigenvalue generate a subspace L_m which is invariant under G. Now if L_m is a proper subspace of L_n, that is, if L_m is not the same as L_n, then L_n has an invariant subspace and as shown in Section 3.2.1, the representation $\Gamma^{(l)}$ must be reducible which is contrary to the hypothesis. Therefore L_m must be identical

[4] P is the matrix of some operator in the same space L_n in which $\Gamma^{(l)}$ is defined.

with L_n making all the eigenvalues of P equal to each other and equal to, say, $c_j \equiv c$, giving $P=cE$.

There is one more possibility in the above treatment, that is, the invariant subspace L_m may contain only the null vector. However, this case is excluded from consideration because if x is a null vector, it trivially satisfies the eigenvalue equation $Px=cx$ with an arbitrary eigenvalue c.

Hence the theorem is proved.

Second proof: We shall first show that any hermitian matrix which commutes with every matrix of an irreducible representation is a constant multiple of the unit matrix.

Let H be a hermitian matrix which commutes with all the matrices of the representation $\Gamma^{(i)}$, so that

$$H\Gamma^{(i)}(A)=\Gamma^{(i)}(A)\ H \text{ for all } A\in G. \tag{3.29}$$

Let U be the unitary transformation which diagonalizes H, i.e.,

$$U^{-1}HU=H_d,\ UH_dU^{-1}=H, \tag{3.30}$$

where H_d is a diagonal matrix with diagonal elements, say d_i, which are the eigenvalues of H. (The matrix H is of order n, the dimension of the representation $\Gamma^{(i)}$.)

Let us suppose that the eigenvalues of H are not all the same. Let us pick up a certain eigenvalue which is repeated, say, k times where $1\leq k\leq n$. By a rearrangement of the columns of U, the order of the eigenvalues d_i in H_d can be changed at will[5]. Let such a rearrangement be made to bring the chosen equal eigenvalues in the first k positions of H_d, so that

$$d_1=d_2=\ldots=d_k\neq d_\mu,\ k+1\leq\mu\leq n. \tag{3.31}$$

Multiplying (3.29) from the left by U^{-1} and from the right by U, we have

$$U^{-1}HUU^{-1}\Gamma^{(i)}(A)\ U=U^{-1}\Gamma^{(i)}(A)\ UU^{-1}HU,$$

or

$$H_d\Gamma^{(i)\prime}(A)=\Gamma^{(i)\prime}(A)\ H_d, \text{ for all } A\in G, \tag{3.32}$$

where $\Gamma^{(i)\prime}(A)$, etc., are the matrices of a representation equivalent to $\Gamma^{(i)}$. Taking the $(j,\ \mu)$ element of both sides of (3.32), we find

$$d_j\ \Gamma_{i\mu}^{(ji)\prime}(A)=\Gamma_{j\mu}^{(i)\prime}(A)\,d_\mu,$$

or

$$(d_j-d_\mu)\ \Gamma_{j\mu}^{(i)\prime}(A)=0 \text{ for all } A\in G,$$

By (3.31), $d_j\neq d_\mu$ if $1\leq j\leq k$ and $k+1\leq\mu\leq n$. Hence

$$\Gamma_{j\mu}^{(i)\prime}(A)=0 \text{ for } 1\leq j\leq k,\ k+1\leq\mu\leq n, \text{ and all } A\in G. \tag{3.33}$$

[5]Joshi (1975), Section 9, p. 96.

The matrices of $\Gamma^{(l)\prime}$ therefore have the form

$$\begin{array}{c} \overbrace{}^{k} \quad \overbrace{}^{n-k} \\ \left.\begin{array}{c} k \\ n-k \end{array}\right\{ \left[\begin{array}{c|c} & \\ \hline & \end{array}\right. \end{array} \begin{array}{c} \\ \mathbf{0} \\ \\ \end{array} \left.\begin{array}{c} \\ \\ \end{array}\right] . \tag{3.34}$$

This is of the form (3.8), showing that the representation $\Gamma^{(l)\prime}$, and hence its equivalent representation $\Gamma^{(l)}$, must be reducible. But by assumption, $\Gamma^{(l)}$ is an irreducible representation, which is possible if and only if $k=n$, that is, if and only if all the eigenvalues of H are the same. This shows that $H=H_d$ and H must be a scalar matrix.

Now, let P be any matrix which commutes with all the matrices of the representation $\Gamma^{(l)}$. Then, by taking the hermitian conjugate of (3.26), we have

$$P^\dagger \Gamma^{(l)\dagger}(A)=\Gamma^{(l)\dagger}(A)\, P^\dagger,$$

or
$$P^\dagger [\Gamma^{(l)}(A)]^{-1}=[\Gamma^{(l)}(A)]^{-1} P^\dagger,$$

or
$$P^\dagger \Gamma^{(l)}(A^{-1})=\Gamma^{(l)}(A^{-1}) P^\dagger \text{ for all } A \in G. \tag{3.35}$$

Hence $P^\dagger$ also commutes with all the matrices of $\Gamma^{(l)}$. We can define two hermitian matrices H_1 and H_2, such that

$$H_1=(P+P^\dagger)/2,\ H_2=i\,(P^\dagger-P)/2; \tag{3.36a}$$

$$P=H_1+iH_2,\ P^\dagger=H_1-iH_2. \tag{3.36b}$$

If both P and $P^\dagger$ commute with the matrices of $\Gamma^{(l)}$, Eqs. (3.36a) show that H_1 and H_2 also do. As just shown above, H_1 and H_2 must then be constant matrices. From (3.36b) it therefore follows that P must be a constant matrix, completing the proof.

The importance of this theorem lies in the fact that its converse is also true. Thus, if no matrix other than a constant matrix commutes with all the matrices of a representation, then the representation is irreducible. (This fact is used later in Section 4.5.1).

3.3.2 Schur's lemma 2. *If $\Gamma^{(i)}$ and $\Gamma^{(j)}$ are two irreducible representations of dimensions l_i and l_j respectively of a group G and if a matrix M (of order $l_i \times l_j$) satisfies the relation*

$$\Gamma^{(i)}(A)\, M=M\, \Gamma^{(j)}(A) \text{ for all } A \in G, \tag{3.37}$$

then either (a) $M=\mathbf{0}$, *the null matrix, or* (b) $\det M \neq 0$, *in which case* $\Gamma^{(i)}$ *and* $\Gamma^{(j)}$ *are equivalent representations.*

It should be noted that two representations can be equivalent

only if their dimensions are equal. Hence if $l_i \neq l_j$, only case (a) applies.

Proof: Taking the hermitian conjugate of both sides of (3.37), we have

$$M^\dagger \Gamma^{(i)\dagger}(A) = \Gamma^{(j)\dagger}(A) M^\dagger \text{ for all } A \in G,$$

or
$$M^\dagger \Gamma^{(i)}(A^{-1}) = \Gamma^{(j)}(A^{-1}) M^\dagger \text{ for all } A \in G.$$

Multiplying from the right by M, we get

$$M^\dagger \Gamma^{(i)}(A^{-1}) M = \Gamma^{(j)}(A^{-1}) M^\dagger M \text{ for all } A \in G,$$

or
$$M^\dagger M \Gamma^{(j)}(A^{-1}) = \Gamma^{(j)}(A^{-1}) M^\dagger M \text{ for all } A \in G, \qquad (3.38)$$

by using (3.37). Thus the matrix $M^\dagger M$ commutes with $\Gamma^{(j)}(A^{-1})$ for all $A \in G$ and therefore, by the previous lemma, must be a constant matrix:

$$M^\dagger M = cE. \qquad (3.39)$$

We first consider the case $l_i = l_j = n$, say. From (3.39), we have

$$\det(M^\dagger M) = \det(M^\dagger) \det(M) = c^n. \qquad (3.40)$$

If $c \neq 0$, then $\det M \neq 0$ (because $\det M^\dagger = (\det M)^*$); therefore M^{-1} exists and from (3.37), we have

$$\Gamma^{(j)}(A) = M^{-1} \Gamma^{(i)}(A) M \text{ for all } A \in G,$$

showing that $\Gamma^{(i)}$ and $\Gamma^{(j)}$ are equivalent representations. If $c = 0$, then taking the (i, i) element of (3.39), we find

$$\sum_k M_{ik}^\dagger M_{ki} = 0,$$

or
$$\sum_k M_{ki}^* M_{ki} = \sum_k |M_{ki}|^2 = 0,$$

which is possible if and only if $M_{ki} = 0$ for $1 \leq k \leq n$. But i is arbitrary and can take any value from 1 to n; hence $M = 0$.

In the second case, when $l_i \neq l_j$, we can assume without loss of generality that $l_i < l_j$. We supplement the matrix M by writing $(l_j - l_i)$ rows of zeros to give a new matrix M':

$$M' = \begin{bmatrix} \overbrace{\quad M \quad}^{l_j} \\ \cdots\cdots \\ \quad 0 \quad \end{bmatrix} \begin{matrix} \} l_i \\ \\ \} l_j - l_i \end{matrix} \qquad (3.41a)$$

This gives

$$M'^\dagger = \left[\overbrace{M^\dagger}^{l_i} \;\vdots\; \overbrace{0}^{l_j - l_i} \right] \} l_j. \qquad (3.41b)$$

It can then be easily seen by matrix multiplication that $M'^{\dagger}M'=M^{\dagger}M$, and hence

$$\det(M'^{\dagger}M')=\det(M^{\dagger}M),$$

or

$$\det(M'^{\dagger})\det(M')=c^n,$$

by using (3.40). Here, we have put $l_j=n$. However, by inspection of (3.41), $\det(M')=\det(M'^{\dagger})=0$; hence $c=0$, and $M^{\dagger}M=\mathbf{0}$. Once again, taking the (i, i) elelemt of $M^{\dagger}M$, we see that $M=\mathbf{0}$.

This completes the proof of the lemma.

3.3.3 The orthogonality theorem. As an application of the above two lemmas, let us construct a matrix M given by

$$M=\sum_{A\in G}\Gamma^{(i)}(A)\,X\,\Gamma^{(j)}(A^{-1}), \tag{3.42}$$

where $\Gamma^{(i)}$ and $\Gamma^{(j)}$ are two inequivalent irreducible representations of dimensions l_i and l_j respectively of a group G of order g, and X is an arbitrary matrix of order $l_i\times l_j$ independent of the group elements. Multiplying both sides of (3.42) from the left by $\Gamma^{(i)}(B)$, where $B\in G$, we get

$$\begin{aligned}\Gamma^{(i)}(B)M&=\Gamma^{(i)}(B)\sum_{A\in G}\Gamma^{(i)}(A)\,X\,\Gamma^{(j)}(A^{-1})\\&=\sum_{A\in G}\Gamma^{(i)}(BA)\,X\,\Gamma^{(j)}(A^{-1})\\&=\sum_{C\in G}\Gamma^{(i)}(C)\,X\,\Gamma^{(j)}(C^{-1}B)\text{ where }BA=C\\&=\sum_{C\in G}\Gamma^{(i)}(C)\,X\,\Gamma^{(j)}(C^{-1})\,\Gamma^{(j)}(B)\\&=M\,\Gamma^{(j)}(B),\end{aligned} \tag{3.43}$$

for all $B\in G$. Therefore, by the second lemma of Schur, we have that $M=\mathbf{0}$.

Taking the (k, s) element of (3.42), we obtain

$$\sum_{A\in G}\sum_{p,\,q}\Gamma_{kp}^{(i)}(A)\,X_{pq}\,\Gamma_{qs}^{(j)}(A^{-1})=0. \tag{3.44}$$

For our purpose, we now conveniently choose the arbitrary matrix X to be a matrix all of whose elements are zero except the (m, n) element which we take to be unity, i.e., $X_{pq}=\delta_{pm}\,\delta_{qn}$. Then, we have, from

the above equation

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{ns}^{(j)}(A^{-1})=0,$$

or

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{sn}^{(j)*}(A)=0,$$

$$\text{for } 1\leq k,\ m\leq l_i,\ 1\leq n,\ s\leq l_j. \tag{3.45a}$$

Put in words, this *implies that the product of the* (k,m) *element of the irreducible representation* $\Gamma^{(i)}$ *with the complex conjugate of the* (s,n) *element of the irreducible representation* $\Gamma^{(j)}$, *summed over the group elements, equals zero.*

Next, we construct a matrix N by replacing $\Gamma^{(j)}$ in (3.42) by $\Gamma^{(i)}$, that is,

$$N=\sum_{A\in G} \Gamma^{(i)}(A)\,X\,\Gamma^{(i)}(A^{-1}). \tag{3.46}$$

By a treatment that led to (3.43), we can show that

$$\Gamma^{(i)}(A)\,N=N\,\Gamma^{(i)}(A) \text{ for all } A\in G.$$

Therefore, by Schur's first lemma, we see that N must be a constant matrix, say, $N=aE$, where E is the unit matrix of order l_i. Again, taking the (k,s)-th element of (3.46), we get

$$\sum_{A\in G}\sum_{p,q} \Gamma_{kp}^{(i)}(A)\,X_{pq}\,\Gamma_{qs}^{(i)}(A^{-1})=a\delta_{ks}. \tag{3.47}$$

As before, if we take $X_{pq}=\delta_{pm}\,\delta_{qn}$, then

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{ns}^{(i)}(A^{-1})=a\delta_{ks}. \tag{3.48}$$

To draw any conclusion from (3.48), we must first find the scalar a. For this purpose, we take the traces of the matrices on both sides of (3.46), giving

$$\begin{aligned}
\text{trace } N=al_i&=\sum_{k=1}^{l_i}\sum_{A\in G}\sum_{p,q} \Gamma_{kp}^{(i)}(A)\,X_{pq}\,\Gamma_{qk}^{(i)}(A^{-1}),\\
&=\sum_{p,q} X_{pq}\sum_{A\in G}\sum_{k} \Gamma_{qk}^{(i)}(A^{-1})\,\Gamma_{kp}^{(i)}(A)\\
&=\sum_{p,q} X_{pq}\sum_{A\in G} \Gamma_{qp}^{(i)}(E)\\
&=g\sum_{p,q} X_{pq}\,\delta_{pq}=g\ \text{trace } X,
\end{aligned}$$

or

$$a=g\ (\text{trace } X)/l_i. \tag{3.49}$$

But, due to our choice of X, trace $X=0$ unless $m=n$, in which case trace $X=1$. In short, trace $X=\delta_{mn}$. Hence, we get from (3.48),

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{ns}^{(i)}(A^{-1})=(g/l_i)\,\delta_{ks}\,\delta_{mn}, \qquad (3.45b)$$

for $1\leq k, m, n, s\leq l_i$. Now we combine the two results (3.45a) and (3.45b) in one single equation:

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{ns}^{(j)}(A^{-1})=(g/l_i)\,\delta_{ij}\,\delta_{ks}\,\delta_{mn}, \qquad (3.50)$$

or

$$\sum_{A\in G} \Gamma_{km}^{(i)}(A)\,\Gamma_{sn}^{(j)*}(A)=(g/l_i)\,\delta_{ij}\,\delta_{ks}\,\delta_{mn}.$$

This is known as the *great orthogonality theorem* for the irreducible representations of a group and occupies a central position in the theory of group representations.

3.4 Interpretation of the Orthogonality Theorem

Eq. (3.50) has a very elegant interpretation in the language of linear vector spaces. Let c be the total number of distinct irreducible representations of a finite group $G=\{E, A, B, \ldots\}$ of order g. Let us think of $\Gamma_{km}^{(i)}$ as a function of the elements of the group G. This function $\Gamma_{km}^{(i)}$ is defined only at the g discrete 'points' E, A, B, etc. If we were to plot the function $\Gamma_{km}^{(i)}$ against the variable A, it may look something like that shown in Fig. (3.1).

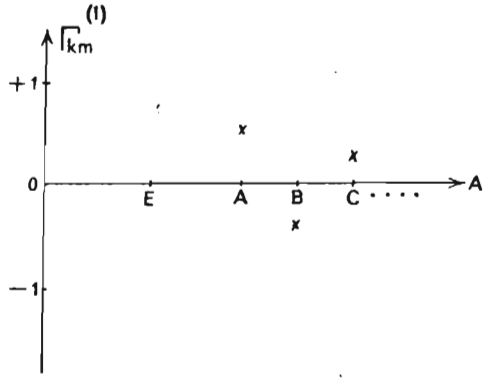


FIGURE 3.1 The (k, m) matrix element of the irreducible representation $\Gamma^{(i)}$ as a function of the group elements

We have one such function for every different value of i, k, m $(1\leq i\leq c,\ 1\leq k,\ m\leq l_i)$, and hence the total number of functions

is $\sum_{i=1}^{c} l_i^2$ (we have l_i^2 functions for each value of i). All such functions define a g-dimensional vector space because a function in this space can be completely specified by giving its g 'components'. This space is generally referred to as the *group space*.

The left-hand side of (3.50) is then just the scalar product of the two functions $\Gamma_{km}^{(i)}$ and $\Gamma_{sn}^{(j)}$ [see (2.35)]:

$$(\Gamma_{sn}^{(j)}, \Gamma_{km}^{(i)}) \equiv \sum_{A \in G} \Gamma_{sn}^{(j)*}(A)\, \Gamma_{km}^{(i)}(A). \tag{3.51}$$

Eq. (3.50) then implies that all the different functions such as $\Gamma_{km}^{(i)}$ are orthogonal to each other. However, we do not yet know whether they are complete, that is, whether they span the full space or not. Nevertheless, since the number of independent vectors in a vector space cannot exceed its dimension, we have the relation

$$\sum_{i=1}^{c} l_i^2 \leq g. \tag{3.52}$$

This is the condition which, as we stated earlier, limits the number of the irreducible representations of a group G of order g. We shall later show that the equality sign holds in (3.52). We shall call $\Gamma_{km}^{(i)}$ the *representation vectors* in the group space.

This idea of the group space may be a little difficult to grasp in the first reading. However, to give an analogy, it is very similar to the two-dimensional spin space of spin functions of a particle with $s=1/2$. The basis functions in this space are $\chi^{1/2}(s_z)$ and $\chi^{-1/2}(s_z)$ (where s_z is a component of the spin s), each function itself being defined only at the two discrete values of its argument $s_z = \pm 1/2$. Any other spinor (a function in the spin space) can then be expressed as a linear combination of the two basis functions. In general, if the spin of the particle is j, then the spin functions define a $(2j+1)$-dimensional space with the $2j+1$ basis functions $\chi^{j}(j_z)$, $\chi^{j-1}(j_z)$, ..., $\chi^{-j}(j_z)$ (where j_z is a component of j), each function being defined at the $2j+1$ values of its argument $-j \leq j_z \leq j$.

3.5 Characters of a Representation

We now introduce another important idea. We have seen that the matrices of a representation of a group in a given vector space are not unique, for they depend on the choice of the basis vectors in the vector space and even on the ordering of the basis vectors. However,

all such representations must be related to each other by some similarity transformation and must therefore be equivalent to each other, for all of them are defined in the same vector space. Now, we know that the trace of a matrix is invariant under a similarity transformation. Hence we see that the traces of all the matrices of a representation would uniquely characterize a representation irrespective of the choice of the basis vectors.

Let Γ be a representation (reducible or irreducible) of a group G. We define the *characters* of the representation Γ as the set of the traces of all the matrices of the representation Γ, i. e.,

$$\chi(A) = \sum_k \Gamma_{kk}(A). \tag{3.53}$$

Obviously, if the representation is one-dimensional, the character is the same as the representation. Also, the characters of conjugate elements in a representation are the same, because the trace of a matrix is invariant under a similarity transformation. Thus, if A and B are conjugate elements, then there exists an element C such that $A=C^{-1}BC$, or

$$\Gamma(A)=\Gamma(C^{-1})\,\Gamma(B)\,\Gamma(C);$$

taking the trace of both sides gives

$$\text{trace}\,(\Gamma(A))=\text{trace}\,(\Gamma(B)),$$

or
$$\chi(A)=\chi(B), \tag{3.54}$$

where we have used the cyclic property of trace, that is, for any matrices P, Q and R, we have

$$\text{trace}(PQR)=\text{trace}(QRP)=\text{trace}(RPQ).$$

All the elements in a class thus have the same character in a representation. *The character is therefore a function of the classes just as a representation is a function of the group elements.*

3.5.1 Orthogonality of characters. We can immediately transform (3.50) into an orthogonality relation for the characters of the irreducible representations of a group. Setting $k=m$ and $s=n$ in (3.50), summing over k and s and using (3.53), we get

$$\sum_{A\in G} \chi^{(i)}(A)\,\chi^{(j)*}(A)=\frac{g}{l_i}\,\delta_{ij}\;\; l_i=g\,\delta_{ij}. \tag{3.55}$$

Here, $\chi^{(i)}(A)$ is the character of the element A in the representation $\Gamma^{(i)}$, etc. If n_k is the number of elements in the class C_k of the group then (3.55) reduces to

$$\sum_k \sqrt{\frac{n_k}{g}}\,\chi_k^{(i)}\,\sqrt{\frac{n_k}{g}}\,\chi_k^{(j)*}=\delta_{ij}, \tag{3.56}$$

where $\chi_k^{(i)}$ is the character of an element A in the class C_k in the representation $\Gamma^{(i)}$, etc., and the summation is over all the distinct classes of G.

This is the orthogonality relation for the characters of the irreducible representations of a group and, written in the form (3.56), once again suggests that $(\sqrt{n_k/g})\,\chi_k^{(i)}$ can be thought of as the orthonormal basis functions in a *class space* whose dimension equals the number of classes in G. We have one such independent basis function for each irreducible representation of the group and therefore, as before, we have the condition

number of irreducible representations of G

$$\leq \textit{number of classes of } G. \tag{3.57}$$

That, in fact, the equality sign holds in (3.57) also will be shown in Section 3.7. We shall call $\chi^{(i)}$ the *character vectors* in the class space.

Taking the equality sign in (3.57), the orthogonality relation (3.56) can be expressed in an alternative form as[6]

$$\sum_{i=1}^{c} \chi_k^{(i)*}\,\chi_l^{(i)} = \frac{g}{n_k}\,\delta_{kl}. \tag{3.58}$$

The sum is over all the inequivalent irreducible representations of G and (3.58) denotes the orthogonality of the characters for different classes. Though it does not contain any new information, it is helpful in writing down the characters of a group by inspection.

We can derive a useful relation for the products of the characters of an irreducible representation $\Gamma^{(\alpha)}$. To this end, we consider the product of two classes defined in Section 1.3.1 :

$$C_i C_j = \sum_k a_{ijk}\,C_k. \tag{1.16}$$

Let us add the matrices representing the elements of the class C_i in the irreducible representation $\Gamma^{(\alpha)}$ and denote the resulting matrix by $P_{i\alpha}$, i.e.,

$$P_i^{\alpha} = \sum_{A\in C_i} \Gamma^{(\alpha)}(A). \tag{3.59}$$

[6]This can be obtained by using the fact that if all the rows of a finite square matrix are normalized and orthogonal to each other, then its columns must also be normalized and orthogonal to each other. Thus, if U is a finite square matrix with $UU^{\dagger} = E$, then $U^{\dagger}U = E$.

Similarly, of course, we can construct the matrices for all the classes of G. For any $B \in G$, we now have

$$[\Gamma^{(\alpha)}(B)]^{-1} P_i^{\alpha} \Gamma^{(\alpha)}(B) = \sum_{A \in C_i} [\Gamma^{(\alpha)}(B)]^{-1} \Gamma^{(\alpha)}(A) \Gamma^{(\alpha)}(B)$$

$$= \sum_{A \in C_i} \Gamma^{(\alpha)}(B^{-1}AB)$$

$$= \sum_{A \in C_i} \Gamma^{(\alpha)}(A), \tag{3.60}$$

where we have used (3.5) and the fact that as A runs over the class C_i, $B^{-1}AB$ also runs over the class C_i. It therefore follows that

$$\Gamma^{(\alpha)}(B) P_i^{\alpha} = P_i^{\alpha} \Gamma^{(\alpha)}(B) \text{ for all } B \in G, \tag{3.61}$$

that is, P_i^{α} commutes with all the matrices of the irreducible representation $\Gamma^{(\alpha)}$. By Schur's first lemma, this means that P_i^{α} must be a constant matrix:

$$P_i^{\alpha} = \lambda_i^{\alpha} E. \tag{3.62}$$

Taking the trace of both sides of (3.59), we have

$$\lambda_i^{\alpha} l_{\alpha} = n_i \chi_i^{(\alpha)},$$

or

$$\lambda_i^{\alpha} = (n_i/l_{\alpha}) \chi_i^{(\alpha)}. \tag{3.63}$$

From Eq. (1.16) and from the definition of the matrices P_i^{α} in (3.59), we have

$$P_i^{\alpha} P_j^{\alpha} = \sum_k a_{ijk} P_k^{\alpha},$$

or

$$\lambda_i^{\alpha} \lambda_j^{\alpha} = \sum_k a_{ijk} \lambda_k^{\alpha}, \tag{3.64}$$

by using (3.62). Substituting (3.63) in the above, we get

$$\frac{n_i}{l_{\alpha}} \chi_i^{(\alpha)} \frac{n_j}{l_{\alpha}} \chi_j^{(\alpha)} = \sum_k a_{ijk} \frac{n_k}{l_{\alpha}} \chi_k^{(\alpha)},$$

or

$$n_i n_j \chi_i^{(\alpha)} \chi_j^{(\alpha)} = l_{\alpha} \sum_k a_{ijk} n_k \chi_k^{(\alpha)}. \tag{3.65}$$

Once again, this relation is extremely useful in constructing the characters of the irreducible representations of a group.

3.5.2 Reduction of a reducible representation. It very often happens that we have a representation of a group which is, in general, a reducible one. Such a representation, say Γ, may be written as a linear combination of the irreducible representations as in (3.25). We can find the number of times an irreducible representation $\Gamma^{(i)}$ occurs in the reduction of Γ. For this we take the traces of both sides of (3.25). If $\chi(A)$, etc., denote the characters of the elements

in the representation Γ, then we have

$$\chi(A)=\sum_i a_i\chi^{(i)}(A), \tag{3.66}$$

for all $A\in G$. Multiplying both sides by $\chi^{(j)*}(A)$ and summing over all the elements of G, we get

$$\sum_{A\in G}\chi^{(j)*}(A)\chi(A)=\sum_i a_i \sum_{A\in G}\chi^{(j)*}(A)\chi^{(i)}(A)$$
$$=a_j g,$$

or

$$a_i=\frac{1}{g}\sum_{A\in G}\chi^{(i)*}(A)\chi(A). \tag{3.67}$$

This gives a method for obtaining the coefficients in (3.25). The characters of the irreducible representations are called *primitive* or *simple characters*, while the characters of the reducible representations are called *compound characters*. A compound character can be expressed as a linear combination of the simple characters of a group as in (3.66).

3.5.3 A criterion for irreducibility. Let Γ be a representation of a group G with the character χ. We can write the character χ as a linear combination of the simple characters of G as in (3.66) with the coefficients a_i given by (3.67). Let us multiply (3.66) by its complex conjugate equation, sum over all the group elements and divide by g, the order of G. We obtain

$$\frac{1}{g}\sum_{A\in G}\chi^*(A)\chi(A)=\frac{1}{g}\sum_{i,j}a_i^*a_j\sum_{A\in G}\chi^{(i)*}(A)\chi^{(j)}(A).$$
$$=\sum_i |a_i|^2. \tag{3.68}$$

If this quantity turns out to be equal to 1 for the representation Γ, it follows that all the a_i's must be zero except one, say a_k, which must be equal to unity (remember that the a_i's are nonnegative integers). It follows that the representation Γ must be identical with (or equivalent to) the irreducible representation $\Gamma^{(k)}$. We thus have a very simple criterion for the irreducibility of a representation: The *necessary and sufficient* condition for a representation to be irreducible is that its characters satisfy the equation

$$\sum_{A\in G}\chi^*(A)\chi(A)=g,$$

or

$$\sum_k n_k\chi_k^*\chi_k=g, \tag{3.69}$$

where χ_k is the character of the k-th class of the group.

3.6 The Example of C_{4v}

As an example of our preceding discussion of the representations and their characters, we now take up the case of the group C_{4v} treated in Chapter 1. We shall illustrate how to find its irreducible representations and the corresponding characters. In practice, it is easier to find the simple characters of a group before its irreducible representations.

3.6.1 The character table of C_{4v}. We shall take for granted the equality sign in (3.52) and (3.57) until it is proved in the next section. Since C_{4v} has five classes, it must have five irreducible representations, say, $\Gamma^{(1)}$, $\Gamma^{(2)}$, $\Gamma^{(3)}$, $\Gamma^{(4)}$ and $\Gamma^{(5)}$, whose dimensions may be denoted by l_1, l_2, l_3, l_4 and l_5 respectively. These must be connected by (3.52):

$$l_1^2+l_2^2+l_3^2+l_4^2+l_5^2=8. \tag{3.70}$$

The only possible solution (with integral l_i) is when four of the l_i's equal 1 and the remaining one equals 2. The order of the l_i's is immaterial and hence we conveniently choose $l_1=l_2=l_3=l_4=1$ and $l_5=2$. We can then construct the character table by making use of the orthogonality relations (3.56) and (3.58). It is shown in Table (3.1) for the group C_{4v}.

TABLE 3.1 THE CHARACTER TABLE FOR C_{4v}

classes / characters	C_1 (E)	C_2 (C_4, C_4^3)	C_3 (C_4^2)	C_4 (m_x, m_y)	C_5 (σ_d, σ_v)
$\chi^{(1)}$	1	1	1	1	1
$\chi^{(2)}$	1	−1	1	−1	1
$\chi^{(3)}$	1	−1	1	1	−1
$\chi^{(4)}$	1	1	1	−1	−1
$\chi^{(5)}$	2	0	−2	0	0

The first row is obtained very easily by writing unity for the character of each class. This corresponds to the identity representation which we have discussed in Section 3.1. Since the matrix for E

in any representation is just the unit matrix, its trace or character is l_i, the dimension of the representation; and this gives the first column of the table. For one-dimensional representations, the character is identical with the representation, and hence, for the representations $\Gamma^{(1)}$ through $\Gamma^{(4)}$, the characters themselves must satisfy the multiplication table. For the elements whose square equals E (such as C_4^2, m_x, σ_u, etc.), the only allowed characters are then ± 1. The multiplication Table (1.2) for C_{4v} shows that $m_x m_y = C_4^2$ (or $\sigma_u \sigma_v = C_4^2$). This indicates that whether m_x and m_y are both represented by $+1$ or by -1 (remembering that elements in the same class have the same characters), $\chi(C_4^2)$ must be $+1$ in all the one-dimensional representations. This gives us the characters of C_4^2 in $\Gamma^{(2)}$, $\Gamma^{(3)}$ and $\Gamma^{(4)}$.

For the elements C_4 and C_4^3, with $(C_4)^4 = (C_4^3)^4 = E$, the one-dimensional representations could be the powers[7] of $i = \sqrt{-1}$. But again, since $(C_4)^2 = (C_4^3)^2 = C_4^2$, $\chi(C_4)$ and $\chi(C_4^3)$ can only be ± 1 for $\Gamma^{(2)}$, $\Gamma^{(3)}$ and $\Gamma^{(4)}$. Now we invoke the orthogonality relation; every new row of characters must be orthogonal to all the previous rows, and must satisfy the normalization condition (3.60). This can be achieved by taking $+1$ for one of the classes C_2, C_4 and C_5 in the representations $\Gamma^{(2)}$, $\Gamma^{(3)}$ and $\Gamma^{(4)}$, and -1 for the remaining two classes. This completely determines the characters for the first four representations. The fifth row is obtained simply by using the orthogonality relations for the columns [Eq. (3.58)].

The arguments given above for the group C_{4v} are perfectly general and can be used in finding the character table for any finite group. We can always easily get the first row and the first column as indicated above. In the case of one-dimensional representations, the other entries are determined by using the criterion given in the footnote 7 and an extensive use of the multiplication table. In the case of irreducible representations of dimensions more than one, the orthogonality relations between the rows and between the columns can be used. For more complicated groups, Eq. (3.59) involving the products of characters should be used.

Since determination of the character table is one of the most important exercises in group theory, we shall discuss another example

[7] In general, if the order of an element A is n, i.e. $A^n = E$, its only one-dimensional representations can be powers of $\exp(2\pi i/n)$, since these are the only numbers whose n-th power equals unity. Moreover, they are 'unitary' numbers, that is, numbers whose inverses equal their complex conjugates respectively.

Flow-chart for determining the character table of a finite group	*The character table of C_{5v}*
1. The number of irreducible representations of group equals the number of its classes.	1. Since C_{5v} has four classes, it must have four distinct irreducible representatons.
2. The dimensions of the irreducible representations are determined by the equation $$\sum_{i=1}^{c} l_i^2 = g.$$ Remembering that l_i are positive integers, this equation has a unique solution, apart from the arbitrariness as to which of the possible values we choose for $l_1, l_2, \ldots, l_c$, respectively.	2. The dimensions of the four irreducible representations of C_{5v} would be given by $$l_1^2 + l_2^2 + l_3^2 + l_4^2 = 10,$$ which is satisfied when we choose the four numbers to be 1, 1, 2, 2. We may choose $l_1 = l_2 = 1$, $l_3 = l_4 = 2$.
3. We now start constructing the character table. We make a $c \times c$ table with classes shown at the top and the c irreducible representations on the left, denoted by $\Gamma_1, \Gamma_2, \ldots, \Gamma_c$.	3. The four classes of C_{5v} are (E), $(2C_5)$, $(2C_5^2)$, $(5m)$. We label the four irreducible representations $\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$. The character table would be a 4×4 table. A blank character table is drawn showing the four classes at the top and the four irreducible representations on the left, as shown below in Step 5.
4. Every group has a representation in which each element is represented by unity, which is called the identity representation. This gives one row of the character table, say the first row.	4. We may choose the first one-dimensional representation Γ_1 to be the identity representation and fill up the first row of the character table by writing unity below each of the four classes, as shown in the table below.

5. In any representation, the identity element E is represented by a unit matrix. Hence the character of the representation for the class (E) is the dimension of the representation. These have already been worked out for the irreducible representations in Step 2 above. This gives the column corresponding to the class (E) in the character table. The character table as obtained so far looks as shown below.

G	C_1 (E)	C_2	...	C_c
Γ_1	1	1	...	1
Γ_2	l_2			
.	.			
.	.			
.	.			
Γ_c	l_c			

6. If there are any other one-dimensional irreducible representations, their characters may now be worked out. In a one-dimensional representation, the characters are identical to the corresponding matrices and hence the characters must themselves satisfy the multiplication table of the group. In particular, if $A^n = E$ for a certain element A, then $[\Gamma(A)]^n = \Gamma(E)$, and for a one-dimensional representation, this leads to $[\chi(A)]^n = 1$ or $\chi(A) = 1^{1/n}$. Thus in a one-dimensional representation, the ***possible*** characters of an element A of order n are the n nth roots of unity.

5. Since the dimensions of the irreducible representations of C_{5v} as worked out in Step 2 above are 1, 1, 2, 2, these will also be the entries in the column for class (E). The character table as obtained so far looks as shown below.

C_{5v}	C_1 (E)	C_2 $(2C_5)$	C_3 $(2C_5^2)$	C_4 $(5m)$
Γ_1	1	1	1	1
Γ_2	1			
Γ_3	2			
Γ_4	2			

6. The group has one more one-dimensional representation, Γ_2. The reflections of the class C_4 are of order 2, while all the rotations of classes C_2 and C_3 are of order 5. This gives the *possible* characters for class C_4 to be ± 1, and the *possible* characters for classes C_2 and C_3 to be x, x^2, x^3, x^4, 1, where $x = \exp(2\pi i/5)$.

Now consider two distinct reflections from class C_4, and denote them by m_i and m_j $(1 \leqslant i, j \leqslant 5$ with $i \neq j)$. We can infer the nature of the product $m_i m_j$ without knowing the full multiplication table of the group. To begin

Then using some multiplication properties of the group elements and the fact that every new row of characters must be orthogonal to all the previous rows, all the one-dimensional characters can be worked out.

7. For higher dimensional representations, we must use the orthogonalily relation, that is, every new row of characters (in general, complex numbers) must be ortho-

with, $m_i m_j$ must belong to the group. Next, the product of two reflections is a rotation because such an operation leaves the sense of the coordinate system unchanged. Further, since m_i and m_j are *distinct* reflections, their product cannot be equal to E. This leaves us with the possibility that $m_i m_j$ belongs to C_2 or C_3. In fact, if we take the product of m_i with the *remaining* four reflections, two of them must give the class C_2 and the other two the class C_3.

This means that in the representation Γ_2, the characters must satisfy $\chi_2(m_i)\,\chi_2(m_j) = \chi_2(C_5)$ or $\chi_2(C_5^2)$, $i \neq j$. As determined earlier, the possible characters of m_i are ± 1, and m_i and m_j must have the same character as they belong to a class. Hence their product must give $+1$, so that $\chi_2(C_5) = \chi_2(C_5^2) = 1$. In order that Γ_2 may be orthogonal to Γ_1, the only possibility now remains that $\chi_2(m_i) = -1$. The character table obtained so far looks as shown below.

C_{5v}	(E)	$(2C_5)$	$(2C_5^2)$	$(5m)$
Γ_1	1	1	1	1
Γ_2	1	1	1	-1
Γ_3	2			
Γ_4	2			

7. To proceed further, let us assume that the characters of Γ_3 are $(2\ a\ b\ c)$, where a, b, c may be complex numbers. Orthogonalizing this to the characters of Γ_1 and Γ_2 (using

gonal to all the previous rows. It must also satisfy the normalization condition (criterion for irreducibility), that is the sum of absolute squares of the characters for all the *elements* must equal the order of the group. The orthogonality of the columns of the character table, Eq. (3.58), can also be used. Also if all the classes of a group are self-inverse, then all the irreducible representations of the group have real characters (see Problem 3.13). If these equations are not sufficient, the relation (3.65) involving product of characters can be used.

(3.55) with $i = 3$ and $j = 1$ or 2), we get

$$2 + 2a + 2b + 5c = 0,$$
$$2 + 2a + 2b - 5c = 0,$$

giving $1 + a + b = 0$, $c = 0$. Then the normalization of Γ_3 ((3.55) with $i = j = 3$ or (3.69)) gives

$$4 + 2|a|^2 + 2|b|^2 + 5|c|^2 = 10 \Rightarrow |a|^2 + |b|^2 = 3.$$

If $a = a_1 + ia_2$, $b = b_1 + ib_2$, we have so far only three equations to determine four real numbers. These are

$$1 + a_1 + b_1 = 0, \quad \text{(i)}$$
$$a_2 + b_2 = 0, \quad \text{(ii)}$$
$$a_1^2 + a_2^2 + b_1^2 + b_2^2 = 3. \quad \text{(iii)}$$

We may now use (3.65). If we work out the product of class $C_2 = (C_5, C_5^4)$ with itself, we find that

$$C_2 C_2 = (C_5^2, E, E, C_5^3) = 2C_1 + C_3.$$

Therefore with $i = j = 2$, we get the coefficients in (1.16) as

$$a_{221} = 2, a_{223} = 1, a_{22k} = 0 \text{ for } k = 2, 4.$$

Using this in (3.65) with $\alpha = 3$, we get $a^2 = 2 + b$, or

$$a_1^2 - a_2^2 = 2 + b_1, \quad \text{(iv)}$$
$$2a_1a_2 = b_2. \quad \text{(v)}$$

Combining Eq. (v) with Eq. (ii), we find $a_1 = -\frac{1}{2}$ or $a_2 = 0$. The first solution $a_1 = -\frac{1}{2}$, when substituted in the other equations, leads to $a_2^2 = -5/4$, which is inconsistent. Hence we have the only solution $a_2 = 0$. This

leads to $b_2 = 0$, showing that a and b are real, and gives

$$a = (-1 \pm \sqrt{5})/2,\ b = (-1 \mp \sqrt{5})/2. \qquad \text{(vi)}$$

All the five equations in four unknowns are now consistent.

Apparently there is a two-fold arbitrariness in the choice of sign of the radical in a and b. However, this arbitrariness is only apparent and not real. For we notice that there is another two-dimensional representation Γ_4 of the group. If we denote the characters of Γ_4 by $(2\ p\ q\ r)$, then the orthogonality of Γ_4 with Γ_1 and Γ_2, the normalization of Γ_4, and the class product equation (3.65) give us the same equations for p, q, r as obtained for a, b, c above. Thus we get

$$p = (-1 \pm \sqrt{5})/2,\ q = (-1 \mp \sqrt{5})/2,\ r = 0. \qquad \text{(vii)}$$

But we will have one more condition, that Γ_4 should also be orthogonal to Γ_3. Moreover, Γ_3 and Γ_4 cannot have the same characters, or else they would not be distinct representations. All this leads to the fact that we can choose one sign of the radical in a and q, and the other sign in b and p. We are finally led to the character table shown below.

C_{5v}	(E)	$(2C_5)$	$(2C_5^2)$	$(5m)$
Γ_1	1	1	1	1
Γ_2	1	1	1	−1
Γ_3	2	$(-1+\sqrt{5})/2$	$(-1-\sqrt{5})/2$	0
Γ_4	2	$(-1-\sqrt{5})/2$	$(-1+\sqrt{5})/2$	0

The reader may compare this with the character table of C_{5v} given in Table (7.7) which appears in a slightly different form.

Here we have explicitly shown that all the irreducible representations of C_{5v} have real characters. In fact, by noting that all the classes of C_{5v} are self-inverse, we could have assumed right in the beginning that the characters are real numbers. This would have provided some simplification in Steps 6 and 7.

along with a flow-chart describing the general procedure. The example we consider is the symmetry group C_{5v} of a regular pentagon containing the identity, four successive rotations of $2\pi/5$ (C_5 and its powers), and five reflections in planes perpendicular to the plane of the pentagon. The group has the classes $(E), (2C_5), (2C_5^2), (5\,m)$ so that $g = 10$, $c = 4$. The flow-chart and the example are discussed on the preceding pages. One more example, the character table of the cubic group O, is discussed in Section 7.4.

3.6.2 The irreducible representations of C_{4v}. After having found the character table, it is easy to find the full irreducible representations for the group C_{4v}. The first four irreducible representations are identical to the corresponding characters, as mentioned before. For $\Gamma^{(5)}$, we must choose a suitable set of basis functions. Since C_{4v} is a group of transformations in a two-dimensional space, it would be clear that any two independent vectors of this space can be chosen as the basis to generate $\Gamma^{(5)}$, because these vectors would transform into their own linear combinations under the operations of C_{4v}. Choosing, for convenience, the two orthogonal basis vectors (x, y), we can obtain the matrices of $\Gamma^{(5)}$ very easily. For example, consider the operation of C_4 on the basis vectors:

$$C_4 \begin{bmatrix} y \\ \uparrow \\ \longrightarrow x \end{bmatrix} = \begin{bmatrix} | \\ \longrightarrow y' \\ \downarrow \\ x' \end{bmatrix},$$

or
$$C_4(x, y) = (x', y') = (-y, x) = (x, y) \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}. \tag{3.71}$$

Then, by the definition of a representation [see Eq. (3.2)], we immediately have

$$\Gamma^{(5)}(C_4) = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}. \tag{3.72}$$

We can similarly obtain the other matrices of $\Gamma^{(5)}$. The complete table of the irreducible representations of the group C_{4v} is given in Table (3.2).

The problem of finding an irreducible representation of dimension greater than 1 is essentially the same as that of finding a suitable set of l_i (equal to its dimension) basis functions which transform into their linear combinations on operating with the group elements. This is not always easy. Some methods for obtaining such basis functions are discussed in the next few sections.

TABLE 3.2 THE IRREDUCIBLE REPRESENTATIONS OF C_{4v}

	E	C_4	C_4^2	C_4^3	m_x	m_y	σ_u	σ_v
$\Gamma^{(1)}$	1	1	1	1	1	1	1	1
$\Gamma^{(2)}$	1	−1	1	−1	−1	−1	1	1
$\Gamma^{(3)}$	1	−1	1	−1	1	1	−1	−1
$\Gamma^{(4)}$	1	1	1	1	−1	−1	−1	−1
$\Gamma^{(5)}$	$\begin{bmatrix}1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&1\\-1&0\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}0&-1\\1&0\end{bmatrix}$	$\begin{bmatrix}1&0\\0&-1\end{bmatrix}$	$\begin{bmatrix}-1&0\\0&1\end{bmatrix}$	$\begin{bmatrix}0&-1\\-1&0\end{bmatrix}$	$\begin{bmatrix}0&1\\1&0\end{bmatrix}$

3.7 The Regular Representation

We shall now consider an example of a reducible representation of C_{4v}. The most natural way of obtaining a representation of a finite group is by an inspection of its multiplication table when it is written in such a way that an element in the extreme left column (second operator in the product) is the inverse of the corresponding element in the top row (first operation in the product). This is how we have written Table (1.2) for C_{4v}.

Let us now construct square matrices of order 8 for all the elements of C_{4v} in the following way. The matrix for an element is obtained by replacing the element wherever it occurs in the multiplication table by unity and placing zeros elsewhere. For example, $\Gamma(E)$ would be a unit matrix of order 8. Another matrix, say $\Gamma(C_4)$, would take the form

$$\Gamma(C_4)=\begin{bmatrix}0&1&0&0&0&0&0&0\\0&0&1&0&0&0&0&0\\0&0&0&1&0&0&0&0\\1&0&0&0&0&0&0&0\\0&0&0&0&0&0&0&1\\0&0&0&0&0&0&1&0\\0&0&0&0&1&0&0&0\\0&0&0&0&0&1&0&0\end{bmatrix}. \tag{3.73}$$

Notice that each row or each column contains unity once and only once, as per the rearrangement theorem.

To show that such matrices do indeed generate a representation in general, we label the rows and the columns of the matrices by the group elements themselves, rather than the indices i, j, etc. That is, we can think of the g elements of the group G as 'coordinate axes' in the

g-dimensional group space. Since multiplication by an element simply gives a new arrangement of all the elements (cf., the rearrangement theorem), the operations by the group elements can be thought of as rotations of these coordinate axes into one another in the group space. Then the (B, C) element of the matrix for A in this representation will be given by

$$\Gamma_{B,C}(A)=\delta_{BA,C}, \tag{3.74}$$

where $\delta_{BA,C}=1$ if $BA=C$ (or $B^{-1}C=A$) and zero otherwise. Let D, F and H be some elements of the group G such that $AD=F$. Then, if the matrices such as (3.74) are to represent the group G, we must have

$$\Gamma(A)\,\Gamma(D)=\Gamma(F). \tag{3.75}$$

Taking the (B, C) element of the left-hand side, we find

$$\begin{aligned}\sum_{H\in G}\Gamma_{B,H}(A)\,\Gamma_{H,C}(D) &= \sum_{H\in G}\delta_{BA\,H}\,\delta_{HD,C}\\ &= \delta_{BAD,C}\\ &= \delta_{BF,C}\\ &= \Gamma_{B,C}(F),\end{aligned}$$

which is the (B, C) element of the right-hand side of (3.75), showing that the matrices $\Gamma(A)$, etc., obey the multiplication table of the group.

The representation generated by such matrices is called the *regular representation* of the group, and we shall denote it by Γ^{reg} hereafter.

Clearly, the characters of the elements in this representation are g for the element E and zero for all the other elements. We shall now find which irreducible representations of G are contained in this reducible representation Γ^{reg} and how many times, i.e., our objective is to find the coefficients a_i in

$$\Gamma^{\text{reg}}=\sum_i a_i\,\Gamma^{(i)}. \tag{3.76}$$

From (3.67), we have

$$a_l=\frac{1}{g}\sum_{A\in G}\chi^{(i)*}(A)\,\chi^{\text{reg}}(A),$$

where χ^{reg} is the character of the regular representation. Since $\chi^{\text{reg}}(E)=g$ and $\chi^{\text{reg}}(A)=0$ for $A\neq E$, the above equation becomes

$$a_l=\frac{1}{g}\,\chi^{(l)*}(E)\,g,$$

or

$$a_l=l_l. \tag{3.77}$$

This shows that every irreducible representation of the group occurs in

the reduction of the regular representation as many times as its dimension, so that we have

$$\Gamma^{\text{reg}}=\sum_i l_i\,\Gamma^{(i)}. \tag{3.78}$$

Taking the traces of both the sides of (3.78) for the element E, we get

$$\chi^{\text{reg}}(E)=\sum_i l_i\,\chi^{(i)}(E),$$

or

$$g=\sum_{i=1}^{c} l_i^2. \tag{3.79}$$

This proves that the equality sign holds in (3.52) and therefore the representation vectors $\Gamma_{km}^{(i)}$ [see discussion after (3.52)] form a *complete* set of orthogonal vectors in the group space.

When we have found the irreducible representations of a group whose dimensions satisfy (3.79), there exists no other independent representation vector which is orthogonal to all the representation vectors of the irreducible representations. This, in turn, implies that there is no other character vector which is orthogonal to all the character vectors of the irreducible representations. Therefore, the character vectors of the irreducible representations must also be a *complete* set of orthogonal vectors in the class space. Their number must then equal the dimension of this space, which is equal to the number of classes in the group. This simple argument shows that the equality sign holds in (3.57) also.

3.8 Symmetrized Basis Functions for Irreducible Representations

We now come to the real problem of *how* to reduce a reducible representation. Hereafter, we shall denote reducible representations by $\Gamma^{(a)}$, $\Gamma^{(b)}$, etc., of dimensions a, b, etc., and the irreducible representations by $\Gamma^{(\alpha)}$, $\Gamma^{(\beta)}$, etc., of dimensions l_α, l_β, etc.

In many problems in physics, we have a set of basis functions generating some representation of a group. However, such a representation may in general be a reducible representation. It can be reduced by a suitable choice of the subsets of basis functions, each subset constituting an invariant subspace under the operations of the group elements. We shall now discuss a method for obtaining suitable linear combinations of the basis functions and demonstrate the use of the method.

Suppose that the n basis functions $\{\phi_1, \phi_2, \ldots, \phi_n\}$ in the space L_n generate a representation Γ of the group. The matrix representing

an element A in this representation is given by

$$A\phi_i = \sum_{j=1}^{n} \phi_j \Gamma_{ji}(A). \tag{3.80}$$

Thus, for example, it can be seen that the eight functions ϕ_1, ϕ_2, ..., ϕ_8 of the eight positions 1, 2, ..., 8 shown in Fig. (3.2) form a convenient set of basis functions for the regular representation of C_{4v}. In this figure, the coordinates of the eight points are indicated explicitly. The operation of, say C_4, on the basis functions can be written in the matrix equation

$$\begin{aligned}(\phi_1', \phi_2', \ldots, \phi_8') &= C_4(\phi_1, \phi_2, \ldots, \phi_8) \\ &= (\phi_1, \phi_1, \phi_2, \phi_3, \phi_7, \phi_8, \phi_6, \phi_5) \\ &= (\phi_1, \phi_2, \ldots, \phi_8)\,\Gamma^{\text{reg}}(C_4),\end{aligned} \tag{3.81}$$

where the matrix representing C_4 in the regular representation is given in (3.73).

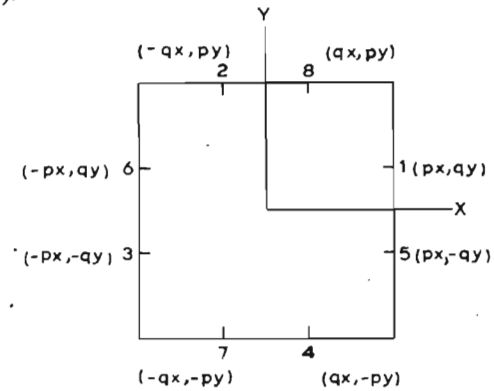


FIGURE 3.2 The eight functions ϕ_i of the positions shown generate the regular representation of C_{4v}

In order to reduce the representation Γ generated in (3.80), we wish to find a suitable unitary transformation matrix U such that

$$U^{-1}\,\Gamma(A)U = \Gamma_{\text{red}}(A), \tag{3.82}$$

for all A in G, where $\Gamma_{\text{red}}(A)$, etc., have the reduced or block-diagonalized form as in (3.24). For this, we write (3.80) in the matrix notation as

$$A\Phi = \Phi\Gamma(A),$$

where Φ stands for the row vector

$$\Phi \equiv (\phi_1, \phi_2, \ldots, \phi_n).$$

If U is the required transformation, then

$$A\Phi U = \Phi U U^{-1}\,\Gamma(A)U$$

or

$$A(\Phi U) = (\Phi U)\,\Gamma_{\text{red}}(A). \tag{3.83}$$

This suggests that if we choose the new basis functions

$$\Psi = \Phi U \tag{3.84}$$

in the space L_n, rather than the basis functions Φ, the matrices of the representation would be in the block-diagonalized form. In an expanded form, (3.84) is

$$\psi_i = \sum_{j=1}^{n} \phi_j U_{ji}. \tag{3.85}$$

For the purpose of finding the coefficients U_{ji} and the proper linear combinations ψ_i, we shall rewrite (3.85) in a different form as

$$\psi_{pm}{}^{\alpha} = \sum_{i=1}^{n} \phi_i U_{\alpha pm}{}^{i}, \tag{3.86}$$

where $\psi_{pm}{}^{\alpha}$ is the m-th basis function for the irreducible representation $\Gamma^{(\alpha)}$ occurring for the p-th time in the reduction of the representation Γ. If

$$\Gamma = \sum_{\alpha=1}^{c} a_\alpha \Gamma^{(\alpha)}, \tag{3.87}$$

then $1 \leq \alpha \leq c$, $1 \leq p \leq a_\alpha$ and $1 \leq m \leq l_\alpha$ (the dimension of $\Gamma^{(\alpha)}$). Eq. (3.86) is the same as (3.85); the matrix $[U_{\alpha pm}{}^{i}]$ is just another label for the matrix $[U_{ji}]$; a set of values of (α, p, m) denotes a column of U and a value of i denotes a row of U. Similarly, $\psi_{pm}{}^{\alpha}$ is just another name for ψ_i. Since the dimension of the matrices on both sides of (3.87) must be the same, we have

$$n = \sum_{\alpha=1}^{c} a_\alpha l_\alpha. \tag{3.88}$$

Now the result of the operation of an element $A \in G$ on $\psi_{pm}{}^{\alpha}$ is to give a linear combination of the l_α functions which generate the irreducible representation $\Gamma^{(\alpha)}$, and which define an l_α-dimensional invariant subspace of the full space L_n. Thus

$$A\psi_{pm}{}^{\alpha} = \sum_{k=1}^{l_\alpha} \psi_{pk}{}^{\alpha} \Gamma_{km}{}^{(\alpha)}(A). \tag{3.89}$$

In such a case, the function $\psi_{pm}{}^{\alpha}$ is said to belong to or *transform according to the m-th column of the irreducible representation* $\Gamma^{(\alpha)}$. Let the basis functions ϕ_i be orthonormal. Since we wish the resulting basis functions $\psi_{pm}{}^{\alpha}$ also to be orthonormal, U must be a unitary matrix and we have

$$\sum_{i=1}^{n} U_{\alpha pm}{}^{i*} U_{\beta qk}{}^{i} = \delta_{\alpha\beta}\delta_{pq}\delta_{mk},$$

$$\sum_{\alpha,p,m} U_{\alpha pm}{}^{i*} U_{\alpha pm}{}^{j} = \delta_{ij}. \tag{3.90}$$

Operating on both sides of (3.86) by an element $A \in G$, we get

$$A\psi_{pm}{}^{\alpha} = \sum_{i=1}^{n} A\phi_i \, U_{\alpha pm}{}^{i}.$$

or

$$\sum_{k=1}^{l_\alpha} \psi_{pk}{}^{\alpha} \, \Gamma_{km}{}^{(\alpha)}(A) = \sum_{i=1}^{n} \sum_{j=1}^{n} \phi_j \, \Gamma_{ji}(A) \, U_{\alpha pm}{}^{i}.$$

Using (3.86) once again in the above equation, we obtain

$$\sum_{k=1}^{l_\alpha} \sum_{s=1}^{n} \phi_s \, U_{\alpha pk}{}^{s} \, \Gamma_{km}{}^{(\alpha)} A = \sum_{i,j=1}^{n} \phi_j \, \Gamma_{ji}(A) \, U_{\alpha pm}{}^{i}.$$

Since ϕ_j are independent functions, the coefficients of each ϕ_j on both sides must be equal. This gives

$$\sum_{k=1}^{l_\alpha} U_{\alpha pk}{}^{s} \, \Gamma_{km}{}^{(\alpha)}(A) = \sum_{i=1}^{n} \Gamma_{si}(A) \, U_{\alpha pm}{}^{i}, \tag{3.91}$$

for all $A \in G$, $1 \leq s \leq n$ and $1 \leq m \leq l_\alpha$. This is a very important relation and is of great help in determining the coefficients $U_{\alpha pm}{}^{i}$, which then immediately give the symmetrized basis functions[8] $\psi_{mp}{}^{\alpha}$. This procedure is very similar to the projection operator technique[9] in which symmetrized basis functions are projected out from a suitable function.

Let us apply (3.91) to the special case of the regular representation of a group. Changing the indices s and i to the group elements B and C respectively and using (3.74), we get

$$\sum_{k=1}^{l_\alpha} U_{\alpha pk}{}^{B} \, \Gamma_{km}{}^{(\alpha)}(A) = \sum_{C \in G} \Gamma_{B,C}^{\text{reg}}(A) \, U_{\alpha pm}{}^{C} = U_{\alpha pm}{}^{BA}, \tag{3.92}$$

for all $A, B \in G$ and $1 \leq m \leq l_\alpha$. Furthermore, if we choose the identity element E for B, we have

$$\sum_{k=1}^{l_\alpha} U_{\alpha pk}{}^{E} \, \Gamma_{km}{}^{(\alpha)}(A) = U_{\alpha pm}{}^{A}. \tag{3.93}$$

This relation, together with (3.90), helps determine the matrix U for the reduction of the regular representation completely.

As an example, we shall apply the above result to the reduction of the regular representation of C_{4v} (with the bases $\phi_1, \phi_2, \ldots, \phi_8$ considered earlier in this section) and to determine the symmetrized

[8] A similar method has been used by Mariot (1962). However, his starting point is different from ours and his method involves some guessing and trial-and-error in the final stage.

[9] Cotton (1971), Section 6.2; Hamermesh (1964), Section 3.18; Tinkham (1964), Section 3.8.

basis functions for the various irreducible representations occurring in Γ^{reg}. Since

$$\Gamma^{\text{reg}} = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \Gamma^{(3)} \oplus \Gamma^{(4)} \oplus 2\Gamma^{(5)},$$

we need eight symmetrized basis functions, one belonging to each of $\Gamma^{(1)}$, $\Gamma^{(2)}$, $\Gamma^{(3)}$ and $\Gamma^{(4)}$, and two sets each of two basis functions belonging to $\Gamma^{(5)}$. Eq. (3.93) connects matrix elements $U_{\alpha pk}{}^{A}$ belonging to the same irreducible representation, i.e., coefficients having the same α and p. We arbitrarily choose one element, say $U_{\alpha pm}{}^{E}=a$, and evaluate the others by letting A run over all the elements of the group. The value of a can be obtained finally by normalization. In the case of an l_α-dimensional irreducible representation, we need to start with l_α arbitrary coefficients which can all be found in the end by normalization (up to a sign factor ± 1, which must be determined by the operation of A on the corresponding symmetrized basis function).

Thus, for obtaining the two sets of basis functions for $\Gamma^{(5)}$, we take

$$U_{5p1}{}^{E}=a,\ U_{5p2}{}^{E}=b. \tag{3.94}$$

On using these in (3.93) together with the irreducible representations of C_{4v} given in Table (3.2), we obtain the following matrix elements:

A :	E	C_4	C_4^2	C_4^3	m_x	m_y	σ_u	σ_v
$U_{5p1}{}^{A}$:	a	$-b$	$-a$	b	a	$-a$	$-b$	b
$U_{5p2}{}^{A}$:	b	a	$-b$	$-a$	$-b$	b	$-a$	a

If we choose the two sets of constants for $p=1$ and $p=2$ as $a=a_1$, $b=b_1$ and $a=a_2$, $b=b_2$, respectively, the orthogonality of all the distinct rows requires that $a_1a_2+b_1b_2=0$. Apart from this condition, we can choose the four constants arbitrarily. We must finally normalize each row (or each column).

The matrix U for the reduction of Γ^{reg} of C_{4v} obtained in this way is given below (we have taken $a_1=b_1=1$, $a_2=-b_2=1$):

$$[U_{\alpha pm}{}^{A}]= \tag{3.95}$$

	α	1	2	3	4	5	5	5	5
	p	1	1	1	1	1	1	2	2
	m	1	1	1	1	1	2	1	2
E		+	+	+	+	+	+	+	+
C_4		+	−	−	+	−	+	+	+
C_4^2		+	+	+	+	−	−	−	+
C_4^3		+	−	−	+	+	−	−	−
m_x		+	−	+	−	+	−	+	+
m_y		+	−	+	−	−	+	−	−
σ_u		+	+	−	−	−	−	+	−
σ_v		+	+	−	−	+	+	−	+

where a factor of $(8)^{-1/2}$ is associated with each positive or negative sign.

One may wonder whether the order of the operators on the left (i.e., the ordering of the rows in (3.95)) is arbitrary and whether one could interchange the rows of the above matrix at will. However, this is not so, and the order is determined by the following consideration. Let us, for the moment, denote the g operators of the group G by $A_1, A_2, \ldots, A_g$. Then, starting from a certain basis function, which we choose to call ϕ_1, the order of the operators is fixed by the relation $A_i\phi_i=\phi_1$, i.e., if an operator brings ϕ_2 into ϕ_1, we shall denote that operator by A_2, etc.[10] This is why we have labeled the points 1, 2, ..., 8 in Fig. (3.2) in a particular fashion. The order of the columns of U is arbitrary except that the columns corresponding to the same irreducible representation (same α and p) must be together.

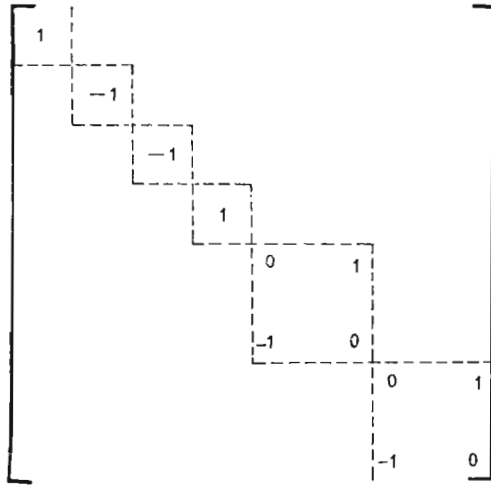
By our starting Eq. (3.86), we then immediately have the symmetrized basis functions for Γ^{reg} of C_{4v}. These are:

$$
\begin{aligned}
\Gamma^{(1)} &: \psi_{11}{}^{1}=(\phi_1+\phi_2+\phi_3+\phi_4+\phi_5+\phi_6+\phi_7+\phi_8)/\sqrt{8}, \\
\Gamma^{(2)} &: \psi_{11}{}^{2}=(\phi_1-\phi_2+\phi_3-\phi_4-\phi_5-\phi_6+\phi_7+\phi_8)/\sqrt{8}, \\
\Gamma^{(3)} &: \psi_{11}{}^{3}=(\phi_1-\phi_2+\phi_3-\phi_4+\phi_5+\phi_6-\phi_7-\phi_8)/\sqrt{8}, \\
\Gamma^{(4)} &: \psi_{11}{}^{4}=(\phi_1+\phi_2+\phi_3+\phi_4-\phi_5-\phi_6-\phi_7-\phi_8)/\sqrt{8}, \\
\Gamma^{(5)} &: \begin{cases} \psi_{11}{}^{5}=(\phi_1-\phi_2-\phi_3+\phi_4+\phi_5-\phi_6-\phi_7+\phi_8)/\sqrt{8}, \\ \psi_{12}{}^{5}=(\phi_1+\phi_2-\phi_3-\phi_4-\phi_5+\phi_6-\phi_7+\phi_8)/\sqrt{8}, \end{cases} \\
\Gamma^{(5)} &: \begin{cases} \psi_{21}{}^{5}=(\phi_1+\phi_2-\phi_3-\phi_4+\phi_5-\phi_6+\phi_7-\phi_8)/\sqrt{8}, \\ \psi_{22}{}^{5}=(-\phi_1+\phi_2+\phi_3-\phi_4+\phi_5-\phi_6-\phi_7+\phi_8)/\sqrt{8}. \end{cases} \qquad (3.96)
\end{aligned}
$$

Thus, starting from the eight-dimensional function space with the basis $\{\phi_1, \phi_2, \ldots, \phi_8\}$, we have successfully reduced it into six subspaces, each of which is invariant under the operations of C_{4v}. Four subspaces are one-dimensional and two are two-dimensional. It can be easily verified that they are indeed invariant subspaces. The operation of $A\in C_{4v}$ on any of the first four functions of (3.96) has the effect of multiplying it by ± 1, whereas a similar operation on $\psi_{pm}{}^{5}$ (fixed p; $m=1, 2$) mixes the two functions $\psi_{p1}{}^{5}$ and $\psi_{p2}{}^{5}$. It can also be seen that the unitary matrix of (3.95) block-diagonalizes all the matrices of the regular representation. For example,

[10]Note that this discussion applies to the regular representation only.

$$U^{-1}\,\Gamma^{\text{reg}}(C_4)\,U=$$



(3.97)

The blocks will, of course, appear in the order in which the columns of U have been arranged.

Let us take the functions ϕ_i to be of the form

$$\phi_i(\mathbf{r})=\exp(i\mathbf{k}.\mathbf{r}_i), \tag{3.98}$$

where $\mathbf{k}$ is a vector of dimensions (length)$^{-1}$ with components k_x and k_y, $\mathbf{r}_i$ are the vectors to the eight points shown in Fig. (3.2). It is of interest to find the behaviour of the symmetrized ψ's for small x and y. Thus, for example, consider

$$\begin{aligned}\psi_{11}{}^2 &\propto \phi_1-\phi_2+\phi_3-\phi_4-\phi_5-\phi_6+\phi_7+\phi_8\\ &\propto \exp i\mathbf{k}.(p\mathbf{x}+q\mathbf{y})-\exp i\mathbf{k}.(q\mathbf{x}-p\mathbf{y})+\exp i\mathbf{k}.(-p\mathbf{x}-q\mathbf{y})\\ &\quad-\exp i\mathbf{k}.(-q\mathbf{x}+p\mathbf{y})-\exp i\mathbf{k}.(p\mathbf{x}-q\mathbf{y})-\exp i\mathbf{k}.(-p\mathbf{x}+q\mathbf{y})\\ &\quad+\exp i\mathbf{k}.(q\mathbf{x}+p\mathbf{y})+\exp i\mathbf{k}.(-q\mathbf{x}-p\mathbf{y})\\ &\propto \sin(qk_y y)\sin(pk_x x)+\sin(pk_y y)\sin(qk_x x).\end{aligned}$$

Retaining only the first term in the expansion for small x and y, we get

$$\psi_{11}{}^2 \propto xy. \tag{3.99}$$

It is then said that the function $\psi_{11}{}^2$ behaves or transforms like xy. This is to say that the function xy is also a suitable basis function for the irreducible representation $\Gamma^{(2)}$ of C_{4v}; the effect of $A\in C_{4v}$ on $\psi_{11}{}^2$ is the same as its effect on xy. In Table (3.3), we have shown how the basis functions for the various irreducible representations transform, leaving the verification to the reader.

TABLE 3.3 BASIS FUNCTIONS FOR THE IRREDUCIBLE REPRESENTATIONS OF C_{4v}

Irreducible representations of C_{4v}	$\Gamma^{(1)}$	$\Gamma^{(2)}$	$\Gamma^{(3)}$	$\Gamma^{(4)}$	$\Gamma^{(5)}$
Basis functions transform like	1	xy	x^2-y^2	$xy(x^2-y^2)$	$\{x, y\}$

It should be noted that the basis functions $\{\psi_{11}^5, \psi_{12}^5\}$ and $\{\psi_{21}^5, \psi_{22}^5\}$ of (3.96) are not unique and therefore the matrix U is also not unique. For example, consider any two linear combinations of ψ_{11}^5 and ψ_{12}^5:

$$\chi_1 = a\psi_{11}^5 + b\psi_{12}^5,$$
$$\chi_2 = c\psi_{11}^5 + d\psi_{12}^5,$$

with the condition $ad \neq bc$, so that χ_1 and χ_2 are two independent functions in this space [see Fig. (3.3)]. It can be shown that χ_1 and χ_2 generate a representation of C_{4v} which is equivalent to the representation $\Gamma^{(2)}$ [see Problem 3.2]. This provides an excellent example of generalized transformations in function spaces and the idea can easily

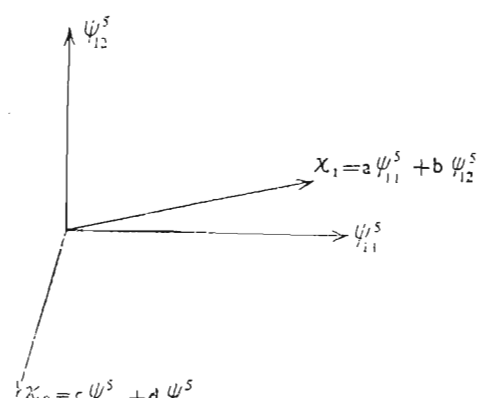


FIGURE 3.3 Any basis can be chosen in a vector space to generate a representation and all such representations are equivalent

be extended to transformations in spaces of more than two dimensions. If the matrix of coefficients $\begin{bmatrix} a & b \\ c & d \end{bmatrix}$ is a unitary matrix, the resulting functions χ_1 and χ_2 are also orthonormal, and the transformation corresponds to a combination of rotations and reflections only.

3.9 Other Reducible Representations

In addition to the regular representation, we can generate other representations of a group. Such representations are, in general, reducible. Thus, starting from any given function ϕ_1 in the Hilbert space of the operators of the group G, we can operate on it with all the elements $A \in G$. Again, in general, this will give us g independent functions

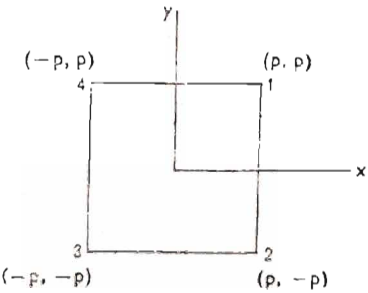


FIGURE 3.4 The four functions of the positions shown generate a representation of C_{4v}

$\phi_1, \phi_2, \ldots, \phi_g$, which generate just the regular representation of G. However if ϕ_1 has special symmetry properties, the number of independent functions is less than g; in fact, it must be an integral divisor of g. As an example, let us start from a function ϕ_1 of the position 1 shown in Fig. (3.4). Applying to this all the operations of C_{4v}, we get three more independent functions of the positions 2, 3 and 4 of Fig. (3.4). Clearly, these four functions generate a representation Γ of C_{4v}, since they transform into each other on the application of the operators of C_{4v}. The matrices of the representation Γ are determined by[11]

$$A\,(\phi_1, \phi_2, \phi_3, \phi_4) = (\phi_1, \phi_2, \phi_3, \phi_4)\,\Gamma\,(A). \tag{3.100}$$

Since there is no four-dimensional irreducible representation of C_{4v}, Γ must be reducible. The characters of the matrices of Γ are found to be[12] as given below:

[11] Note that these are the eight matrices generated in Problem (1.3).

[12] In this particular example, these can be obtained quite easily by an inspection of Fig. (3.4), without having to find all the matrices of Γ explicitly. The character of A is thus the number of functions ϕ_i which remain invariant under A. However, care must be taken in using this simple criterion in other more general problems where fractional coefficients may occur.

Classes	C_1	C_2	C_3	C_4	C_5
	(E)	(C_4, C_4^3)	(C_4^2)	(m_x, m_y)	(σ_u, σ_v)
χ	4	0	0	0	2

Using (3.67), we can find a_i, the number of times an irreducible representation is contained in Γ. We find $a_1=a_2=a_5=1$ and $a_3=a_4=0$, giving

$$\Gamma=\Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \Gamma^{(5)}.$$

In simple cases such as the one we are dealing with, these coefficients can be found by an inspection of the character table of the group, without recourse to (3.67). Thus, notice that if we take the classwise sum of the characters of $\chi^{(1)}$, $\chi^{(2)}$ and $\chi^{(5)}$ of C_{4v} given in Table (3.1), we obtain just the characters of Γ given above.

Now we can apply (3.91) to determine the coefficients $U_{\alpha pm}{}^{i}$ giving the symmetrized linear combinations of ϕ_1, ϕ_2, ϕ_3, and ϕ_4. These are found to be

$$\begin{aligned}
\Gamma^{(1)} &: \quad \psi_{11}{}^{1}=(\phi_1+\phi_2+\phi_3+\phi_4)/2, \\
\Gamma^{(2)} &: \quad \psi_{11}{}^{2}=(\phi_1-\phi_2+\phi_3-\phi_4)/2, \\
\Gamma^{(5)} &: \begin{cases} \psi_{11}{}^{5}=(\phi_1+\phi_2-\phi_3-\phi_4)/2, \\ \psi_{12}{}^{5}=(\phi_1-\phi_2-\phi_3+\phi_4)/2. \end{cases}
\end{aligned} \tag{3.101}$$

The unitary transformation matrix constructed from the coefficients of ϕ_i's above block-diagonalizes all the matrices of the representation Γ.

Thus, in general, whenever the irreducible representations of a group are completely known, (3.91) is adequate to determine all the coefficients $U_{\alpha pm}{}^{i}$ and hence the symmetrized basis functions. In most practical cases, the matrices of the reducible representations have only one nonvanishing element in each row and in each column, leaving only one nonvanishing term on the right hand side of (3.91). Moreover, the irreducible representations of all the crystallographic point groups are at most three-dimensional. This makes the determination of $U_{\alpha pm}{}^{i}$ quite easy.

3.10 Direct Product of Representations

Consider two representations $\Gamma^{(a)}$ and $\Gamma^{(b)}$ (reducible or irreducible) of a group G. Let us take the direct product of the corresponding matrices of the two representations and denote the new matrices by

$$\Gamma(A)=\Gamma^{(a)}(A)\otimes\Gamma^{(b)}(A), \text{ etc.} \tag{3.102}$$

Let $AB=C$ in the group G, and consider the product

$$\begin{aligned}\Gamma(A)\,\Gamma(B)&=[\Gamma^{(a)}(A)\otimes\Gamma^{(b)}(A)]\,[\Gamma^{(a)}(B)\otimes\Gamma^{(b)}(B)]\\&=[\Gamma^{(a)}(A)\,\Gamma^{(a)}(B)]\otimes[\Gamma^{(b)}(A)\,\Gamma^{(b)}(B)]\\&=\Gamma^{(a)}(C)\otimes\Gamma^{(b)}(C)\\&=\Gamma(C).\end{aligned}\tag{3.103}$$

Thus we see that the matrices obtained by taking the direct product of the matrices of two representations also satisfy the multiplication table of the group and hence generate a representation of G. The representation Γ is called the *direct product of the representations* $\Gamma^{(a)}$ and $\Gamma^{(b)}$, and is denoted by $\Gamma=\Gamma^{(a)}\otimes\Gamma^{(b)}$.

The direct product of two representations is, in general, reducible; it certainly is if either $\Gamma^{(a)}$ or $\Gamma^{(b)}$ is reducible. From our discussion of the direct product of matrices in Section 2.5.2, it is clear that the characters of the direct product representation Γ are equal to the products of the corresponding characters of $\Gamma^{(a)}$ and $\Gamma^{(b)}$, i.e.,

$$\chi(A)=\chi^{(a)}(A)\,\chi^{(b)}(A), \text{ etc.}\tag{3.104}$$

Let us first consider the reduction of the direct products of the irreducible representations of G. We denote this by

$$\Gamma^{(i)}\otimes\Gamma^{(j)}=\sum_k x_k{}^{ij}\,\Gamma^{(k)},\tag{3.105a}$$

$$\chi^{(i)}(A)\,\chi^{(j)}(A)=\sum_k x_k{}^{ij}\,\chi^{(k)}(A),\ \forall\ A\in G,\tag{3.105b}$$

where $x_k{}^{ij}$ are nonnegative integers. Then the direct product of any two representations

$$\Gamma^{(a)}=\sum_i a_i\,\Gamma^{(i)} \text{ and } \Gamma^{(b)}=\sum_i b_i\,\Gamma^{(i)}$$

splits into its irreducible components according to

$$\Gamma^{(a)}\otimes\Gamma^{(b)}=\sum_k\Big[\sum_{i,j} a_i\,b_j\,x_k{}^{ij}\Big]\Gamma^{(k)}.\tag{3.106}$$

This can be easily extended to the direct product of more than two representations. In Table (3.4), we have enumerated the direct products of all the irreducible representations of C_{4v} in pairs and their decompositions. We leave its verification to the reader as an exercise.

3.10.1 Basis functions for direct product representations. The basis functions for the direct product representation can easily be obtained by taking the products of the basis functions of the constituent irreducible representations with each other. Thus, let $\{\phi_1,\phi_2,\ldots,\phi_{l_i}\}$ be the basis for the irreducible representation $\Gamma^{(i)}$ and $\{\chi_1,\chi_2,\ldots,\chi_{l_j}\}$

TABLE 3.4 THE DIRECT PRODUCTS OF THE IRREDUCIBLE REPRESENTATIONS OF C_{4v}

$\Gamma^{(1)}$: $\Gamma^{(1)} \otimes \Gamma^{(1)} = \Gamma^{(1)}$;

$\Gamma^{(2)}$: $\Gamma^{(1)} \otimes \Gamma^{(2)} = \Gamma^{(2)}$, $\Gamma^{(2)} \otimes \Gamma^{(2)} = \Gamma^{(1)}$;

$\Gamma^{(3)}$: $\Gamma^{(1)} \otimes \Gamma^{(3)} = \Gamma^{(3)}$, $\Gamma^{(2)} \otimes \Gamma^{(3)} = \Gamma^{(1)}$,
$\Gamma^{(3)} \otimes \Gamma^{(3)} = \Gamma^{(1)}$;

$\Gamma^{(4)}$: $\Gamma^{(1)} \otimes \Gamma^{(4)} = \Gamma^{(4)}$, $\Gamma^{(2)} \otimes \Gamma^{(4)} = \Gamma^{(3)}$,
$\Gamma^{(3)} \otimes \Gamma^{(4)} = \Gamma^{(2)}$, $\Gamma^{(4)} \otimes \Gamma^{(4)} = \Gamma^{(1)}$;

$\Gamma^{(5)}$: $\Gamma^{(1)} \otimes \Gamma^{(5)} = \Gamma^{(5)}$, $\Gamma^{(2)} \otimes \Gamma^{(5)} = \Gamma^{(5)}$,
$\Gamma^{(3)} \otimes \Gamma^{(5)} = \Gamma^{(5)}$, $\Gamma^{(4)} \otimes \Gamma^{(5)} = \Gamma^{(5)}$,
$\Gamma^{(5)} \otimes \Gamma^{(5)} = \Gamma^{(1)} \oplus \Gamma^{(2)} \oplus \Gamma^{(3)} \oplus \Gamma^{(4)}$.

for $\Gamma^{(j)}$. Then the representation $\Gamma = \Gamma^{(i)} \otimes \Gamma^{(j)}$ has the $l_i l_j$ basis functions $\psi_{mn} = \phi_m \chi_n$ ($1 \leq m \leq l_i$, $1 \leq n \leq l_j$). By the definition of a representation, we have

$$A(\psi_{11}, \psi_{12}, \ldots, \psi_{l_i l_j}) = (\psi_{11}, \psi_{12}, \ldots, \psi_{l_i l_j})(\Gamma^{(i)}(A) \otimes \Gamma^{(j)}(A)).$$

From this, the action of A on a particular function ψ_{mn} can be written as

$$A\psi_{mn} = \sum_{(kl)=1}^{l_i l_j} \psi_{kl} [\Gamma^{(i)}(A) \otimes \Gamma^{(j)}(A)]_{kl, mn}$$

$$= \sum_{k=1}^{l_i} \sum_{l=1}^{l_j} \phi_k \chi_l \Gamma_{km}^{(i)}(A) \Gamma_{ln}^{(j)}(A) \quad \text{by (2.87)}$$

$$= (A\phi_m)(A\chi_n). \tag{3.107}$$

This shows how the operation of an operator on a function of the direct product space is to be performed. Here the $l_i l_j$-dimensional space spanned by the basis functions $\{\psi_{mn}\}$ is the direct product of the two spaces spanned by the basis functions $\{\phi_m\}$ and $\{\chi_n\}$ respectively.

In this branch of abstract algebra, we can also take the direct product of a space with itself. Thus, consider a space L_n with the basis functions $\{\phi_1, \phi_2, \ldots, \phi_n\}$. The n^2-dimensional direct product space $L_n \otimes L_n$ has the set of basis functions $\{\phi_1\phi_1, \ldots, \phi_i\phi_j, \ldots, \phi_n\phi_n\}$.

However, one has to be very careful at each stage of the algebra and we must remember that we are dealing with an abstract notation. Therefore, it is necessary to distinguish between the two direct product functions $\phi_i\phi_j$ and $\phi_j\phi_i$ $(i\neq j)$, since in this notation, they stand for two independent vectors in the direct product space. To avoid any ambiguity, one could use primed and unprimed basis functions.

As an example, let us consider the direct product

$$\Gamma\equiv\Gamma^{(5)}\otimes\Gamma^{(5)}=\Gamma^{(1)}\oplus\Gamma^{(2)}\oplus\Gamma^{(3)}\oplus\Gamma^{(4)}; \qquad (3.108)$$

(see Table 3.4). We take the set of functions $\{x, y\}$ as the basis for $\Gamma^{(5)}$. Then the basis functions for the representation Γ are $\{x, y\}\{x', y'\}\equiv\{x^2,\ xy,\ yx,\ y^2\}$. The effect of an operator, say $C_4\in C_{4v}$, on these functions can be readily found to be

$$\begin{aligned} C_4(xx', xy', yx', yy') &= (yy', -yx', -xy', xx') \\ &= (xx', xy', yx', yy')\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} \end{aligned} \qquad (3.109)$$

The validity of (3.107) can now be easily checked; thus

$$C_4(xy)=(C_4x)(C_4y)=-yx.$$

It can also be seen that

$$\begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix} \otimes \begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix},$$

i.e., the matrix representing C_4 in Γ is the direct product of the matrix representing it in $\Gamma^{(5)}$ with itself.

The reduction of (3.108) can now be easily obtained by considering the characters of the representation Γ. The symmetrized linear combinations for the constituent irreducible representations are found to be

$$\begin{aligned} \Gamma^{(1)} &: \psi_1 = [(xx') + (yy')], \\ \Gamma^{(2)} &: \psi_2 = [(xy') + (yx')], \\ \Gamma^{(3)} &: \psi_3 = [(xx') - (yy')], \\ \Gamma^{(4)} &: \psi_4 = [(xy') - (yx')]. \end{aligned} \qquad (3.110)$$

We may mention that the occasion for taking the direct product of two representations of the same group arises when we have a number of identical particles in the system under consideration. Thus, in a two-electron atom such as helium, if the wave function of either electron transforms according to the irreducible representations of a

group, then the combined wave function of the two electrons (neglecting the electron-electron interaction) will transform according to the direct product representations of this group.

3.11 Representations of a Direct Product Group

In this section, we consider the representations of a group which is a direct product of two commuting subgroups. Let $H=\{E\equiv H_1, H_2, \ldots, H_h\}$ and $G=\{E\equiv G_1, G_2, \ldots, G_g\}$ be two groups of order h and g respectively such that all the elements H_i commute with all the elements G_j. Let their direct product group of order $k=hg$ be denoted by $K=\{E\equiv K_{11}, K_{12}, \ldots, K_{1g}, K_{21}, \ldots, K_{hg}\}$, where an element of K is obtained by

$$K_{ij}=H_iG_j. \tag{3.111}$$

Let $H_iH_m=H_p$ and $G_jG_n=G_q$; then

$$\begin{aligned} K_{ij}K_{mn}&=(H_i\,G_j)\,(H_m\,G_n)\\ &=(H_i\,H_m)\,(G_j\,G_n)\\ &=H_p\,G_q\\ &=K_{pq}. \end{aligned} \tag{3.112}$$

Let $\Gamma^{(h)}$ be a representation of H and $\Gamma^{(g)}$ a representation of G. Then

$$\Gamma^{(h)}(H_i)\;\Gamma^{(h)}(H_m)=\Gamma^{(h)}(H_p),$$
$$\Gamma^{(g)}(G_j)\;\Gamma^{(g)}(G_n)=\Gamma^{(g)}(G_q).$$

Taking the direct product of the matrices on the respective sides of the above equations, we have

$$\begin{aligned} \Gamma^{(h)}(H_p)\otimes\Gamma^{(g)}(G_q)&=[\Gamma^{(h)}(H_i)\;\Gamma^{(h)}(H_m)]\otimes[\Gamma^{(g)}(G_j)\;\Gamma^{(g)}(G_n)]\\ &=[\Gamma^{(h)}(H_i)\otimes\Gamma^{(g)}(G_j)][\Gamma^{(h)}(H_m)\otimes\Gamma^{(g)}(G_n)]. \end{aligned} \tag{3.113}$$

If we define new matrices by

$$\Gamma^{(k)}(K_{pq})=\Gamma^{(h)}(H_p)\otimes\Gamma^{(g)}(G_q), \tag{3.114}$$

then (3.113) becomes

$$\Gamma^{(k)}(K_{pq})=\Gamma^{(k)}(K_{ij})\Gamma^{(k)}(K_{mn}). \tag{3.115}$$

Comparing this result with (3.112), it is clear that these direct product matrices form a representation of K. Thus *the direct product of representations of two commuting groups is a representation of the direct product group.*

Now, we go on to show that if both $\Gamma^{(h)}$ and $\Gamma^{(g)}$ are irreducible

representations of H and G respectively, then the direct product $\Gamma^{(k)}=\Gamma^{(h)}\otimes\Gamma^{(g)}$ is an irreducible representation of K. As discussed earlier [see Eq. (3.69)], the condition for irreducibility gives

$$\sum_{H_i\in H}\chi^{(h)}(H_i)\chi^{(h)*}(H_i)=h,$$
$$\sum_{G_i\in G}\chi^{(g)}(G_i)\chi^{(g)*}(G_i)=g, \tag{3.116}$$

where $\chi^{(h)}$ and $\chi^{(g)}$ are the characters of the representations $\Gamma^{(h)}$ and $\Gamma^{(g)}$ respectively. Taking the product of the respective sides of the above equations, we find

$$hg\equiv k=\left[\sum_{H_i\in H}\chi^{(h)}(H_i)\chi^{(h)*}H_i)\right]\left[\sum_{G_j\in G}\chi^{(g)}(G_j)\chi^{(g)*}(G_j)\right]$$
$$=\sum_{H_i\in H}\sum_{G_j\in G}[\chi^{(h)}(H_i)\chi^{(g)}(G_j)][\chi^{(h)*}(H_i)\chi^{(g)*}(G_j)].$$

We can easily deduce from (3.114) that the characters of the representation $\Gamma^{(k)}$ of K are the products of the characters of the respective representations of H and G. Hence the above equation reduces to

$$k=\sum_{K_{ij}\in K}\chi^{(k)}(K_{ij})\chi^{(k)*}(K_{ij}), \tag{3.117}$$

proving that $\Gamma^{(k)}$ is an irreducible representation of K.

Since in the identity representation of any group, each element is represented by unity, the identity representation of K is the direct product of the identity representations of H and G. It can also be seen that if either $\Gamma^{(h)}$ or $\Gamma^{(g)}$ is a reducible representation of H or G, then the direct product representation of K is reducible.

We shall now prove that *all* the irreducible representations of K are the direct products of an irreducible representation of H and one of G. Let the number of the irreducible representations of H be c_h and their dimensions $l_i^{(h)}$ $(1\leq i\leq c_h)$. Let also the number of the irreducible representations of G be c_g and their dimensions $l_j^{(g)}$ $(1\leq j\leq c_g)$. Then, by (3.79), we have

$$\sum_{i=1}^{c_h}[l_i^{(h)}]^2=h,$$
$$\sum_{j=1}^{c_g}[l_j^{(g)}]^2=g.$$

The irreducible representations of K which are obtained by taking the direct products of the irreducible representations of H and G will have

dimensions $l_{ij}{}^{(k)}=l_i{}^{(h)}\,l_j{}^{(g)}$. Consider now the sum of the squares of the dimensions of the irreducible representations of K obtained in this way:

$$\sum_{i=1}^{c_h}\sum_{j=1}^{c_g}[l_{ij}{}^{(k)}]^2=\sum_{i=1}^{c_h}\sum_{j=1}^{c_g}[l_i{}^{(h)}]^2[l_j{}^{(g)}]^2$$
$$=hg$$
$$=k\ ;$$

or
$$\sum_{n=1}^{c_h c_g}[l_n{}^{(k)}]^2=k, \tag{3.118}$$

where we have denoted the dimension of an irreducible representation of K by $l_n{}^{(k)}\equiv l_{ij}{}^{(k)}$. The above equation shows that *the direct products of the irreducible representations of H and G exhaust all the irreducible representations of K*, i.e., there is no irreducible representation of K which cannot be expressed as a direct product of an irreducible representation of H and one of G. If we denote the number of the irreducible representations of K by c_k, then

$$c_k=c_h c_g. \tag{3.119}$$

This is a very important result in the theory of direct product groups since it helps in constructing all the irreducible representations of a bigger group K from those of smaller groups if K can be expressed as the direct product of two or more subgroups. Although we have given an explicit proof of the result here, the same could have been proved using Problem 1.23(iv) together with the fact that the number of irreducible representations of a group is equal to the number of its classes.

3.11.1 Basis functions for representations of the direct product group. The basis functions for a representation $\Gamma^{(k)}$ of K (reducible or irreducible) can be constructed by taking the products of the basis functions of corresponding representations $\Gamma^{(h)}$ and $\Gamma^{(g)}$, of H and G respectively, whose direct product is the representation $\Gamma^{(k)}$. In other words, the Hilbert space of the representation $\Gamma^{(k)}$ is just the direct product of the Hilbert spaces of the representations $\Gamma^{(h)}$ and $\Gamma^{(g)}$.

Let us denote the $l^{(h)}\equiv a$ basis functions of $\Gamma^{(h)}$ by $\{\phi_1, \phi_2, \ldots, \phi_a\}$ and the $l^{(g)}\equiv b$ basis functions of $\Gamma^{(g)}$ by $\{\chi_1, \chi_2, \ldots, \chi_b\}$. Then the representation $\Gamma^{(k)}=\Gamma^{(h)}\otimes\Gamma^{(g)}$ of K has the ab basis functions $\{\psi_{mn}\}$, where $\psi_{mn}=\phi_m\chi_n$ and $1\leq m\leq a$, $1\leq n\leq b$. If an element of K is denoted by $K_{pq}=H_pG_q$, then its operation on a function ψ_{mn} is given by

$$K_{pq}\psi_{mn} = \sum_{(kl)=1}^{ab} \psi_{kl}\, \Gamma_{kl,mn}{}^{(k)}(K_{pq})$$
$$= \sum_{(kl)=1}^{ab} \phi_k \chi_l \left[\Gamma_{km}{}^{(h)}(H_p)\, \Gamma_{ln}{}^{(g)}(G_q)\right]$$
$$= \left[\sum_{k=1}^{a} \phi_k\, \Gamma_{km}{}^{(h)}(H_p)\right] \left[\sum_{l=1}^{b} \chi_l \Gamma_{ln}{}^{(g)}(G_q)\right]$$
$$= (H_p\, \phi_m)\,(G_q \chi_n). \qquad (3.120)$$

Thus, the operators of the two constituent groups act on functions of their respective Hilbert spaces only.

We shall now consider a simple example of the direct product of two groups. Consider the two groups, both of order two, $H=\{E_x, m_x\}$ and $G=\{E_y, m_y\}$, where, as before, the operations m_x and m_y denote reflections in the xz and yz planes, respectively. We have distinguished the identity element in the two groups for the sake of clarity. Since m_x commutes with m_y, we can take the direct product of H and G to give a group of order four with the elements $E=E_xE_y$, $A=E_xm_y$, $B=m_xE_y$, $C=m_xm_y$. The irreducible representations of H and G are as given below:

group H

	E_x	m_x
$\Gamma_1{}^{(h)}$	1	1
$\Gamma_2{}^{(h)}$	1	−1

group G

	E_y	m_y
$\Gamma_1{}^{(g)}$	1	1
$\Gamma_2{}^{(g)}$	1	−1

The irreducible representations of K can then be easily obtained by taking all possible direct products of the irreducible representations of H and G. These are given below:

group K

	E	A	B	C
$\Gamma_1{}^{(k)} \equiv \Gamma_{11}{}^{(k)}$	1	1	1	1
$\Gamma_2{}^{(k)} \equiv \Gamma_{12}{}^{(k)}$	1	−1	1	−1
$\Gamma_3{}^{(k)} \equiv \Gamma_{21}{}^{(k)}$	1	1	−1	−1
$\Gamma_4{}^{(k)} \equiv \Gamma_{22}{}^{(k)}$	1	−1	−1	1

It can be seen that K is isomorphic to the group $\{E, C_4{}^2, m_x, m_y$ which is a subgroup of C_{4v}.

Let us now take ϕ_1 and ϕ_2 as the basis functions for the two irreducible representations of H and χ_1 and χ_2 as those for G. The various operations are then given by

$$\begin{aligned} E_x\phi_1 &= \phi_1,\ m_x\phi_1 = \phi_1, \\ E_x\phi_2 &= \phi_2,\ m_x\phi_2 = -\phi_2; \\ E_y\chi_1 &= \chi_1,\ m_y\chi_1 = \chi_1, \\ E_y\chi_2 &= \chi_2,\ m_y\chi_2 = -\chi_2. \end{aligned} \tag{3.121}$$

An irreducible representation $\Gamma_n^{(k)} \equiv \Gamma_{ij}^{(k)}$ of K will then have the basis functions

$$\psi_{ij} \equiv \phi_i\chi_j,\ i, j = 1, 2.$$

For example, the irreducible representation $\Gamma_2^{(k)} \equiv \Gamma_{12}^{(k)}$ has the basis function $\psi_{12} \equiv \phi_1\chi_2$, which can be easily verified as follows:

$$\begin{aligned} E\psi_{12} &= (E_x\phi_1)(E_y\chi_2) = \phi_1\chi_2 = \psi_{12}, \\ A\psi_{12} &= (E_x\phi_1)(m_y\chi_2) = \phi_1(-\chi_2) = -\psi_{12}, \\ B\psi_{12} &= (m_x\phi_1)(E_y\chi_2) = \phi_1\chi_2 = \psi_{12}, \\ C\psi_{12} &= (m_x\phi_1)(m_y\chi_2) = \phi_1(-\chi_2) = -\psi_{12}. \end{aligned}$$

If there are two distinguishable particles (such as an electron and a proton) whose wave functions transform according to some representations of two different symmetry groups, then the wave function of the system as a whole will transform according to the representations of the direct product group.

PROBLEMS ON CHAPTER 3

(3.1) If the matrix $T(A)$ of Eq. (3.8) is a unitary matrix, show that the rectangular matrix $X(A)$ must be a null matrix. [This is the form of the matrix $\Gamma(A)$ of Eq. (3.23).]

(3.2) Let $\psi_1, \psi_2, \ldots, \psi_n$ be the basis functions for an n-dimensional representation Γ of a group G. Show that any n independent linear combinations of the ψ_i's also generate a representation of G which is equivalent to Γ.

(3.3) If Γ is a representation of a group G, show that Γ^* (whose matrices are the complex conjugates of the corresponding matrices of Γ) is also a representation of G, whereas, Γ^{-1} (whose matrices are the inverses of the corresponding matrices of Γ) and $\Gamma^\dagger$ (whose matrices are the hermitian conjugates of the corresponding matrices of Γ) are not representations of G unless G is an abelian group.

(3.4) If Γ is a representation of a group, show that Γ and Γ^* are both reducible or both irreducible.

(3.5) Construct the character table and the table of the irreducible representations for the group C_{3v}, the symmetry group of an equilateral triangle.

(3.6) Derive Eq. (3.58) from Eq. (3.56).

(3.7) Obtain the character tables and the irreducible representations of (i) a group of order 3; (ii) a cyclic group of order 4; (iii) a noncyclic group of order 4; (iv) a group of order 5; (v) a cyclic group of order 6; (vi) a nonabelian group of order 6; (vii) a cyclic group of order n where n is a positive integer. (Refer to Section 1.8.)

(3.8) Obtain the character table for the group generated in Problem (1.7). (It will be noticed that it is the same as that for C_{4v}. This shows that *two groups having the same character tables are not necessarily isomorphic.*)

(3.9) Obtain the character table of the alternating group A_4.

(3.10) Verify Table (3.4) for the direct products of the irreducible representations of C_{4v}.

(3.11) Let $\Gamma^{(i)}$ and $\Gamma^{(j)}$ be two inequivalent irreducible representations of a group G. Show that the direct product representation $\Gamma^{(i)} \otimes \Gamma^{(j)*}$ does not contain the identity representation. Show also that the direct product of an irreducible representation with its own complex conjugate representation contains the identity representation once and only once.

(3.12) Obtain the direct products of all the irreducible representation of the group C_{3v} and reduce them into direct sums of the irreducible representations.

(3.13) Let C_i^* be the inverse of the class C_i [see Problem (1.18)]. If $C_i^*=C_i$, the class C_i is said to be *self-inverse*. Show that the number of real irreducible characters of a group equals the number of its self-inverse classes.

(3.14) Show that every group has at least one faithful representation.

(3.15) Verify Eq. (3.65) for the characters of C_{4v} given in Table 3.1.

(3.16) Show explicitly (by operating with all the group elements) that the functions xy and x^2-y^2 respectively generate the representations $\Gamma^{(2)}$ and $\Gamma^{(3)}$ of C_{4v}.

(3.17) Generate representations of the group C_{4v} starting from the functions (i) z, (ii) x^2, (iii) x^3, (iv) x^2y, (v) e^{ix}, (vi) $\cos(x)$, (vii) $\cos(mx)\sin(ny)$, (viii) $\exp(ax+by)$ with $a \neq b$. In case the representation is reducible, reduce it and find suitable combinations of functions which generate the constituent irreducible representations.

(3.18) Same as Problem (3.17) for the group C_{3v} with the following functions: (i) z, (ii) xy, (iii) x^2-y^2, (iv) x^2, (v) x^3, (vi) x^2y.

(3.19) Construct the regular representation of the group C_{3v}. Choose a set of six functions which generate the representation. Reduce this representation and obtain six symmetrized basis functions transforming according to the various irreducible representations of C_{3v}.

(3.20) Show that two representations Γ_1 and Γ_2 of a finite group G have no irreducible representation in common if and only if their characters are orthogonal, i.e.,

$$\sum_{k=1}^{c} n_k \chi_{1k} \chi_{2k}^* = 0,$$

where χ_{1k} and χ_{2k} are the characters of the k-th class in Γ_1 and Γ_2 respectively.

(3.21) Show that the two functions $e^{i(x+y)}$ and $e^{i(x+y)}$ generate the regular representation of the group (E, m_x) where m_x is a reflection as defined

in the text. Obtain two linear combinations of these functions transforming according to the irreducible representations of (E, m_x).

(3.22) Show that the function $\exp[i(ax+by)]$ with $a \neq b$ is one of the four functions which generate the regular representation of the group (E, C_4^2, m_x, m_y). Once again, obtain four symmetrized combinations of these functions transforming according to the irreducible representations of the group.

(3.23) Prove that a one-dimensional representation of a group must be irreducible.

Bibliography for Chapter 3

Boerner (1963); Burrow (1965); Dixon (1967); Falicov (1967); Hamermesh (1964); Kahan (1965); Margenau and Murphy (1966), Chapter 15; Meijer and Bauer (1962); Murnaghan (1963); Tinkham (1964); Wigner (1959).

CHAPTER 4

Continuous Groups and Their Representations

In Chapter 1, we introduced the notion of finite and infinite groups and gave a number of examples of both. We saw that infinite groups may be of two categories—discrete and continuous. We shall repeat their definitions here: If the number of elements of a group is denumerably infinite, the group is called *discrete*, whereas if the number of elements is nondenumerably infinite it is called a *continuous* group.

Practically all the theory of groups developed in Chapters 1 and 3 for finite groups holds good in the case of discrete infinite groups. it is when we treat continuous groups that some modifications are needed. In addition to these modifications, many new concepts are introduced which provide a point of contact between the theory of continuous groups and other branches of mathematics. Whereas the theory of finite groups stands alone, without relying on any other part of mathematics, the theory of continuous groups, as remarked by Wigner,[1] often makes extensive use of the theory of ordinary and partial differential equations, topology, etc. In this chapter, we shall develop the theory of continuous groups and their representations.

This chapter is not aimed at providing a rigorous mathematical exposition of the topic at hand. The objective is to introduce to the reader the elementary concepts of continuous groups in an easily comprehensible way.

[1] Talman (1968).

4.1 Topological Groups and Lie Groups

The elements of a continuous group can be characterized by a set of *real parameters* $a_1, a_2, \ldots, a_n$, at least one of which varies continuously over a certain interval. The set of parameters should be both necessary and sufficient to characterize all the elements of the group. In other words, it should not be possible to choose a set containing a smaller number of parameters which can be used to characterize *all* the elements of the group. Let the number of continuous parameters be r ($1 \leq r \leq n$). If this number is finite, the continuous group is said to be *finite* and r is called the *order of the continuous group*.

EXAMPLE 1. The set of all real numbers is a continuous group of order 1 because any real number can be characterized by one parameter, say x, taking values on the interval $[-\infty, \infty]$.

EXAMPLE 2. Consider a linear transformation of a variable x to x' of the form

$$x' = ax + b, \; a, b \in [-\infty, \infty], \; a \neq 0. \tag{4.1}$$

The set of all such transformations is a two-parameter group, an element of which can be symbolically denoted by $T(a, b)$ such that

$$T(a, b)\, x = x' = ax + b. \tag{4.2}$$

The law of composition can be obtained as follows:

$$\begin{aligned} T(a_1, b_1)\, T(a_2, b_2)\, x &= T(a_1, b_1)(a_2 x + b_2) \\ &= a_1 (a_2 x + b_2) + b_1 \\ &= a_1 a_2 x + a_1 b_2 + b_1, \end{aligned} \tag{4.3}$$

so that

$$T(a_3, b_3) \equiv T(a_1, b_1)\, T(a_2, b_2) = T(a_1 a_2, \; a_1 b_2 + b_1); \tag{4.4a}$$

$$a_3 = a_1 a_2, \; b_3 = a_1 b_2 + b_1. \tag{4.4b}$$

From this it can be seen that the identity element is $T(1, 0)$ and the inverse is given by

$$T(c, d) \equiv T^{-1}(a, b) = T(1/a, \; -b/a); \tag{4.5a}$$

$$c = 1/a, \; d = -b/a. \tag{4.5b}$$

Note that a_3 and b_3 are analytic functions of a_1, b_1, a_2, b_2 in (4.4b) and so are c and d of a and b in (4.5b).

EXAMPLE 3. The set of all displacements in a three-dimensional real vector space of the form

$$x' = x + a, \; y' = y + b, \; z' = z + c, \tag{4.6}$$

is a three-parameter, continuous group. If we denote the translation

operator by $T(a, b, c)$, the identity element is $T(0, 0, 0)$ and the inverse of $T(a, b, c)$ is $T(-a, -b, -c)$.

EXAMPLE 4. Consider a linear homogeneous transformation of two variables of the form

$$x' = a_{11}x + a_{12}y,$$
$$y' = a_{21}x + a_{22}y, \tag{4.7}$$

or, in the vector form

$$\mathbf{r}' = A\mathbf{r}, \tag{4.8}$$

with

$$\det A = |a_{ij}| \neq 0. \tag{4.9}$$

The set of all such transformations, obtained by giving all possible real values to a_{ij} subject to the condition (4.9), is a group. It is a four-parameter, continuous group, known as the *linear group* in two dimensions and denoted by $GL(2)$. It can be seen that this group is isomorphic to the group of all nonsingular matrices of order two under multiplication.

EXAMPLE 5. Consider a linear homogeneous transformation of n variables (a generalization of Example 4):

$$x_i' = \sum_{j=1}^{n} a_{ij}x_j, \quad 1 \leq i \leq n, \quad |a_{ij}| \neq 0. \tag{4.10}$$

The set of all such transformations is a continuous, n^2-parameter group known as the linear group in n dimensions and denoted by $GL(n)$. This group is isomorphic to the group of all nonsingular matrices of order n under multiplication.

EXAMPLE 6. The set of all rotations about an axis is a continuous group of order 1, whose parameter may conveniently be chosen to be the angle of rotation, say θ, taking values on the interval $[-\pi, \pi]$ or $[0, 2\pi]$. This group, denoted by $SO(2)$, will be discussed in more detail in Section 4.2.

EXAMPLE 7. The set of all rotations about all axes passing through a fixed point in the three-dimensional space is a group whose elements can be characterized by the Euler angles α, β, γ. The group, denoted by $SO(3)$, is to be discussed later in Section 4.3.

4.1.1 Topological groups. Owing to the continuous nature of the group elements, it is desirable to introduce a topology in the group.

For simplicity, we shall restrict ourselves to groups whose elements can be put in a one-to-one correspondence with the points of a subset of an r-dimensional real inner product space S_r. We shall refer to this subset as the *parameter space*.

Let[2] $P(x)$ be the point of S_r corresponding to the element x of the group G. $P(x)$ is said to be the *image* of the element x.

Consider now a *neighbourhood* of the point $P(x)$ in S_r. This is the set of all points P' of S_r for which

$$\|P'-P(x)\|<\epsilon, \tag{4.11}$$

where ϵ is a real positive number. This is also called the ϵ-neighbourhood of $P(x)$ and we shall denote it by N_ϵ [see Fig. (4.1)]. The points of this neighbourhood N_ϵ are then the images of the elements constituting a neighbourhood Z_ϵ of the element x of G. Symbolically, the neighbourhood Z_ϵ of x is the set of elements x' in G for which

$$\|P(x')-P(x)\|<\epsilon. \tag{4.12}$$

By using these concepts, we can define the limit and the continuity of the laws of composition and inversion of the group elements.

Thus, consider a composition of group elements such as

$$x_1x_2=x_3. \tag{4.13}$$

The law of composition of the group elements is said to be *continuous* in x_2 if for every $\epsilon>0$, it is possible to find a real number $\delta_\epsilon>0$ such that for all x belonging to the neighbourhood $Z_{\delta\epsilon}$ of x_2 (i.e., all x for

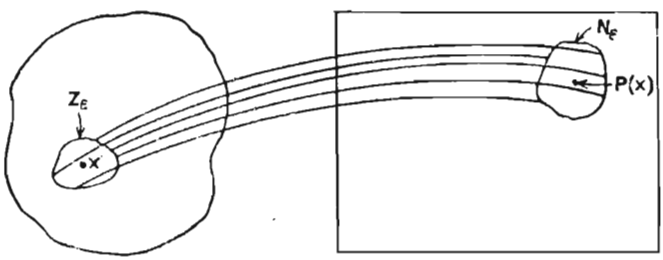


FIGURE 4.1 The neighbourhood N_ϵ of $P(x)$ in S_r is the set of the images of elements in the neighbourhood Z_ϵ of x in G

which $\|P(x)-P(x_2)\|<\delta_\epsilon$), the element x_1x belongs to the neighbourhood Z_ϵ of x_3 (i.e., $\|P(x_1x)-P(x_3)\|<\epsilon$). What this means is that a small change in one of the factors in the product produces

[2]In this chapter, we shall denote the elements of the continuous group by x with primes or subscripts.

a small change in the product. Similarly, of course, we can define the continuity of the law of inversion of the group elements [see Fig. (4.2) and Problem (4.1)], which means that a small change in an element produces a small change in its inverse.

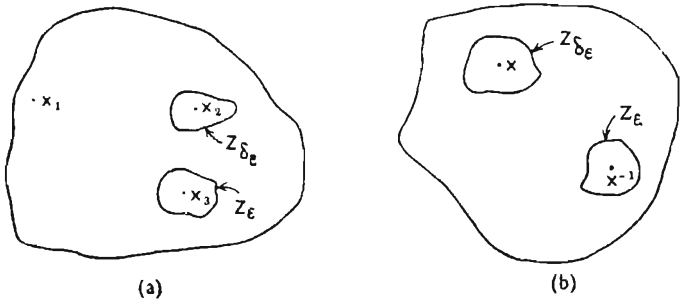


FIGURE 4.2 (a) The continuity of the law of composition: for every $x \in Z_{\delta\epsilon}$, the neighbourhood of x_2, $x_1 x \in Z_\epsilon$, the neighbourhood of x_3, where $x_1 x_2 = x_3$. (b) The continuity of the inversion of the group elements: for every $x' \in Z_{\delta\epsilon}$, the neighbourhood of x, $x'^{-1} \in Z_\epsilon$, the neighbourhood of x^{-1}, where $xx^{-1} = e$, the identity element

We are now in a position to define a *topological group*: it is a group in which the law of composition and the law of inversion are continuous in all the group elements.

4.1.2 Connectedness and compactness. Consider any two elements x_1 and x_2 of a topological group G with images $P(x_1)$ and $P(x_2)$ in S_r. If it is possible to connect $P(x_1)$ and $P(x_2)$ by one or more paths lying entirely within the parameter space, the parameter space is said to be *connected*; otherwise it is *disconnected.* Let G be a group whose parameter space is connected and consider a path connecting $P(x_1)$ and $P(x_2)$. The set of elements of G whose images are the points of the path connecting $P(x_1)$ and $P(x_2)$ will be called a *path connecting x_1 and x_2*. A group is then said to be *connected* if there exists a path connecting any two group elements, or, in other words, if its parameter space is connected.

As an example, we see that the group of rotations about an axis is a connected group, as is also the group of proper rotations in three dimensions.

It is important to note that the property of connectedness is different from the continuous nature of the group, which depends on the continuous variation of one or more of the group parameters. Thus

a continuous group may not be connected, an important example of which, as we shall see later, is the rotation-inversion group in three dimensions. As shown in Fig. (4.3), it means that the parameter space of a continuous disconnected group consists of two or more disjoint subsets such that each subset is a connected space, but it is not possible to go continuously from a point of one subset to a point in another without going outside the parameter space.

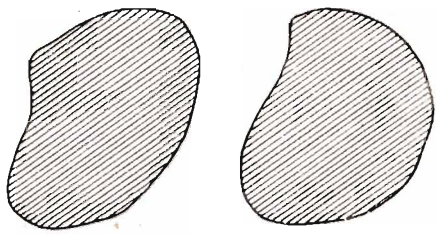


FIGURE 4.3 A plausible structure of the parameter space of a continuous but disconnected group

A continuous connected group may further be *simply connected* or *multiply connected* depending on the topology of the parameter space. A subset of the Euclidean space S_r is said to be *k-fold connected* if there are precisely k distinct paths connecting any two points of the subset which cannot be brought into each other by continuous deformation without going outside the subset. The structure of multiply connected spaces is shown in Fig. (4.4). A connected group is then said to be *k-fold connected* if its parameter space is k-fold connected.

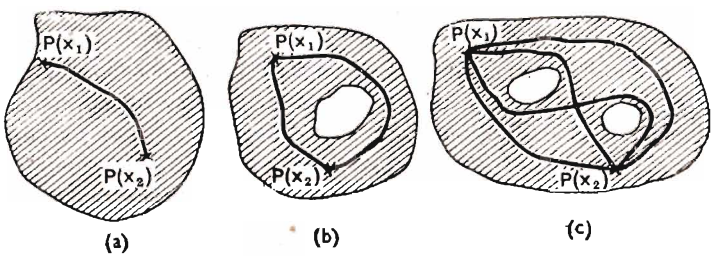


FIGURE 4.4 Plausible structures for (a) a simply connected space, (b) a doubly connected space, and (c) a fourfold connected space. In each case, the space under consideration is the lined region

If a topological group has r continuous parameters and $n-r$ discrete parameters, its parameter space will consist of $n-r$ disjoint subspaces.

There is a one-to-one correspondence between any two disjoint pieces of the group space and when the analytical properties of the group are discussed, only the piece (subspace) containing the identity element is generally implied.

Finally, a topological group is said to be *compact* if its parameter space is a compact space, that is, a closed[3] and bounded[4] space.

4.1.3 Lie groups. The dependence of the elements x_1, x_2, etc., of a topological group G on its r continuous parameters can be written explicitly as $x_1 \equiv x_1(a_1, a_2, \ldots, a_r)$, $x_2 \equiv x_2(b_1, b_2, \ldots, b_r)$, etc. Let $x_1 x_2 = x_3(c_1, c_2, \ldots, c_r)$ and $x_1^{-1} = x_4(d_1, d_2, \ldots, d_r)$. The parameters of x_3 and x_4 can be expressed as functions of the parameters of x_1 and x_2, that is,

$$c_i \equiv c_i(a_1, \ldots, a_r; b_1, \ldots, b_r),$$
$$d_i \equiv d_i(a_1, \ldots, a_r), \tag{4.14}$$

for $1 \leqslant i \leqslant r$. A topological group is called an r-dimensional *Lie group* if there exists a neighbourhood N of the identity element e such that the continuous parameters of the product of two elements and those of the inverse of an element in N are continuous differentiable functions of the parameters of the elements, that is, if c_i's and d_i's of (4.14) are analytic functions of a_i's and b_i's for elements in N provided that x_3 and x_4 lie in N when x_1 and x_2 do. In addition, there will be laws for combining the other $n-r$ discrete parameters.

It is convenient to choose the continuous parameters of a Lie group such that the image of the identity element e is the origin of the parameter space, i.e., $e \equiv x(0, 0, \ldots, 0)$. With this parametrization, an element near the identity may be written, due to the analytical properties of the Lie group, as

$$x(0, 0, \ldots, \epsilon_j, \ldots, 0) \simeq x(0, 0, \ldots, 0) + i\epsilon_j I_j(0, 0, \ldots, 0), \tag{4.15}$$

to first order in ϵ_j. The operator I_j can be obtained from (4.15) and is given by

$$I_j = \lim_{\epsilon_j \to 0} \left[\frac{1}{i\epsilon_j} \{x(0, \ldots, \epsilon_j, \ldots, 0) - x(0, 0, \ldots, 0)\} \right]. \tag{4.16}$$

All the properties of a Lie group can be derived from the r operators $I_j (1 \leqslant j \leqslant r)$ which need to be defined only near the identity element of the group.

[3] A set is *closed* if every Cauchy sequence of elements of the set has a limit element which also belongs to the set. See Section 2.1.4.

[4] See Simmons (1963), p. 58.

By the successive application of the product rule, we can arrive at an element of the group a finite distance away from the identity. Thus, suppose we wish to generate the element $x(0, 0, \ldots, a_j, \ldots, 0)$. Let us write $a_j = N\epsilon_j$, where N is a large positive integer so that ϵ_j is a small quantity. Then

$$\begin{aligned} x(0, 0, \ldots, a_j, \ldots, 0) &= [x(0, 0, \ldots, \epsilon_j, \ldots, 0)]^N \\ &= [e + i\epsilon_j I_j]^N \\ &= [e + i(a_j/N) I_j]^N. \end{aligned} \tag{4.17}$$

Allowing N to tend to infinity and using the algebraic identity

$$\lim_{N \to \infty} (1 + x/N)^N = \exp(x),$$

this becomes

$$x(0, 0, \ldots, a_j, \ldots, 0) = \exp(i a_j I_j), \tag{4.18}$$

which is an exact result. The exponential function on the right-hand side of (4.18) is to be understood as being formally equivalent to its expansion in the powers of the operator I_j. For a general element of the group, we can easily extend the above result to obtain

$$x(a_1, a_2, \ldots, a_r) = \exp\left[\sum_{j=1}^{r} i a_j I_j\right]. \tag{4.19}$$

All the elements of the Lie group belonging to the subset containing the identity can be obtained by giving various values to the parameters a_j on the respective prescribed intervals. The operators I_j are therefore called the *generators* of the Lie group. A Lie group with r continuous parameters has r generators.

The infinitesimal elements of a Lie group themselves constitute an abelian group. Thus, let

$$\begin{aligned} x_k &\equiv x(0, 0, \ldots, \epsilon_k, \ldots, 0) = e + i\epsilon_k I_k, \\ x_j &\equiv x(0, 0, \ldots, \epsilon_j, \ldots, 0) = e + i\epsilon_j I_j. \end{aligned}$$

Then

$$x_k x_j = x_j x_k \simeq e + i(\epsilon_k I_k + \epsilon_j I_j), \tag{4.20}$$

to first order in the ϵ's, which is again an infinitesimal element of G.

4.1.4 Representation of a continuous group. Let a set of matrices $\Gamma(x)$ generate a representation of the Lie group G. We say that Γ is a *continuous representation* of G if

$$\Gamma(x) \to \Gamma(x') \text{ as } x \to x'. \tag{4.21}$$

The group G is homomorphic to the group Γ of matrices and the matrices of Γ can be characterized by the same parameters as used for characterizing the elements of G. Eq. (4.21) then means that as the

values of the parameters are continuously changed from those for x to those for x' in the parameter space, the corresponding matrix $\Gamma(x)$ goes continuously to $\Gamma(x')$.

If we restrict ourselves to the consideration of the continuous representations of a compact continuous group, then we have the following important theorems which we shall state without proof. These are, in a way, extensions of some of the results which hold good for finite groups to the case of continuous groups:

(a) *Any representation has an equivalent representation whose matrices are unitary.* We have proved this for finite groups in Section 3.2.2.

(b) *Any unitary representation is completely reducible, i.e., can be brought to the form* (3.24),

(c) *Any irreducible representation is finite dimensional.*

4.2 The Axial Rotation Group $SO(2)$

Consider the set of rotations of a circle about an axis normal to the plane of the circle and passing through its centre. Each element of this set can be characterized by one parameter which can be chosen to be the angle of rotation ϕ which takes values on the interval $[0, 2\pi]$. This is clearly a one-parameter, continuous, connected, abelian, compact, Lie group, known as the *axial rotation group*, and is denoted by $SO(2)$. Since rotations by ϕ and $\phi+2\pi n$ (n an integer) are identical, the parameter space is the subset $[0, 2\pi]$ of the real line. The group is infinitely manifold connected because there are infinitely many paths connecting any two group elements which cannot be brought into each other by continuous deformation without going outside the space. The path which goes around the circle n times is not identical to one which goes around it $n+1$ times [see Fig. (4.5)].

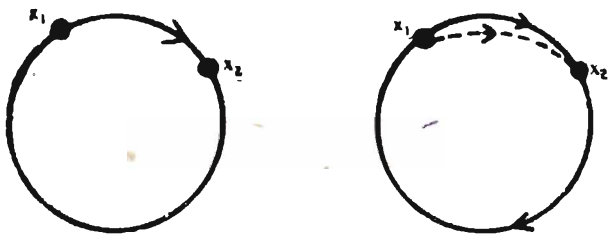


FIGURE 4.5 The group $SO(2)$ is infinitely manifold connected

If we denote an element of this group by $T(\phi)$, the law of composition is

$$T(\phi)\,T(\theta)=T(\theta)\,T(\phi)=\begin{cases}T(\phi+\theta) \text{ if } \phi+\theta<2\pi,\\ T(\phi+\theta-2\pi) \text{ if } \phi+\theta\geq 2\pi.\end{cases} \tag{4.22}$$

The identity element is $T(0)$ and the inverse of $T(\phi)$ is $T(2\pi-\phi)$.

The transformations of a cartesian coordinate system (x, y) in the plane of the circle under the rotations of the group $SO(2)$ can be used to generate a representation of the group. The operation of an element $T(\phi)$ on (x, y) is given by

$$T(\phi)(x,y)\equiv(x'.y')=(x,y)\begin{bmatrix}\cos\phi & \sin\phi\\ -\sin\phi & \cos\phi\end{bmatrix}. \tag{4.23}$$

The matrix of transformation on the right-hand side is an orthogonal matrix of order 2. With every element $T(\phi)$ of the group can thus be associated a 2×2 orthogonal matrix with determinant $+1$ and the correspondence is clearly one-to-one. The set of all orthogonal matrices of order 2 having determinant $+1$ is a group which is isomorphic to the axial rotation group and therefore provides a two-dimensional representation for it. This matrix group is also denoted by the same symbol $SO(2)$.

Since the axial rotation group is abelian, all its irreducible representations must be one-dimensional. To obtain all such irreducible representations, we take the help of the product rule (4.22) and note that the only numbers (1×1 matrices) which satisfy it are of the form

$$\chi(\phi)=\exp(c\phi), \tag{4.24}$$

where c is a number and $\chi(\phi)$ is the character of $T(\phi)$. But since $T(2\pi)=e$, the identity, and e must be represented by unity in any one-dimensional representation, we have $\exp(2\pi c)=1$, giving $c=im$ where m is an integer, or

$$\chi^{(m)}(\phi)=\exp(im\phi). \tag{4.25}$$

For every integral value of m we have an irreducible representation of $SO(2)$ given by (4.25). The orthogonality theorem (3.55) for characters becomes in this case

$$\int_0^{2\pi}\chi^{(m)*}(\phi)\,\chi^{(m')}(\phi)\,d\phi=2\pi\delta_{mm'}. \tag{4.26}$$

If we allow multivalued representations, it can be seen that $\chi^{(m)}(\phi)=\exp(im\,\phi/2)$, $\chi^{(m)}(\phi)=\exp(im\,\phi/3)$, etc., can also be used as representations of $SO(2)$, because it is evident that

$$\exp(im\,\phi/k)\exp(im\,\theta/k)=\exp[im(\phi+\theta)/k],$$

satisfying the group multiplication law; here k is any integer. In general, $x^{(m)}(\phi)=\exp(im\,\phi/k)$ gives us a k-valued representation of $SO(2)$. However, it is found that in constructing mathematical models of real physical systems, only single-valued and double-valued representations occur. Further discussion of such representations can be found at the end of Section 4.5.3.

4.2.1 Generators of $SO(2)$. Since $SO(2)$ is a one-parameter group, it has only one generator. The generator will depend on which group isomorphic to $SO(2)$ is under consideration. We shall illustrate this by considering four examples.

EXAMPLE 1. The group of the complex numbers $\{\exp(im\phi)\}$ for $0\leq\phi<2\pi$, fixed m. This group is clearly isomorphic to $SO(2)$. By (4.16), the generator is given by

$$\begin{aligned} I &= \lim_{\phi\to 0}\left\{\frac{1}{i\phi}\left[\exp(im\phi)-1\right]\right\} \\ &= m. \end{aligned} \tag{4.27}$$

By (4.18), any element of the group can be written as $\exp(im\phi)$, which is trivially true in this case.

EXAMPLE 2. The group of all orthogonal matrices of order 2 with determinant $+1$. We have seen that a typical element of this group can be written as $\begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix}$. The generator is therefore

$$\begin{aligned} I &= \lim_{\phi\to 0}\left[\frac{1}{i\phi}\left\{\begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix}-\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}\right\}\right] \\ &= \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \end{aligned} \tag{4.28}$$

which is one of the Pauli spin matrices commonly denoted by σ_y. Any 2×2 orthogonal matrix with determinant $+1$ can then be written as

$$\begin{bmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{bmatrix} = \exp(i\phi\sigma_y), \tag{4.29}$$

a verification of which is left to Problem (4.4).

EXAMPLE 3. Consider a circle of radius a and let x measure the distance along the circumference. Let $f\equiv f(x)$ and let $T(\phi)$ stand for a rotation of the function f through an angle ϕ about an axis normal to the circle and passing through its centre. Since f is defined only on the

circle, $T(\phi)$ has the effect of translating it by a distance $a\phi$, i.e., $T(\phi)f(x)=f(x+a\phi)$. The generator I is then an operator whose effect on $f(x)$ is

$$\begin{aligned} If(x) &= \lim_{\phi\to 0}\left\{\frac{1}{i\phi}\left[T(\phi)f(x)-ef(x)\right]\right\} \\ &= \lim_{\phi\to 0}\left\{\frac{1}{i\phi}\left[f(x+a\phi)-f(x)\right]\right\} \\ &= -ia\,\partial f/\partial x. \end{aligned} \tag{4.30}$$

Thus, the operator is proportional to the quantum mechanical momentum operator $p_x=-i\hbar\partial/\partial x$ and is given by

$$I=ap_x/\hbar. \tag{4.31}$$

An operator of the group can then be written as

$$T(\phi)=\exp(i\phi\, ap_x/\hbar). \tag{4.32}$$

EXAMPLE 4. Let $f\equiv f(x,y)$ and let the operator $T(\phi)$ stand for an orthogonal transformation of the coordinate system as in (4.23). The operation of $T(\phi)$ on f then gives

$$T(\phi)f(x,y)=f(x\cos\phi+y\sin\phi,\ -x\sin\phi+y\cos\phi). \tag{4.33}$$

The generator can be found out as follows.

$$\begin{aligned} If(x,y) &= \lim_{\phi\to 0}\frac{1}{i\phi}\times\left[f(x\cos\phi+y\sin\phi,-x\sin\phi+y\cos\phi)-f(x,y)\right] \\ &= \lim_{\phi\to 0}\left\{\frac{1}{i\phi}\left[y\phi\partial f/\partial x-x\phi\partial f/\partial y\right]\right\} \\ &= -i(y\partial/\partial x-x\partial/\partial y)f(x,y). \end{aligned} \tag{4.34}$$

Hence

$$I=-L_z/\hbar, \tag{4.35}$$

where L_z is the component of the angular momentum operator normal to the plane (x, y):

$$L_z=i\hbar\,(y\partial/\partial x-x\partial/\partial y)=xp_y-yp_x=-i\hbar\partial/\partial\phi. \tag{4.36}$$

An orthogonal transformation of the coordinates in the two-dimensional plane (x, y) is then given by

$$T(\phi)=\exp(-i\phi L_z/\hbar). \tag{4.37}$$

4.3 The Three-Dimensional Rotation Group $SO(3)$

Consider the set of all orthogonal transformations in a three-

dimensional real vector space (i.e., a space defined over the field of real numbers). It is a group which we shall denote by $O(3)$. It can also be alternatively defined as the group of all 3×3 orthogonal matrices. The two groups are isomorphic to each other.

If R is an orthogonal matrix, it satisfies the equation

$$R\tilde{R} = \tilde{R}R = E, \tag{4.38}$$

where E is the unit matrix and $\tilde{R}$ is the transposed matrix of R. Taking the determinants of both the sides of (4.28) and noting that $\det \tilde{R}=\det R$, we have

$$(\det R)^2=1 \Rightarrow \det R=\pm1. \tag{4.39}$$

The matrices of the group $O(3)$ are thus divided into two sets—one containing the matrices with determinant $+1$ and the other containing the matrices with determinant -1. It can be easily checked that the first set is a group. We shall denote this group—the group of all real orthogonal matrices of order 3 with determinant $+1$—by $SO(3)$.

Considering the isomorphism of the orthogonal matrices with the orthogonal transformations, we see that an orthogonal matrix with determinant $+1$ corresponds to a pure rotation or *proper rotation* of the coordinate system. An orthogonal matrix with determinant -1 corresponds to an orthogonal transformation which can be expressed as the product of a proper rotation with the inversion. Such transformations are called *improper rotations*. The matrix corresponding to the operation of inversion is the negative of the unit matrix:

$$J = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{4.40}$$

The inversion and the identity constitute a group of order 2. Since inversion commutes with all the rotations,[5] we have the important relation

$$O(3)=SO(3)\otimes(E, J). \tag{4.41}$$

The group (E, J) has only two one-dimensional irreducible representations. The representations of $O(3)$ can therefore be easily obtained from those of $SO(3)$ by the theory of the direct product of groups. We shall therefore consider below the irreducible representations of $SO(3)$ only. The group $O(3)$ is called the three-dimensional *rotation-inversion* group.

[5]In the matrix group, J is a constant matrix. Hence it commutes with all square matrices of order 3.

The parameters of $SO(3)$ can be chosen in various ways. Let us choose a cartesian coordinate system (x, y, z) in the space under consideration. We may denote a rotation through an angle ψ about an axis $\mathbf{u}$ by $R_{\mathbf{u}}(\psi)$. It requires two parameters to fix a direction with respect to the coordinate system. For example, we may choose the two parameters to be the angular polar coordinates (θ, ϕ) of a point on the axis $\mathbf{u}$. The three group parameters θ, ϕ and ψ are shown in Fig. (4.6).

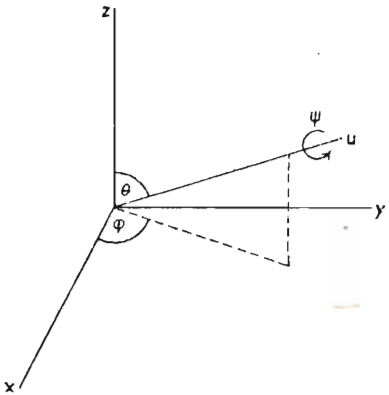


FIGURE 4.6 The three parameters θ, ϕ and ψ of $SO(3)$

An alternative method is to express the rotations in terms of the Eular angles. This is a more convenient way for developing the theory further. A rotation through the Eular angles (α, β, γ) denoted by $R(\alpha, \beta, \gamma)$ consists of the following three successive rotations: (i) a rotation through α about the z axis, followed by (ii) a rotation through β about the new y axis, followed by (iii) a rotation through γ about the transformed z axis. Thus,

$$R(\alpha, \beta, \gamma) = R_z(\gamma)\, R_y(\beta)\, R_z(\alpha). \tag{4.42}$$

The matrix of transformation corresponding to the element $R(\alpha, \beta, \gamma)$ can be easily found out. Consider first the element $R_z(\alpha)$; its matrix of transformation is clearly

$$\begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Writing down similar matrices for $R_y(\beta)$ and $R_z(\gamma)$ and taking the

product in accordance with (4.42), we obtain[6]

$$R(\alpha, \beta, \gamma)= \begin{bmatrix} \cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma & \sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma-\sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma+\cos\alpha\cos\gamma & -\sin\beta\sin\gamma \\ -\cos\alpha\sin\beta & -\sin\alpha\sin\beta & -\cos\beta \end{bmatrix}. \quad (4.43)$$

This is an orthogonal matrix with determinant $+1$ and gives the general element of the matrix group $SO(3)$.

The generators of $SO(3)$ can be obtained by considering an infinitesimal rotation through an angle ϵ about an axis $\mathbf{u}$. The group of rotation $R_{\mathbf{u}}(\phi)$ for $0\leq\phi<2\pi$, which is a subgroup of $SO(3)$, is isomorphic to $SO(2)$ and hence, in the manner in which we obtained (4.35), we get

$$I_{\mathbf{u}} = -L_{\mathbf{u}}/\hbar, \quad (4.44)$$

where $L_{\mathbf{u}} = \mathbf{L}\cdot\hat{\mathbf{u}}$ is the component of the angular momentum operator $\mathbf{L}$ along $\mathbf{u}$, $\hat{\mathbf{u}}$ being a unit vector along $\mathbf{u}$. Since any rotation can be expressed as the product of three rotations about the cartesian coordinate axes, we see that we need the three operators

$$I_x=-L_x/\hbar,\ I_y=-L_y/\hbar,\ I_z=-L_z/\hbar. \quad (4.45)$$

Any rotation operator can then be written as

$$R_{\mathbf{u}}(\phi)=\exp\left[-i\phi\,(\mathbf{L}\cdot\hat{\mathbf{u}})/\hbar\right]. \quad (4.46)$$

While expanding the exponential, it should be remembered that the components of the angular momentum operator $\mathbf{L}$ do not commute with each other.

The full rotation-inversion group $O(3)$ has four parameters which may be taken to be $(\alpha, \beta, \gamma, d)$, where α, β, and γ are the parameters of $SO(3)$ and d denotes the determinant of an element and can take values ± 1. The parameter space of $O(3)$ thus consists of two disconnected regions. It is therefore a four-parameter group, three of which are continuous. It is a continuous, compact, Lie group which is, however, not connected.

4.3.1 Irreducible representations of $SO(3)$. As usual, it is easier to find the characters, rather than the actual matrices, of the irreducible representations of $SO(3)$. As discussed at the end of Section 3.6.2, the problem is to find a suitable set of basis functions

[6]For more details, see Messiah (1965), Section C.10; Ziman (1969), Section 7.9.

which transform into their linear combinations on operating with the elements of $SO(3)$. It is well known that the set of the $2l+1$ spherical harmonics $Y_l^m(\theta, \phi)$, where $l=0, 1, 2, 3, \ldots$, and $-l \leq m \leq l$, transform into their own linear combinations on rotating the coordinate system. If the transformation properties of $Y_l^m(\theta, \phi)$ under rotations are known then, of course, we immediately have the matrices of the irreducible representations generated by the $2l+1$ functions $Y_l^m(\theta, \phi)$. We shall take this up later, indicating at present a method to determine the characters of the irreducible representations generated by $Y_l^m(\theta, \phi)$.

Let us first consider the class structure of the group $SO(3)$. Consider the two operations $R_{\mathbf{u}}(\alpha)$ and $R_{\mathbf{v}}(\alpha)$ which denote rotations through the same angle α about two distinct axes $\mathbf{u}$ and $\mathbf{v}$ (both passing through the origin). Since there exists in $SO(3)$ an operation which can bring the axis $\mathbf{u}$ into the axis $\mathbf{v}$, by rule (iii) of Section 1.3 for finding classes, we see that $R_{\mathbf{u}}(\alpha)$ and $R_{\mathbf{v}}(\alpha)$ must belong to the same class. In other words, if $R_{\mathbf{w}}(\beta)$, say, is the rotation which brings the axis $\mathbf{u}$ into the axis $\mathbf{v}$, then $R_{\mathbf{u}}(\alpha)$ and $R_{\mathbf{v}}(\alpha)$ are related through a similarity transformation

$$R_{\mathbf{u}}(\alpha) = [R_{\mathbf{w}}(\beta)]^{-1} R_{\mathbf{v}}(\alpha) R_{\mathbf{w}}(\beta). \tag{4.47}$$

It should be clear that β is the angle between $\mathbf{u}$ and $\mathbf{v}$ and $\mathbf{w}$ is perpendicular to both of them. We thus have the important result: *In the group $SO(3)$, rotations through a given angle about all axes belong to a class.* In any representation, therefore, characters of the elements of $SO(3)$ depend only on the angle of rotation, not on the axis of rotation.

It is thus not necessary to know the complicated transformation properties of the spherical harmonics under all rotations. We may choose the axis of rotation to be the z axis; the operation of $R_z(\alpha)$ on a spherical harmonic $Y_l^m(\theta, \phi)$ is then known to be

$$R_z(\alpha)\, Y_l^m(\theta, \phi) = Y_l^m(\theta, \phi - \alpha) = \exp(-im\alpha)\, Y_l^m(\theta, \phi). \tag{4.48}$$

The matrix representing $R_z(\alpha)$ with the basis $\{Y_l^m(\theta, \phi)\}$ (for $-l \leq m \leq l$) is therefore a diagonal matrix given by[7]

$$R_z(\alpha) = \begin{bmatrix} e^{-il\alpha} & & & & \\ & e^{-i(l-1)\alpha} & & \mathbf{O} & \\ & & \cdot & & \\ & & & \cdot & \\ & \mathbf{O} & & & e^{i(l-1)\alpha} \\ & & & & e^{il\alpha} \end{bmatrix} \tag{4.49}$$

[7] Although the operator $R_z(\alpha)$ has a diagonal representation in (4.49), it should not be thought that this is a reducible representation. A rotation about any other axis except the z axis will be represented by a nondiagonal matrix because of the mixing of the spherical harmonics.

The character of $R_z(\alpha)$ is then easily found to be

$$\begin{aligned}\chi^{(l)}(\alpha) &= \sum_{m=-l}^{l} e^{im\alpha} \\ &= e^{-il\alpha}(1+e^{i\alpha}+e^{-i\alpha}+\ldots+e^{2il\alpha}) \\ &= \frac{\exp[\,i\,(l+\tfrac{1}{2})\alpha]-\exp[-i(l+\tfrac{1}{2})\alpha]}{\exp(i\alpha/2)-\exp(-i\alpha/2)} \\ &= \frac{\sin(l+\tfrac{1}{2})\alpha}{\sin(\alpha/2)}. \end{aligned} \tag{4.50}$$

Coming to the actual representations, we have

$$R(\alpha,\beta,\gamma)\,Y_l^m(\theta,\phi) = \sum_{m'=-l}^{l} Y_l^{m'}(\theta,\phi)\,D_{m',m}^{(l)}(\alpha,\beta,\gamma). \tag{4.51}$$

The spherical harmonics generate a $(2l+1)$-dimensional irreducible representation. The identity element is $R(0,0,0)$, and from (4.50), we see that $\chi^{(l)}(0)=2l+1$, as it should be. The representation is denoted by $D^{(l)}$. For $l=0,1,2,\ldots$, these give *all* the continuous and single-valued irreducible representations of $SO(3)$. A method to obtain the matrices $D^{(l)}(\alpha,\beta,\gamma)$ is discussed in Section 4.5.3.

4.3.2 Connectedness of $SO(3)$. We have seen that every rotation of $SO(3)$ can be characterized by a vector whose length is equal to the angle of rotation and whose direction is along the axis of rotation. The end-points of all such vectors thus fill a sphere of radius π. Every element of $SO(3)$, except those denoting rotations through π, has associated with it a unique point *inside* the sphere. However, since the rotations through π and $-\pi$ about an axis denote the same element, we must identify all diametrically opposite points of the sphere under consideration, that is, we must think of *two diametrically opposite points as being the same point*. This introduces some important topological connectedness properties in the group $SO(3)$.

Consider two elements R_1 and R_2 of $SO(3)$. There are two distinct paths connecting the images of R_1 and R_2 in the parameter space as shown in Fig. (4.7); a direct path (a) from R_1 to R_2 and a path (b) which first goes to the point x on the surface of the sphere, makes a jump to the diametrically opposite point x' and then goes to R_2. The path (b) cannot be made to coincide with the path (a) by a continuous distortion because as we move the point x on the surface of the sphere its equivalent point x' also moves remaining always diametrically opposite to x.

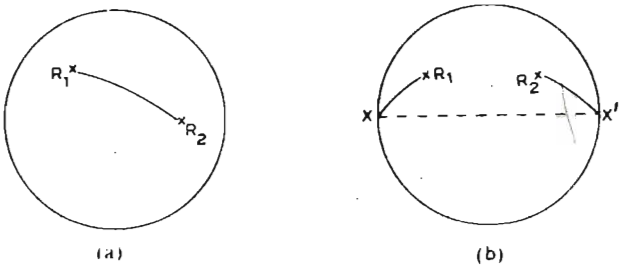


FIGURE 4.7 Two distinct paths connecting the image points of R_1 and R_2: (a) a direct path and (b) a path which makes a jump across diametrically opposite points

We can now show that any other path connecting R_1 and R_2 can be brought into coincidence with one of the two paths of Fig. (4.7) by a continuous distortion. Thus consider a path $R_1xx'yy'R_2$ which makes two jumps across the surface of the sphere as shown in Fig. (4.8). In this figure, it is shown that this path can be continuously distorted to make it a path of type (a). As we let x approach y on the surface of the sphere, x' approaches y'. Finally, as x and y coincide, so do x' and y', and the path is clearly of type (a). Similarly, it can be shown that a path which makes n jumps across the surface is of type (a) or (b) depending on whether n is even or odd.

The group $SO(3)$ is therefore *doubly connected.*

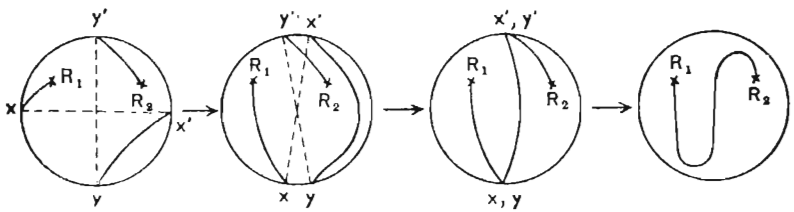


FIGURE 4.8 Continuous distortion of a path making two jumps across the surface of the sphere to a path of type (a)

4.3.3 The group $O(n)$. It should be clear that the set of all real orthogonal matrices of order n is a group. This group is denoted by $O(n)$ and is a continuous, compact, Lie group, which is, however, not connected. It can be alternatively thought of as the set of all orthogonal transformations in a real n-dimensional vector space. If x_i are the orthonormal basis vectors in this space, a transformation

of $O(n)$ leaves the quadratic form $\sum_{i=1}^{n} x_i^2$ invariant. The parameter space of $O(n)$ consists of two disconnected pieces, one corresponding to matrices with determinant $+1$ (proper rotations) and the other to matrices with determinant -1 (reflections). The subgroup containing proper rotations is a connected, $n(n-1)/2$-parameter,[8] Lie group, denoted by $SO(n)$. $O(n)$ has one discrete parameter in addition to the $n(n-1)/2$ continuous parameters of $SO(n)$.

For example, $O(4)$ is the group of all orthogonal transformations which leave the quadratic form $x^2+y^2+z^2+u^2$ invariant. If we regard x, y, z, u as the cartesian coordinate axes in a four-dimensional Euclidean space, the six parameters of $SO(4)$ can be thought of as representing rotations in the six coordinate planes. From the theory of $SO(2)$ and $SO(3)$ [Eqs. (4.34) and (4.45)], it can be seen that the six generators of $SO(4)$ can be conveniently taken to be

$$\begin{aligned} &A_1=-i(y\partial/\partial z-z\partial/\partial y),\ A_2=-i(z\partial/\partial x-x\partial/\partial z),\\ &A_3=-i(x\partial/\partial y-y\partial/\partial x),\\ &B_1=-i(x\partial/\partial u-u\partial/\partial x),\ B_2=-i(y\partial/\partial u-u\partial/\partial y),\\ &B_3=-i(z\partial/\partial u-u\partial/\partial z). \end{aligned} \tag{4.52}$$

The commutators of these generators with each other are found to be

$$\begin{aligned} &[A_1, A_2]=iA_3,\ [B_1, B_2]=iA_3,\\ &[A_1, B_1]=0,\ [A_1, B_2]=iB_3,\ [A_1, B_3]=-iB_2, \end{aligned} \tag{4.53}$$

and others obtained by cyclic permutations of the indices in each of the above.

Changing to a new set of linearly independent generators defined by

$$J_l=\tfrac{1}{2}(A_l+B_l),\ K_l=\tfrac{1}{2}(A_l-B_l),\ l=1, 2, 3, \tag{4.54}$$

we see that the commutators become

$$[J_1, J_2]=iJ_3,\quad [K_1, K_2]=iK_3, \tag{4.55a}$$

$$[J_l, K_j]=0,\quad l, j=1, 2, 3, \tag{4.55b}$$

with permutation of indices in (4.55a). This shows that each of the sets (J_1, J_2, J_3) and (K_1, K_2, K_3) generates the group $SO(3)$, so that $SO(4)$ is isomorphic to the direct product of $SO(3)$ with itself. A physical application of this group is discussed in Section 5.8.1.

[8] An orthogonal matrix of order n has $n(n-1)/2$ independent elements.

4.4 The Lorentz Group

It is of interest to consider the group of transformations which leave the quadratic form $x_1^2+x_2^2+\ldots+x_p^2-x_{p+1}^2-\ldots-x_n^2$ $(0<p<n)$ invariant. These groups are known as the *pseudorotation groups.*[9] Although some authors[10] also refer to all such groups as the Lorentz group, it is customary to restrict the phrase *Lorentz group* to the case of the above quadratic form with $n=4$, $p=3$, i.e., $x_1^2+x_2^2+x_3^2-x_4^2$, owing to its importance in the special theory of relativity, where the four-dimensional space-time continuum is described by the metric

$$ds^2=dx^2+dy^2+dz^2-c^2dt^2. \tag{4.56}$$

The pseudorotation group is denoted by the symbol $O_{p,\,n-p}$, and there is no loss of generality in choosing $p\geqslant n-p$. The simplest of the pseudorotation groups occurs when $p=1$, $n=2$, that is the group $O_{1,\,1}$, which leaves the quadratic form x^2-y^2 invariant. A general transformation of $O_{1,1}$ is of the form

$$\begin{aligned} x' &= x\cosh\theta+y\sinh\theta, \\ y' &= x\sinh\theta+y\cosh\theta, \end{aligned} \tag{4.57}$$

where θ is real and $-\infty<\theta<\infty$, so that

$$x'^2-y'^2=x^2-y^2. \tag{4.58}$$

Each element of the group can be characterized in terms of a real parameter θ, and the set of matrices

$$\begin{bmatrix} \cosh\theta & \sinh\theta \\ \sinh\theta & \cosh\theta \end{bmatrix}, \quad -\infty<\theta<\infty, \tag{4.59}$$

gives a two-dimensional representation of the group. In addition, the group $O_{1,\,1}$ also contains reflections (such as $x\to-x$, $y\to y$), the matrices corresponding to which have determinant -1. It is therefore a continuous, one-parameter, Lie group, which is noncompact because the parameter space is unbounded, and not connected because the parameter space is divided into two disjoint subspaces. Also note that the transformations of the pseudorotation group are not orthogonal.

In analogy with Example 4, Section 4.2.1, the single generator of the group can be found to be

$$B=-i\,(x\partial/\partial y+y\partial/\partial x). \tag{4.60}$$

If we put $y=iv$, so that $x^2-y^2=x^2+v^2$, a transformation which leaves

[9] Englefield (1972), Section 1.9.
[10] Hamermesh (1962), p. 307.

x^2-y^2 invariant also leaves x^2+y^2 unchanged. But the group of the quadratic form x^2+y^2 is just the group $SO(2)$, with transformations given by

$$x'=x\cos\theta+y\sin\theta,$$
$$y'=-x\sin\theta+y\cos\theta. \tag{4.61}$$

If we put $\alpha=i\theta$, (4.61) reduces to (4.57), so that the pseudorotation group can be thought of as a group of rotations through imaginary angles or as a group of rotations of coordinate axes where one of the coordinates is imaginary.

Coming to the quadratic form $x^2+y^2-z^2$, we see that this will be invariant under ordinary rotations [of the form of (4.61)] in the xy-plane and under Lorentz rotations [of the form of (4.57)] in the xz- and yz-planes. Thus, the group of the quadratic form $x^2+y^2-z^2$, that is, the group $O_{2,1}$, is a three-parameter, continuous, noncompact, Lie group. The three generators of the group can be chosen to be

$$B_1=-i(y\partial/\partial z+z\partial/\partial y),\quad B_2=-i(x\partial/\partial z+z\partial/\partial x),$$
$$A_3=-i(x\partial/\partial y-y\partial/\partial x). \tag{4.62}$$

Their commutators with each other are easily worked out to be

$$[B_1, B_2]=iA_3,\ [B_2, A_3]=-iB_1,\ [A_3, B_1]=-iB_2. \tag{4.63}$$

The negative sign in the last two commutation relations of (4.63) is characteristic of the fact that B_1 and B_2 generate imaginary rotations.

Finally, let us consider the group which leaves the quadratic form $x^2+y^2+z^2-u^2$ invariant. This Lorentz group evidently contains as a subgroup the group $O(3)$ of real orthogonal transformations in the three-dimensional space (x, y, z). In addition, it also contains imaginary rotations in the xu-, yu- and zu-planes. Thus, it is a six-parameter, continuous, noncompact, Lie group. The six generators can be chosen to be A_j and B_k, $j, k=1, 2, 3$, where

$$A_1=-i(y\partial/\partial z-z\partial/\partial y),\ A_2=-i(z\partial/\partial x-x\partial/\partial z),$$
$$A_3=-i(x\partial/y\partial-y\partial/\partial x),$$
$$B_1=-i(x\partial/\partial u+u\partial/\partial x),\ B_2=-i(y\partial/\partial u+u\partial/\partial y),$$
$$B_3=-i(z\partial/\partial u+u\partial/\partial z). \tag{4.64}$$

The commutation relations among these generators are found to be identical to those of (4.53) except that the second equation of (4.53) shows a change in sign; they are given by

$$[A_1, A_2]=iA_3,\ [B_1, B_2]=-iA_3,$$
$$[A_1, B_1]=0,\ [A_3, B_2]=iB_3,\ [A_1, B_3]=-iB_2, \tag{4.65}$$

with others obtained by cyclic permutation of the indices in each of the above.

For further reading, the reader is referred to the literature.[11]

4.5 The Special Unitary Group $SU(2)$

Let u and v be a pair of vectors in a two-dimensional vector space defined over the field of complex numbers. A rotation in this space transforms u and v into their linear combinations:

$$u'=au+bv,\ v'=cu+dv; \tag{4.66a}$$

or

$$[u',\ v']=[u,\ v]\begin{bmatrix} a & c \\ b & d \end{bmatrix}, \tag{4.66b}$$

where a, b, c, d are complex numbers and hence the transformation matrix involves 8 parameters. If we consider only those rotations which leave the quadratic form $uu^*+vv^*=|u|^2+|v|^2$ invariant, we see that the matrix of transformation in (4.66b) must be a unitary matrix. In other words, if we require that $|u'|^2+|v'|^2=|u|^2+|v|^2$, then from (4.66), we obtain the conditions

$$aa^*+cc^*=1,\ bb^*+dd^*=1,\ ab^*+cd^*=0. \tag{4.67}$$

Since the scalars are complex, the last of Eqs. (4.67) is equivalent to two conditions. These conditions thus reduce the number of parameters in (4.66) from 8 to 4. By using (4.67), it can be deduced that the most general unitary matrix of order two involving four real parameters can be expressed in the form[12]

$$\begin{bmatrix} \cos\theta\, e^{i\alpha} & \sin\theta\, e^{i\gamma} \\ -\sin\theta\, e^{i(\beta-\gamma)} & \cos\theta\, e^{i(\beta-\alpha)} \end{bmatrix}, \tag{4.68}$$

whose determinant is $\exp(i\beta)$. Here α, β, γ and θ are the four real parameters.

The set of all such transformations is the group $U(2)$ which is isomorphic to the group of all unitary matrices of order 2. It is a 4-parameter, continuous, connected, compact, Lie group.

The subgroup of $U(2)$ which contains all the unitary matrices of order 2 with determinant $+1$ is of particular interest in physics. It is the set of matrices whose general element is

$$\begin{bmatrix} a & -b^* \\ b & a^* \end{bmatrix} \text{ with } aa^*+bb^*=1. \tag{4.69}$$

[11] Wybourne (1974).

[12] See Eq. (5.50) of Joshi (1984).

it is known as the *unitary unimodular group* or the *special unitary group* and is denoted by $SU(2)$. Owing to the additional condition on the determinant, $SU(2)$ is a three-parameter group. In what follows, we shall denote the general element (4.69) of this group by $R(a, b)$.

4.5.1 Irreducible representations of $SU(2)$. The matrices of (4.69) themselves provide us with a representation of $SU(2)$. Other representations can be obtained by considering the transformations of the following $2j+1$ symmetric products of u and v of degree $2j$:

$$f_j^m = \frac{u^{j+m}\, v^{j-m}}{[(j+m)!\,(j-m)!\,]^{1/2}}, \tag{4.70}$$

where $m=-j, -j+1, \ldots, j-1, j$, and j is an integer or half an odd integer. Because u and v transform into their linear combinations as per (4.69), it is clear that the $2j+1$ functions of (4.70) also transform into their own linear combinations under the transformations of $SU(2)$. This provides us with a $(2j+1)$-dimensional representation of $SU(2)$ whose matrices can be obtained by applying $R(a, b)$ on f_j^m and using (4.69):

$$R(a, b) f_j^m = \frac{1}{[(j+m)!\,(j-m\,!]^{1/2}} (au+bv)^{j+m}(-b^*u+a^*v)^{j-m}. \tag{4.71}$$

Expanding the brackets by the binomial theorem, we find

$$\begin{aligned} R(a, b) f_j^m &= \sum_{k,l} \frac{1}{[(j+m)!\,(j-m)!\,]^{1/2}} \quad \frac{(j+m)!}{k!\,(j+m-k)!} \\ &\quad \times (au)^{j+m-k}\,(bv)^k \,\frac{(j-m)!}{l!\,(j-m-l)!}\,(-b^*u)^{j-m-l}(a^*v)^l \\ &= \sum_{k,l} \frac{[(j+m)!\,(j-m)!\,]^{1/2}}{k!\,(j+m-k)!\,l!\,(j-m-l)!}\, a^{j+m-k}\,(a^*)^l \\ &\quad \times b^k(-b^*)^{j-m-l}\, u^{2j-k-l}\, v^{k+l}. \end{aligned} \tag{4.72}$$

Although the upper limits of k and l in the summation are $j+m$ and $j-m$ respectively and the lower limit for both is zero, we need not mention these explicitly. We can take account of it by saying that k and l take all integral values which keep the arguments of *all* the factorials in the denominator nonnegative.

We can now express the right-hand side of (4.72) as a linear combination of f_j^m's. If we make a change of variables by defining

$m'=j-k-l$, we have $2j-k-l=j+m'$, $k+l=j-m'$, and (4.72) becomes

$$R(a, b)\, f_j^m = \sum_{m'=-j}^{j} f_j^{m'}\, D_{m'm}^{(j)}(a,b), \tag{4.73a}$$

with

$$D_{m'm}^{(j)}(a, b) = \sum_k \frac{[(j+m)!\,(j-m)!\,(j+m')!\,(j-m')!]^{1/2}}{(j+m-k)!k!(j-m'-k)!(m'-m+k)!} \times a^{j+m-k}\,(a^*)^{j-m'-k}\,b^k\,(-b^*)^{m'-m+k}. \tag{4.73b}$$

Here, again, k takes all possible integral values so that none of the factorials in the denominator has a negative argument (for given values of j, m and m'). The limits of k may thus be different for different values of m and m'. If we kept track of the limits while making the change of variables, we would arrive at the same result. Thus the lower limit of k is determined by the value of $m-m'$. If $m'-m<0$, the lower limit of k is $m-m'$, while if $m'-m\geqslant 0$, the lower limit of k is 0. Similarly, the upper limit of k is governed by the two factors $j+m-k$ and $j-m'-k$ and is equal to the smaller of the two integers $j+m$ and $j-m'$.

The functions f_j^m defined in (4.70) clearly constitute a set of $2j+1$ independent functions in the $(2j+1)$-dimensional Hilbert space L_{2j+1} which is the space of the representation $D^{(j)}$ of (4.73). We note that

$$\sum_{m=-j}^{j} |f_j^m|^2 = \sum_m \frac{|u^{j+m}\, v^{j-m}|^2}{(j+m)!\;(j-m)!}.$$

But the right-hand side is the binomial expansion of $(|u|^2+|v|^2)^{2j}/(2j)!$; hence we have

$$\sum_m |f_j^m|^2 = \frac{1}{(2j)!}(|u|^2+|v|^2)^{2j}. \tag{4.74}$$

Since $|u|^2+|v|^2$ is invariant under the transformations of $SU(2)$, $\sum_m |f_j^m|^2$ is also invariant, showing that our representations $D^{(j)}$ are unitary.

We can show that the representations $D^{(j)}$ are irreducible. We shall use the converse of Schur's first lemma to prove this, that is, we shall show that if a matrix P commutes with $D^{(j)}(a, b)$ for all a and b (with $aa^*+bb^*=1$) then P must be a constant matrix. To this end, we work out the matrices of $D^{(j)}$ for two particular cases. Choos-

ing first $a=\exp(i\alpha/2)$, $b=0$ with α real, we find that only the term with $k=0$ in (4.73b) survives, giving

$$D_{m'm}^{(j)}(e^{i\alpha/2}, 0)=\delta_{m'm}e^{im\alpha}. \tag{4.75}$$

Secondly, if we let $m'=j$ in the general matrix element (4.73b), we see again that the only allowed value of k is 0, giving

$$D_{jm}^{(j)}(a, b)=\left[\frac{(2j)!}{(j+m)!\,(j-m)!}\right]^{\frac{1}{2}} a^{j+m}(-b^*)^{j-m}. \tag{4.76}$$

Now, if P commutes with all the matrices of $D^{(j)}$ of the form (4.75), which are all diagonal with distinct elements, then P must also be a diagonal matrix,[13] i.e., $P_{ik}\equiv p_i\delta_{ik}$. Considering the (j, m) element of the matrix equation $PD^{(j)}(a, b)=D^{(j)}(a, b)P$ and using (4.76), we find that $p_jD_{jm}^{(j)}=D_{jm}^{(j)}p_m$. Since $D_{jm}^{(j)}(a, b)$ is not identically equal to zero, it follows that $p_j=p_m$, that is, P must be a constant matrix. Thus no matrix other than a constant matrix commutes with all the matrices $D^{(j)}$ (a, b). It therefore follows that $D^{(j)}$ is an irreducible representation. It turns out that $D^{(j)}$ is the only irreducible representation of $SU(2)$ of dimension $2j+1$. Moreover, since the dimensions of the representations $D^{(j)}$ differ for different values of j, they are not equivalent to one another. In other words, *the group $SU(2)$ has one and only one inequivalent irreducible representation of every integral order.*

The characters of $D^{(j)}$ can now be easily found out. To this end, we shall first determine the class-structure of $SU(2)$. In fact, we shall show that all those elements of $SU(2)$ of the form (4.69) which have the same real part of the parameter a belong to a class of $SU(2)$. This can be done by obtaining the eigenvalues of a general element of $SU(2)$. If λ is an eigenvalue of the unitary matrix (4.69), it can be deduced that λ satisfies the quadratic

$$\lambda^2-(a+a^*)\lambda+1=0.$$

The two eigenvalues are thus

$$\lambda_1=[\beta+(\beta^2-4)^{1/2}]/2,\ \lambda_2=[\beta-(\beta^2-4)^{1/2}]/2, \tag{4.77}$$

where $\beta=a+a^*$ is a real number. Now from the condition $aa^*+bb^*=1$, it is clear that $-1\leq\mathrm{Re}\,(a)\leq 1$, where $\mathrm{Re}\,(a)$ is the real part of a, so that $-2\leq\beta\leq 2$. Eqs. (4.77) then show that $\lambda_2=\lambda_1^*$. Moreover, it is also clear from (4.77) that $\lambda_1\lambda_2=1$. It follows that $|\lambda_1|=|\lambda_2|=1$. Hence, defining α by the relations

$$\cos(\alpha/2)=\beta/2,\ \sin(\alpha/2)=(1-\beta^2/4)^{1/2},$$

we find that the two eigenvalues become

$$\lambda_1=\exp(i\alpha/2),\ \lambda_2=\exp(-i\alpha/2). \tag{4.78}$$

[13] See Joshi (1984), Example 3.1, p. 31.

Since $-2\leq\beta\leq 2$, we have $-1\leq\cos(\alpha/2)\leq 1$ and $0\leq\sin(\alpha/2)\leq 1$. This gives $0\leq\alpha\leq 2\pi$. Since the eigenvalues depend only on the real part of a, all elements of $SU(2)$ having the same $\mathrm{Re}(a)$ will have the same eigenvalues and hence will be conjugate to each other. Every real value of α on the interval $[0, 2\pi]$ thus determines a class of $SU(2)$.

Now we can obtain the character of a class (characterized by α) in the irreducible representation $D^{(j)}$. Since all the elements in a class have the same character, we can obviously choose the simplest element in the class under consideration to obtain the characters. Consider the element $R(a,b)$ of $SU(2)$ for which $a=\exp(i\alpha/2)$, $b=0$. The matrix representing this element in $D^{(j)}$ has already been found out in (4.75). The trace of this matrix gives the character of the element under consideration. Thus,

$$\chi^{(j)}(e^{i\alpha/2}, 0)=\sum_{m=-j}^{j} D_{mm}{}^{(j)}(e^{i\alpha/2}, 0)$$

$$=\sum_{m=-j}^{j} e^{im\alpha}$$

$$=\frac{\sin(j+\frac{1}{2})\,\alpha}{\sin(\alpha/2)}. \tag{4.79}$$

This is analogous to the characters (4.50) of the rotation group $SO(3)$, with the important difference that for $SU(2)$, j can take nonnegative integral *as well as* half-odd-integral values, whereas for $SO(3)$, l can take only nonnegative integral values.

4.5.2 Homomorphism of $SU(2)$ on $SO(3)$. Consider the functions of (4.70) for the particular case $j=1$. We have the three functions

$$x_1\equiv f_1{}^1=u^2/\sqrt{2},\ x_2\equiv f_1{}^0=uv,\ x_3\equiv f_1{}^{-1}=v^2/\sqrt{2}. \tag{4.80}$$

Their transformation by a general element $R(a, b)$ of $SU(2)$ gives

$$\begin{aligned} x_1' &= R(a,b)\,x_1=a^2\,x_1+ab x_2+b^2\,x_3,\\ x_2' &= R(a,b)\,x_2=-2ab^*\,x_1+(aa^*-bb^*)\,x_2+2a^*\,bx_3,\\ x_3' &= R(a,b)\,x_3=b^{*2}\,x_1-a^*\,b^*\,x_2+a^{*2}\,x_3. \end{aligned} \tag{4.81}$$

Defining three new variables

$$x=x_1-x_3,\ y=-i(x_1+x_3),\ z=x_2, \tag{4.82a}$$

and their inverse transformation

$$x_1=(x+iy)/2,\ x_2=z,\ x_3=(-x+iy)/2, \tag{4.82b}$$

with similar expressions for the primed variables, we see that (4.81) becomes

$$x'=\tfrac{1}{2}(a^2+a^{*2}-b^2-b^{*2})\,x+\frac{i}{2}(a^2-a^{*2}+b^2-b^{*2})\,y$$
$$+(ab+a^*\,b^*)\,z,$$
$$y'=-\frac{i}{2}(a^2-a^{*2}-b^2+b^{*2})\,x+\tfrac{1}{2}(a^2+a^{*2}+b^2+b^{*2})\,y$$
$$-i\,(ab-a^*\,b^*)\,z,$$
$$z'=-(a^*\,b+ab^*)\,x+i(a^*\,b-a\,b^*)\,y+(aa^*-bb^*)\,z. \tag{4.83}$$

We notice that all the coefficients in (4.83) are real. Moreover, remembering that $aa^*+bb^*=1$, it can be shown that $x'^2+y'^2+z'^2=x^2+y^2+z^2$. Starting from a unitary matrix $R(a, b)$ of order 2 with determinant $+1$, we have thus succeeded in associating with it a real orthogonal matrix of order 3 with determinant $+1$, which corresponds to a pure rotation in the three-dimensional real vector space of (x, y, z) and hence is an element of $SO(3)$.

We shall now show the converse, that is, that all the rotations of $SO(3)$ are associated with one (or more?) element of $SU(2)$. Any general rotation through the Euler angles (α, β, γ) can be expressed as the product of three rotations in accordance with (4.42). Choosing first a unitary transformation with $a=\exp(i\alpha/2)$, $b=0$, Eqs. (4.83) give

$$x'=x\cos\alpha-y\sin\alpha,\ y'=x\sin\alpha+y\cos\alpha,\ z'=z, \tag{4.84}$$

the element $R(e^{i\alpha/2}, 0)$ of $SU(2)$ corresponds to the rotation through α about the z-axis of the group $SO(3)$, or

$$R(e^{i\alpha/2}, 0)=\begin{bmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{bmatrix}\to\begin{bmatrix} \cos\alpha & \sin\alpha & 0 \\ -\sin\alpha & \cos\alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{4.85}$$

Similarly, choosing $a=\cos(\beta/2)$, $b=\sin(\beta/2)$, we see that

$$R\left(\cos\frac{\beta}{2}, \sin\frac{\beta}{2}\right)=\begin{bmatrix} \cos\dfrac{\beta}{2} & -\sin\dfrac{\beta}{2} \\ \sin\dfrac{\beta}{2} & \cos\dfrac{\beta}{2} \end{bmatrix}\to\begin{bmatrix} \cos\beta & 0 & \sin\beta \\ 0 & 1 & 0 \\ -\sin\beta & 0 & \cos\beta \end{bmatrix}. \tag{4.86}$$

By using (4.85) and (4.86) in (4.42) we then find that the unitary transformation

$$\begin{bmatrix} e^{i\gamma/2} & 0 \\ 0 & e^{-i\gamma/2} \end{bmatrix}\begin{bmatrix} \cos\dfrac{\beta}{2} & -\sin\dfrac{\beta}{2} \\ \sin\dfrac{\beta}{2} & \cos\dfrac{\beta}{2} \end{bmatrix}\begin{bmatrix} e^{i\alpha/2} & 0 \\ 0 & e^{-i\alpha/2} \end{bmatrix}$$

corresponds to the rotation $R(\alpha, \beta, \gamma)$ of $SO(3)$, or

$$\begin{bmatrix} \cos\frac{\beta}{2}\, e^{i(\alpha+\gamma)/2} & -\sin\frac{\beta}{2}\, e^{i(\gamma-\alpha)/2} \\ \sin\frac{\beta}{2}\, e^{i(\alpha-\gamma)/2} & \cos\frac{\beta}{2}\, e^{-i(\alpha+\gamma)/2} \end{bmatrix} \rightarrow R(\alpha, \beta, \gamma). \qquad (4.87)$$

We must now examine whether this correspondence between $SU(2)$ and $SO(3)$ is an isomorphism or homomorphism. We have already seen in (4.83) that each unitary matrix of $SU(2)$ corresponds to a unique rotation of $SO(3)$. We must now determine how many matrices of $SU(2)$ are associated with each rotation of $SO(3)$. We notice from (4.87) that the two rotations $R(0, 0, 0)$ and $R(0, 2\pi, 0)$, both of which denote the identity element of $SO(3)$, have associated with them the two unitary matrices

$$E=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ and } -E=\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}.$$

In fact, we notice that the operations $R(\alpha, \beta, \gamma)$ and $R(\alpha, \beta+2\pi, \gamma)$, which represent the same element of $SO(3)$, correspond to two distinct unitary matrices of $SU(2)$, one of which is the negative of the other. There is thus a 2-to-1 homomorphism of $SU(2)$ on $SO(3)$.

4.5.3 Representations of $SO(3)$ from representations of $SU(2)$. While discussing the irreducible representations of $SO(3)$ in Section 4.3.1, we really obtained only their characters in (4.50), but did not obtain the complete matrices $D^{(l)}(\alpha, \beta, \gamma)$ for the irreducible representations which appear in (4.51). We can obtain these from the irreducible representations $D^{(j)}$ of $SU(2)$ generated in (4.73). Since we have just proved that $SU(2)$ is homomorphic on $SO(3)$, we could obtain a representation of $SO(3)$ by starting from a representation of $SU(2)$ and picking out only those matrices which correspond to the elements of $SO(3)$. Eq. (4.87) shows that the unitary matrix of order 2 of $SU(2)$ for which

$$a=\cos(\beta/2)\, e^{i(\alpha+\gamma)/2},\ b=\sin(\beta/2)\, e^{i(\alpha-\gamma)/2},$$

corresponds to the element $R(\alpha, \beta, \gamma)$ of $SO(3)$. Hence a representation of $SO(3)$ can be obtained by associating the matrix which represents the element $R(a, b)$ of $SU(2)$, i.e., the matrix $D^{(j)}(a, b)$ with the element $R(\alpha, \beta, \gamma)$ of $SO(3)$. The required matrix is thus

$$D_{m'm}^{(l)}(\alpha, \beta, \gamma) \equiv D_{m'm}^{(j)}\left(\cos\frac{\beta}{2}\, e^{i(\alpha+\gamma)/2},\ \sin\frac{\beta}{2}\, e^{i(\alpha-\gamma)/2}\right)$$

$$=\sum_k (-1)^{m'-m+k} \frac{[(j+m)!(j-m)!(j+m')!(j-m')!]^{1/2}}{(j+m-k)!(j-m'-k)!k!(m'-m+k)!}$$

$$\times e^{i\alpha m} e^{im'\gamma} \left(\cos\frac{\beta}{2}\right)^{2j+m-m'-2k} \left(\sin\frac{\beta}{2}\right)^{m'-m+2k}. \quad (4.88)$$

We notice from (4.85) that the element $R(e^{i\alpha/2}, 0)$ of $SU(2)$ corresponds to the element $R(\alpha, 0, 0)$ of $SO(3)$. The characters of the elements of the rotation group $SO(3)$ can therefore be obtained from the special form (4.79) with $\beta=\gamma=0$;

$$\chi^{(j)}(\alpha)=\frac{\sin(j+\frac{1}{2})\alpha}{\sin(\alpha/2)}. \quad (4.89)$$

We thus see that for integral values of j, these characters coincide with those of $D^{(j)}$ obtained in (4.50). In other words, the representations $D^{(j)}$ for integral j are identical to the representations $D^{(j)}$. However, for half-odd-integral values of j, each rotation of $SO(3)$ is the image of two matrices $\pm D^{(j)}(\alpha, \beta, \gamma)$ due to the 2-to-1 correspondence noted at the end of the previous subsection.

Thus, for example, the identity element E is the image of the two matrices

$$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ and } \begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}.$$

Another element, say a rotation through π about the y axis ($\beta=\pi$, $\alpha=\gamma=0$; $R(0, \pi, 0)$), is the image of the two matrices $\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}$ and $\begin{bmatrix} 0 & 1 \\ -1 & 0 \end{bmatrix}$ because $R(0, 3\pi, 0)$ is identical to $R(0, \pi, 0)$. Let us, for the moment, denote $R(0, \pi, 0)$ by C_2. If we choose the representative matrices to be

$$D(E)=\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \text{ and } D(C_2)=\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix},$$

then we find that

$$D(E)\,D(C_2)=\begin{bmatrix} 0 & -1 \\ 1 & 0 \end{bmatrix}=D(C_2)\,D(E)=D(C_2),$$

but

$$D(C_2)D(C_2)=\begin{bmatrix} -1 & 0 \\ 0 & -1 \end{bmatrix}=-D(C_2^2)=-D(E). \quad (4.90)$$

In general, if R and S are two rotations of $SO(3)$, we would have

$$D^{(j)}(R)\;D^{(j)}(S)=\pm D^{(j)}(RS) \quad (4.91)$$

for half-odd-integral values of j. Such representations are known as *double-valued representations.*

The origin of this ambiguity in sign is easy to trace. Consider the two elements $R(a, b)$ and $R(-a, -b)$ of $SU(2)$. From the form of the matrix elements (4.73b), it is easily seen that

$$D_{m'm}^{(j)}(-a, -b)=(-1)^{2j} D_{m'm}^{(j)}(a, b),$$

so that

$$D^{(j)}(-a, -b)=\begin{cases} D^{(j)}(a, b) \text{ for integral } j, \\ -D^{(j)}(a, b) \text{ for half-odd-integral } j. \end{cases}$$

Thus, in the irreducible representations with integral j, the elements $R(a, b)$ and $R(-a, -b)$ are represented by the same matrix while in those with half-odd-integral j, they are represented by two matrices one of which is the negative of the other. In particular, when $j=\frac{1}{2}$, we just have the matrix group $SU(2)$ with

$$R(a, b)=\begin{bmatrix} a & -b^* \\ b & a^* \end{bmatrix}, \quad R(-a, -b)=\begin{bmatrix} -a & b^* \\ -b & -a^* \end{bmatrix}$$

When we consider the homomorphism of $SU(2)$ on $SO(3)$, we would have an ambiguity in sign as in (4.91). We may conclude that the representations $D^{(j)}$ of $SU(2)$ with integral j are the single-valued representations of $SO(3)$ identical to $D^{(j)}$ considered earlier, whereas the representations $D^{(j)}$ of $SU(2)$ with half-odd-integral j are the double-valued representations of $SO(3)$.

The ambiguity in the sign can be removed by considering a group which has twice the number of elements of $SO(3)$. In the new group, a rotation through 2π about any axis is *not* identical to the identity element but only a rotation through 4π is the identity. We thus define a new element $\bar{E}$ to mean the rotation through 2π about, say, the z axis. The group we have constructed then has all the rotations of $SO(3)$ *plus* the products of $\bar{E}$ with all the elements of $SO(3)$. It should be obvious that the representations $D^{(j)}$ for half-odd-integral values of j are *single-valued representations* of the new group. The new group is said to be the *double group* of $SO(3)$ and is often denoted by $SO'(3)$. It is isomorphic to $SU(2)$. But notice that $SO(3)$ is not a subgroup of $SO'(3)$; in fact the elements of $SO(3)$ now do not constitute a group because these are *now not closed under multiplication.* Consider, for example, an element C_n of $SO(3)$ denoting a rotation through $2\pi/n$ (n a positive integer) about some axis. Then the n-th power of this element is not equal to the identity element; it equals the element $\bar{E}$ which we have defined above, and which does not belong to $SO(3)$. It is only $(C_n)^{2n}$ which equals the identity of the group $SO'(3)$.

It should be pointed out that such cases arise in physics whenever we are dealing with particles or systems of particles which have spin angular momenta. For example, the orbital angular momentum of electrons is an integral multiple of $\hbar$ while the spin angular momentum is $\frac{1}{2}\hbar$. Thus, if we are dealing with a system containing an odd number of electrons the total angular momentum is a half-odd-integral multiple of $\hbar$. It is well-known in this case that the wave function of the system does not return to its original value after a rotation through 2π but becomes negative of its original value, returning to its original value only after a rotation through 4π. In the language of group theory, this means that *the symmetry of the wave function is governed by the irreducible representations of the corresponding double group* rather than those of the original symmetry group. We shall deal with some more double groups in greater detail in Chapter 7.

It should be realized that the existence of the double-valued representations of $SO(3)$ is a consequence of its being doubly connected. In general, if G is a k-fold connected continuous Lie group, then it has single-valued, double-valued, triple-valued, ..., and k-valued representations. If C_n denotes an n-fold rotation about some axis and is an element of G, then $(C_n)^n$ is the identity element E in the group G. Let us now construct a group G' in which only a rotation through $2k\pi$, and not a rotation through 2π, about any axis is the identity element. Let us define E_1 as a rotation through 2π, E_2 as a rotation through 4π, ..., E_{k-1} as a rotation through $2(k-1)\pi$ and, finally, E_0 as a rotation through $2k\pi$ which is the identity element of G'. Then it is clear that

$$G' = G \cup E_1 G \cup E_2 G \cup \ldots \cup E_{k-1} G.$$

The set G, which is a subset of G', is not now closed under multiplication, because $(C_n)^n = E_1$ is not the identity element and does not belong to G. The group G' is homomorphic to G with a k-to-1 correspondence. Every representation of G' therefore gives a representation of G. However, some of these will be single-valued, some double-valued, ..., and some k-valued representations of G. The group G' is called the *universal covering group* of G. Although such groups are of topological interest by themselves, no physical situation has yet been found to require the use of more than doubly connected groups.

4.5.4 Direct product of representations of $SU(2)$. It is of interest to obtain the direct products of the irreducible representations of $SU(2)$ and to reduce them into linear combinations of the irreducible representations. Consider the direct product $D = D^{(j)} \otimes D^{(j')}$

of two irreducible representations of $SU(2)$. Let the characters of D be denoted by χ; these are then the products of the corresponding characters of $D^{(j)}$ and $D^{(j')}$. Thus,

$$\chi(\alpha)=\chi^{(j)}(\alpha)\,\chi^{(j')}(\alpha)=\sum_{m=-j}^{j} e^{im\alpha}\sum_{m'=-j'}^{j'} e^{im'\alpha}$$

$$=\sum_{m=-j}^{j}\sum_{m'=-j'}^{j'} e^{i(m+m')\alpha}$$

$$=\sum_{J=|j-j'|}^{j+j'}\sum_{M=-J}^{J} e^{iM\alpha}=\sum_{J=|j-j'|}^{j+j'}\chi^{(J)}(\alpha). \qquad (4.92)$$

This gives a very simple formula for the direct product of two irreducible representations:

$$D^{(j)}\otimes D^{(j')}=\sum_{J=|j-j'|}^{j+j'} D^{(J)}, \qquad (4.93)$$

showing that each representation occurs at most once in the reduction of the direct product. Moreover, only those irreducible representations are contained in the reduction whose 'J'-values satisfy the triangular inequality $|j-j'|\leq J\leq j+j'$. Eq. (4.93) is known as the *Clebsch-Gordan series*.

4.6 Generators of $U(n)$ and $SU(n)$

The group of all unitary matrices of order n is known as $U(n)$, whereas the group of all unitary matrices of order n with determinant $+1$ is denoted by $SU(n)$ (SU stands for *special unitary*). Clearly, $SU(n)$ is a subgroup of $U(n)$. Since a unitary matrix of order n has n^2 independent elements, $U(n)$ is a continuous, connected, n^2-parameter, compact, Lie group. The elements of the group $SU(n)$ have one more condition to satisfy (that their determinant be $+1$), so that $SU(n)$ is a continuous, connected, (n^2-1)-parameter, compact, Lie group.

It is fairly easy to obtain the n^2 generators of $U(n)$. For this we note that if H is a hermitian matrix, $\exp(iH)$ is a unitary matrix. The converse is also true, i.e., if U is any unitary matrix, then it can be expressed in the form

$$U=\exp(iH), \qquad (4.94)$$

where H is a hermitian matrix. Now any linear combination of hermitian matrices with real coefficients is again a hermitian matrix.[14] Hence

[14]Note that the set of all hermitian matrices of order n is an n^2-dimensional real vector space.

there can be at most n^2 independent hermitian matrices of order n. Let $H_1, H_2, \ldots, H_N$ be a set of n^2 independent hermitian matrices of order n, where we have denoted $N \equiv n^2$ for the sake of convenience. Let a_j $(1 \leq j \leq N)$ be n^2 real independent parameters. Then it is clear that any unitary matrix of order n can be written as

$$U = \exp\left[i \sum_{j=1}^{N} a_j H_j \right], \tag{4.95}$$

or, in other words, *all* the elements of $U(n)$ can be generated from the right-hand side of (4.95) by giving all possible values to the N real parameters a_j. The N independent hermitian matrices H_j are thus the generators of $U(n)$. Obviously they are not unique, and any N independent linear combinations of these could equally well be used as the generators of $U(n)$.

If A is any square matrix, it can be easily seen that[15]

$$\det(e^A) = e^{\text{trace}A}. \tag{4.96}$$

Using (4.94), we therefore see that

$$\det U = \det(e^{iH}) = \exp(i \text{ trace } H). \tag{4.97}$$

All the diagonai elements of a hermitian matrix are real and hence trace $H \equiv \alpha$ is a real number. This shows in passing that det $U = \exp(i\alpha)$ is a number of unit magnitude.

Coming to $SU(n)$, we make use of the fact that its elements have their determinants equal to $+1$. Thus if we denote an element of $SU(n)$ by $U_0 = \exp(iH_0)$, then it follows from the condition det $U_0 = 1$ that trace $H_0 = 0$. Now, as before,[16] there can be at most $n^2 - 1$ independent *traceless* hermitian matrices of order n, and these can be conveniently chosen to be the generators of $SU(n)$ along with $n^2 - 1$ real independent parameters.

It is convenient to choose the $n^2 - 1$ generators of $SU(n)$ first and then add to this set the unit matrix of order n to obtain the n^2 generators of $U(n)$.

As an example, the three generators of $SU(2)$ can be chosen to be the Pauli spin matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}, \tag{4.98}$$

which are a set of three independent traceless hermitian matrices of

[15] See Joshi (1984), Example 12.12, p. 134.

[16] The set of all traceless hermitian matrices of order n is an (n^2-1)-dimensional real vector space.

order 2. For the generators of $U(2)$, we could then choose the set $(E, \sigma_x, \sigma_y, \sigma_z)$ where E is the unit matrix of order 2.

4.7 Lie Algebra and Representations of a Lie Group

Consider a Lie group with r continuous parameters a_k having the r generators $I_1, I_2, \ldots, I_r$. We have seen that any element of the Lie group can be expressed in the form

$$x(a_1, a_2, \ldots, a_r) = \exp\left(i \sum_{k=1}^{r} a_k I_k\right). \tag{4.19}$$

In the case of a finite group, we have seen that all the properties of the group can be obtained from the structure of its multiplication table. What is the equivalent of the multiplication table for a continuous group? We can show that for a Lie group, the commutators of its generators determine the structure of the group.

Thus, consider two particular elements of the Lie group of the form

$$x(0, 0, \ldots, a_k, \ldots, 0) = \exp(i a_k I_k),$$
$$x(0, 0, \ldots, a_l, \ldots, 0) = \exp(i a_l I_l).$$

The product of these two elements, $\exp(i a_k I_k) \exp(i a_l I_l)$, must belong to the group and hence must be expressible in the form (4.19) with some values of the parameters a_k. Now since the generators of a Lie group do not, in general, commute with each other,[17] there is no simple way of writing this product element. We may, however, use the fact that such a product involves the commutator of I_k and I_l. For the product $\exp(i a_k I_k) \exp(i a_l I_l)$ to belong to the group, it therefore follows that the commutator $[I_k, I_l]$ must be a linear combination of the generators, i.e.,

$$[I_k, I_l] = \sum_{j=1}^{r} c_{kl}{}^{j} I_j, \quad 1 \leq k, l \leq r; \tag{4.99}$$

where $c_{kl}{}^{j}$ are certain coefficients. The commutators of pairs of generators of a Lie group determine the structure of the Lie group completely in analogy with the multiplication table for a finite group. The coefficients $c_{kl}{}^{j}$ are therefore known as the *structure constants* of the Lie group. They are a characteristic property of the Lie group and do not depend on any particular representation of the generators. However, they are not unique, since the generators of a Lie group are themselves not unique.

[17] They commute only when the Lie group under consideration is abelian.

As we have remarked before, any linear combination of the generators with real coefficients can also be used as a generator of the group. It is then clear that the r generators of a Lie group are the bases for an r-dimensional real linear vector space.

Eq. (4.99) takes us one step further—it provides us with a law of composition between any two elements of the vector space such that the resulting vector is also an element of the vector space. The set of real linear combinations of the generators of a Lie group is, in fact, a Lie algebra (see footnote 2 in Chapter 2).

Quite generally, a *Lie algebra* is a real r-dimensional vector space L with elements $(x, y, z, \ldots)$ endowed with a law of composition for any two elements of L denoted by $[x, y]$ such that

(i) $[x, y] \in L$,

(ii) $[x, y]=-[y, x]$,

(iii) $[x, [y, z]]+[y, [z, x]]+[z, [x, y]]=0$,

for all $x, y, z \in L$. The law of composition $[x, y]$ is known as the *commutator of x and y*. A set of r independent vectors of L is called a *basis of the Lie algebra* in analogy with the basis for a vector space.

Since the commutators of the generators of a Lie group defined in (4.99) satisfy the above properties, we obtain the following relations among the structure constants:

$$c_{kl}{}^{j}=-c_{lk}{}^{j},$$

$$\sum_{m=1}^{r} [c_{kl}{}^{m}\, c_{jm}{}^{s}+c_{lj}{}^{m}\, c_{km}{}^{s}+c_{jk}{}^{m}\, c_{lm}{}^{s}]=0. \tag{4.100}$$

Moreover, since the generators I_k are hermitian, (4.99) shows that the structure constants $c_{kl}{}^{j}$ are purely imaginary.

The importance of the Lie algebra lies in the fact that we may generate a representation of the Lie group by considering a matrix representation of the Lie algebra. Thus, if we are able to find a set of r square matrices all of order p, say, such that they satisfy the commutation relations (4.99) with the given structure constants, then using these for the I_k's in (4.19), we would generate a p-dimensional representation of the Lie group. We can therefore take it as a general rule that *a representation of a Lie algebra can be used to generate a representation of the associated Lie group.*

As an example, we shall apply the above discussion to $SU(2)$. Its generators given in (4.98) satisfy the commutation relations

$$[\sigma_j, \sigma_k]=2i \sum_{l} \epsilon_{jkl}\, \sigma_l, \tag{4.101}$$

where ϵ_{jkl} is the fully antisymmetric tensor of rank 3 whose only non-vanishing elements are

$$\epsilon_{123}=\epsilon_{231}=\epsilon_{312}=-\epsilon_{213}=-\epsilon_{132}=-\epsilon_{321}=1. \tag{4.102}$$

The indices, j,k,l stand for any of x,y,z or for 1,2,3. Hereafter, the six equations in (4.102) will be abbreviated into a single equation and will be written as '$\epsilon_{123}=1$ and all permutations with proper signs'. The components of the tensor ϵ_{jkl} multiplied by $2i$ are evidently the structure constants of $SU(2)$. The Lie algebra of $SU(2)$ is thus the set of all real linear combinations of σ_x, σ_y and σ_z.

Let us now look at the following three matrices:

$$\lambda_1=\begin{bmatrix}0&1&0\\1&0&0\\0&0&0\end{bmatrix},\ \lambda_2=\begin{bmatrix}0&-i&0\\i&0&0\\0&0&0\end{bmatrix},\ \lambda_3=\begin{bmatrix}1&0&0\\0&-1&0\\0&0&0\end{bmatrix}. \tag{4.103}$$

It can be easily verified that they satisfy the same commutation relations as the generators σ's, i.e.

$$[\lambda_j, \lambda_k]=2i\sum_l \epsilon_{jkl}\lambda_l. \tag{4.104}$$

The λ's thus generate a representation of the Lie algebra of $SU(2)$ and can therefore be used to generate a three-dimensional representation of $SU(2)$ itself.

The maximum number of mutually commuting generators of a Lie group is called its *rank*. The rank of $SO(3)$ is thus 1 because no two of its generators L_x, L_y and L_z commute with each other. The rank of $SU(2)$ is also 1.

An operator which commutes with *all* the generators of a Lie group is known as a *Casimir operator* for the Lie group. According to a theorem due to Racah, the number of independent Casimir operators of a Lie group is equal to its rank. It was recognized by Casimir himself that one such operator could always be constructed by taking a suitable bilinear combination of the generators.

The one and only Casimir operator of $SO(3)$ is thus $\mathbf{L}^2\equiv L_x^2+L_y^2+L_z^2$, which commutes with each of L_x, L_y and L_z. The only Casimir operator of $SU(2)$ is similarly $\underline{\sigma}^2=\sigma_x^2+\sigma_y^2+\sigma_z^2$.

Since the Casimir operators of a Lie group can be diagonalized simultaneously with its generators, the eigenvalues of the Casimir operators may be used to label the irreducible representations of the Lie group. Thus, the Casimir operator $\mathbf{L}^2$ of $SO(3)$ has the eigenvalue $l(l+1)$, where l takes on all nonnegative integral values, and hence the irre-

ducible representations of $SO(3)$ may be labeled by the index l as we have already done in Section 4.3. We have seen that the dimension of the representation $D^{(l)}$ is $2l+1$. Similarly, the Casimir operator $\underline{\sigma}^2$ of $SU(2)$ has, in general, the eigenvalues $j(j+1)$ where j takes all non-negative integral and half-odd-integral values (the representation (4.98) for the generators is a special case with $j=\frac{1}{2}$). The irreducible representations of $SU(2)$ can therefore be labeled by j. These are the representations $D^{(j)}$ considered earlier and are of dimension $2j+1$.

4.8 The Special Unitary Group $SU(3)$

As should be clear from the name, $SU(3)$ is the group of all unitary matrices of order 3 with determinants $+1$. It has $3^2-1=8$ generators which are usually denoted by $\lambda_1, \lambda_2, \ldots, \lambda_8$. Although these can be chosen in many ways, it has become a convention to use the following traceless matrices as the generators of $SU(3)$:

$$\lambda_1=\begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \lambda_2=\begin{bmatrix} 0 & -i & 0 \\ i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \lambda_3=\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

$$\lambda_4=\begin{bmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \lambda_5=\begin{bmatrix} 0 & 0 & -i \\ 0 & 0 & 0 \\ i & 0 & 0 \end{bmatrix}, \quad \lambda_6=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix},$$

$$\lambda_7=\begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & -i \\ 0 & i & 0 \end{bmatrix}, \quad \lambda_8=\frac{1}{\sqrt{3}}\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -2 \end{bmatrix}. \tag{4.105}$$

Their commutators can be worked out and are found to be

$$[\lambda_j, \lambda_k]=2i\sum_l f_{jkl}\lambda_l, \tag{4.106}$$

where the only nonvanishing components of f_{jkl} are

$$\begin{aligned} &f_{123}=1, \\ &f_{147}=f_{516}=f_{246}=f_{257}=f_{345}=f_{637}=\tfrac{1}{2}, \\ &f_{458}=f_{678}=\sqrt{3}/2, \\ &\text{and all permutations with proper signs.} \end{aligned} \tag{4.107}$$

It must be realized that these structure constants are a characteristic property of $SU(3)$ and do not depend on the particular representation chosen in (4.105).

We see from (4.105) that λ_3 and λ_8 are diagonal matrices and hence commute with each other. We can verify (from the structure constants

(4.107)) that no other matrix of (4.105) commutes with *both* λ_3 and λ_8. The rank of $SU(3)$ is thus 2.

The group $SU(3)$ therefore has two Casimir operators. One of them is a quadratic combination of the generators:

$$C_1 = \sum_{i=1}^{8} \lambda_i^2. \tag{4.108}$$

It can be verified without difficulty that C_2 commutes with all the generators, i.e., $[C_1, \lambda_i]=0$ for $1 \leq i \leq 8$ (see Problem 4.7). The other Casimir operator is a complicated trilinear combination of the generators.

The eigenvalues of the two Casimir operators of $SU(3)$ may be labeled by two running indices p and q, and then an irreducible representation of $SU(3)$ may be denoted by (p, q), where p and q take all nonnegative integral values. The dimension of this irreducible representation is found to be[18]

$$d=(1+p)(1+q)(2+p+q)/2. \tag{4.109}$$

It has become a convention to denote an irreducible representation merely by its dimension. That is, instead of specifying it by (p, q), we denote it simply by **d** or **d*** according as whether $p<q$ or $p>q$. If $p=q$, there is only one irreducible representation of the corresponding dimension denoted by **d**.

Thus, the lowest order irreducible representation of $SU(3)$ is that for which $p=q=0$, or $(0, 0) \equiv \mathbf{1}$. Some of the other irreducible representations are $(0, 1) \equiv \mathbf{3}$, $(1, 0) \equiv \mathbf{3}^*$, $(0, 2) \equiv \mathbf{6}$, $(2, 0) \equiv \mathbf{6}^*$, $(1, 1) \equiv \mathbf{8}$, $(0, 3) \equiv \mathbf{10}$, etc. The direct products of these irreducible representations can be taken and reduced in terms of the irreducible representations. Without going into detail,[19] we list below a few particular cases of decomposition:

$$\begin{aligned} \mathbf{3} \otimes \mathbf{3} &= \mathbf{6} \oplus \mathbf{3}^*, \\ \mathbf{3} \otimes \mathbf{3}^* &= \mathbf{8} \oplus \mathbf{1}, \\ \mathbf{3} \otimes \mathbf{3} \otimes \mathbf{3} &= \mathbf{10} \oplus \mathbf{8} \oplus \mathbf{8} \oplus \mathbf{1}. \end{aligned} \tag{4.110}$$

4.8.1 Physical applications of $SU(2)$ and $SU(3)$. Just as the orbital wave functions of an electron (spherical harmonics) generate, or transform according to, the irreducible representations $D^{(l)}$ of $SO(3)$ in accordance with (4.51), we can see that the spin functions of

[18] See Fonda and Ghirardi (1970) for a detailed treatment of $SU(3)$.

[19] For the rules for reducing the direct products of the irreducible representations of $SU(3)$, see, for example, Fonda and Ghirardi (1970).

an electron would generate the representations of $SU(2)$. Consider a single electron with a spin angular momentum $\mathbf{s}=\frac{1}{2}\hbar\underline{\sigma}$ where $\underline{\sigma}\equiv(\sigma_x, \sigma_y, \sigma_z)$ and σ_i are the Pauli spin matrices. The two orthonormal spin functions may be denoted by $\chi^{(\frac{1}{2})}$ and $\chi^{(-\frac{1}{2})}$ which are simultaneous eigenfunctions of $\mathbf{s}^2$ and s_z. Under an orthogonal coordinate transformation, these spin functions undergo a unitary transformation in the complex two-dimensional Hilbert space of $\chi^{(\frac{1}{2})}$ and $\chi^{(-\frac{1}{2})}$. This space is known as the *spinor space* and any vector (which is any linear combination of the two basis functions) of this space is called a *spinor*. The spin functions $\chi^{(\frac{1}{2})}$ and $\chi^{(-\frac{1}{2})}$ thus generate a two-dimensional representation of $SU(2)$ which we recognize to be $D^{(\frac{1}{2})}$.

Let us now consider the case of two electrons. Since the spin functions of each electron transform according to $D^{(\frac{1}{2})}$, the spin functions of the combined system will transform according to the direct product representation $D^{(\frac{1}{2})}\otimes D^{(\frac{1}{2})}$. This is a four-dimensional representation of $SU(2)$. From the decomposition law (4.93) for the direct products of irreducible representations of $SU(2)$, we see that

$$D^{(\frac{1}{2})}\otimes D^{(\frac{1}{2})}=D^{(1)}\oplus D^{(0)}. \tag{4.111}$$

If we denote the spin functions of the first electron by $\chi_1(+)$ and $\chi_1(-)$, and those of the second electron by $\chi_2(+)$ and $\chi_2(-)$, then the basis functions for the direct product representation of (4.111) are clearly the four functions $[\chi_1(+)\chi_2(+), \chi_1(+)\chi_2(-), \chi_1(-)\chi_2(+), \chi_1(-)\chi_2(-)]$. By using the standard methods, we can obtain four symmetrized linear combinations of these functions such that one of them will generate the representation $D^{(0)}$ and the remaining three will generate $D^{(1)}$. These, when normalized, are found to be

$$\begin{aligned} D^{(0)}:\quad & \psi_{0,0}=\frac{1}{\sqrt{2}}[\chi_1(+)\chi_2(-)-\chi_1(-)\chi_2(+)]; \\ D^{(1)}:\quad & \begin{cases}\psi_{1,1}=\chi_1(+)\chi_2(+), \\ \psi_{1,0}=\dfrac{1}{\sqrt{2}}[\chi_1(+)\chi_2(-)+\chi_1(-)\chi_2(+)], \\ \psi_{1,-1}=\chi_1(-)\chi_2(-). \end{cases} \end{aligned} \tag{4.112}$$

The total spin of the system in the state $\psi_{0,0}$ is zero (a singlet state), while in any of the three states $\psi_{1,1}$, $\psi_{1,0}$, and $\psi_{1,-1}$ it is $\hbar$ (the triplet state).

The $SU(2)$ finds another important application in the isotopic spin formalism of elementary particles. In the long list of elementary particles, it can be seen that there are a large number of pairs such that

the two members of a pair have practically identical properties except their electrical charges. An obvious example is a proton and a neutron, all of whose properties are almost the same except their electromagnetic properties. We may then treat the proton and the neutron as the two states of a single *nucleon field*. We denote the two states by $|p>$ and $|n>$ and define an operator τ_3 whose eigenstates they are with the eigenvalues $+\frac{1}{2}$ and $-\frac{1}{2}$ respectively, i.e.,

$$\tau_3|p>=\tfrac{1}{2}|p>,\ \tau_3|n>=-\tfrac{1}{2}|n>. \tag{4.113}$$

The states $|p>$ and $|n>$ now span a two-dimensional Hilbert space in which the operator τ_3 would have the same representation as that of σ_z given in (4.98). In analogy with the electron spin problem, we make the hypothesis that there exists an operator $\underline{\tau}$, to be called the *isotopic spin operator*, which is given by

$$\underline{\tau}^2=\tau_1^2+\tau_2^2+\tau_3^2,$$

whese τ_1, τ_2 and τ_3 are the components of the vector operator $\underline{\tau}$. All physically observable states must be simultaneous eigenfunctions of $\underline{\tau}^2$ and τ_3. The states $|p>$ and $|n>$ thus generate the two-dimensional irreducible representation $D^{(\frac{1}{2})}$ of $SU(2)$. The charge of the nucleon in any of the eigenstates is $Q=\frac{1}{2}+\tau_3$.

The formalism is mathematically exactly analogous to that of the electron spin problem. Just as we do not treat an electron with spin 'up' and an electron with spin 'down' as two different types of particles but regard them merely as two states of a single entity called 'electron', we must teach ourselves to regard the proton and the neutron as the two states of a single 'nucleon'. It must be realized that the coincidence between the two cases is not merely accidental. It emerges from the fact that in quantum mechanics, unlike in classical mechanics, the angular momentum is a purely mathematically defined operator which corresponds to some physical observables.[20] Thus, the isotopic spin operator is as much an angular momentum as the operator for orbital or spin angular momentum of an electron.

The study of elementary particles has shown that there are certain groups of particles which can be assigned further quantum numbers—such as baryon number, strangeness, hypercharge, etc.—in addition to the isotopic spin angular momentum. It was therefore suggested that the symmetry group of these particles may be larger than $SU(2)$ and may, in fact, be $SU(3)$. Thus, there are a number of groups of parti-

[20] For the quantum mechanical definition of angular momentum, see Section 6.4.1.

cles whose states transform according to the irreducible representations of $SU(3)$, that is, they are degenerate with each other for strong interactions but are distinguished by their electrical charges and strangeness. The basic triplet transforming according to the irreducible representation **3** of $SU(3)$ is (p, n, Λ), where Λ is a hyperon. It is well-established now that there are groups of eight and ten elementary particles which correspond to the irreducible representations **8** and **10** of $SU(3)$. In fact, when Gell-Mann[21] proposed the $SU(3)$ scheme, he could fit only nine of the then known elementary particles into the ten states of the representation **10**, leaving one gap. The particle with properties predicted by Gell-Mann was soon observed in the laboratory and named Ω^-. The story is essentially parallel to that of Mendeleev's periodic table with gaps which were later filled by the discovery of new atoms.

PROBLEMS ON CHAPTER 4

(4.1) By referring to Fig. (4.2b), state the definition of the continuity of inversion for a topological group.

(4.2) Show that the following sets are groups:

(a) The set of matrices $\begin{bmatrix} 1 & \alpha \\ 0 & 1 \end{bmatrix}$ with $-\infty < \alpha < \infty$;

(b) The set of matrices

$$A(u)=\begin{bmatrix} (1-u^2/c^2)^{-1/2} & -u(1-u^2/c^2)^{-1/2} \\ -uc^{-2}(1-u^2/c^2)^{-1/2} & (1-u^2/c^2)^{-1/2} \end{bmatrix}$$

with $-c \leq u \leq c$, where c is a real positive constant. Use the relativistic law of addition of velocities, $w=(u+v)/(1+uv/c^2)$.

(4.3) Show that the sets of transformations (a) $x'=ax$, $y'=by$; (b) $x'=ax$, $y'=y/a$, $a\neq 0$, are Lie groups and obtain their infinitesimal generators.

(4.4) Prove Eq. (4.29). [Hint: Expand the right-hand side in the formal exponential series and use the property of the Pauli spin matrix that $\sigma_y^2=E$.]

(4.5) What is the group $U(1)$? Show that $U(n)=SU(n)\otimes U(1)$.

(4.6) Show that in an even-dimensional real vector space, inversion is equivalent to a proper rotation.

(4.7) Show that the operator of (4.108) is a Casimir operator for $SU(3)$, i.e., that $[C_1, \lambda_i]=0$ for $1 \leq i \leq 8$.

(4.8) Let H be a hermitian matrix of order n and let $U=\exp(iH)$. Let H be expanded with a suitable number of rows and columns of zeros to give a hermitian matrix of order m:

$$H'=\begin{bmatrix} H & 0 \\ 0 & 0 \end{bmatrix}.$$

[21] Ne'eman and Gell-Mann (1964).

(a) Show that $\exp(iH')=\begin{bmatrix} U & 0 \\ 0 & E \end{bmatrix}$, where E is the unit matrix of order $m-n$.

(b) Show that the set of matrices $\begin{bmatrix} U & 0 \\ 0 & E \end{bmatrix}$, where U is any unitary matrix, is a group isomorphic to $U(n)$. [In this sense, it is often said that $U(n)$ is a subgroup of $U(m)$ if $n<m$.]

(c) Show that, in the above sense, $SU(n)$ is a subgroup of $SU(m)$ if $n<m$.

(4.9) Let $a_i^\dagger$ and a_i denote the operators for the creation and the annihilation of a nucleon respectively, where i stands for p (proton) or n (neutron). These operators follow the boson commutation relations:

$$[a_i,\ a_j^\dagger]=\delta_{ij},\ [a_i,\ a_j]=[a_i^\dagger,\ a_j^\dagger]=0.$$

(a) Show that the operaters $\tau_x=a_p^\dagger a_n+a_n^\dagger a_p$, $\tau_y=-i(a_p^\dagger a_n-a_n^\dagger a_p)$, $\tau_z=a_p^\dagger a_p-a_n^\dagger a_n$ satisfy the commutation relations (4.101). [They therefore generate the algebra of $SU(2)$. This is the neutron-proton isospin algebra.]

(b) Show that the operator $E=a_p^\dagger a_p+a_n^\dagger a_n$ commutes with all the τ's. [The operators E, τ_x, τ_y, τ_z thus generate the algebra of $U(2)$.]

(4.10) A system contains three electrons each with spin $\frac{1}{2}\hbar$. Show that the system can exist in a quartet state (with spin $S=3\hbar/2$) and two distinct doublet states (each with spin $S=\frac{1}{2}\hbar$). Obtain the symmetrized spin functions for these states.

(4.11) The transformation of a vector $\mathbf{r}=(x,\ y,\ z)$ under rotations is determined by the matrix $R(\alpha,\ \beta,\ \gamma)$ given in (4.43). If we define the *spherical* or *standard* components of $\mathbf{r}$ by

$$r_1=-(x+iy)/\sqrt{2},\ r_0=z,\ r_{-1}=(x-iy)/\sqrt{2},$$

show that these components transform according to

$$r_n'=\sum_{m=-1}^{+1} r_m D_{mn}^{(1)}(\alpha,\ \beta,\ \gamma),\ n=-1,\ 0,\ 1,$$

where the elements $D_{mn}^{(1)}(\alpha, \beta, \gamma)$ are defined in (4.88). [See also (6.77) for the case $j=1$.]

Bibliography for Chapter 4

Carruthers (1966); Edmonds (1968); Englefield (1972); Falicov (1967); Fonda and Ghirardi (1970); Gelfand, Minlos and Shapiro (1963); Gottfried (1966); Gourdin (1968); Hamermesh (1964); Heine (1960); Hermann (1966); Kahan (1965); Lipkin (1965); Loebl (1968); Meijer and Bauer (1962); Messiah (1965), Chapter 13; Naimark (1964); Rose (1967); Schiff (1968), Chapter 7; Sudarshan and Mukunda (1974); Tinkham (1964); Wigner (1959); Wybourne (1974).

CHAPTER 5

Group Theory in Quantum Mechanics. I

The fundamental problem of quantum physics is to investigate the Schroedinger equation

$$\mathcal{H}\psi = E\psi, \tag{5.1}$$

where $\mathcal{H}$ is a linear hermitian operator suited to the problem at hand and ψ and E are its eigenfunction and eigenvalue respectively. The operator $\mathcal{H}$ may correspond to any physical observable such as position, momentum, angular momentum (spin or orbital), energy, and so on. In general, there are several solutions which satisfy (5.1) and which may be denoted by ψ_i with the corresponding eigenvalues E_i. The number of eigenfunctions of $\mathcal{H}$ in most quantum mechanical problems is in fact infinite. It is an axiom of quantum mechanics that the set of all eigenfunctions of a hermitian operator is a complete set. These eigenfunctions define a Hilbert space on which the operator acts.

In general, it is very difficult to find the exact eigenfunctions and eigenvalues of an operator, except in some very simple 'exactly solvable' cases. However, the problem can be considerably simplified by using group theoretical methods. In this chapter, we shall establish the connection between group theory and quantum mechanics by showing how the use of group theory helps in (a) simplifying the eigenvalue problem, (b) classifying the various eigenfunctions of an operator by the irreducible representations of the symmetry group of the operator, and

(c) describing their general properties by the consideration of the symmetry properties of the operator.

5.1 Hilbert Spaces in Quantum Mechanics

Before we begin applications of group theory, we shall illustrate in this section that with every hermitian operator corresponding to a physical observable, there is associated a Hilbert space on which the operator acts. We shall do this by considering a few typical examples.

5.1.1 One-dimensional square-well potential with perfectly rigid walls. The potential is of the form $V(x)=+\infty$ for $|x|>a$ and $V(x)=0$ for $|x|<a$, where a is some finite positive constant. The eigenfunctions of this problem are known to be[1] $\psi_n(x)=\sin(n\pi x/2a)$ for even n and $\psi_n(x)=\cos(n\pi x/2a)$ for odd n, where n takes all positive integral values and x takes values on the interval $[-a, a]$. It is clear that these eigenfunctions constitute an orthogonal set on $[-a, a]$ and hence can be chosen to be the basis functions of the Hilbert space of the Hamiltonian of the problem. Let us denote this space by L.

One might jump to the conclusion that this is the direct sum of the spaces L_e and L_o discussed in Section 2.3.2. A little reflection, however, shows that this is not so because only alternate values of n are allowed in the sine and the cosine functions. How can we then describe this space in words? It is not the space of *all* periodic functions with period $4a$. A little thought again tells us that it is the space of all continuous, square integrable functions which vanish at the boundaries[2] $|x|=a$. Any function in this space L can be expanded as a linear combination of the complete set of basis functions as follows.

$$\psi(x)=\sum_{n=1}^{\infty} c_n\psi_n(x)$$

$$=\sum_{n=1}^{\infty} a_n \sin(n\pi x/a)+\sum_{n=0}^{\infty} b_n \cos[(2n+1)\pi x/2a]. \quad (5.2)$$

Consider now the case when the potential is not constant in the region $|x|<a$ but still has perfectly rigid walls at $|x|=a$. The eigenfunctions will no longer be simple sine or cosine functions but must still satisfy the same boundary conditions,[3] that is, they must vanish at $|x|$

[1] Schiff (1968), p. 39.

[2] This shows in passing the importance of boundary conditions in quantum mechanics.

[3] Schiff (1968), Section 8.

$=a$. This implies that the eigenfunctions of the new problem must also belong to the Hilbert space L of the original problem and therefore can be expanded[4] as in (5.2). As is well-known, a function such as $\psi(x)$ of (5.2) denotes a wave-packet (whose spatial extension depends on the relative magnitudes of the coefficients a_n and b_n) and this is just what we expect to obtain for the problem at hand.

5.1.2 The hydrogen-like atom. The Hamiltonian of an electron in a hydrogen-like atom in the centre of mass coordinates is

$$\mathcal{H}=-\hbar^2\nabla^2/2\mu+V(r), \tag{5.3}$$

where $V(r)=-Ze^2/r$, Z is the charge at the nucleus, e the electronic charge, r the radial distance from the nucleus and μ the effective mass. The eigenfunctions of this problem are known to be[5]

$$\psi_{nlm}(\mathbf{r})=R_{nl}(r)\ Y_l^m(\theta, \phi), \tag{5.4}$$

where $R_{nl}(r)$ is the solution of the radial Schroedinger equation, $Y_l^m(\theta, \phi)$ is a spherical harmonic and $\mathbf{r}=(r, \theta, \phi)$ in spherical polar coordinates. These functions are orthonormal if the functions R_{nl} are normalized; thus

$$\int \psi_{nlm}(\mathbf{r})\psi^*_{n'l'm'}(\mathbf{r})\ d^3r=\delta_{nn'}\delta_{ll'}\delta_{mm'}. \tag{5.5}$$

These eigenfunctions therefore constitute the basis functions for the infinite-dimensional Hilbert space. The boundary conditions here are that each eigenfunction $\psi_{nlm}(\mathbf{r})\to 0$ as $r\to\infty$. Any function (continuous and square integrable) satisfying these boundary conditions can be expanded as a linear combination of the bound state eigenfunctions of (5.4). One must bear in mind, however, that this is *not the full* Hilbert space of the Hamiltonian (5.3); the full Hilbert space would include the eigenfunctions corresponding to the continuous eigenvalues in addition to those of (5.4).

5.1.3 Angular momentum. If $\mathbf{J}$ denotes the angular momentum operator of a physical system, it is known that its components do not commute with each other but that $\mathbf{J}^2$ commutes with all the components of $\mathbf{J}$. The problem is therefore to construct simultaneous

[4]This is the philosophy behind the precept in perturbation theory that the eigenfunctions of the perturbed problem can be expanded as linear combinations of the eigenfunctions of the unperturbed problem, provided the boundary conditions are the same.

[5]We have disregarded the spin of the electron and have restricted ourselves to the bound energy levels.

eigenfunctions of $\mathbf{J}^2$ and, say J_z. It is not necessary to obtain the explicit eigenfunctions. The eigenfunctions may be characterized by two indices[6] j and μ and an eigenfunction may be denoted in the Dirac notation by $|j\mu>$. The set of all such eigenfunctions for $j=0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, and $\mu=-j, -j+1, \ldots, j-1, j$ is a complete set in the infinite-dimensional Hilbert space of the angular momentum operator. The action of the components of this operator on a basis function is given by

$$\begin{aligned}
&\mathbf{J}^2|j\mu> = j(j+1)\hbar^2|j\mu>,\\
&J_z|j\mu> = \mu\hbar\,|j\mu>,\\
&(J_x+iJ_y)|j\mu> = [j(j+1)-\mu(\mu+1)]^{1/2}\hbar\,|j,\ \mu+1>,\\
&(J_x-iJ_y)|j\mu> = [j(j+1)-\mu(\mu-1)]^{1/2}\hbar\,|j,\ \mu-1>.
\end{aligned} \tag{5.6}$$

Eqs. (5.6) show that the infinite-dimensional Hilbert space of $\mathbf{J}$ splits into a direct sum of an infinite number of finite-dimensional Hilbert subspaces. The dimension of a subspace corresponding to a particular allowed j-value is $(2j+1)$ and the corresponding basis functions are $|j\mu>$ for $-j \leq \mu \leq j$. This is the familiar *spin space* of a system whose angular momentum is $j\hbar$ and is the space in which the representation $D^{(j)}$ of $SU(2)$ is defined.

5.1.4 Electron in a periodic potential. Let us finally consider an electron in a crystal lattice. The eigenfunctions of the Hamiltonian in this case can be put in the Bloch form

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}\cdot\mathbf{r})\, u_{n\mathbf{k}}(\mathbf{r}), \tag{5.7}$$

where $u_{n\mathbf{k}}(\mathbf{r})$ is a periodic function with the periodicity of the lattice. The boundary conditions here are the periodic boundary conditions. The number of the allowed values of the vector $\mathbf{k}$ is equal to the number of unit cells in the crystal and n is the band index which takes all positive integral values (and also takes account of the states in the bands obtanined from the core levels). These eigenfunctions constitute a basis for the infinite-dimensional Hilbert space of the crystal Hamiltonian and any function with the same periodic boundary conditions can be expressed as a linear combination of functions in this complete set.

The examples of Sections 5.1.1, 5.1.2 and 5.1.4 show that when the operator under consideration is the Hamiltonian, its Hilbert space is determined by the boundary conditions rather than the actual form of the potential.

[6] Schiff (1968), Section 27; Messiah (1965), Section 13.1

5.2 Transformations of a Function

Let R be an operator referring to a transformation of the coordinate system $\mathbf{e}_i$, i.e.,

$$R\mathbf{e}_i=\mathbf{e}_i',\ i=1, 2, 3, \ldots, \tag{5.8}$$

where $\mathbf{e}_i'$ are the axes of the transformed coordinate system. Eq. (5.8) can also be written in full as

$$\mathbf{e}_i'=\sum_j \mathbf{e}_j R_{ji},\ i=1, 2, 3, \ldots, \tag{5.9}$$

where $[R_{ij}]$ is the representation of the operator R with the bassis $\{\mathbf{e}_i\}$.

We are interested in knowing how the form of a function (defined in the space of $\{\mathbf{e}_i\}$) changes when the coordinate system undergoes a transformation. To begin with, let us consider a simple function of one variable (one-dimensional space) such as $f(x)=\cos x$. For the coordinate transformation, we take the translation of the origin of the coordinate to the point $x=a$. If we denote this transformation by R, the new coordinate can be denoted by

$$x\rightarrow x'\equiv Rx=x-a. \tag{5.10}$$

It is then obvious that the inverse transformation will be $R^{-1}\ x=x+a$.

What happens to the function $f(x)$ in the new coordinate system? Let us denote the transformed function of x' by $f_t(x')$ and denote by P_R the operator corresponding to R operating on functions of[7] x. Then we can write algebraically

$$P_R f(x)\equiv f_t(x'). \tag{5.11}$$

In our case, with $f(x)=\cos x$, it would be clear from Fig. (5.1) that the transformed function takes the form $f_t(x')=\cos(x'+a)$. Dropping the primes, this can be written in the form $f_t(x)=\cos(x+a)$, or

$$P_R f(x)=\cos\ (R^{-1}\ x). \tag{5.12}$$

The same result would be obtained if we kept the coordinate system fixed and moved the function $f(x)=\cos x$ by a distance a to the left (the active point of view). As discussed in Chapter 1, this shows in general that a transformation of the coordinate system $\mathbf{e}_i$ is equivalent to the inverse transformation applied on the function f. Generalizing this result to the three-dimensional space of position vectors, this means that the value of the transformed function f_t at a point $\mathbf{r}$ is the same as the value of the original function f at the point $R^{-1}\mathbf{r}$. We therefore have

$$f_t\ (\mathbf{r})=P_R f(\mathbf{r})=f(R^{-1}\ \mathbf{r}). \tag{5.13}$$

[7]Note that the operator R acts on the coordinate x only.

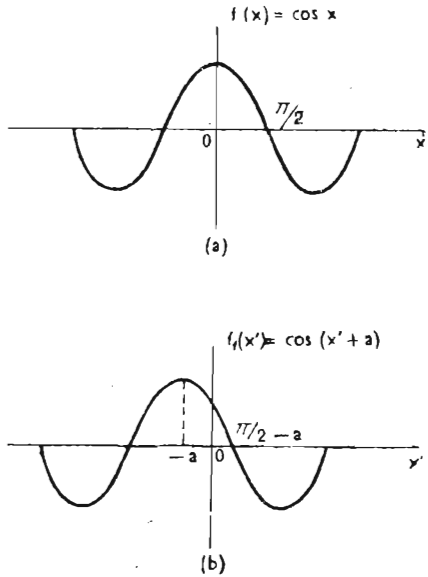


FIGURE 5.1 (a) The function $f(x)=\cos x$; (b) The coordinate transformation in which the origin is shifted to the point $x=a$, so that $x'=x-a$ and $f_t(x')=\cos(x'+a)$

Since this transformation is very important, it would be worth considering one more example in the three-dimensional space. Let us take the function to be

$$f(\mathbf{r})=\exp i\,(k_1x_1+k_2x_2+k_3x_3), \tag{5.14}$$

where (x_1, x_2, x_3) are the components of $\mathbf{r}$ in the orthonormal system $\{\mathbf{e}_i\}$ and k_i are scalars of dimensions (length)$^{-1}$. Let R be a rotation of the coordinate axes through 90° about $\mathbf{e}_3$, that is,

$$\begin{aligned} R(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3) &\equiv (\mathbf{e}_1', \mathbf{e}_2', \mathbf{e}_3') \\ &= (\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)\begin{bmatrix} 0 & -1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \end{aligned} \tag{5.15}$$

The function $f(\mathbf{r})$ has the value given by (5.14) at a point $P=(x_1, x_2, x_3)$. In the primed system, the point P (see Fig. (5.2)) has the coordinates (x_1', x_2', x_3'), where $x_1'=x_2$, $x_2'=-x_1$, $x_3'=x_3$. Since the value of the function f at the point P has not changed during the transformation (or, in other words, the value of the function f at the point P is independent of the coordinate system), the form of the transformed function must be

$$f_i(\mathbf{r}')=\exp i\,(-k_1x_2'+k_2x_1'+k_3x_3'). \tag{5.16}$$

Since $\mathbf{r}'$ is only a label for the argument of f_i, we may drop the primes and write

$$f_i(\mathbf{r})=\exp i(-k_1x_2+k_2x_1+k_3x_3). \tag{5.17}$$

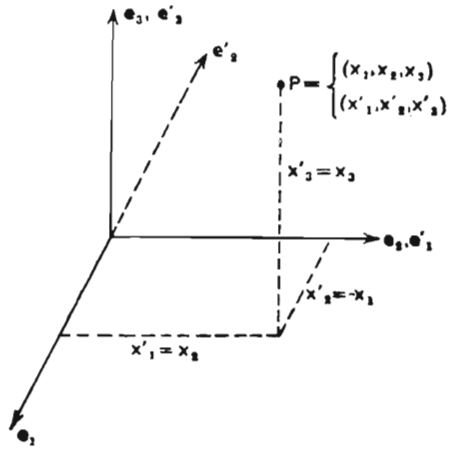


FIGURE 5.2 The transformation of the coordinate system $\mathbf{e}_i$ to $\mathbf{e}_i'$

This form of the transformed function can evidently be obtained by the operation

$$R^{-1}(x_1, x_2, x_3)=(-x_2, x_1, x_3)$$
$$=(x_1, x_2, x_3)\begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix}. \tag{5.18}$$

The matrix obtained in the above equation is the inverse of that obtained in (5.15). Hence, once again we have

$$f_i(\mathbf{r})=P_Rf(\mathbf{r})=f(R^{-1}\,\mathbf{r}),$$

which is just (5.13). Here it should be emphasized that the function f of (5.14) is identically the same as the function f_i of (5.17); the only difference is that in (5.14), the position $\mathbf{r}$ is measured in the original coordinate system, whereas in (5.17), it is measured in the transformed system.

Consider now the effect of the successive transformation of the coordinate system by the application of the operators R and S. Let P_R and P_S be the operators which act on functions of $\mathbf{r}$ and which corres-

pond to R and S respectively. The result of the first operation, by (5.13), is

$$P_R f(\mathbf{r}) = f(R^{-1}\,\mathbf{r}) \equiv F(\mathbf{r}), \tag{5.19}$$

which defines the function $F(\mathbf{r})$. Now the result of the operation of P_S on $F(\mathbf{r})$ is

$$P_S\, F(\mathbf{r}) = F\,(S^{-1}\,\mathbf{r}). \tag{5.20}$$

On replacing $\mathbf{r}$ by $S^{-1}\,\mathbf{r}$ in (5.19), we get

$$F(S^{-1}\,\mathbf{r}) = f(R^{-1}\,S^{-1}\,\mathbf{r}).$$

Using (5.19) and (5.20) in the above equation, we have

$$P_S\, P_R f(\mathbf{r}) = f(R^{-1}\,S^{-1}\,\mathbf{r}). \tag{5.21}$$

Note the interchange in the order of the inverse operators in the argument of the function f on the right-hand side of the above equation.

5.3 Space and Time Displacements

5.3.1 Space displacements. Consider a physical system represented by a wave function $\psi(\mathbf{r})$. Let the physical system be displaced through a vector $\underline{\rho}$. Since this is equivalent to displacing the coordinate system through $-\underline{\rho}$, the wave function representing the physical system, according to our previous discussion, will be

$$\psi'\,(\mathbf{r}) = \psi\,(\mathbf{r}-\underline{\rho}). \tag{5.22}$$

If we denote the corresponding translation operator by $P_r(\underline{\rho})$ (the subscript r stands for space displacements), then we have

$$P_r(\underline{\rho})\;\psi\,(\mathbf{r}) \equiv \psi'\,(\mathbf{r}) = \psi\,(\mathbf{r}-\underline{\rho}). \tag{5.23}$$

Our aim now is to obtain an expression for the translation operator $P_r\,(\underline{\rho})$. We first consider the particular case when the displacement $\underline{\rho}$ is parallel to the x axis. Since the wave function of a physical system is a continuous and differentiable function at all points of the space, we can expand $\psi(\mathbf{r}-\underline{\rho})$ in a Taylor series:

$$\begin{aligned}\psi\,(\mathbf{r}-\underline{\rho}) &\equiv \psi\,(x-\rho,\, y,\, z)\\ &= \left\{1-\rho\,\frac{\partial}{\partial x}+\frac{\rho^2}{2\,!}\,\frac{\partial^2}{\partial x^2}-\ldots\right\}\psi\,(x,\, y,\, z)\\ &= \exp\left(-\rho\frac{\partial}{\partial x}\right)\psi\,(x,\, y,\, z).\end{aligned} \tag{5.24}$$

Extending this to any general displacement $\underline{\rho}$, we have

$$\begin{aligned}\psi(\mathbf{r}-\underline{\rho}) &= \exp\,(-\underline{\rho}\cdot\nabla)\;\psi(\mathbf{r})\\ &= \exp(-i\,\underline{\rho}\cdot\mathbf{p}/\hbar)\;\psi(\mathbf{r}),\end{aligned} \tag{5.25}$$

where $\mathbf{p}=-i\hbar\nabla$ is the quantum mechanical operator corresponding to the linear momentum of the system. Comparing this with (5.23), we find

$$P_r(\underline{\rho})=\exp(-i\underline{\rho}\cdot\mathbf{p}/\hbar). \tag{5.26}$$

Since $\underline{\rho}$ is real and $\mathbf{p}$ is a hermitian operator, $P_r(\underline{\rho})$ is a unitary operator.

It now remains to verify whether the displaced function still characterizes a possible state of the system. For this, we first note that the function $\psi(\mathbf{r})$, being a wave function of the system, satisfies the time-dependent Schroedinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r})=\mathcal{H}\psi(\mathbf{r}), \tag{5.27}$$

where $\mathcal{H}$ is the Hamiltonian of the system. We now calculate the time derivative of the displaced function which gives

$$\begin{aligned} i\hbar\frac{\partial}{\partial t}\psi'(\mathbf{r})&=i\hbar P_r(\underline{\rho})\frac{\partial}{\partial t}\psi(\mathbf{r})=P_r(\underline{\rho})\,\mathcal{H}\psi(\mathbf{r}) \\ &=P_r(\underline{\rho})\,\mathcal{H}\,P_r\dagger(\underline{\rho})\psi'(\mathbf{r}). \end{aligned} \tag{5.28}$$

It is then clear that the function $\psi'(\mathbf{r})$ satisfies the time-dependent Schroedinger equation with the same Hamiltonian $\mathcal{H}$ if and only if

$$P_r(\underline{\rho})\,\mathcal{H}P_r\dagger(\underline{\rho})=\mathcal{H}, \quad \text{or} \quad [P_r(\underline{\rho}),\mathcal{H}]=0. \tag{5.29}$$

On looking at the form of the unitary operator $P_r(\underline{\rho})$ given in (5.26), we note that (5.29) holds for *all* vectors $\underline{\rho}$ if and only if $\mathbf{p}$ commutes with $\mathcal{H}$. This implies that *if the physical system is invariant under all space translations, its linear momentum is a constant of motion, or is conserved.*

The set of all translation operators $P_r(\underline{\rho})$ (for all values of $\underline{\rho}$) clearly is an abelian, continuous, connected, three-parameter, non-compact group. The law of composition for this group is simply

$$P_r(\underline{\rho})\,P_r(\underline{\delta})=P_r(\underline{\delta})\,P_r(\underline{\rho})=P_r(\underline{\rho}+\underline{\delta}).$$

This is the symmetry group of the physical system under consideration.

It would be instructive to consider two simple examples of the concept discussed here. Consider first the case of a free particle whose Hamiltonian contains only the kinetic energy part: $\mathcal{H}=-\hbar^2\nabla^2/2m \equiv\mathbf{p}^2/2m$. Its wave function is of the form $\exp(i\mathbf{k}\cdot\mathbf{r})$ where $\mathbf{k}$ denotes the wave vector of the particle. If we displace the system through a vector $\underline{\rho}$, the new function $\exp[i\mathbf{k}\cdot(\mathbf{r}-\underline{\rho})]$ also represents a possible state of the free particle. This must be true for any vector $\underline{\rho}$ because the momentum of the particle commutes with $\mathcal{H}$ and is therefore a constant of motion ($\mathbf{p}=\hbar\mathbf{k}$).

Consider next the case of an electron in a hydrogen atom. The wave function of the electron is of the form $R_{nl}(r)\, Y_l^m(\theta, \phi)$. Here the position vector **r** is measured in a coordinate system whose origin is at the nucleus. If we displace the system through some vector so that the nucleus is no longer at the origin of coordinates, the displaced function cannot be put in the standard form and hence does not denote a possible state of the system. The linear momentum is therefore not a constant of motion for an electron in a hydrogen atom which is of course a well-known result.

5.3.2 Time displacements. In analogy with the space displacement of a physical system considered above, we may displace a system in time and try to find out whether the displaced function represents a possible state of the system.

Thus, let $\psi(t)$ be the wave function[8] of a physical system and let $P_t(\tau)$ denote the operator for translating the functions of time by an amount τ. We then have

$$P_t(\tau)\,\psi(t) \equiv \psi'(t) = \psi(t-\tau). \tag{5.30}$$

We may expand the function $\psi(t-\tau)$ in a Taylor series about the point t and we then find that

$$P_t(\tau)\,\psi(t) = \exp(-\tau\,\partial/\partial t)\,\psi(t). \tag{5.31}$$

We therefore have

$$P_t(\tau) = \exp(-\tau\,\partial/\partial t). \tag{5.32}$$

Now, the quantum mechanical energy operator is given by $\mathcal{H} = i\hbar\partial/\partial t$. If $\mathcal{H}$ is itself independent of time, that is, if the energy is a constant of motion, then we can replace $\partial/\partial t$ in the exponential in (5.32) by $\mathcal{H}$ and obtain

$$P_t(\tau) = \exp(i\tau\,\mathcal{H}/\hbar), \tag{5.33}$$

which is a unitary operator because τ is real and $\mathcal{H}$ is hermitian.

This again shows that if a physical system is invariant under *all* time displacements, then the energy of the system is a constant of motion. The transformed function in this case still obeys the Schroedinger equation. All the time translation operators $P_t(\tau)$ commute with the Hamiltonian, i.e.,

$$[P_t(\tau), \mathcal{H}] = 0, \text{ all } \tau. \tag{5.34}$$

The set of all time translation operators is again an abelian, conti-

[8] We are not interested in the other variables on which ψ may depend; these are therefore suppressed here.

nuous, connected, one-parameter, noncompact group which is the symmetry group of the physical system.

Once again, we may consider the example of the hydrogen atom. If we have an isolated hydrogen atom, with no perturbations, its Hamiltonian is invariant under all time displacements. If the atom is in a particular state at a given instant of time, it will continue to remain in the same state for all time and the total energy of the system will be an invariant. On the other hand, if we apply a time-dependent perturbation, the Hamiltonian is no longer invariant under time translations, the atom may make transitions from one state to another and the energy of the atom does not remain a constant of motion.

5.4 Symmetry of the Hamiltonian

In the previous section we have seen by means of two examples that when a system possesses a certain symmetry, there is a corresponding physical observable which remains a constant of motion. We shall develop this concept here in its complete generality. We shall hereafter use the operator $\mathcal{H}$ of (5.1) to mean the Hamiltonian (the energy operator) of the system.

The Hamiltonian $\mathcal{H}$ is itself a function of the various parameters of the system such as the position vector, time, momentum, angular momentum, etc., and it reflects the symmetry of the system it describes. Its familiar form in the single-particle approximation is

$$\mathcal{H}=-\frac{\hbar^2\nabla^2}{2m}+V, \tag{5.35}$$

where the first term is the kinetic energy operator for the particle it describes and V contains all the other terms. The Laplacian ∇^2 is invariant under all orthogonal transformations of the coordinate system (that is, under the rotation-inversion group $O(3)$). Hence, the symmetry of $\mathcal{H}$ is essentially governed by the symmetry of the function V. Thus, if (5.35) refers to an electron in a hydrogen atom, the potential energy of the electron is spherically symmetric, and $\mathcal{H}$ would be invariant under the group $O(3)$; if it refers to an electron in a crystal, $\mathcal{H}$ would be invariant under the symmetry transformations of the crystal (that is, the operations of the space group of the crystal, to be discussed in Chapter 7).

Let us consider the operation of P_R, which corresponds to some coordinate transformation R, on the Schroedinger equation (5.1):

$$P_R\,\mathcal{H}\psi=P_R\,E\psi,$$

or $$(P_R \mathcal{H} P_R^{-1})(P_R \psi) = E P_R \psi,$$

or $$\mathcal{H}'(P_R \psi) = E(P_R \psi), \tag{5.36}$$

where

$$\mathcal{H}' = P_R \mathcal{H} P_R^{-1} \tag{5.37}$$

is the Hamiltonian referred to the transformed coordinate system. If the operator P_R is such that $\mathcal{H}' = \mathcal{H}$, which means that the form of the Hamiltonian function in the new coordinate system is the same as its form in the original one, then from (5.37), we find that

$$\mathcal{H} P_R = P_R \mathcal{H}. \tag{5.38}$$

This shows that the Hamiltonian commutes with all the operators under which it is invariant.

The set of all transformations R which leave the system invariant is a group. The set of the corresponding transformations P_R leaves the Hamiltonian of the system invariant and hence also is a group. The two groups are isomorphic to each other and they will both be denoted by the same symbol G. It is known as the *symmetry group of the Hamiltonian* or *the group of the Schroedinger equation*. (See Problem 5.7.)

The commutation relation (5.38), when used in (5.36), implies that

$$\mathcal{H}(P_R \psi) = E(P_R \psi), \tag{5.39}$$

that is, $P_R \psi$ is also an eigenvector of $\mathcal{H}$ with the same eigenvalue E. The function $P_R \psi$ is thus degenerate with ψ, unless it is a multiple of ψ.

5.4.1 Symmetry and degeneracy. Starting from a given eigenfunction ψ_1 of $\mathcal{H}$ with the eigenvalue E, we can generate a set of independent eigenfunctions $\psi_1, \psi_2, \ldots, \psi_n$ ($n \leqslant g$, the order of G) by operating with all the elements of the group G. These functions form a basis for a representation of G which may be reducible or irreducible. However, if all possible symmetry transformations which leave the Hamiltonian invariant have been included in the group G, then the representation generated by the degenerate eigenfunctions must, in general, be an irreducible one. Conversely, the eigenfunctions belonging to an irreducible representation of G (occurring for a particular time) can be transformed into each other by the operations of the elements of G, and hence they must be degenerate, as is clear from (5.39).

Now we may ask the question: Do the eigenfunctions transforming according to different representations of G always have different eigenvalues? In general, they should. This is due to the fact that if, for example, ψ and ϕ are functions belonging to different irreducible

representations of G, then there is no operation of G which mixes them. But it may happen that we have failed to include all the symmetry transformations of the Hamiltonian in the group G, in which case, the representation generated by the degenerate eigenfunctions may be a reducible one. The basis functions belonging to two or more constituent irreducible representations may then be degenerate. However, if this happens consistently, that is, if we find that the basis functions belonging to two or more irreducible representations of G are always degenerate, we may conclude that we have overlooked some symmetry of the Hamiltonian. When we have considered all possible symmetry transformations of the Hamiltonian, the basis functions belonging to different irreducible representations of G must, in general, have different eigenvalues.

We can, however, hardly ever be certain in practice that we have discovered all the invariances of a physical system. An excellent example of this will be found when we discuss the dynamical symmetry of physical systems in Section 8 of this chapter.

It may still happen that for certain values of the parameters (such as the nuclear charge, the electronic mass, the interatomic distances in molecules and crystals, etc., on which the eigenfunctions depend), two or more eigenfunctions belonging to different irreducible representations have the same energy eigenvalue. This degeneracy is not demanded by the symmetry of the system and cannot be inferred from group theoretical considerations. This is called *accidental degeneracy* as against the *essential degeneracy* which arises due to the symmetry of the system and which we have hitherto discussed. The essential degeneracy can be removed by lowering the symmetry of the system. On the other hand, the position of the accidental degeneracy changes on changing the parameters, which have no effect on essential degeneracy.

To take an example, consider a simple two level Fermi system shown in Fig. (5.3). Both the levels A and B are doubly degenerate, i.e.,

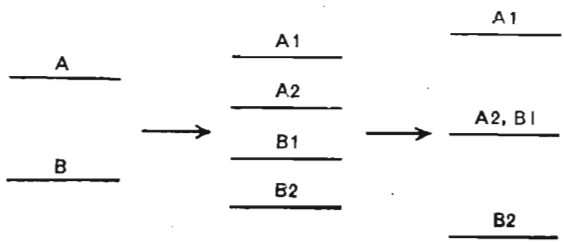


FIGURE 5.3 The splitting of levels under a magnetic field and the accidental degeneracy of $A2$ and $B1$

each level can accommodate two fermions, one with spin 'up' and one with spin 'down'. If we apply a magnetic field, each level splits into two. The separations between the two levels $A1$ and $A2$ and between $B1$ and $B2$ increase linearly on increasing the intensity of the magnetic field. Fig. (5.4) shows the variation of the energies of the four levels with the intensity of the magnetic field. It is clear that for some value of the magnetic field, the energies of the two levels $A2$ and $B1$ will coincide, such as at the point P in Fig. (5.4).

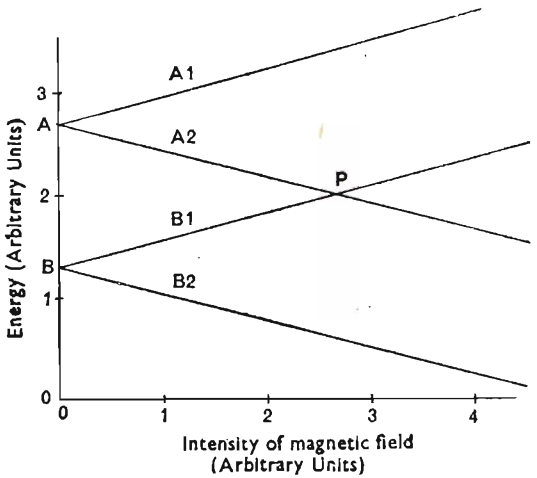


FIGURE 5.4 The double degeneracies at A and B are essential whereas the double degeneracy at P is accidental

The double degeneracy of the two levels A and B in the absence of the magnetic field is due to the symmetry of the system. The 'up' spin is not distinguishable from the 'down' spin in the absence of a magnetic field, and hence it is an essential degeneracy. On the other hand, the double degeneracy at P in Fig. (5.4) for a particular value of the magnetic field is an accidental degeneracy, as it is not warranted by symmetry considerations. The essential degeneracy at A and B is removed only by lowering the symmetry of the system but the position of the accidental degeneracy can be changed by changing the charge or the mass of the fermions (or even by changing the velocity of light, since the Bohr magneton depends on it).

We shall come across a number of other examples of the two types of degeneracy while treating various problems in the remaining part of this book.

5.4.2 Good quantum numbers. Let us come back to our discussion about the connection between the dimensions of the irreducible representations and the degeneracies of the energy levels. The importance of this result, as we shall soon see, is that it provides a means of labeling the energy levels and the eigenfunctions of the system by the irreducible representations of its symmetry group and determines the various degeneracies to be expected.

Thus, if ψ_{pm}^{α} is an eigenfunction belonging to the m-th column of the α-th irreducible representation occurring for the p-th time in the energy level scheme, then α and p are suitable indices for labeling the eigenvalues which may be denoted by $E_{\alpha p}$. For example, the Hamiltonian of an electron in a hydrogen atom has rotational invariance. The eigenfunctions of the problem are $R_{nl}\, Y_l^m(\theta, \phi)$ and the energy levels of the electron can be labeled by the indices n and l (n corresponds to p here). Anticipating the result of our further discussion, we may consider the example of an electron in a periodic lattice. The irreducible representations of the group of the Hamiltonian in this case are characterized by a wave vector $\mathbf{k}$, and therefore, we may denote the eigenfunctions by $\psi_{n\mathbf{k}}(\mathbf{r})$ and the energy eigenvalues by $E_n(\mathbf{k})$, where n is now the band index.

This is indeed the group theoretical explanation of *good quantum numbers*. Thus, for an electron in a hydrogen atom, n and l are good quantum numbers; for an electron in a crystal, n and $\mathbf{k}$ are good quantum numbers. A good quantum number is that characteristic of the eigenfunction of the physical system which remains invariant under the symmetry transformations of the system, and is, therefore, the most suitable variable to label the eigenfunctions and the eigenvalues of the system.

In the light of this discussion, the time-independent Schroedinger equation for any system can be put in the most general form

$$\mathcal{H}\psi_{pm}^{\alpha} = E_{\alpha p}\, \psi_{pm}^{\alpha}, \tag{5.40}$$

where α, p and m are the good quantum numbers. While the eigenfunction is characterized by these three parameters, the eigenvalue depends only on α and p. The degeneracy of the level $E_{\alpha p}$ is therefore the number of values m takes which is the dimension of the α-th irreducible representation.

5.5 Reduction Due to Symmetry

If an arbitrary choice of basis functions is made, the Hamiltonian

would in general have nonvanishing matrix elements between any pair of basis functions. The Hamiltonian matrix would then have diagonal as well as off-diagonal elements. However, we shall see in this section that with a suitable choice of the basis functions, the Hamiltonian matrix can be put in a block-diagonalized form, considerably simplifying the problem of obtaining its eigenvalues.

5.5.1 **Orthogonality of basis functions.** As a first step towards our objective, we shall show that if the elements of a group are unitary operators, then the basis functions belonging to different irreducible representations of the group or to two different columns of the same irreducible representation are orthogonal.

Let $\psi_{pm}{}^{\alpha}$ be a basis function transforming according to the m-th column of the irreducible representation $\Gamma^{(\alpha)}$ (of the symmetry group G) occurring for the p-th time in the energy level scheme. Let also $\psi_{qn}{}^{\beta}$ be a basis function transforming according to the n-th column of the irreducible representation $\Gamma^{(\beta)}$ occurring for the q-th time in the energy level scheme. Since the scalar product of two functions is invariant under a unitary transformation, we have

$$(\psi_{pm}{}^{\alpha}, \psi_{qn}{}^{\beta}) = (A\psi_{pm}{}^{\alpha}, A\psi_{qn}{}^{\beta}), \tag{5.41}$$

for all $A \in G$. Writing explicitly the operation of A on the basis functions in the right-hand side of the above equation, we have

$$(\psi_{pm}{}^{\alpha}, \psi_{qn}{}^{\beta}) = \left(\sum_{k=1}^{l_\alpha} \psi_{pk}{}^{(\alpha)} \Gamma_{km}{}^{(\alpha)}(A), \sum_{l=1}^{l_\beta} \psi_{ql}{}^{\beta} \Gamma_{ln}{}^{(\beta)}(A) \right) \tag{5.42}$$

$$= \sum_{k=1}^{l_\alpha} \sum_{l=1}^{l_\beta} \Gamma_{km}{}^{(\alpha)*}(A) \Gamma_{ln}{}^{(\beta)}(A) (\psi_{pk}{}^{\alpha}, \psi_{ql}{}^{\beta}). \tag{5.43}$$

Let us restrict ourselves to finite groups for the moment. Since the left-hand side of the above equation is independent of the group element A, we may sum the right-hand side over all the group elements and divide by g, the order of G. By using the orthogonality relation between the irreducible representations, we then find

$$(\psi_{pm}{}^{\alpha}, \psi_{qn}{}^{\beta}) = \frac{1}{g} \sum_{k=1}^{l_\alpha} \sum_{l=1}^{l_\beta} \sum_{A \in G} \Gamma_{km}{}^{(\alpha)*}(A) \Gamma_{ln}{}^{(\beta)}(A) (\psi_{pk}{}^{\alpha}, \psi_{ql}{}^{\beta})$$

$$= \delta_{\alpha\beta} \delta_{mn} (1/l_\alpha) \sum_{k=1}^{l_\alpha} \sum_{l=1}^{l_\beta} \delta_{kl} (\psi_{pk}{}^{\alpha}, \psi_{ql}{}^{\beta}). \tag{5.44}$$

This shows that the basis functions $\psi_{pm}{}^{\alpha}$ and $\psi_{qn}{}^{\beta}$ are orthogonal if

$\alpha \neq \beta$ or $m \neq n$,

However, if $\alpha=\beta$ and $m=n$, we find from the above equation that

$$(\psi_{pm}^{\alpha}, \psi_{qm}^{\alpha})=\frac{1}{l_\alpha} \sum_{k=1}^{l_\alpha} (\psi_{pk}^{\alpha}, \psi_{qk}^{\alpha}). \tag{5.45a}$$

Since the right-hand side is independent of m, we have an important result that

$$(\psi_{pm}^{\alpha}, \psi_{qm}^{\alpha})=(\psi_{pk}^{\alpha}, \psi_{qk}^{\alpha}), \tag{5.45b}$$

for $1 \leq m, k \leq l_\alpha$, i.e., the scalar product of two basis functions both transforming according to the same column of the same irreducible representation, is independent of the column index.

Although we have derived these results for a finite group, it would suffice to say that they hold good for compact continuous groups also.

Thus, if we have a number of basis functions transforming according to the various irreducible representations of a group, the only scalar products that are likely to exist are those between basis functions transforming according to the same column of the same irreducible representation.[9]

We have obtained the above result for the basis functions of the irreducible representations of any group in general. However, if we are considering the eigenfunctions of the Hamiltonian, which are at the same time basis functions for the irreducible representations of its symmetry group, then we can go one step further. It is known from elementary quantum mechanics that if ψ_{pm}^{α} and ψ_{qn}^{β} are two eigenfunctions of $\mathcal{H}$ having two different eigenvalues $E_{\alpha p}$ and $E_{\beta q}$, then they must be orthogonal. Combining this with the above orthogonality relation (5.44), we see that the set of *all* eigenfunctions of the Hamiltonian, if they are chosen so as to form basis functions for the irreducible representations of its symmetry group, is an orthogonal set. In other words, the matrix representing $\mathcal{H}$ with such eigenfunctions for the basis is a diagonal matrix.

5.5.2 Block-diagonalization of the Hamiltonian. The situation discussed above when the Hamiltonian is fully diagonalized is really only an ideal case and obtains when we know the eigenfunctions of the Hamiltonian. However, in practice, we do not know the eigenfunctions of the Hamiltonian beforehand. We may, nevertheless, con-

[9]Even these may vanish, of course, in particular cases due to reasons other than those of symmetry.

struct a set of approximate eigenfunctions generating the various irreducible representations of the symmetry group of the Hamiltonian and use them as a starting point towards determining the required eigenfunctions. We can show that if we construct the matrix representing the Hamiltonian with these basis functions, it will be in a block-diagonalized form, though not in the fully diagonalized form.

Thus, as before, let $\psi_{pm}{}^{\alpha}$ and $\psi_{qn}{}^{\beta}$ be two basis functions as defined in the previous subsection. These are now not necessarily the eigenfunctions of the Hamiltonian. Our object is then to find the matrix element of the Hamiltonian between these two states, i.e., $(\psi_{pm}{}^{\alpha}, \mathcal{H}\psi_{qn}{}^{\beta})$. Since $\mathcal{H}$ is invariant under all operations of its symmetry group, it is easy to see that the function $\mathcal{H}\psi_{qn}{}^{\beta}$ has the same symmetry as $\psi_{qn}{}^{\beta}$. For, let A be a symmetry element in the group, so that

$$A\,\psi_{qn}{}^{\beta} = \sum_{l} \psi_{ql}{}^{\beta}\, \Gamma_{ln}{}^{(\beta)}(A) \;\forall\; A \in G. \tag{5.46}$$

Now consider the operation of A on the function $\mathcal{H}\psi_{qn}{}^{\beta}$. Using the fact that A commutes with $\mathcal{H}$, we have

$$A\,(\mathcal{H}\psi_{qn}{}^{\beta}) = \mathcal{H}A\,\psi_{qn}{}^{\beta} = \sum_{l} (\mathcal{H}\psi_{ql}{}^{\beta})\, \Gamma_{ln}{}^{(\beta)}(A) \;\forall\; A \in G. \tag{5.47}$$

This shows that $\mathcal{H}\psi_{qn}{}^{\beta}$ also transforms under the symmetry group according to the n-th column of the irreducible representation $\Gamma^{(\beta)}$. Hence the scalar product of $\psi_{pm}{}^{\alpha}$ with $\mathcal{H}\psi_{qn}{}^{\beta}$ will involve factors like $\delta_{\alpha\beta}\,\delta_{mn}$ in accordance with (5.44). The only nonvanishing matrix elements of $\mathcal{H}$ will thus be between functions of the form $\psi_{pm}{}^{\alpha}$ and $\psi_{qm}{}^{\alpha}$ i.e.,

$$(\psi_{pm}{}^{\alpha}, \mathcal{H}\psi_{qn}{}^{\beta}) = \delta_{\alpha\beta}\,\delta_{mn}\,(\psi_{pm}{}^{\alpha}, \mathcal{H}\psi_{qm}{}^{\alpha}). \tag{5.48}$$

The Hamiltonian matrix would therefore be in a block-diagonalized form the dimensions of the blocks being equal to the number of values the index p takes; these are the numbers a_{α} defined in (3.87). The dimension of the biggest block will be the maximum number of times an irreducible representation occurs in the energy level scheme, i.e., the largest of the a_{α}'s. The problem is then considerably simplified because it has essentially been reduced to that of determining the eigenvalues of the blocks separately.

To illustrate this by an example, let us consider a very simple case of a Hamiltonian which is invariant under the inversion operator J. Let U_J be the unitary operator corresponding to J which operates on functions of the position vector. As we have seen before, the operator U_J then commutes with $\mathcal{H}$:

$$U_J\,\mathcal{H} = \mathcal{H}\,U_J. \tag{5.49}$$

Applying the operator U_J to both the sides of (5.1) from the left

(where ψ is an unknown eigenfunction of $\mathcal{H}$) and using (5.49), we get

$$\mathcal{H}(U_J\psi)=E(U_J\psi). \tag{5.50}$$

Let ϕ be an eigenfunction of U_J; then

$$U_J\phi=c\phi, \tag{5.51}$$

where c is the eigenvalue of U_J corresponding to ϕ. Since the double operation of J leaves the coordinate system invariant, we have

$$(U_J)^2\phi=cU_J\phi=c^2\phi\equiv\phi;$$

hence

$$c=\pm 1. \tag{5.52}$$

In fact, any physically acceptable function which is purely even or purely odd under coordinate inversion will be an eigenfunction of U_J with the eigenvalue $+1$ or -1 respectively.

Let the eigenfunction ψ of $\mathcal{H}$ be written as the sum of an even function and an odd function. Thus, let

$$\psi=\phi_e+\phi_0, \tag{5.53a}$$

where

$$\phi_e=(\psi+U_J\psi)/2,\ \phi_0=(\psi-U_J\psi)/2. \tag{5.53b}$$

If ψ is neither purely even nor purely odd under inversion, $U_J\psi$ would be independent of ψ and both would be degenerate eigenfunctions of $\mathcal{H}$. Any two independent linear combinations of ψ and $U_J\psi$, such as ϕ_e and ϕ_0, will then also be eigenfunctions of $\mathcal{H}$ with the same eigenvalue E. In the language of group theory, we see that ϕ_e and ϕ_0 are the symmetrized basis functions for the irreducible representations of the inversion group (E, J). It would obviously be convenient to work with the eigenfunctions ϕ_e and ϕ_0 rather than with ψ and $U_J\psi$, because the matrix element of $\mathcal{H}$ between ϕ_e and ϕ_0 would be zero.

We must extend the above result to include *all* the eigenfunctions of $\mathcal{H}$. Let $\{\psi_1, \psi_2, \ldots, \psi_n\}$ be the eigenfunctions of $\mathcal{H}$ defining a Hilbert space L_n where n may be finite or infinite. From the above discussion, it follows that every eigenfunction must be *either* (i) purely even or purely odd, *or* (ii) degenerate with another eigenfunction. In case of degeneracy we can choose two suitable linear combinations which are purely even or purely odd. Hence we can choose *all* the eigenfunctions of $\mathcal{H}$ to be purely even or purely odd under coordinate inversion, that is, which are simultaneous eigenfunctions of $\mathcal{H}$ and U_J.[10] We therefore see that

[10]This is in conformity with an important result in quantum mechanics that simultaneous eigenfunctions can be found for two commuting operators (or, in matrix algebra, simultaneous eigenvectors can be found for two commuting matrices).

each eigenfunction of the Hamiltonian, which has space inversion symmetry, has a definite *parity* which is *even* or *odd* depending on the action of U_J on the eigenfunction.

Except in the case of very simple systems, the exact solution of (5.1) is very difficult; that is, it is difficult to find the exact eigenfunctions of $\mathcal{H}$. However, in general, we can choose a set of n suitable basis functions ψ_i which form an invariant subspace of the infinite-dimensional Hilbert space of $\mathcal{H}$. These basis functions ψ_i are not necessarily the eigenfunctions of $\mathcal{H}$ and, therefore, we may write the operation of $\mathcal{H}$ on a function ψ_i as

$$\mathcal{H}\psi_i = \sum_{j=1}^{n} \psi_j \mathcal{H}_{ji}. \tag{5.54}$$

As in the discussion of Section 2.4.2, our aim now is to find the eigenfunctions of $\mathcal{H}$ as correctly as possible by constructing linear combinations of ψ_i's. If we are able to find all the n eigenfunctions χ_i of $\mathcal{H}$, then, as in (2.69), we have

$$\mathcal{H}\chi_i = E_i\chi_i. \tag{5.55}$$

But as we have just mentioned, it is difficult to obtain the exact eigenfunctions. We can still construct approximate 'zeroth order' eigenfunctions $\chi_i^{(0)}$ by taking suitable linear combinations of ψ_i's, such that in the equation

$$\mathcal{H}\chi_i^{(0)} = \sum_{j=1}^{n} \chi_j^{(0)} \mathcal{H}_{ji}, \tag{5.56}$$

the off-diagonal elements $\mathcal{H}_{ji}$ $(j \neq i)$ are much smaller than the diagonal elements $\mathcal{H}_{ii}$. When this has been achieved, we say that we have obtained the eigenfunctions and the eigenvalues of $\mathcal{H}$ to a certain order of approximation which depends on how small the off-diagonal elements are compared to the diagonal elements. To this order of approximation, we may write the above equation as

$$\mathcal{H}\chi_i^{(0)} = E_i^{(0)} \chi_i^{(0)}, \quad E_i^{(0)} = \mathcal{H}_{ii}. \tag{5.57}$$

Group theory is of great assistance in this process. Thus, in the example considered earlier in this subsection, a great deal of simplification would be obtained by using the invariance of $\mathcal{H}$ under inversion and by choosing the approximate eigenfunctions of $\mathcal{H}$ to be simultaneous eigenfunctions of U_J. Let these n basis functions be arranged in such a way that the first m are even and the remaining $n-m$ are odd. Then the matrix representing $\mathcal{H}$ with these basis functions will

appear in the block-diagonalized form

$$[\mathcal{H}_{ij}]=\begin{bmatrix} \overbrace{\quad\quad}^{m} & \overbrace{\quad\quad}^{n-m} \\ \vdots & \vdots \\ \cdots\cdots & \mathbf{O} \\ \vdots & \vdots \\ \mathbf{O} & \cdots\cdots \end{bmatrix} \begin{matrix} \\ \\ \}\, m \\ \\ \}\, n-m \end{matrix} \tag{5.58}$$

It should then be clear that by considering all the symmetry transformations of $\mathcal{H}$, we can further diagonalize the matrix for $\mathcal{H}$. Group theory tells us, as we shall see in Section 5.7, which elements of the $\mathcal{H}$-matrix ought to be zero on the grounds of symmetry, although it does not tell us anything about the nonvanishing elements.

It may be mentioned here that the expansion (5.54) in terms of the n basis functions ψ_i is itself an approximation. In principle, n should be infinite; but for practical reasons, we take it to be finite. We are usually interested only in the lowest few eigenvalues of $\mathcal{H}$ and these are not much affected if n is chosen to be sufficiently large and the corresponding n-dimensional subspace is chosen properly. The approximation of taking n to be finite is then a very good one.

5.6 Perturbation and Level Splitting

As is well-known in elementary quantum mechanics, only a few problems are exactly solvable. In the general case, a considerable simplification ensues if the Hamiltonian can be split into two parts such as

$$\mathcal{H}=\mathcal{H}_0+V, \tag{5.59}$$

where the first part $\mathcal{H}_0$ is simple so that its eigenvalues can be obtained relatively easily and the second part V has a small effect on the eigenvalues of $\mathcal{H}_0$.

Let G be the group of symmetry transformations of $\mathcal{H}_0$. In general, all the operations of G will not leave V invariant, or in other words, the group K of symmetry transformations of V will be smaller than G. We shall assume that the group K is a subgroup of G. The full Hamiltonian $\mathcal{H}$ remains invariant only under the symmetry transformations common to both $\mathcal{H}_0$ and V. This implies that K is also the symmetry group of $\mathcal{H}$.

By assumption, the eigenfunctions of $\mathcal{H}_0$ are known. As discussed before, these can be grouped into invariant subsets (according to their degeneracy) where each subset forms the basis for an irredu-

cible representation of G. Let us denote the eigenvalues of $\mathcal{H}_0$ by $E_\alpha^{(0)}$, which is l_α-fold degenerate so that there are l_α independent eigenfunctions $\{\psi_1, \psi_2, \ldots, \psi_{l\alpha}\}$, all having the same eigenvalue $E_\alpha^{(0)}$. These l_α eigenfunctions form a basis for an irreducible representation $\Gamma^{(\alpha)}$ of G. If we now imagine that the perturbation V is 'switched on', the group of symmetry of the system will be reduced to K. Since K is a subgroup of G, the functions $\{\psi_i\}$ will still generate an l_α-dimensional representation of K; but this representation will in general be a reducible one. We can then reduce this representation by the standard technique discussed in Chapter 3. Thus, we get new subsets from the set of functions $\{\psi_i\}$ such that a function in a subset mixes only with the functions of the same subset under the operations of the group K. These subsets must all belong to different eigenvalues (except in the case of accidental degeneracy) and hence the original energy level $E_\alpha^{(0)}$ 'splits' into a number of energy levels due to the lowering of symmetry.

We shall illustrate this by an example. Consider a simple two-dimensional square molecule or a crystal having a square lattice. The group of symmetry of the system is our group C_{4v}. Suppose the crystal is compressed along one of the edges of the square. The symmetry of the resulting system (a primitive rectangular lattice) is lower than that

TABLE 5.1 THE CHARACTER TABLE OF C_{2v} AND THE CHARACTERS OF THE ELEMENTS OF C_{2v} IN THE IRREDUCIBLE REPRESENTATIONS OF C_{4v}

		E	C_4^2	m_x	m_y
Character table of C_{2v}	D_1	1	1	1	1
	D_2	1	1	−1	−1
	D_3	1	−1	1	−1
	D_4	1	−1	−1	1
Characters of the elements of C_{2v} in the irreducible representations of C_{4v}	$\Gamma^{(1)}$	1	1	1	1
	$\Gamma^{(2)}$	1	1	−1	−1
	$\Gamma^{(3)}$	1	1	1	1
	$\Gamma^{(4)}$	1	1	−1	−1
	$\Gamma^{(5)}$	2	−2	0	0

of the square. In fact, the symmetry group of the compressed lattice is $K=\{E, C_4^2, m_x, m_y\}$ which is denoted by C_{2v} in crystallography. We shall see how the levels corresponding to the various irreducible representations of C_{4v} split on applying the perturbation.

The group C_{2v} has four elements and it is an abelian group. It has, therefore, four irreducible representations, all one-dimensional. In Table (5.1), we have shown the character table of C_{2v} and the characters for the elements of C_{2v} in the irreducible representations of the group C_{4v}.

Since the levels belonging to the irreducible representations $\Gamma^{(i)}$ of C_{4v} for $1\leq i\leq 4$ are nondegenerate, they cannot split further. On examining Table (5.1), we find that a basis function transforming according to $\Gamma^{(1)}$ or $\Gamma^{(3)}$ under C_{4v} will transform according to D_1 under the operations of C_{2v}. Similarly, a basis function transforming according to $\Gamma^{(2)}$ or $\Gamma^{(4)}$ under C_{4v} will transform according to D_2 under the operations of C_{2v}. Lastly, a level belonging to the irreducible representation $\Gamma^{(5)}$ of C_{4v} must be split on compressing the crystal as there is no two-dimensional irreducible representation of C_{2v}. Let the two degenerate functions ψ_1^5 and ψ_2^5 be the basis functions for $\Gamma^{(5)}$. These functions now generate a representation of C_{2v} whose characters are given in the last row of Table (5.1). By inspection of the characters, it can be easily seen that, as far as the group C_{4v} is concerned, we can symbolically write

$$\Gamma^{(5)}\rightarrow D_3\oplus D_4. \tag{5.60}$$

The basis functions for D_3 and D_4 are simply ψ_1^5 and ψ_2^5 respectively, as can be readily verified by operating on these functions by the elements of C_{2v}. Thus, any level belonging to $\Gamma^{(5)}$ in the molecule or lattice splits into two nondegenerate levels belonging to the irreducible representations D_3 and D_4 in a crystal having the symmetry group C_{2v}.

One of the most important and celebrated cases—the splitting of the electronic energy levels of an atom in a cubic crystal field—will be treated in Section 7.6.

5.7 The Matrix Element Theorem and Selection Rules

Let the Hamiltonian of a system be given by (5.59) and let us assume that, to begin with, the perturbation V has been switched off. Let ψ_{pm}^{α} denote the eigenfunctions of $\mathcal{H}_0$; these describe the stationary states of the unperturbed system. That is to say, if the system is in some

state $\psi_{pm}{}^{\alpha}$ at a given instant, it will continue to remain in the same state, provided there is no perturbation on the Hamiltonian $\mathcal{H}_0$. The application of a perturbation of lower symmetry not only splits the energy levels of the system as discussed in the previous section but also induces transitions of the system from one eigenstate of $\mathcal{H}_0$ to another. Thus, there is a nonvanishing probability that after some time the system may be found in some other eigenstate of $\mathcal{H}_0$. The group theoretical matrix element theorem allows us to predict which transitions are forbidden purely on the grounds of symmetry of the eigenfunctions and the perturbation. We shall now take up this study.

5.7.1 The matrix element theorem. Let $\psi_{pm}{}^{\alpha}$ and $\psi_{qn}{}^{\beta}$ be two eigenfunctions of $\mathcal{H}_0$, which are also among the basis functions generating the irreducible representations of the group of $\mathcal{H}_0$. Let the perturbation V be now applied to the system. We can use the eigenfunctions of $\mathcal{H}_0$ to generate a representation of the operator V. This is easily obtained by considering the operation of V on an eigenfunction, say $\psi_{pm}{}^{\alpha}$, and expanding the resulting function in a complete set of all eigenfunctions of $\mathcal{H}_0$. Thus,

$$V\psi_{pm}{}^{\alpha} = \sum_{\beta, q, n} \psi_{qn}{}^{\beta}\, c(\alpha, p, m; \beta, q, n), \tag{5.61}$$

where $c(\alpha, p, m; \beta, q, n)$ are scalars. These coefficients can be determined by taking the scalar product of $V\psi_{pm}{}^{\alpha}$ with some other eigenfunction and using the orthogonality between the eigenfunctions. This gives

$$c(\alpha, p, m; \beta, q, n) = (\psi_{qn}{}^{\beta},\ V\psi_{pm}{}^{\alpha}), \tag{5.62}$$

which is just the matrix element of the perturbation V between the basis states $\psi_{qn}{}^{\beta}$ and $\psi_{pm}{}^{\alpha}$. With these coefficients, (5.61) becomes

$$V\psi_{pm}{}^{\alpha} = \sum_{\beta, q, n} \psi_{qn}{}^{\beta}\, (\psi_{qn}{}^{\beta},\ V\psi_{pm}{}^{\alpha}). \tag{5.63}$$

The transition from the state $\psi_{pm}{}^{\alpha}$ to the state $\psi_{qn}{}^{\beta}$ under the perturbation V will be forbidden if the matrix element of V given in (5.62) vanishes.

It is seen from (5.63) that the function $V\psi_{pm}{}^{\alpha}$ is not a function of 'pure' symmetry, but is a linear combination of a number of basis functions. We therefore have the *matrix element theorem*: *If the function* $V\psi_{pm}{}^{\alpha}$ *does not contain a part transforming according to the n-th column of the irreducible representation* $\Gamma^{(\beta)}$, *the matrix element* (5.62) *must vanish* (*for all values of q*). This means then that in this case the transition between the states $\psi_{pm}{}^{\alpha}$ and $\psi_{qn}{}^{\beta}$ under the action of the perturbation V is forbidden.

We may use the function $V\psi_{pm}{}^{\alpha}$ itself to generate a representation of the symmetry group G of $\mathcal{H}_0$. Such a representation, say Γ, would in general be a reducible one, because $V\psi_{pm}{}^{\alpha}$ is *not* an eigenfunc-

tion of $\mathcal{H}_0$ (unless V commutes with $\mathcal{H}_0$).

The perturbation V itself is a function of the coordinates (or, it acts on the coordinates) and hence can be used to generate a representation, say Γ_V, of the group G. The function $V\psi_{pm}{}^{\alpha}$, considered as a product of the two functions V and $\psi_{pm}{}^{\alpha}$, therefore generates a representation which must be the direct product[11] of Γ_V and $\Gamma^{(\alpha)}$, i.e.,

$$\Gamma = \Gamma_V \otimes \Gamma^{(\alpha)} \equiv \sum_{\gamma} a_\gamma \Gamma^{(\gamma)}, \tag{5.64}$$

where we have expressed Γ as the direct sum of the irreducible representations of G. It is then clear that the matrix element (5.62) will vanish if the direct product $\Gamma_V \otimes \Gamma^{(\alpha)}$ does not contain the irreducible representation $\Gamma^{(\beta)}$.

Note that this is a weaker condition than the one stated earlier in the matrix element theorem. Thus, in order to determine whether a certain element such as (5.62) survives, we should first apply the weaker but simpler condition to find out whether $\Gamma_V \otimes \Gamma^{(\alpha)}$ contains $\Gamma^{(\beta)}$. If this gives a negative result, there is no need to apply the stricter condition. But if this gives a positive result, we must go further and find out whether $V\psi_{pm}{}^{\alpha}$ contains a part transforming according to the n-th column of $\Gamma^{(\beta)}$.

An equivalent condition can be obtained by taking the direct product of Γ with $\Gamma^{(\beta)*}$. The condition is that the matrix element of V between $\psi_{qn}{}^{\beta}$ and $\psi_{pm}{}^{\alpha}$ vanishes if the representation $\Gamma^{(\beta)*} \otimes \Gamma_V \otimes \Gamma^{(\alpha)}$ does not contain the identity representation of G.[12]

Thus we see that the symmetry of the system forbids certain transitions. Group theory, however, does not give any information about the matrix elements of V which do not vanish due to symmetry. It must be emphasized that such matrix elements may also vanish due to some other reasons or merely by accident.

5.7.2 Selection rules for electric dipole transitions. To illustrate the working of the matrix element theorem, we shall consider the selection rules for electric dipole transitions of an electron in a molecule with the symmetry group C_{4v}. Another example will be treated in the next chapter where we shall obtain the selection rules for electronic

[11] As a special case, we can see that $\mathcal{H}_0$ is invariant under all operations of G, so that it generates the identity representation of G. Hence $\mathcal{H}_0\psi_{pm}{}^{\alpha}$ has the same symmetry as $\psi_{pm}{}^{\alpha}$.

[12] Note that the equivalence of the two conditions is a consequence of the result of Problem (3.11).

transitions in isolated atoms. The electric dipole moment operator is $\underset{\sim}{\mu}=e\mathbf{r}$; it is a vector operator with components $e(x, y, z)$. This will be the operator V of the above theory and it can easily be seen that it generates the representation $\Gamma_V=\Gamma^{(1)}\oplus\Gamma^{(5)}$ of C_{4v} (the operator ez generates $\Gamma^{(1)}$ and the two components $e(x, y)$ generate $\Gamma^{(5)}$. Suppose we wish to find out whether the transition between two states belonging respectively to $\Gamma^{(1)}$ and $\Gamma^{(2)}$ is allowed or not; we then work out the direct product $\Gamma_V \otimes \Gamma^{(2)}=(\Gamma^{(1)} \oplus \Gamma^{(5)}) \otimes \Gamma^{(2)}=\Gamma^{(2)} \oplus \Gamma^{(5)}$, by using Table (3.4). Since this does not contain $\Gamma^{(1)}$, we conclude that the transition $\Gamma^{(1)}\leftrightarrow\Gamma^{(2)}$ under the influence of the electric dipole radiation is forbidden.

Working out the selection rules for all possible transitions in a similar fashion, we find that the allowed transitions for electromagnetic radiation polarized in the z direction (the component ez) are $\Gamma^{(i)}\leftrightarrow\Gamma^{(i)}$ for $1\leq i\leq 5$. The allowed transitions under electromagnetic radiation polarized in the (x,y)-plane (the components ex and ey) are $\Gamma^{(i)}\leftrightarrow\Gamma^{(5)}$ for $1\leq i\leq 4$. The remaining transitions are forbidden under the influence of the electric dipole moment operator; these are $\Gamma^{(1)}\leftrightarrow\Gamma^{(2)}$, $\Gamma^{(3)}$, $\Gamma^{(4)}$; $\Gamma^{(2)}\leftrightarrow\Gamma^{(3)}$, $\Gamma^{(4)}$ and $\Gamma^{(3)}\leftrightarrow\Gamma^{(4)}$.

Consider now the selection rules for the matrix elements of the electric dipole moment operator between two states of given symmetries. Applying the weaker condition on the direct product of the irreducible representations, we have seen above that the transitions $\Gamma^{(5)}\leftrightarrow\Gamma^{(4)}$ and $\Gamma^{(5)}\leftrightarrow\Gamma^{(5)}$ are allowed. But suppose we now wish to find out whether the transition from a state $\psi_{p_1}{}^5$ to a state $\psi_{q_2}{}^5$ or $\psi_{r_1}{}^4$ is allowed or not (the notation here is obvious). The matrix elements under consideration are $(\psi_{q_2}{}^5, \underset{\sim}{\mu}\psi_{p_1}{}^5)$ and $(\psi_{r_1}{}^4, \underset{\sim}{\mu}\psi_{p_1}{}^5)$. Now $\psi_{p_1}{}^5$ transforms according to the first column of $\Gamma^{(5)}$ like x and $\underset{\sim}{\mu}$ has three components which transform according to $\Gamma^{(1)}$ and the two columns of $\Gamma^{(5)}$. The product function $\underset{\sim}{\mu}\psi_{p_1}{}^5$ therefore has three parts which may be denoted by $x\psi_{p_1}{}^5$, $y\psi_{p_1}{}^5$ and $z\psi_{p_1}{}^5$. By operating with all the elements of C_{4v}, we then clearly see that the function $z\psi_{p_1}{}^5$ which is like zx transforms according to the first column of $\Gamma^{(5)}$, the function $y\psi^5{}_{p_1}$ like xy transforms according to $\Gamma^{(2)}$ (See Table 3.3) and $x\psi_{p_1}{}^5$ like x^2 is one of the two functions which generate the representation $\Gamma^{(1)} \oplus \Gamma^{(3)}$ (see Problem (3.17)). The function $\underset{\sim}{\mu}\psi_{p_1}{}^5$ thus does not contain any part transforming according to $\Gamma^{(4)}$ or to the second column of $\Gamma^{(5)}$. Both the matrix elements under consideration therefore must vanish and the corresponding transitions are forbidden. On the other hand, it should be obvious that a transition between, say, $\psi_{p_1}{}^5$ and $\psi_{q_1}{}^5$ is allowed because $\underset{\sim}{\mu}\psi_{p_1}{}^5$ contains a part transforming

according to the first column of $\Gamma^{(5)}$. This should make it clear that when the weaker test gives a positive result, the stronger test must further be applied to check whether the transition is really allowed.

The working out of the selection rules for magnetic dipole transitions is left to Problem 5.2. We may only mention that the magnetic dipole moment operator is an axial vector. Its x and y components therefore still generate $\Gamma^{(5)}$ but its[13] z component generates $\Gamma^{(4)}$.

5.8 Dynamical Symmetry

We have so far discussed symmetries of physical systems which may be termed *geometrical symmetries* (except the time translation symmetry) because they refer to the external geometrical structure of the system. These include rotations, reflections and inversion. In this section, we shall consider a different type of symmetry which is known as the internal symmetry and which relates to the particular form of the force law or the interaction between different parts of the system.

We have discussed earlier in this chapter the relation between symmetry and degeneracy and have learnt to expect some kind of symmetry or invariance associated with a physical system if the eigenvalue spectrum for its observables shows degeneracy. For example, the Hamiltonian of an electron in a hydrogen atom is invariant under all rotations so that the geometrical symmetry group is $O(3)$. Our discussion of the previous chapter tells us that the irreducible representations $D^{(l)}$ have dimensions $2l+1$ so that these would be the expected degeneracies of the energy levels of the electron. But we know that in fact all the levels with a given value of the principal quantum number n and all values of l between 0 and $n-1$ are degenerate. The actual degeneracy[14] is thus

$$\sum_{l=0}^{n-1} (2l+1) = n^2. \tag{5.65}$$

As we shall soon see, these degeneracies arise from the internal symmetry of the hydrogen atom.

The operators of the geometrical symmetry group are those under

[13] An axial vector has the same rotational properties as a polar vector but is invariant under inversion. A reflection can be thought of as a rotation through π about a line normal to the plane of reflection followed by inversion. The effect of m_x, m_y, σ_u and σ_v on the z component of an axial vector is therefore to multiply it by -1.

[14] We have neglected the spin degeneracy here.

which the potential energy of the particle remains invariant. However, there are other operations which involve simultaneous transformation of the coordinates and the momenta and which leave invariant the Hamiltonian as a whole. These are usually called dynamical symmetries. We shall consider two rather simple cases, the hydrogen atom and the isotropic harmonic oscillator, and see that their dynamical symmetry groups are $O(4)$ and $SU(3)$, respectively. The dynamical symmetry group of a system of course contains its geometrical symmetry group as a subgroup.

5.8.1 The hydrogen atom. An electron in a hydrogen-like atom with nuclear charge Ze experiences a potential energy given by

$$V(\mathbf{r}) = -Ze^2/r, \tag{5.66}$$

where e is the electronic charge and r is the distance of the electron form the nucleus. The potential energy, being spherically symmetric, is invariant under the geometrical symmetry group $O(3)$. The full Hamiltonian of an electron in a hydrogen-like atom is

$$\mathcal{H}(\mathbf{r}) = \frac{\mathbf{p}^2}{2\mu} - \frac{Ze^2}{r}. \tag{5.67}$$

In classical mechanics this is the familiar Kepler's problem and the classical orbit for a particle with the potential energy (5.66) is known to be an ellipse with the centre of attraction at one of the foci. It must be recognized that the mere spherical symmetry of the potential is not sufficient to make the orbit of a particle closed, though it is sufficient to make it lie in a plane. It is only when the potential is Coulombian that the orbit becomes a closed ellipse; see Fig. (5.5). In case of the Coulomb potential, therefore, we have an additional invariant such as the vector OA or OP. In quantum mechanics, it is known that the vector

$$\mathbf{M}' = \frac{1}{2\mu}(\mathbf{p} \times \mathbf{L} - \mathbf{L} \times \mathbf{p}) - \frac{Ze^2\mathbf{r}}{r}, \tag{5.68}$$

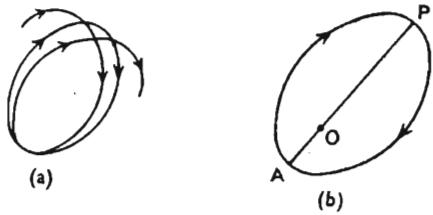


FIGURE 5.5 The orbit of a classical particle around a centre of force O with (a) an arbitrary spherically symmetric potential, and (b) a Coulombian potential of the form $V(r) \propto 1/r$

known as the *Runge-Lenz vector*, is a constant of motion. that is, it commutes with the Hamiltonian. Here, **L** is the orbital angular momentum operator which is normal to the plane of the orbit. From (5.68) we can easily see that

$$\mathbf{M}'\cdot\mathbf{L}=0, \tag{5.69}$$

so that $\mathbf{M}'$ is a vector in the plane of the orbit. The orbital angular momentum also commutes with the Hamiltonian and is a constant of motion. We thus have

$$[\mathbf{M}', \mathcal{H}]=0, \quad [\mathbf{L}, \mathcal{H}]=0. \tag{5.70}$$

Using the commutation relations between the components of **r** and **p**, we can show, after a somewhat lengthy calculation, that

$$\mathbf{M}'^2=\frac{2\mathcal{H}}{\mu}(\mathbf{L}^2+\hbar^2)+Z^2e^4. \tag{5.71}$$

We now have six operators (three components each of **L** and $\mathbf{M}'$) which correspond to the invariants of the problem at hand. We may use these operators to generate unitary transformations[15] (as in (4.19)) under which the Hamiltonian would be invariant because of (5.70). In accordance with the theory of continuous groups outlined in the previous chapter, we therefore work out the commutation relations between the components of **L** and $\mathbf{M}'$ with each other. There will be fifteen commutators which are given below in five equations, each standing for three equations obtainable from it by cyclic permutation of x, y and z.

$$[L_x, L_y]=i\hbar L_z, [M_x', L_x]=0, [M_x', L_y]=i\hbar M_z',$$
$$[M_x', L_z]=-i\hbar M_y', [M_x', M_y']=-\frac{2i\hbar}{\mu}\mathcal{H}L_z. \tag{5.72}$$

The components of **L** by themselves constitute a closed algebra and, as seen in the previous chapter, can be used to generate the Lie group $O(3)$. But, as Eqs. (5.72) show, the six operators **L** and $\mathbf{M}'$ do not form a closed algebra because of the appearance of a new operator, the Hamiltonian $\mathcal{H}$, in the commutator of the components of $\mathbf{M}'$. However, let us work with a particular bound state energy level ($E<0$) of the hydrogen atom and restrict ourselves to the invariant subspace (of the full space) which corresponds to the eigenvalue E. In this subspace, we can replace $\mathcal{H}$ by E, and define a new operator by[16]

$$\mathbf{M}=(-\mu/2E)^{\frac{1}{2}}\mathbf{M}'. \tag{5.73}$$

[15]This was first suggested by Pauli.

[16]The operator **M** acts only on the invariant subspace corresponding to the eigenvalue E.

In the first four commutators of (5.72), the components of **M** simply replace those of **M′**. The last commutator, however, takes the form

$$[M_x, M_y]=i\hbar L_z. \tag{5.74}$$

The algebra of the six operators **L** and **M** is then obviously a closed one. These can therefore be used to generate a six-parameter Lie group which will be the dynamical symmetry group of the hydrogen atom.

To show that this group is $O(4)$, we define six new operators by writing

$$J_{ij}=\sum_k \epsilon_{ijk} L_k, \text{ for } i,j,k=x,y,z; \tag{5.75a}$$

$$J_{iw}=-J_{wi}=M_i. \tag{5.75b}$$

Here, ϵ_{ijk} is the fully antisymmetric tensor of rank three. The commutation relations between these operators can be worked out and are found to be

$$\begin{aligned}&[J_{xy}, J_{yz}]=i\hbar J_{zx}, \ [J_{xw}, J_{yz}]=0,\\ &[J_{xw}, J_{zx}]=i\hbar J_{zw}, \ [J_{xw}, J_{yw}]=i\hbar J_{xy},\\ &[J_{xw}, J_{yx}]=i\hbar J_{yw},\end{aligned} \tag{5.76}$$

where, again, each equation stands for three equations obtained from it by cyclic permutation of x, y and z. The six operators $J_{\rho\sigma}$ ($\rho, \sigma=x, y, z, w$) are the infinitesimal generators of a group whose operations leave the quadratic form $x^2+y^2+z^2+w^2$ invariant, i.e., the group of all real orthogonal transformations in a four-dimensional vector space, or $O(4)$. We have one operator for generating rotations in each of the six coordinate planes.

It is particularly convenient to construct the following linear combinations of **L** and **M**:

$$\mathbf{A}=\tfrac{1}{2}(\mathbf{L}+\mathbf{M}), \ \mathbf{B}=\tfrac{1}{2}(\mathbf{L}-\mathbf{M}), \tag{5.77}$$

so that the commutation relations between the components of **A** and **B** are

$$\begin{aligned}&\mathbf{A}\times\mathbf{A}=i\hbar\,\mathbf{A}, \ \mathbf{B}\times\mathbf{B}=i\hbar\,\mathbf{B},\\ &[A_i, B_j]=0 \text{ for } i,j=x,y,z.\end{aligned} \tag{5.78}$$

Moreover, since **L** and **M** both commute with $\mathcal{H}$, it follows that **A** and **B** also do. The above equations then show that the Lie algebras of **A** and **B** are separately closed, so that each of them can be used to generate the $SU(2)$ group. This tells us that $O(4)$ is homomorphic to $SU(2)\otimes SU(2)$.

The rank of $O(4)$ is seen from (5.72) to be 2; we may choose the two commuting generators to be any one component of **A** and any one

component of **B**. There are therefore two Casimir operators which commute with all the six generators. These are obviously $\mathbf{A}^2$ and $\mathbf{B}^2$ or any two independent linear combinations of these. Their eigenvalues, in analogy with the theory of $SU(2)$, may be written as

$$\mathbf{A}^2=a(a+1)\,\hbar^2,\quad \mathbf{B}^2=b\,(b+1)\,\hbar^2, \tag{5.79}$$

where a and b take all nonnegative integral or half-odd-integral values. Taking the sum and the difference of $\mathbf{A}^2$ and $\mathbf{B}^2$, we find that

$$C\equiv\mathbf{A}^2+\mathbf{B}^2=\tfrac{1}{2}\,(\mathbf{L}^2+\mathbf{M}^2),\quad C'\equiv\mathbf{A}^2-\mathbf{B}^2=\mathbf{L}\cdot\mathbf{M}. \tag{5.80}$$

Using (5.69) and (5.73), the second of the above equations shows that $C'=0$, so that our physical system (the hydrogen atom) corresponds only to that part of $O(4)$ for which $\mathbf{A}^2=\mathbf{B}^2$ or $a(a+1)=b(b+1)$. This gives the two solutions $a=b$ and $a=-(b+1)$; the second solution must, however, be discarded since a and b are restricted to nonnegative values. This tells us that only those representations of $O(4)$ represent the states of the hydrogen atom for which $a=b$, i.e., representations of the form (a, a).

The eigenvalues of the Casimir operator C then become

$$C=2a(a+1)\,\hbar^2. \tag{5.81}$$

Using Eqs. (5.71), (5.73) and (5.80), we then have that

$$\begin{aligned} C&=\tfrac{1}{2}\left[\mathbf{L}^2-\frac{\mu}{2E}\left\{\frac{2E}{\mu}(\mathbf{L}^2+\hbar^2)+Z^2e^4\right\}\right]\\ &=-\tfrac{1}{2}\left[\hbar^2+\frac{\mu Z^2e^4}{2E}\right]. \end{aligned} \tag{5.82}$$

Using (5.81) in the above equation, this finally gives

$$E=-\frac{\mu Z^2e^4}{2\hbar^2(2a+1)^2}. \tag{5.83}$$

If we make the identification $n=2a+1$, so that n takes all positive integral values, (5.83) agrees with the more familiar quantum mechanical result for the energy levels of an electron in a hydrogen atom. Since the dimension of the irreducible representation (a, a) of $O(4)$ is $(2a+1)^2=n^2$, this also explains the n^2-fold degeneracy of the levels.

We have remarked earlier in this chapter in Section 5.4.1 that the degeneracies of the eigenvalue spectrum of a physical system are related to the dimensions of the irreducible representations of its symmetry group. We have also mentioned that if the eigenfunctions belonging to different irreducible representations of a group are always degenerate, we may conclude that we have overlooked some symmetry of the system and the symmetry group must be larger than the one that has been found. The present case provides an excellent example of this situation.

On the basis of the group $O(3)$, the expected degeneracies were only $2l+1$. But we find in actual practice that all the levels of an electron with different values of l, but with same n, are always degenerate, i.e., for each value of n, the levels with all allowed values of l are degenerate. This fact itself would suggest that the symmetry group of the hydrogen atom is larger than $O(3)$. We have now found that the Hamiltonian of the hydrogen atom is invariant under $O(4)$ and we then get the correct degeneracies for the energy levels.

5.8.2 The isotropic harmonic oscillator. It is known that the energy levels of a three-dimensional isotropic harmonic oscillator are highly degenerate and the degeneracy of each level is larger than that required by the geometric symmetry group $O(3)$. Once again, we shall see that this is due to the fact that the dynamical symmetry group of a three-dimensional isotropic harmonic oscillator is $SU(3)$.

The Hamiltonian of an isotropic harmonic oscillator is

$$\begin{aligned}\mathcal{H} &= \frac{\mathbf{p}^2}{2\mu} + \frac{k\mathbf{r}^2}{2} \\ &= \frac{1}{2\mu} \sum_{j=1}^{3} (p_j^2 + \mu^2\omega^2 r_j^2),\end{aligned} \tag{5.84}$$

where $\omega^2 = k/\mu$ and p_j and r_j are the cartesian components of $\mathbf{p}$ and $\mathbf{r}$ respectively. We shall work with the raising and lowering operators for the eigenvalues of $\mathcal{H}$ defined by

$$\begin{aligned}a_j &= \frac{1}{(2\mu\hbar\omega)^{\frac{1}{2}}}(p_j - i\omega\mu r_j), \\ a_j^\dagger &= \frac{1}{(2\mu\hbar\omega)^{\frac{1}{2}}}(p_j + i\omega\mu r_j).\end{aligned} \tag{5.85}$$

Using the commutation relations between p_i and r_j, the commutation relations between a_i and $a_j^\dagger$ can be found to be

$$\begin{aligned}[a_i, a_j^\dagger] &= \delta_{ij}, \\ [a_i, a_j] &= [a_i^\dagger, a_j^\dagger] = 0.\end{aligned} \tag{5.86}$$

Inverting the transformation (5.85) and substituting in (5.84), the Hamiltonian becomes

$$\mathcal{H} = \hbar\omega \sum_j (a_j^\dagger a_j + \tfrac{1}{2}) = \frac{\hbar\omega}{2} \sum_j \{a_j^\dagger, a_j\}, \tag{5.87}$$

where $\{A, B\} = AB + BA$ denotes the anticommutator of A and B.

The commutators of the raising and the lowering operators with the Hamiltonian turn out to be

$$[\mathcal{H}, a_i^\dagger]=\hbar\omega a_i^\dagger, [\mathcal{H}, a_i]=-\hbar\omega a_i. \tag{5.88}$$

The *occupation number operator* $a_i^\dagger a_i$ has eigenvalues n_i, where n_i can take any nonnegative integral value. The eigenvalues of the Hamiltonian (5.87) are therefore

$$E_n=\left(n+\frac{3}{2}\right)\hbar\omega, \tag{5.89}$$

where

$$n=n_1+n_2+n_3;\ n_1, n_2, n_3=0, 1, 2, \ldots. \tag{5.90}$$

The degeneracy of the level E_n is then easily seen to be[17] $(n+1)(n+2)/2$. The angular momentum operator can be worked out by using the inverse transformation of (5.85) and is found to be

$$L_j=(\mathbf{r}\times\mathbf{p})_j=\frac{i\hbar}{2}\sum_{k,l=1}^{3}\epsilon_{jkl}\,(a_k a_l^\dagger-a_k^\dagger a_l). \tag{5.91}$$

We can further show that operators of the form $a_i^\dagger a_j$ commute with the Hamiltonian. The operator $a_i^\dagger a_j$ has the effect of transferring a quantum from the j-direction to the i-direction and hence leaves the total number of quanta unchanged. There are nine such operators and it can be shown that they generate the algebra of $U(3)$. We see from (5.87) that the operator for the total quantum number is given by

$$\sum_{i=1}^{3} a_i^\dagger a_i=\frac{\mathcal{H}}{\hbar\omega}-\frac{3}{2}, \tag{5.92}$$

and hence it commutes with all the operators $a_i^\dagger a_j$. Eight other independent linear combinations of the operators $a_i^\dagger a_j$ can be constructed which generate the algebra of $SU(3)$. These are

$$\begin{aligned}
&\lambda_1=a_1^\dagger a_2+a_2^\dagger a_1, && \lambda_2=-i(a_1^\dagger a_2-a_2^\dagger a_1),\\
&\lambda_3=a_1^\dagger a_1-a_2^\dagger a_2, && \lambda_4=a_1^\dagger a_3+a_3^\dagger a_1,\\
&\lambda_5=-i(a_1^\dagger a_3-a_3^\dagger a_1), && \lambda_6=a_2^\dagger a_3+a_3^\dagger a_2,\\
&\lambda_7=-i(a_2^\dagger a_3-a_3^\dagger a_2), && \lambda_8=\frac{1}{\sqrt{3}}(a_1^\dagger a_1+a_2^\dagger a_2-2a_3^\dagger a_3)
\end{aligned} \tag{5.93}$$

It is left as an exercise to show that they satisfy the commutation relations (4.106). The dynamical symmetry group of a three-dimensional isotropic harmonic oscillator[18] is therefore $SU(3)$.

[17] This is the total number of distinct ways in which a positive integer can be split into the sum of three nonnegative integers.

[18] The dynamical symmetry group of an n-dimensional isotropic harmonic oscillator is $SU(n)$.

5.9 Time Reversal and Space Inversion Symmetries

In this chapter, we have so far considered some of the important continuous groups such as the groups of space and time translations and of generalized rotations in an n-dimensional (real or complex) vector space. In the present section, we shall consider two more symmetries which many physical systems possess. They are the time-reversal symmetry and the space inversion symmetry.[19] These symmetries have some very interesting consequences.

5.9.1 Time-reversal symmetry. Many physical systems contain an invariance under the reversal of the direction of propagation of time. This is true of classical systems as well as quantum mechanical systems. Thus, in classical mechanics, a system which has only conservative (velocity-independent) forces is invariant under the operation of time-reversal. Since the force is mass times acceleration and the acceleration is the second derivative of the position vector with respect to time, the force is unchanged if t is replaced by $-t$. However, if a particle is moving in a medium with friction or viscosity, the medium exerts on the particle velocity-dependent forces; if these involve an odd power of velocity, the motion of the particle is not invariant under time-reversal.

In a system with time-reversal symmetry, the path of a particle remains the same after time-reversal but the direction of propagation of the particle is reversed. The velocity itself, being the first derivative of the position vector with respect to time, is reversed. For example,

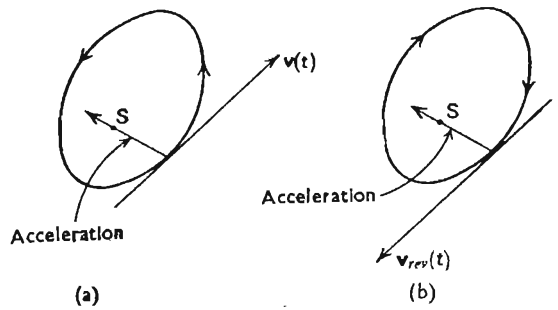


FIGURE 5.6 The path of a planet around the sun S. The velocity of the planet after time-reversal in (b) is given by $\mathbf{v}_{rev}(t) = -\mathbf{v}(t)$, where $\mathbf{v}(t)$ is its velocity before time-reversal in (a). The acceleration is invariant under time-reversal

[19] Some authors also call this space reflection symmetry.

in the classical Kepler problem of the motion of a planet around the sun, the orbit of the planet would remain the same if the direction of propagation of time were reversed, but the direction of motion of the planet will be reversed (see Fig. 5.6). This is also true of a charged particle in an electric field since the force on the charged particle due to the field is $q\mathbf{E}$ (where q is the charge and $\mathbf{E}$ the electric field) which is independent of the velocity of the particle (see Fig. 5.7). In a magnetic field, however, the motion of a charged particle is not time-reversal invariant. This is because the magnetic field exerts a force proportional to $\mathbf{v} \times \mathbf{H}$ (where $\mathbf{v}$ is the velocity and $\mathbf{H}$ is the magnetic field) which involves the first power of velocity (see Fig. 5.8).

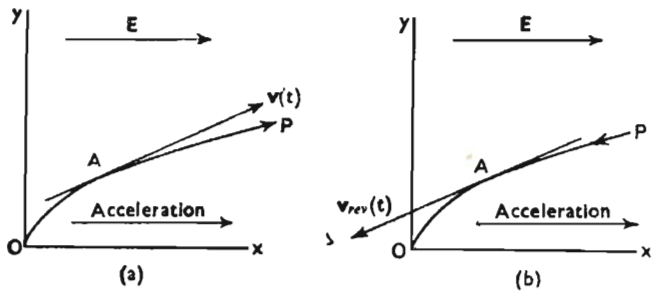


FIGURE 5.7 (1) The path OAP of a charged particle in an electric field $\mathbf{E}$ which is along the x axis and the particle has a constant velocity component along the y axis. (b) The particle traverses back its path along PAO when the time reversal is applied at the point P.

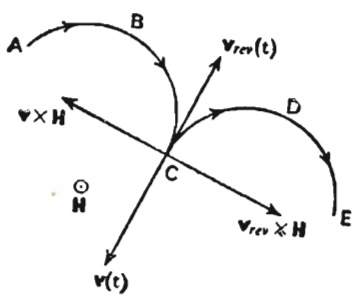


FIGURE 5.8 A charged particle executes a circular path ABC in a magnetic field $\mathbf{H}$ (normal to the plane, denoted by ⊙). When time-reversal is applied at C, the instantaneous velocity is reversed, reversing the direction of the force $\mathbf{v} \times \mathbf{H}$. The particle does not retrace its path and the system is not invariant under time-reversal.

5.9.2 Time-reversal operator for spinless particles. Consider a particle in a static potential $V(\mathbf{r})$. Its classical Hamiltonian is

$$\mathcal{H}(\mathbf{p}, \mathbf{r}) \equiv \frac{\mathbf{p}^2}{2m} + V(\mathbf{r}) = \mathcal{H}(-\mathbf{p}, \mathbf{r}). \tag{5.94}$$

Since it depends quadratically on the momentum, and hence on velocity, it is invariant under time-reversal. It is then clear that if $\mathbf{r} \equiv \mathbf{r}(t)$ is a solution of the equation of motion, $\mathbf{r}_{rev}(t) \equiv \mathbf{r}(-t)$ is also a solution of the equation. The position of the particle at time t in one solution is the same as its position at time $-t$ in the time-reversed solution. The velocity and the momentum of the particle in one solution are opposite to those in the time-reversed solution.

We are thus led to define a transformation of the dynamical variables under which $\mathbf{r}$ and $\mathbf{p}$ go respectively to $\mathbf{r}$ and $-\mathbf{p}$. This transformation, called the *time-reversal*, will be denoted by T and it has the following properties:

$$T\mathbf{r}T^\dagger = \mathbf{r}, \quad T\mathbf{p}T^\dagger = -\mathbf{p}. \tag{5.95}$$

Consider now a quantum mechanical system described by the time-dependent Schroedinger equation

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \left\{-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})\right\}\psi(\mathbf{r}, t). \tag{5.96}$$

Replacing t by $-t$ and taking the complex conjugate of both sides of the above equation, we have

$$i\hbar \frac{\partial}{\partial t}\psi^*(\mathbf{r}, -t) = \left\{-\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r})\right\}\psi^*(\mathbf{r}, -t). \tag{5.97}$$

This shows that $\psi^*(\mathbf{r}, -t)$ is also a solution of the Schroedinger equation if $\psi(\mathbf{r}, t)$ is. The state $\psi^*(\mathbf{r}, t)$ thus develops in the $+t$ direction exactly as the state $\psi(\mathbf{r}, t)$ develops in the $-t$ direction.

For spinless particles, we thus see that the complex conjugation operator, which we shall denote by K, has the effect of reversing the direction of propagation of time. This can also be seen from the fact that in the usual representation of wave mechanics, the matrices for $\mathbf{r}$ and $\mathbf{p}$ are respectively real and purely imaginary, so that the complex conjugation operator K has the following effect on $\mathbf{r}$ and $\mathbf{p}$:

$$K\mathbf{r}K^\dagger = \mathbf{r}, \quad K\mathbf{p}K^\dagger = -\mathbf{p}. \tag{5.98}$$

For spinless particles, therefore, the time-reversal operator is just the complex conjugation operator apart from a phase factor. If we choose the phase factor to be unity, we have

$$T = K. \tag{5.99}$$

The operation of T on a wave function gives its complex conjugate; thus,

$$T\psi(\mathbf{r}) = \psi^*(\mathbf{r}). \tag{5.100}$$

The invariance of the Hamiltonian under the transformation $\mathbf{p} \to -\mathbf{p}$ is then equivalent to saying that it commutes with T, i.e.,

$$[T, \mathcal{H}] = 0. \tag{5.101}$$

Remembering that $\mathbf{p} = -i\hbar\nabla$, we see that (5.101) will hold if $\mathcal{H}$ does not contain any odd powers of $\mathbf{p}$, i.e., if $\mathcal{H}$ is real, as is the case for stationary physical systems.

The time-reversal operator is clearly not a linear operator. It is, in fact, an antiunitary operator (which is the combination of an antilinear and a unitary operator). Thus, an operator T acting on a vector space L is said to be antiunitary if for every $\psi, \phi \in L$,

$$(T\phi, T\psi) = (\psi, \phi) = (\phi, \psi)^*, \tag{5.102a}$$

$$T(a\phi + b\psi) = a^* T\phi + b^* T\psi, \tag{5.102b}$$

where a and b are scalars. The complex conjugation operator K is also an antiunitary operator.

5.9.3 Time-reversal operator for particles with spin. If we desire to extend the concept of time-reversal to the most general case of particles having angular momenta, we would require the transformation properties of angular momentum under the time-reversal operator. From (5.95) we see that the orbital angular momentum transforms according to

$$T(\mathbf{r} \times \mathbf{p})\, T^\dagger = -(\mathbf{r} \times \mathbf{p}), \tag{5.103}$$

i.e., the orbital angular momentum anticommutes with the time-reversal operator. Since the spin is an angular momentum, we expect that it will also anticommute with T; thus if $\mathbf{s}$ and $\mathbf{j}$ are the spin angular momentum and the total angular momentum operators respectively, we have

$$T\mathbf{s}T^\dagger = -\mathbf{s}, \quad T\mathbf{j}T^\dagger = -\mathbf{j}. \tag{5.104}$$

In the standard $(\mathbf{r}, s_z)$ representation in which the z component of the angular momentum operator is taken to be diagonal, the matrices representing s_x and s_z are real whereas the matrix representing s_y is purely imaginary.[20] Under the action of the complex conjugation operator, we therefore have

$$Ks_xK^\dagger = s_x, \quad Ks_yK^\dagger = -s_y, Ks_zK^\dagger = s_z. \tag{5.105}$$

For a particle with spin, we therefore write

$$T = UK, \tag{5.106}$$

[20] Schiff (1968), p. 203.

so that, since K^2 equals the identity, we have

$$TK=U, \tag{5.107}$$

where U is to be determined. Since T and K are both antiunitary operators, their product U must be a unitary operator. Referring to Eqs. (5.95), (5.98), (5.104) and (5.105), we find that the effect of the unitary transformation U is given by

$$U\mathbf{r}\,U^\dagger=\mathbf{r},\ U\mathbf{p}\,U^\dagger=\mathbf{p},$$

$$Us_x\,U^\dagger=-s_x,\ Us_y\,U^\dagger=s_y,\ Us_z\,U^\dagger=-s_z. \tag{5.108}$$

Since U commutes with both $\mathbf{r}$ and $\mathbf{p}$, U has an effect only on the spin variables of the particle. The last three equations of (5.108) in fact show that U corresponds to *a rotation through π about the y axis in the spin space of the particle.* The operator for such a rotation can be written in accordance with (4.46) as

$$U=\exp(-i\pi s_y/\hbar), \tag{5.109}$$

giving

$$T=\exp(-i\pi s_y/\hbar)\,K. \tag{5.110}$$

In the particular case of a spin-$\frac{1}{2}$ particle, $s_y=\frac{1}{2}\hbar\sigma_y$ and it follows from (4.29) that

$$\exp(-i\pi\sigma_y/2)=-i\sigma_y, \tag{5.111}$$

so that

$$T=-i\sigma_y\,K. \tag{5.112}$$

The above result can be easily extended to a system of n particles having arbitrary spin angular momenta. If $\mathbf{s}_l$ denotes the spin angular momentum operator for the l-th particle, then we may write T as the product of the U's for each particle and K. Thus,

$$T=\exp(-i\pi s_{1y}/\hbar)\ldots\exp(-i\pi s_{ny}/\hbar)\,K, \tag{5.113}$$

where s_{ly} is the y component of $\mathbf{s}_l$. Since each s_{ly} is purely imaginary, each exponent in (5.113) is real and hence commutes with K. Moreover, the s_{ly}'s also commute with each other, for the operator s_{ly} acts on the spin variables of the l-th particle only. The order of the factors in (5.113) is thus immaterial.

5.9.4 Kramers' theorem. Taking the square of the operator in (5.113), we get

$$T^2=\exp(-2i\pi s_{1y}/\hbar)\ldots\exp(-2i\pi s_{ny}/\hbar). \tag{5.114}$$

Each factor on the right-hand side of the above equation denotes a rotation through 2π. The l-th factor will be equal to $+1$ or -1 according as the spin of the l-th particle is an integral or a half-odd-

integral multiple of $\hbar$. T^2 is thus equal to $+1$ or -1 depending on whether the number of half-odd-integral spin particles in the system is even or odd.

As discussed earlier in this subsection, if ψ is an eigenfunction of the system (which has time-reversal symmetry), then $T\psi$ is also an eigenfunction. Assuming that ψ is a nondegenerate eigenfunction, we see that $T\psi$ must be a multiple of ψ, say,

$$T\psi = c\psi. \tag{5.115}$$

Operating once again by T, we have

$$T^2\psi = T[c\psi] = c^* T\psi = c^* c\psi. \tag{5.116}$$

Thus, if $T^2=+1$, then $|c|^2=1$ and c is just a phase factor. But if $T^2=-1$, there is no number c for which $|c|^2=-1$, so that the eigenfunction $T\psi$ must be linearly independent of ψ. Since both ψ and $T\psi$ have the same eigenvalue, we have at least twofold degeneracy. Since ψ and $T\psi$ are independent eigenvectors, and since $T^2\psi=-\psi$ is a multiple of the original eigenvector ψ, the net degeneracy of the level must be even. We therefore have the *Kramers' theorem* which states that *every energy level of a system with an odd number of electrons in the presence of any electric field but no magnetic field is evenfold degenerate*. This is known as *Kramers' degeneracy*.

We can further show that when $T^2=-1$, ψ and $T\psi$ are orthogonal. For this, we replace ϕ by $T\psi$ in (5.102a) to get

$$(T^2\psi,\ T\psi) = (\psi,\ T\psi),$$

or

$$-(\psi,\ T\psi) = (\psi,\ T\psi),$$

since $T^2=-1$. This shows that $(\psi, T\psi)=0$, so that ψ and $T\psi$ are orthogonal.

It must be emphasized that Kramers' degeneracy is removed by the application of an *external* magnetic field. This introduces terms like $\mathbf{v}\times\mathbf{H}$, $\mathbf{L}\cdot\mathbf{H}$ or $\mathbf{s}\cdot\mathbf{H}$ in the Hamiltonian, and these are not invariant under time-reversal. An external magnetic field thus destroys the time-reversal symmetry.

One is likely to ask the question: What is the effect of the *internal* magnetic fields? A system containing moving charged particles always has internal magnetic fields. Do they destroy the time-reversal symmetry of the system? The answer is *no*. The reason is that when the time-reversal is applied on such a system, the velocities of all the charged particles are reversed, reversing the currents and therefore the directions of the internal magnetic fields. This leaves the terms such as $\mathbf{v}\times\mathbf{H}$, $\mathbf{L}\cdot\mathbf{H}$ or $\mathbf{s}\cdot\mathbf{H}$ (where $\mathbf{H}$ is now the internal magnetic field) invariant under time-reversal. Thus the internal magnetic fields need not bother

us while considering the time-reversal symmetry.[21] It is for this reason that interaction terms such as spin-orbit and spin-spin interactions do not destroy the time-reversal symmetry of the Hamiltonian.

5.9.5 Space inversion symmetry. The operator of space inversion has the effect of reversing the position coordinates of all the particles of the system under consideration and has no effect on the angular momentum variables of the particles. We have already introduced this operator earlier in Section 5.5.2 where we denoted it by J. We have seen there that if the Hamiltonian of a system has inversion symmetry, the eigenfunctions can be chosen to be purely even or purely odd; in other words, the eigenfunctions have a definite *parity*.

Let $\psi(\mathbf{r})$ be an arbitrary function and $\psi'(\mathbf{r})$ the function obtained after applying the space inversion. Then

$$\psi'(J\mathbf{r})=w\psi(\mathbf{r}), \tag{5.117}$$

where w is a number to be discussed soon. The fact that the number w appears in (5.117) but not in (5.22) or (5.30) is a consequence of the discrete nature of the transformation of space inversion. We also have

$$U_J\psi(\mathbf{r})=\psi'(\mathbf{r})=w\psi(-\mathbf{r}), \tag{5.118}$$

where we have used (5.117) in the last step and U_J is the operator defined in Section 5.5.2. One more application of U_J on (5.118) gives

$$U_J{}^2\psi(\mathbf{r})=wU_J\psi(-\mathbf{r})=w^2\psi(\mathbf{r}). \tag{5.119}$$

Two inversions restore the original coordinate system, so that the norm of the function $\psi(\mathbf{r})$ cannot change on the application of $U_J{}^2$; it may at most be multiplied by a phase factor of unit magnitude. Thus w^2, and hence w, must be a complex number of unit magnitude. We shall now show that $w^2=+1$ or -1 according as the spin of the system is integral or half-odd-integral.

Suppose that G is the symmetry group of the system (excluding the space inversion symmetry) and that $\psi(\mathbf{r})$ is one of the basis functions for generating a certain representation of G. If the net spin of the system is integral, the representations of G are single-valued and the identity element E is represented only by the unit matrix. Therefore, $U_J{}^2\psi(\mathbf{r})=E\psi(\mathbf{r})=\psi(\mathbf{r})$ and it follows from (5.119) that $w^2=1$ or $w=\pm1$. However, if the net spin of the system is half-odd-integral, the group G also admits double-valued representations. The identity element in this case corresponds to two matrices, the unit matrix and the negative

[21] Whether a magnetic field is to be treated as *internal* or *external*, of course, simply depends on how we define our physical system.

unit matrix. We therefore have $U_J^2\psi(\mathbf{r})=E\psi(\mathbf{r})=\pm\psi(\mathbf{r})$, so that $w^2=\pm 1$ and $w=1,-1,i$, or $-i$.

We expect each kind of particle to have a definite value of w. We note that all the results of physical significance such as selection rules, etc., are unaffected by the choice of w because all the physically observable quantities contain products like $\psi_i^*\psi_j$ (where ψ_i and ψ_j are different states of the particle), which have a factor $w^*w=1$.

If a function remains invariant under space inversion ($w=+1$), it is said to be of *even parity* and a particle represented by such a function is called a *scalar* particle. On the contrary, if a function changes sign under space inversion ($w=-1$), it is said to be of *odd parity* and the particle represented by it is said to be a *pseudoscalar* particle. As per the current convention, the nucleons are assigned even parity while the pions are assigned odd parity.

PROBLEMS ON CHAPTER 5

(5.1) What are the generators of the group of space displacements and of the group of time displacements?

(5.2) Find the selection rules for the magnetic dipole transitions if the symmetry group is C_{4v}.

(5.3) Find the selection rules for the electric and the magnetic dipole transitions if the symmetry group is C_{3v}.

(5.4) (a) Prove the commutation relations (5.88).

(b) Show that $a_i\dagger\, a_j$ commutes with the Hamiltonian (5.87).

(5.5) Show that the operators in (5.93) satisfy the commutation rules (4.106) of $SU(3)$ with the same constants as given in (4.107)

(5.6) Show that the dynamical symmetry group of a two-dimensional isotropic harmonic oscillator is $SU(2)$.

(5.7) Let $G=(R, S, T,\ldots)$ be the group of transformations which leave a physical system invariant. Let P_R, P_S, etc., be the corresponding operators which act on functions and leave the Hamiltonian of the system invariant. Show that the operators P_R, P_S, etc., also constitute a group which is isomorphic to the group G. [Hint: Using (5.21), show that if P_R corresponds to R and P_S to S, then $P_R P_S$ corresponds to RS.]

Bibliography for Chapter 5

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CHAPTER 6

Group Theory in Quantum Mechanics. II

The symmetry properties of atoms play a very important role in the study of their structures. Since in atoms, we have to deal with a number of identical particles, the electrons, one of the obvious symmetry elements is the permutation symmetry. The same is true of nuclei where we have a system containing a number of identical nucleons. It is well known that this has led to the postulate of Heisenberg and Dirac that the wave functions of a system of identical fermions must be antisymmetric under the interchange of two identical particles, enabling us to express the wave functions in the form of Slater determinants. In addition to the permutation symmetry, atoms also possess rotational invariances; they are invariant under all operations of the group $SO(3)$ in the single-particle model. Although many atomic problems can be solved without its aid, group theory becomes almost inevitable when the system contains a large number of atoms, such as in molecules and crystals. Even in atomic physics, group theoretical methods provide a touch of elegance and generality and the various results can be better understood in the light of the group theoretical interpretation.

In this chapter, we shall study mainly three topics—symmetries of atomic systems, the problem of addition of two angular momenta and irreducible tensor operators.

6.1 Atomic Symmetries

We shall consider in this section the important atomic symmetry groups, which as we have mentioned, are the three-dimensional rotation-inversion group and the symmetric group. We shall work in the *single-particle model* assuming that each electron in the atom moves in the average potential of the nucleus and the rest of the electrons. The potential is then spherically symmetric so that the Hamiltonian of an electron in an atom is invariant under the rotation-inversion group.

6.1.1 The rotation-inversion group. We have already discussed in Chapter 4 the three-dimensional rotation group $SO(3)$ and the rotation-inversion group $O(3)$. In this subsection, we shall consider the irreducible representations of $O(3)$. We have seen that

$$O(3)=SO(3) \otimes (E, J), \tag{6.1}$$

where J is the inversion operator. Let us denote the two irreducible representations of the group (E, J) by $\Gamma^{(+)}$ and $\Gamma^{(-)}$, where

$$\Gamma^{(+)}(X)=+1, \; X=E \text{ or } J;$$
$$\Gamma^{(-)}(E)=+1, \; \Gamma^{(-)}(J)=-1. \tag{6.2}$$

$\Gamma^{(+)}$ is clearly the identity representation of the group (E, J). The irreducible representations of $O(3)$ are then the direct products of the irreducible representations of $SO(3)$ with those of (E, J). If we denote the irreducible representations of $O(3)$ by $D^{(l,\sigma)}$, then

$$D^{(l,\sigma)}=D^{(l)} \otimes \Gamma^{(\sigma)}, \tag{6.3}$$

where σ stands for $+$ or $-$. Since $\Gamma^{(\sigma)}$ are one-dimensional representations, the dimension of $D^{(l,\sigma)}$ is the same as that of $D^{(l)}$, i.e., $2l+1$. The group $O(3)$ thus has *two distinct irreducible representations of every odd order.*

To obtain the actual matrices of the irreducible representation $D^{(l,\sigma)}$, we note that the elements of $O(3)$ can be divided into two categories, $\{X\}$ and $\{JX\}$, where X runs over the group $SO(3)$. The matrices of $D^{(l,\sigma)}$ are therefore given by

$$D^{(l,\sigma)}(EX)=D^{(l)}(X) \otimes \Gamma^{(\sigma)}(E)=D^{(l)}(X), \tag{6.4a}$$
$$D^{(l,\sigma)}(JX)=D^{(l)}(X) \otimes \Gamma^{(\sigma)}(J), \tag{6.4b}$$

so that

$$D^{(l,+)}(JX)=D^{(l)}(X), \quad D^{(l,-)}(JX)=-D^{(l)}(X), \tag{6.4c}$$

for all $X \in SO(3)$. The classes of $O(3)$ are quite simply related to those of $SO(3)$. In fact, each class $\{R_u(\alpha)\}$ of $SO(3)$ gives two classes of $O(3)-\{ER_u(\alpha)\}$ and $\{JR_u(\alpha)\}$. The character of a class in the

irreducible representation $D^{(l,\sigma)}$ can be found by using (6.4). This gives

$$\chi^{(l,\sigma)}(E\alpha)=\chi^{(l)}(\alpha),$$
$$\chi^{(l,+)}(J\alpha)=\chi^{(l)}(\alpha), \chi^{(l,-)}(J\alpha)=-\chi^{(l)}(\alpha), \tag{6.5}$$

where $\chi^{(l)}(\alpha)$ is given by (4.50) and we have denoted the classes of $O(3)$ by $(E\alpha)$ and $(J\alpha)$ for brevity; the class $(E\alpha)$ contains all rotations through α while $(J\alpha)$ contains the elements denoting all rotations through α followed by inversion.

The eigenfunctions of an electron in an atom may thus belong to any of the irreducible representations $D^{(l,\sigma)}$. If an eigenfunction belongs to $D^{(l,+)}$, it remains invariant under the inversion and is said to be of *even parity*; the corresponding spectral term is said to be *positive* or *even*. If an eigenfunction belongs to $D^{(l,-)}$ it changes sign under the action of J and is said to be of *odd parity* and the corresponding spectral term is said to be *negative* or *odd*. The parity of a wave function of a system of particles depends only on the space coordinates of the particles and not on their spins. The spin angular momentum (or any angular momentum) is invariant under the inversion of the position coordinates.

It is, however, found that not all the irreducible representations $D^{(l,\sigma)}$ occur in a one-electron atom. This is due to the fact that the one-electron wave functions are homogeneous polynomials of degree l in x, y and z, where l is the orbital quantum number. Such a polynomial clearly gets multiplied by $(-1)^l$ on coordinate inversion which takes x to $-x$, y to $-y$ and z to $-z$. The only irreducible representations that occur are thus $D^{(0,+)}$, $D^{(1,-)}$, $D^{(2,+)}$, $D^{(3,-)}$, etc., corresponding to the spectral terms s, p, d, f, etc., which alternate in parity. This is not true in a many-electron atom as we shall see below. Table (6.1) shows the various electronic levels along with the irreducible representations to which the eigenfunctions of the one-electron atom belong.

In a many-electron atom, the parity of the combined wave function of all the electrons is $(-1)^k$ where $k = \sum_i l_i$ and l_i is the orbital quantum number of the i-th electron. Total orbital and total spin quantum numbers denoted by L and S are obtained respectively from the individual l_i and s_i of the electrons by vector addition method, with $M_L = \Sigma m_{li}$ and $M_s = \Sigma m_{si}$. Here m_{li} and m_{si} are respectively the quantized projections of $\mathbf{l}_i$ and $\mathbf{s}_i$. The spectral term of the atom is characterized by the value of L; $L=0, 1, 2, 3, \ldots$, correspond respectively to the lables S, P, D, $F, \ldots$.

Unlike the case of a one-electron atom, the S, P, D, etc., functions of a many-electron atom may have either parity. For example,

whereas the p functions of a one-electron atom must have an odd parity, the P functions of a many-electron atom can have either even or odd parity depending on whether $\sum_i l_i$ is even or odd. Thus, consider the case of two electrons. If both the electrons are in the p shell, their wave functions transform according to $D^{(1,-)}$. The product wave function therefore transforms according to the direct product representation

$$D^{(1,-)} \otimes D^{(1,-)} = D^{(0,+)} \oplus D^{(1,+)} \oplus D^{(2,+)}. \qquad (6.6)$$

TABLE 6.1 THE ELECTRONIC LEVELS IN A ONE-ELECTRON ATOM

Nomenclature	l	Parity	Representation	Degeneracy[1]
$1s$	0	even	$D^{(0,+)}$	1
$2s$	0	even	$D^{(0,+)}$	1
$2p$	1	odd	$D^{(1,-)}$	3
$3s$	0	even	$D^{(0,+)}$	1
$3p$	1	odd	$D^{(1,-)}$	3
$3d$	2	even	$D^{(2,+)}$	5
$4s$	0	even	$D^{(0,+)}$	1
$4p$	1	odd	$D^{(1,-)}$	3
$4d$	2	even	$D^{(2,+)}$	5
$4f$	3	odd	$D^{(3,-)}$	7
.				
.				
.				

This shows that the atom can have $L=0$, 1 or 2, and in any of these states, its parity will be even. On the other hand, if one electron is in the p shell and one in the d shell, the product wave function would transform according to

$$D^{(1,-)} \otimes D^{(2,+)} = D^{(1,-)} \oplus D^{(2,-)} \oplus D^{(3,-)}, \qquad (6.7)$$

i.e., the atom can have $L=1$, 2 or 3, and in any of these states, its parity is odd. From this consideration, we have a very important rule: *Whereas the parity of a one-electron wave function is linked to its orbital quantum number l, the parity of a many-electron wave function is indepen-*

[1]We have disregarded the electron spin here. If this is taken into account, the appropriate symmetry group is $SU(2)$ rather than $O(3)$ and the degeneracies must be further multiplied by 2.

dent of the total orbital quantum number L but depends on the l values of the constituent electrons. We shall find this of great utility in obtaining the selection rules later in this chapter.

6.1.2 Angular symmetry of wave functions and spherical harmonics. We have seen in Chapter 4 that the $2l+1$ spherical harmonics $Y_l^m(\theta, \phi)$ for $-l \leq m \leq l$ generate the irreducible representation $D^{(l)}$ of $SO(3)$. The eigenfunctions of a one-electron atom are of the form $R_{nl}(r)\, Y_l^m(\theta, \phi)$ where $R_{nl}(r)$ is spherically symmetric. The angular dependence of the eigenfunctions is therefore completely contained in the spherical harmonics Y_l^m. For the sake of completeness, we shall list in this subsection the first few spherical harmonics and the corresponding atomic eigenfunctions. Table (6.2) gives the symmetry of the eigenfunctions for $l=0$, 1, 2 and 3 and their angular parts which are obtained by using the transformation

$$x=r \sin\theta \cos\phi,\ y=r \sin\theta \sin\phi,\ z=r \cos\theta, \tag{6.8}$$

TABLE 6.2 THE ANGULAR SYMMETRY OF THE ATOMIC EIGENFUNCTIONS FOR $l=0$, 1, 2 AND 3

l	Symmetry of the eigenfunction	Angular part of the eigenfunction
0	s:1	constant
1	p: x	$\sin\theta \cos\phi$
	p: y	$\sin\theta \sin\phi$
	p: z	$\cos\theta$
2	d: xy	$\sin^2\theta \sin 2\phi$
	d: yz	$\sin\theta \cos\theta \sin\phi$
	d: zx	$\sin\theta \cos\theta \cos\phi$
	d: x^2-y^2	$\sin^2\theta \cos 2\phi$
	d: $2z^2-x^2-y^2$	$3\cos^2\theta-1$
3	f: $2z^3-3z(x^2+y^2)$	$5\cos^3\theta-3\cos\theta$
	f: $x(4z^2-x^2-y^2)$	$\sin\theta(5\cos^2\theta-1)\cos\phi$
	f: $y(4z^2-x^2-y^2)$	$\sin\theta(5\cos^2\theta-1)\sin\phi$
	f: $z(x^2-y^2)$	$\sin^2\theta \cos\theta \cos 2\phi$
	f: xyz	$\sin^2\theta \cos\theta \sin 2\phi$
	f: x^3-3xy^2	$\sin^3\theta \cos 3\phi$
	f: $3x^2y-y^3$	$\sin^3\theta \sin 3\phi$

which is valid on the surface of a sphere of radius r. Table (6.3) gives the linear combinations[2] of these functions which are proportional to the spherical harmonics of degree l and order m. The Y_l^m's form a *complete orthonormal set* of square-integrable functions on the unit sphere.

TABLE 6.3 THE STANDARD SYMMETRIZED COMBINATIONS WHICH GENERATE THE REPRESENTATIONS $D^{(l)}$ OF $SO(3)$

$D^{(l)}$	The linear combination	is proportional to the spherical harmonic
$D^{(0)}$	1	$Y_0^0=1/\sqrt{4\pi}$
$D^{(1)}$	$x\pm iy$	$Y_1^{\pm 1}=\mp\sqrt{\frac{3}{8\pi}}\sin\theta\exp(\pm i\phi)$
	z	$Y_1^0=\sqrt{\frac{3}{4\pi}}\cos\theta$
$D^{(2)}$	$2z^2-x^2-y^2$	$Y_2^0=\sqrt{\frac{5}{16\pi}}(3\cos^2\theta-1)$
	$zx\pm iyz$	$Y_2^{\pm 1}=\mp\sqrt{\frac{15}{8\pi}}\sin\theta\cos\theta\exp(\pm i\phi)$
	$(x^2-y^2)\pm i(2xy)$	$Y_2^{\pm 2}=\sqrt{\frac{15}{32\pi}}\sin^2\theta\exp(\pm 2i\phi)$
$D^{(3)}$	$2z^3-3z(x^2+y^2)$	$Y_3^0=\sqrt{\frac{7}{16\pi}}(5\cos^3\theta-3\cos\theta)$
	$(x\pm iy)(4z^2-x^2-y^2)$	$Y_3^{\pm 1}=\mp\sqrt{\frac{21}{64\pi}}\sin\theta(5\cos^2\theta-1)\times\exp(\pm i\phi)$
	$z(x^2-y^2)\pm 2ixyz$	$Y_3^{\pm 2}=\sqrt{\frac{105}{32\pi}}\sin^2\theta\cos\theta\exp(\pm 2i\phi)$
	$(x^3-3xy^2)\pm i(3x^2y-y^3)$	$Y_3^{\pm 3}=\mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\exp(\pm 3i\phi)$

6.1.3 The symmetric group. We have introduced the symmetric group in Section 1.7. We shall consider here a few additional properties of these groups.

[2]For the shapes of these functions, see White (1934), p. 63.

Firstly, we shall discuss the class structure of the symmetric group S_n. There is a particularly simple way for obtaining the number of classes of S_n; the rule is that the number of classes of S_n is equal to the number of ways in which the integer n can be partitioned into a sum of positive integers. Each of these ways is related uniquely to a class of S_n.

Thus, for $n=3$, we can write 3 as 3, 2+1 and 1+1+1, so that the number of classes of S_3 is 3. The class corresponding to (3) contains elements in which all the three objects undergo *cyclic* permutations; these are the elements A and B defined in (1.36). The partition 2+1 gives us a class containing the elements which denote the cyclic permutation of two objects (transposition) leaving the third object unchanged; such elements of S_3 are C, D and F. Finally, the partition 1+1+1 gives us the element in which each object is unchanged—the identity element. The classes of S_3 are therefore (E), (A,B) and (C,D,F).

For, $n=4$, we have five ways of partitioning: 4, 3+1, 2+2, 2+1+1, 1+1+1+1. The last partition gives the identity element. The class corresponding to the partition 2+1+1 contains elements which involve one transposition leaving the remaining two objects unchanged; there are 6 such elements. The partition 2+2 means two interchanges in pairs; this class contains 3 elements. The elements in the class corresponding to the partition 3+1 consist of cyclic permutations on three objects leaving the fourth unchanged; these are 8 in number. Lastly, the class corresponding to the partition 4 consists of the remaining 6 elements.

Example. We shall consider the group S_4 and obtain its classes. We shall employ a simpler notation than that used in Section 1.7, although the definition of an operation will remain the same. Thus, an element of S_4, say (2 4 3 1), will mean that the second object is to be brought to the first position, the fourth to the second position, the third remains where it is, while the first object is to be taken to the fourth position. For example, the operation of the permutation (2 4 3 1) on (2 3 1 4), according to the above definition, will be

$$(2\ 4\ 3\ 1)(2\ 3\ 1\ 4) = (3\ 4\ 1\ 2).$$

We can now directly write the classes of S_4 by the rule given above. The partition 1 + 1 + 1 + 1 gives the permutation in which each object is in its own position, that is, the identity element $E = (1\ 2\ 3\ 4)$. The next partition 2 + 1 + 1 gives a class of six elements A_i, $1 \leqslant i \leqslant 6$, each of which consists of a transposition between one pair of objects, leaving the other two unchanged. These six transpositions expressed

as products of the generators (1 2), (1 3), (1 4) are

$$A_1 = (1\ 2) \equiv (2\ 1\ 3\ 4),$$
$$A_2 = (1\ 3) \equiv (3\ 2\ 1\ 4),$$
$$A_3 = (1\ 4) \equiv (4\ 2\ 3\ 1),$$
$$A_4 = (2\ 3) \equiv (1\ 3\ 2\ 4) = (1\ 2)\ (1\ 3)\ (1\ 2),$$
$$A_5 = (2\ 4) \equiv (1\ 4\ 3\ 2) = (1\ 2)\ (1\ 4)\ (1\ 2),$$
$$A_6 = (3\ 4) \equiv (1\ 2\ 4\ 3) = (1\ 3)\ (1\ 4)\ (1\ 3).$$

The next partition 2 + 2 gives the class (B_1, B_2 B_3) each element of which consists of two transpositions in pairs. The elements are explicitly given by

$$B_1 = (1\ 2)\ (3\ 4) \equiv (2\ 1\ 4\ 3) = (1\ 2)\ (1\ 3)\ (1\ 4)\ (1\ 3),$$
$$B_2 = (1\ 3)\ (2\ 4) \equiv (3\ 4\ 1\ 2) = (1\ 3)\ (1\ 2)\ (1\ 4)\ (1\ 2),$$
$$B_3 = (1\ 4)\ (2\ 3) \equiv (4\ 3\ 2\ 1) = (1\ 4)\ (1\ 2)\ (1\ 3)\ (1\ 2).$$

The partition 3 + 1 gives eight elements, in each of which one object is kept fixed and the other three are cyclically permuted :

$$C_1 = (1\ 3\ 4\ 2),\ C_2 = (1\ 4\ 2\ 3),\ C_3 = (3\ 2\ 4\ 1),\ C_4 = (4\ 2\ 1\ 3),$$
$$C_5 = (2\ 4\ 3\ 1),\ C_6 = (4\ 1\ 3\ 2),\ C_7 = (2\ 3\ 1\ 4),\ C_8 = (3\ 1\ 2\ 4).$$

Finally the partition 4 gives us the permutations having the property that no object remains in its own place, nor do any two objects undergo a simple transposition. This gives the six elements

$$D_1 = (2\ 3\ 4\ 1),\ D_2 = (2\ 4\ 1\ 3),\ D_3 = (3\ 1\ 4\ 2),$$
$$D_4 = (3\ 4\ 2\ 1),\ D_5 = (4\ 1\ 2\ 3),\ D_6 = (4\ 3\ 1\ 2).$$

It is left as an exercise to express the elements of classes (C_i) and (D_i) as products of generators. We see that the classes (E), (B_i) and (C_i) consist of even permutations while (A_i) and (D_i) consist of odd permutations.

We thus see that the groups S_3 and S_4 have 3 and 5 classes respectively. These will also be the number of their distinct irreducible representations. Their dimensions can then be found by using the condition (3.79). This gives the dimensions of the irreducible representations of S_3 to be 1, 1 and 2. For S_4, we find the dimensions to be 1, 1, 2, 3 and 3.

The classes of S_n for any value of n can in general be found by the same method. It turns out that for every value of n, S_n has two, and only two, distinct irreducible representations of dimension one. One of them is obviously the identity representation in which each element of S_n corresponds to unity. In the other one-dimensional representation, the even permutations of S_n correspond to $+1$ while the odd permutations to -1. We shall denote this irreducible representation of S_n by Γ_{odd}.

This is a very important result for us, because we can immediately recognize that it is connected with the construction of symmetric and antisymmetric wave functions of a system of n identical particles. Thus, let $\psi(1, 2, \ldots, n)$ denote a particular state of the system and let us construct the wave function

$$\Psi_{\text{even}} = \sum_{A \in S_n} A\psi(1, 2, \ldots, n). \tag{6.9}$$

It is then clear that the operation of any element of S_n on Ψ_{even} leaves it unchanged, i.e.,

$$A\Psi_{\text{even}} = \Psi_{\text{even}} \quad \forall \quad A \in S_n. \tag{6.10}$$

The wave function Ψ_{even} therefore generates the identity representation of S_n. On the other hand, if we construct the wave function

$$\Psi_{\text{odd}} = \sum_{A \in S_n} (-1)^a A\psi(1, 2, \ldots, n). \tag{6.11}$$

where a is the number of transpositions in the element A, then we find that

$$A\Psi_{\text{odd}} = (-1)^a \Psi_{\text{odd}}. \tag{6.12}$$

The wave function Ψ_{odd} thus changes sign under a transposition of any two elements.

If we have a system of n identical bosons, its wave function must be of the form Ψ_{even} which generates the identity representation of S_n. A system of n identical fermions, on the other hand, must be represented by a wave function of the form Ψ_{odd} which generates the representation Γ_{odd} of S_n. If we assume that there are no interactions between the particles, the state function $\psi(1, 2, \ldots, n)$ can be expressed as the product of single-particle eigenfunctions according to

$$\psi(p_1, p_2, \ldots, p_n) = u_1(p_1)\, u_2(p_2) \ldots u_n(p_n), \tag{6.13}$$

where $u_i(p_j)$ is the wave function of the j-th particle in the i-th single-particle orbital. Here p_j denotes all the coordinates (position and spin projection) of the j-th particle. The antisymmetrized wave function of the system transforming according to Γ_{odd} is then the *Slater determinant*

$$\Psi_{\text{odd}} = \frac{1}{\sqrt{n!}} \begin{vmatrix} u_1(1) & u_1(2) \ldots u_1(n) \\ u_2(1) & u_2(2) \ldots u_2(n) \\ \cdot & \\ \cdot & \\ \cdot & \\ u_n(1) & u_n(2) \ldots u_n(n) \end{vmatrix}. \tag{6.14}$$

For example, if we have three identical particles whose coordinates and spins are symbolized by 1, 2 and 3, and three spin-orbitals, then the wave function of a particular state of the system may be written as

$$\psi(p_1, p_2, p_3)=u_1(p_1)\,u_2(p_2)\,u_3(p_3), \tag{6.15}$$

where each p_i can take values 1, 2 or 3 and no two p_i's can have the same value. The antisymmetrized basis function is then

$$\begin{aligned}\Psi_{\text{odd}}&=\frac{1}{\sqrt{6}}\begin{vmatrix} u_1(1) & u_1(2) & u_1(3)\\ u_2(1) & u_2(2) & u_2(3)\\ u_3(1) & u_3(2) & u_3(3)\end{vmatrix}\\ &=[\psi(1\,2\,3)-\psi(2\,1\,3)+\psi(2\,3\,1)-\psi(3\,2\,1)\\ &\quad+\psi(3\,1\,2)-\psi(1\,3\,2)]/\sqrt{6}.\end{aligned} \tag{6.16}$$

6.2 Selection Rules for Atomic Transitions

We have seen that the states of a many-electron atom may belong to all the irreducible representations of $O(3)$ but that the states of a one-electron atom belong only to some irreducible representations of $O(3)$. It is therefore natural that the selection rules for the two systems would be different. We shall consider the two cases separately.

6.2.1 A many-electron atom. We shall first obtain the selection rules for electric dipole transitions of a many-electron atom. The electric dipole moment operator $\underline{\mu}=\epsilon(x, y, z)$ is a polar vector (which changes sign under inversion) and it clearly generates the representation $D^{(1,-)}$ of $O(3)$. The transition of a many-electron atom from a state $D^{(L,\sigma)}$ to a state $D^{(L',\sigma')}$ under the electric dipole radiation would then be allowed if the direct product representation $D^{(1,-)}\otimes D^{(L,\sigma)}$ contains $D^{(L',\sigma')}$. Now, we have

$$D^{(1,-)}\otimes D^{(L,\sigma)}=\begin{cases} D^{(L-1,-\sigma)}\oplus D^{(L,-\sigma)}\oplus D^{(L+1,-\sigma)} & \text{if } L\neq 0.\\ D^{(1,-\sigma)} \text{ if } L=0.\end{cases} \tag{6.17}$$

The second part of the above equation shows that the transition between two states with $L=0$ is forbidden. The representation $D^{(L',\sigma')}$ appears in the direct product if

$$\left.\begin{aligned} L'&=\begin{cases} L,\ L\pm 1 \text{ if } L\neq 0,\\ 1 \text{ if } L=0;\end{cases}\\ \text{and}\quad \sigma'&=-\sigma.\end{aligned}\right\} \tag{6.18a}$$

If we denote $L'-L=\wedge L$, this gives us the selection rules for electric

dipole transitions:

$$\Delta L=0,\ \pm 1\ (0\leftarrow/\rightarrow 0);\ \text{parity change.} \qquad (6.18b)$$

Since the electric dipole moment operator does not act on the spin variables of the atom, we also have the selection rule $\Delta S=0$.

6.2.2 A one-electron atom. It is well known that the spectral terms of one-electron atoms like hydrogen and the alkalies are particularly simple. Once again, we examine the direct product $D^{(l,\sigma)}\otimes D^{(1,-)}$ for obtaining the selection rules for electric dipole transitions. This gives us an equation similar to (6.17) with L replaced by l. However, we must now take into account the fact that the parity of a one-electron atomic wave function is linked to its l value. Thus, if there is a state of the atom belonging to the representation $D^{(l,\sigma)}$, there cannot be any state of the atom belonging to $D^{(l,-\sigma)}$ but there are states belonging to $D^{(l\pm 1,-\sigma)}$. This therefore forbids transitions for which $l'=l$ and gives us the selection rule

$$\Delta l=\pm 1,\ \text{parity change.} \qquad (6.19)$$

On the other hand, the magnetic dipole moment operator generates the representation $D^{(1,+)}$ and we have, for $l\neq 0$,

$$D^{(1,+)}\otimes D^{(l,\sigma)}=D^{(l-1,\sigma)}\oplus D^{(l,\sigma)}\oplus D^{(l+1,\sigma)}. \qquad (6.20)$$

The only allowed transition among these is therefore $D^{(l,0)}\leftrightarrow D^{(l,\sigma)}$, and we have the selection rule

$$\Delta l=0,\ \text{no change in parity.} \qquad (6.21)$$

Moreover, since the magnetic dipole moment operator also does not act on the spin variables, we have

$$\Delta s=0. \qquad (6.22)$$

6.3 Zeeman Effect

In this section, we shall study the Zeeman effect which stems from the splitting of the atomic energy levels in a magnetic field.

Consider an atom in a state j having a $(2j+1)$-fold degenerate energy level E_{nj}. If the atom is placed in a steady uniform magnetic field **H**, assumed to be along the z axis, the degeneracy of the level E_{nj} is totally lifted and it splits into $2j+1$ nondegenerate levels. This result can easily be obtained group theoretically.

Let ψ_j^m be the $2j+1$ degenerate eigenfunctions (for $-j\leq m\leq j$) for the level E_{nj}. The symmetry group of the atom is $SO(3)$ if j is integral and $SU(2)$ if j is half-odd-integral. If the group is $SO(3)$, ψ_j^m contains

the spherical harmonic $Y_j^m(\theta, \phi)$, while if the group is $SU(2)$, ψ_j^m has the same transformation properties as the function f_j^m defined in Section 4.5.1. In either case, a rotation through α about the z axis has the effect

$$R_z(\alpha)\psi_j^m = \exp(im\alpha)\ \psi_j^m. \tag{6.23}$$

Let λV be the perturbation arising from the applied magnetic field, where λ is a parameter.[3] The perturbation λV and therefore the perturbed system (i.e., atom + magnetic field) are invariant only under rotations about the z axis. The symmetry group of the physical system is thus $SO(2)$, which is a subgroup of $SO(3)$ or $SU(2)$. Since $SO(2)$ is an abelian group, it has only one-dimensional irreducible representations. This is sufficient to show that the function ψ_j^m cannot remain degenerate for all values of m between $-j$ and j. The function ψ_j^m now belongs to the m-th irreducible representation of $SO(2)$ and thus the $(2j+1)$-fold degeneracy is completely lifted by the magnetic field.

The operation of the perturbation V on an eigenfunction ψ_j^m of the unperturbed system is, in general, to mix all the degenerate eigenfunctions. We can therefore write:

$$V\psi_j^m = \sum_{m'=-j}^{j} \psi_j^{m'} v_{m'm}, \tag{6.24}$$

where $v_{m'm} = (\psi_j^{m'},\ V\psi_j^m)$ is the matrix element of V between two degenerate unperturbed eigenfunctions. The matrix element of V between two nondegenerate eigenfunctions $\psi_{j'}^{m'}$ and ψ_j^m will be identically zero because the operation of V on ψ_j^m does not mix any function with different j value. Since V is invariant under $SO(2)$, $V\psi_j^m$ has the same transformation properties under $SO(2)$ as ψ_j^m, i.e.,

$$R_z(\alpha)(V\psi_j^m) = \exp(im\alpha)(V\psi_j^m). \tag{6.25}$$

Thus, the function $V\psi_j^m$ also belongs to the m-th irreducible representation of $SO(2)$ and, by the matrix element theorem, we see that $(\psi_j^{m'},\ V\psi_j^m)$ will be proportional to $\delta_{m'm}$, or

$$v_{m'm} \equiv v_m\ \delta_{m'm}, \tag{6.26}$$

which defines v_m as being the expectation value of V in an unperturbed state ψ_j^m. The matrix representing V with $\{\psi_j^m\}$ as the basis is thus diagonal and v_m are its eigenvalues. The new energy levels are then clearly given by

[3] The parameter λ is being used here to facilitate the separation of the various orders of perturbation. This is the usual and well known technique in perturbation theory.

$$E_{njm} = E_{nj} + \lambda \nu_m, -j \leq m \leq j. \tag{6.27}$$

This is as far as we can go with the help of group theory. The actual calculation of ν_m's will depend on the explicit nature of the perturbation and the exact atomic eigenfunctions.

The number of components into which a line splits under a magnetic field helps determine the j value of the unperturbed state. It was by this method that Sommerfeld originally suggested that j must be given integral as well as half-odd-integral values.

6.4 Addition of Angular Momenta

It is often necessary in many quantum mechanical problems to couple two or more angular momenta and obtain the angular momentum of the combined system. We may be dealing with a single particle with two angular momenta (orbital and intrinsic) or with a system of two particles (such as two electrons in the same atom). Our aim in this section would be to obtain the possible values for the total angular momentum and its quantized projection and to obtain the eigenstates of the combined system as (symmetrized) linear combinations of the separate eigenstates of the two angular momenta.

Before going to the proper problem of addition of angular momenta, we shall discuss in the first subsection below the quantum mechanical nature of angular momentum. This subsection is included here merely for the sake of completeness although its results have in fact been used previously in this book.

6.4.1 Angular momentum in quantum mechanics. In classical mechanics, the angular momentum is an easily comprehensible entity. It is defined as $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ where $\mathbf{r}$ is the position vector and $\mathbf{p}$ is the linear momentum and is related to $\mathbf{r}$ by $\mathbf{p} = m\, d\mathbf{r}/dt$ where m is the mass of the system. The angular momentum depicts the rotational properties of the system. For example, if a system has rotational symmetry about an axis, the component of angular momentum along that axis is a constant of motion. If the system is invariant under all rotations, the angular momentum $\mathbf{L}$ is conserved.

Although these results hold good in quantum mechanics also, it is not possible to take the former definition of angular momentum over to quantum mechanics. This is because in accordance with the basic axioms of quantum mechanics, $\mathbf{r}$ and $\mathbf{p}$ are themselves not classical quantities but the *position vector operator* and the *linear momentum operator*, respectively, related to each other by $\mathbf{p} = -i\hbar\nabla_{\mathbf{r}}$

or $\mathbf{r}=-i\hbar\nabla_{\mathbf{p}}$. We may, of course, still define $\mathbf{L}=\mathbf{r}\times\mathbf{p}$ and call it the *angular momentum operator*. If the system possesses full rotational symmetry, the operator $\mathbf{L}$ would commute with the Hamiltonian and would therefore be a constant of motion. However, this is not the only invariant of a quantum mechanical isotropic system. A quantum mechanical system possesses other *degrees of freedom* (the intrinsic spin angular momentum, the isotopic spin angular momentum, etc.) the observables corresponding to which are invariants if the Hamiltonian is invariant under rotations in its Hilbert space. These additional degrees of freedom have no classical analogue.

As the whole structure of quantum mechanics is based on operators corresponding to observables, we will have to define angular momentum in quantum mechanics abstractly and mathematically. For this, we shall first define an angular momentum operator.

An operator $\mathbf{A}$ with Cartesian components A_x, A_y and A_z is said to be an *angular momentum operator* if

(i) the operators A_i $(i=x, y, z)$ correspond to physical observables,

(ii) they transform under rotations like the components of a vector (i.e., the matrix associated with the transformation is the same as (4.43)), and

(iii) they obey the following commutation relations:

$$[A_x, A_y]=i\hbar A_z,\ [A_y, A_z]=i\hbar A_x,\ [A_z, A_x]=i\hbar A_y. \qquad (6.28)$$

The physical observable associated with the operator $\mathbf{A}$ will then be called an *angular momentum.*

The operator $\mathbf{L}=\mathbf{r}\times\mathbf{p}$ is a particular example of an angular momentum operator, because it satisfies the above three axioms. The observable associated with it is called the *orbital angular momentum.* The intrinsic spin angular momentum operator $\mathbf{S}$ and the isotopic spin angular momentum operator $\boldsymbol{\tau}$ are other examples of an angular momentum operator. The physical observables associated with them are respectively called *spin angular momentum*[4] (or simply *spin*) and *charge.*

Hereafter, we shall frequently call the angular momentum operator simply the angular momentum and denote it in general by $\mathbf{J}$.

The square of the angular momentum $\mathbf{J}^2=J_x^2+J_y^2+J_z^2$ commutes with each of the components of $\mathbf{J}$ as can be verified from (6.28). However, (6.28) shows that no two components of $\mathbf{J}$ commute with each other. In any representation, therefore, not more than one component of $\mathbf{J}$ can be diagonalized at a time. By convention, we choose

[4] It is a mere fantasy to imagine that a particle having spin angular momentum is really rotating about itself; *spin* is merely the name given to the additional degree of freedom possessed by many particles such as electrons, neutrons, etc., and by many composite systems such as nuclei, atoms, molecules, etc.

basis states for representation which are simultaneous eigenstates of $\mathbf{J}^2$ and J_z. It is found that $\mathbf{J}^2$ can have eigenvalues $j(j+1)\hbar^2$ with $j=0, \frac{1}{2}, 1, \frac{3}{2}, 2, \ldots$, and J_z can have eigenvalues $m\hbar$ where $m=-j, -j+1, \ldots, j$. A common eigenstate of $\mathbf{J}^2$ and J_z can be denoted by $|jm\rangle$ with

$$J^2 |jm\rangle = j(j+1)\hbar^2 |jm\rangle, \quad J_z |jm\rangle = m\hbar |jm\rangle. \tag{6.29}$$

Normally, there would be other operators too which commute with both $\mathbf{J}^2$ and J_z. Correspondingly, the system would have good quantum numbers other than j and m. We should strictly denote a common eigenstate of all the commuting operators by $|Njm\rangle$ where N is the set of all the other good quantum numbers. These quantum numbers are, however, not relevant to the rotational properties of the eigenstate $|Njm\rangle$. They govern, for example, among other things, the radial dependence of the eigenstates. We shall often drop these, except where necessary, and write an eigenstate simply as $|jm\rangle$ although its dependence on the other quantum numbers would be implicit.

The two operators $J_\pm = J_x \pm iJ_y$ which are hermitian conjugates of each other have respectively the effect of increasing and decreasing the z component of the angular momentum by unity. Thus,[5]

$$\begin{aligned} J_+ |jm\rangle &= [j(j+1)-m(m+1)]^{\frac{1}{2}}\hbar\, |j, m+1\rangle, \\ J_- |jm\rangle &= [j(j+1)-m(m-1)]^{\frac{1}{2}}\hbar\, |j, m-1\rangle. \end{aligned} \tag{6.30}$$

The coefficients in the above equations are the elements of the matrices representing J_+ and J_- with the basis $\{|jm\rangle\}$. The representation of $\mathbf{J}^2$ and its components (J_x, J_y and J_z or $J_\pm$ and J_z) with this basis is called the *standard representation* of angular momentum. It is evident that in this representation, only the matrix for J_y is purely imaginary while all the other matrices are real. The matrices for $\mathbf{J}^2$ and J_z are, of course, diagonal whereas those for J_x, J_y, J_+ and J_- are block-diagonalized with blocks of dimensions $2j+1$. The states $\{|jm\rangle\}$ generate the representation $D^{(j)}$ of $SU(2)$ under generalized rotations in the Hilbert space of the operators $\mathbf{J}^2$ and $\mathbf{J}$, so that we have

$$U_R |jm\rangle = \sum_{m'} |jm'\rangle D_{m'm}^{(j)}(R), \tag{6.31}$$

where we have denoted a rotation such as $R_{\mathbf{u}}(\phi)$ or $R(\alpha, \beta, \gamma)$ of $SO(3)$ by U_R for brevity and convenience.

In particular cases, it is not necessary that all the allowed values of j should occur. For example, if the orbital angular momentum $\mathbf{L}^2$ is under consideration, its allowed eigenvalues are $l(l+1)$ where l takes only nonnegative integral values, excluding all the half-odd-integral

[5]See Heine (1960), Section 8; Schiff (1968), Section 27.

values. Moreover, for a given value of j, there may be more than one sets of $(2j+1)$ linearly independent eigenfunctions corresponding to it (for different values of the remaining quantum numbers N).

6.4.2 Addition of two angular momenta and symmetrized combinations of eigenstates. Let $\mathbf{J}_1$ and $\mathbf{J}_2$ be two angular momenta. If each component of $\mathbf{J}_1$ commutes with every component of $\mathbf{J}_2$, then it can be shown that $\mathbf{J}=\mathbf{J}_1+\mathbf{J}_2$ is also an angular momentum. Thus, consider the commutator

$$\begin{aligned}[J_x, J_y] &\equiv [J_{1x}+J_{2x},\ J_{1y}+J_{2y}] \\ &= [J_{1x},\ J_{1y}]+[J_{2x}, J_{2y}] \\ &= i\,\hbar\,(J_{1z}+J_{2z}) \\ &= i\,\hbar\,J_z, \end{aligned} \tag{6.32}$$

which is identical to the first of Eqs. (6.28). Similarly, by cyclic permutations of x, y and z, we find that $[J_y, J_z]=i\hbar J_x$ and $[J_z, J_x]=i\hbar J_y$, so that $\mathbf{J}$ is an angular momentum. The commutators of $\mathbf{J}$ with $\mathbf{J}_1$ or $\mathbf{J}_2$ are found to be

$$\begin{aligned}&[J_x, J_{ix}]=[J_{1x}+J_{2x},\ J_{ix}]=0, \\ &[J_x, J_{iy}]=[J_{1x}+J_{2x},\ J_{iy}]=i\,\hbar J_{iz}, \\ &[J_x, J_{iz}]=[J_{1x}+J_{2x},\ J_{iz}]=-i\hbar J_{iy}, \end{aligned} \tag{6.33}$$

with $i=1$ or 2, and similar equations obtained by cyclic permutations of x, y and z.

Let $|\,j_1 m_1>$ be the eigenstates of $\mathbf{J}_1^2$ and J_{1z} and $|\,j_2 m_2>$ those of $\mathbf{J}_2^2$ and J_{2z}. The combined eigenstates of these four mutually commuting operators are just the products of the individual eigenstates which may be denoted by $|\,j_1 m_1>\,|\,j_2 m_2> \equiv |\,j_1 m_1,\ j_2 m_2>$. For given values of j_1 and j_2, these are altogether $(2j_1+1)(2j_2+1)$ in number, and have the properties

$$\begin{aligned}&\mathbf{J}_i^2\,|\,j_1 m_1,\ j_2 m_2> = j_i(j_i+1)\,\hbar^2\,|\,j_1 m_1,\ j_2\,m_2>, \\ &J_{iz}\,|\,j_1 m_1,\ j_2 m_2\ > = m_i\hbar\,|\,j_1 m_1,\ j_2 m_2>. \end{aligned} \tag{6.34}$$

The $(2j_1+1)(2j_2+1)$ eigenstates transform according to the representation $D^{(j_1)} \otimes D^{(j_2)}$ of $SU(2)$. This representation can be reduced to a sum of irreducible representations as in (4.93) where each irreducible representation $D^{(j)}$ occurs once for values of j between $|\,j_1-j_2\,|$ and j_1+j_2. Each representation $D^{(j)}$ has associated with it $(2j+1)$ states which are just linear combinations of $|\,j_1 m_1,\ j_2 m_2>$. The number of these states is

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1)=(2j_1+1)(2j_2+1), \tag{6.35}$$

as it should be.

In order to construct the new eigenstates, we note that the square of the total angular momentum $\mathbf{J}^2$ commutes with both $\mathbf{J}_1^2$ and $\mathbf{J}_2^2$, and so does J_z. For obtaining these eigenstates we choose the set of linearly independent mutually commuting operators to be $(\mathbf{J}_1^2, \mathbf{J}_2^2, \mathbf{J}^2, J_z)$ instead of the set $(\mathbf{J}_1^2, J_{1z}, \mathbf{J}_2^2, J_{2z})$. The eigenvalues of $\mathbf{J}^2$ may be denoted by $j(j+1)\hbar^2$ where $|j_1-j_2| \leq j \leq j_1+j_2$ and a common eigenstate of the former set of operators may be denoted by $|jm>$ where $m\hbar$ is the eigenvalue of J_z in the state $|jm>$. We express this state as a linear combination of the states $|j_1 m_1, j_2 m_2>$ in the form

$$|jm> = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1 m_1, j_2 m_2> C(j_1 m_1, j_2 m_2; jm). \tag{6.36}$$

The coefficients of expansion[6] can be obtained by taking the scalar product of the above equation with some state, say $|j_1 m_1', j_2 m_2'>$, and using the orthonormality of these states. This gives

$$<j_1 m_1', j_2 m_2' | jm> = C(j_1 m_1', j_2 m_2'; jm). \tag{6.37}$$

Eq. (6.36) then becomes

$$|jm> = \sum_{m_1, m_2} |j_1 m_1, j_2 m_2><j_1 m_1, j_2 m_2 | jm>. \tag{6.38}$$

These are the eigenstates we are seeking and have the properties

$$\mathbf{J}^2 |jm> = j(j+1)\hbar^2 |jm>, \quad J_z |jm> = m\hbar |jm>, \tag{6.39}$$
$$\mathbf{J}_i^2 |jm> = j_i(j_i+1)\hbar^2 |jm>, \quad i=1, 2.$$

The coefficients $<j_1 m_1, j_2 m_2 | jm>$ are called *Clebsch-Gordan coefficients* or *Wigner coefficients* or *vector coupling coefficients*. Operating on the state (6.38) with $J_z = J_{1z} + J_{2z}$, we have

$$m\hbar |jm> = \sum_{m_1, m_2} (m_1+m_2)\hbar |j_1 m_1, j_2 m_2> \times <j_1 m_1, j_2 m_2 | jm>. \tag{6.40}$$

Using (6.38) once again on the left-hand side of the above equation, we get

$$\sum_{m_1, m_2} (m-m_1-m_2)\hbar |j_1 m_1, j_2 m_2><j_1 m_1, j_2 m_2 | jm> = 0. \tag{6.41}$$

Since the states $|j_1 m_1, j_2 m_2>$ are linearly independent for different

[6] It can be shown that these coefficients are independent of the other quantum numbers N; see Messiah (1965), Section XIII. 27.

values of m_1 and m_2, the above equation is satisfied if and only if

$$(m-m_1-m_2)<j_1\, m_1, j_2\, m_2\,|\,j\, m>=0. \tag{6.42}$$

This shows that

$$<j_1\, m_1, j_2\, m_2\,|\,j\, m>=0 \text{ unless } m=m_1+m_2. \tag{6.43}$$

This shows that the z component of the total angular momentum must be equal to the sum of the z components of the individual angular momenta.[7] In short, the conditions for the nonvanishing of the *C-G* coefficient[8] $<j_1\, m_1, j_2\, m_2\,|\,j\, m>$ are

$$|j_1-j_2\,|\leq j\leq j_1+j_2,\ m=m_1+m_2,$$

and

$$|m|\leq \mathrm{j}. \tag{6.44}$$

The *C-G* coefficients of (6.38) are just the elements of the transformation from one basis to another in the $(2j_1+1)(2j_2+1)$-dimensional Hilbert space. If the set of initial states $\{|j_1 m_1, j_2 m_2>\}$ and the set of final states $\{|jm>\}$ are both assumed to be orthonormal, the matrix of these elements is a $(2j_1+1)(2j_2+1)$-dimensional unitary matrix.

The largest value of m is j_1+j_2, and this can occur only when j also has its largest value equal to j_1+j_2. Thus, if $j=m=j_1+j_2$, it can be seen from the rules (6.44) that the only *C-G* coefficient in (6.38) to be different from zero is that for which $m_1=j_1$ and $m_2=j_2$, giving

$$|j_1+j_2, j_1+j_2>=|j_1 j_1, j_2 j_2><j_1 j_1, j_2 j_2\,|\,j_1+j_2, j_1+j_2>. \tag{6.45}$$

Now, since both the states $|j_1+j_2, j_1+j_2>$ and $|j_1 j_1, j_2 j_2>$ are normalized, the *C-G* coefficient in the above equation can at most be a complex number with unit magnitude. By convention, we choose the phase such that this coefficient is $+1$:

$$<j_1 j_1, j_2 j_2\,|\,j_1+j_2, j_1+j_2>=1. \tag{6.46}$$

We shall see that with this and a similar convention explained later, all the *C-G* coefficients turn out to be real so that the unitary matrix of transformation in fact reduces to an orthogonal matrix.

6.4.3 Calculation of Clebsch-Gordan coefficients. We shall show that the $(2j_1+1)(2j_2+1)$-dimensional matrix of the *C-G* coefficients

[7] This rule is quite general and holds good for the addition of more than two angular momenta also.

[8] We shall write '*C-G* coefficients' instead of 'Clebsch-Gordan coefficients' for the sake of brevity.

reduces to a direct sum of smaller matrices with one block corresponding to each allowed value of $m=m_1+m_2$.

Since the matrix of transformation in (6.38) is unitary and since all the elements are real by the phase conventions, we have

$$<j_1 m_1, j_2 m_2 \mid j\ m>^* = <j_1 m_1, j_2\ m_2 \mid j\ m>, \tag{6.47a}$$

$$\sum_{j=\mid j_1-j_2\mid}^{j_1+j_2} \sum_{m=-j}^{j} <j_1 m_1, j_2 m_2 \mid j\ m><j_1\ m_1', j_2\ m_2' \mid j\ m> = \delta_{m_1 m_1'}\delta_{m_2 m_2'}, \tag{6.47b}$$

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} <j_1\ m_1, j_2\ m_2 \mid j\ m><j_1\ m_1, j_2\ m_2 \mid j'\ m'> = \delta_{mm'}\,\delta_{jj'}. \tag{6.47c}$$

Notice that the rows and the columns of this matrix are labeled by *different schemes*. Each row is labeled by the dual symbol (m_1, m_2), while each column is labeled by the dual symbol (j, m). For example, for given values of j_1 and j_2, the first row would be called the (j_1, j_2)-row (because $m_1=j_1$, $m_2=j_2$), while the first column would be (j_1+j_2, j_1+j_2)-column (because $j=m=j_1+j_2$). For this reason, it is not easy to write down the transpose of an element $<j_1\ m_1, j_2\ m_2 \mid j\ m>$. In other words, it is not true that the element $<j\ m \mid j_1\ m_1, j_2\ m_2>$ is the transpose of $<j_1\ m_1, j_2\ m_2 \mid j\ m>$. By convention, we shall mean by both these symbols the same element, i.e.,

$$<j\ m \mid j_1\ m_1, j_2\ m_2> \equiv <j_1\ m_1, j_2\ m_2 \mid j\ m>, \tag{6.48}$$

both of which stand for an element in the (m_1, m_2)-row and the (j, m)-column.

We have already shown that the largest value of m occurs when $j=m=j_1+j_2$ and only one *C-G* coefficient survives in this case. The next largest value of m is j_1+j_2-1 and this may occur in two ways: when $j=j_1+j_2$ or $j=j_1+j_2-1$. Also, since $m=m_1+m_2$, we must have either $m_1=j_1$, $m_2=j_2-1$, or $m_1=j_1-1$, $m_2=j_2$. This shows that the two final states $\mid j_1+j_2, j_1+j_2-1>$ and $\mid j_1+j_2-1, j_1+j_2-1>$ are both linear combinations of only the two initial states $\mid j_1\ j_1, j_2\ j_2-1>$ and $\mid j_1\ j_1-1, j_2 j_2>$; or, in accordance with (6.38), we can write

$$\begin{aligned}
&\mid j_1+j_2, j_1+j_2-1> \\
&\quad = \mid j_1\ j_1, j_2\ j_2-1><j_1\ j_1, j_2\ j_2-1 \mid j_1+j_2, j_1+j_2-1> \\
&\qquad + \mid j_1\ j_1-1, j_2\ j_2><j_1 j_1-1, j_2\ j_2 \mid j_1+j_2, j_1+j_2-1>, \\
&\mid j_1+j_2-1, j_1+j_2-1> \\
&\quad = \mid j_1\ j_1, j_2\ j_2-1><j_1\ j_1, j_2\ j_2-1 \mid j_1+j_2-1, j_1+j_2-1> \\
&\qquad + \mid j_1\ j_1-1, j_2\ j_2><j_1\ j_1-1, j_2\ j_2 \mid j_1+j_2-1, j_1+j_2-1>.
\end{aligned} \tag{6.49}$$

Thus, in the second and the third rows and columns of the *C-G* matrix, there would be only two nonvanishing coefficients. As we proceed further, we can see that if the columns are labeled in decreasing order of m, the *C-G* matrix would be in a block-diagonal form. The dimensions of the blocks increase to begin with from unity onwards and then again decrease to unity for the lowest value of m which occurs when $-m=j=j_1+j_2$ and $m_1=-j_1$, $m_2=-j_2$.

To obtain the *C-G* coefficients explicitly, we shall first obtain their recursion relations connecting one to the others, from which the coefficients can be calculated knowing one of them. For this, we apply the raising operator $J_+=J_{1+}+J_{2+}$ to both the sides of (6.38), use (6.30) and divide by $\hbar$ throughout to obtain

$$\begin{aligned}&[j(j+1)-m(m+1)]^{\frac{1}{2}} \mid j, m+1\rangle \\ &= \sum_{m_1, m_2} \{[j_1(j_1+1)-m_1(m_1+1)]^{\frac{1}{2}} \mid j_1\ m_1+1, j_2\ m_2\rangle \\ &\qquad +[j_2(j_2+1)-m_2(m_2+1)]^{\frac{1}{2}} \mid j_1\ m_1, j_2\ m_2+1\rangle\} \\ &\qquad\qquad \times\langle j_1\ m_1, j_2\ m_2 \mid j\ m\rangle. \end{aligned} \tag{6.50}$$

On the left-hand side, we substitute for $\mid j, m+1\rangle$ again from (6.38). On the right-hand side, we change the variable of summation to $m_1'=m_1+1$ in the first term, leaving m_2 unchanged, and to $m_2'=m_2+1$ in the second term, leaving m_1 unchanged. The first term, for example, then becomes

$$\sum_{m_1'=-j_1+1}^{j_1+1} \sum_{m_2=-j_2}^{j_2} [j_1(j_1+1)-(m_1'-1)\,m_1']^{\frac{1}{2}} \mid j_1\ m_1', j_2\ m_2\rangle \times\langle j_1\ m_1'-1, j_2\ m_2 \mid j\ m\rangle.$$

Now, it can be seen that for $m_1'=j_1+1$ or $-j_1$, the radical in the square brackets above vanishes. The range of summation over m_1' can therefore be replaced by $-j_1$ to j_1. Dropping the prime in m_1' finally, the first term becomes

$$\sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} [j_1(j_1+1)-m_1(m_1-1)]^{\frac{1}{2}} \mid j_1\ m_1, j_2\ m_2\rangle \times\langle j_1\ m_1-1, j_2\ m_2 \mid jm\rangle.$$

The second term in (6.50) is treated in a similar fashion. Then, noting that the states $\mid j_1 m_1, j_2 m_2\rangle$ are orthogonal, we equate their coefficients on both the sides and obtain

$$\begin{aligned}&[j(j+1)-m(m+1)]^{\frac{1}{2}}\langle j_1\ m_1, j_2\ m_2 \mid j, m+1\rangle \\ &=[j_1(j_1+1)-m_1(m_1-1)]^{\frac{1}{2}}\langle j_1\ m_1-1, j_2\ m_2 \mid j\ m\rangle \\ &+[j_2(j_2+1)-m_2(m_2-1)]^{\frac{1}{2}}\langle j_1\ m_1, j_2\ m_2-1 \mid j\ m\rangle. \end{aligned} \tag{6.51}$$

Similarly, operating on both sides of (6.38) by the lowering operator

$J_- = J_{1-} + J_{2-}$ instead of J_+ and following the same procedure as above, we can obtain another relation given below.

$$[j(j+1) - m(m-1)]^{\frac{1}{2}} < j_1 m_1, j_2 m_2 \mid j, m-1 >$$
$$= [j_1(j_1+1) - m_1(m_1+1)]^{\frac{1}{2}} < j_1 m_1 + 1, j_2 m_2 \mid j m >$$
$$+ [j_2(j_2+1) - m_2(m_2+1)]^{\frac{1}{2}} < j_1 m_1, j_2 m_2 + 1 \mid j m >. \quad (6.52)$$

These two recursion relations are sufficient to obtain all the *C-G* coefficients by starting from the first coefficient (6.46) which is the only coefficient with $m = j_1 + j_2$.

Suppose, for example, that next we wish to obtain all the *C-G* coefficients with $m = j_1 + j_2 - 1$. Putting $m_1 = j_1$, $m_2 = j_2 - 1$, $j = j_1 + j_2$ and $m = j_1 + j_2$ in (6.52) and using the selection rules (6.44) together with (6.46), we obtain

$$< j_1 j_1, j_2 j_2 - 1 \mid j_1 + j_2, j_1 + j_2 - 1 > = [j_2/(j_1 + j_2)]^{\frac{1}{2}}. \quad (6.53)$$

Similarly, if we put $m_1 = j_1 - 1$, $m_2 = j_2$ and $j = m = j_1 + j_2$ in (6.52), we find

$$< j_1 j_1 - 1, j_2 j_2 \mid j_1 + j_2, j_1 + j_2 - 1 > = [j_1/(j_1 + j_2)]^{\frac{1}{2}}. \quad (6.54)$$

These are the two *C-G* coefficients with $j = j_1 + j_2$ and $m = j_1 + j_2 - 1$. There are two more *C-G* coefficients with $m = j_1 + j_2 - 1$ and both of these have $j = j_1 + j_2 - 1$. These can be calculated by using the orthogonality relations (6.47). To clarify the procedure, we have shown in Table (6.4) the matrix elements under consideration, where we have denoted the matrix elements of (6.53) and (6.54) respectively by a and b. The elements to be calculated are denoted by c and d. The normalization of

TABLE 6.4 THE CALCULATION OF *C-G* COEFFICIENTS

m_1 \ m_2		j	j_1+j_2	j_1+j_2	j_1+j_2-1	·	·	·
		m	j_1+j_2	j_1+j_2-1	j_1+j_2-1	·	·	·
j_1	j_2		1	0	0	0	·	·
j_1	j_2-1		0	a	c	0	·	·
j_1-1	j_2		0	b	d	0	·	·
·	·		0	0	0	·		
·	·		·	·	·		·	
·	·		·	·	·			·

the (j_1, j_2-1)-row gives $a^2+c^2=1$, which, by using (6.53) for a, gives

$$c^2=j_1/(j_1+j_2). \tag{6.55}$$

Similarly, the normalization of the (j_1-1, j_2)-row together with (6.54) for b gives

$$d^2=j_2/(j_1+j_2). \tag{6.56}$$

The orthogonality of the two columns under consideration requires $ac+bd=0$ or $c=-d\,(b/a)=-d(j_1/j_2)^{\frac{1}{2}}$. This shows that c and d are both real and have opposite signs. Here, again, there is an arbitrary choice for the sign which is fixed according to the convention that the first of these elements, for which $j=m$ and $m_1=j_1$ and which has the general form $<j_1 j_1, j_2\, j-j_1 \mid jj>$, is real and positive. This gives

$$c\equiv<j_1 j_1, j_2 j_2-1 \mid j_1+j_2-1, j_1+j_2-1>=[j_1/(j_1+j_2)]^{\frac{1}{2}}, \tag{6.57a}$$

$$d\equiv<j_1 j_1-1, j_2 j_2 \mid j_1+j_2-1, j_1+j_2-1>=-[j_2/(j_1+j_2)]^{\frac{1}{2}}. \tag{6.57b}$$

Next, we consider the value $m=j_1+j_2-2$. This will give a 3×3 submatrix of C-G coefficients for $j=j_1+j_2$, j_1+j_2-1, j_1+j_2-2 and for $(m_1, m_2)=(j_1, j_2-2)$, (j_1-1, j_2-1), (j_1-2, j_2). The first two columns (for $j=j_1+j_2$ and j_1+j_2-1) can be obtained by using (6.53), (6.54) and (6.57) in (6.52). The last column (for $j=j_1+j_2-2=m$) is obtained by the orthonormalization of the rows. The process of normalization again leaves an arbitrary sign which is fixed by the convention that the first element of the last column is real and positive.

A repetition of this procedure determines all the remaining blocks of the desired matrix. The matrices of the C-G coefficients for some particular small values of j_1 and j_2 are given in Table (6.5).

TABLE 6.5 THE MATRICES OF THE C-G COEFFICIENTS

(a) $j_1=j_2=\frac{1}{2}$

		j	1	1	0	1
		m	1	0	0	−1
m_1	m_2					
1/2	1/2		1			0
1/2	−1/2			$\sqrt{1/2}$	$\sqrt{1/2}$	
−1/2	1/2			$\sqrt{1/2}$	$-\sqrt{1/2}$	
−1/2	−1/2		0			1

(b) $j_1=1, j_2=\frac{1}{2}$

m_1	m_2	j = 3/2	3/2	1/2	3/2	1/2	3/2
		m = 3/2	1/2	1/2	−1/2	−1/2	−3/2
1	1/2	1					
1	−1/2		$\sqrt{1/3}$	$\sqrt{2/3}$		0	
0	1/2		$\sqrt{2/3}$	$-\sqrt{1/3}$			
0	−1/2				$\sqrt{2/3}$	$\sqrt{1/3}$	
−1	1/2	0			$\sqrt{1/3}$	$-\sqrt{2/3}$	
−1	−1/2						1

(c) $j_1=j_2=1$

m_1	m_2	j = 2	2	1	2	1	0	2	1	2
		m = 2	1	1	0	0	0	−1	−1	−2
1	1	1								
1	0		$\sqrt{1/2}$	$\sqrt{1/2}$			0			
0	1		$\sqrt{1/2}$	$-\sqrt{1/2}$						
1	−1				$\sqrt{1/6}$	$\sqrt{1/2}$	$\sqrt{1/3}$			
0	0				$\sqrt{2/3}$	0	$-\sqrt{1/3}$			
−1	1				$\sqrt{1/6}$	$-\sqrt{1/2}$	$\sqrt{1/3}$			
0	−1							$\sqrt{1/2}$	$\sqrt{1/2}$	
−1	0	0						$\sqrt{1/2}$	$-\sqrt{1/2}$	
−1	−1									1

The Wigner's 3-j symbols which are related to the C-G coefficients, have been extensively numerically tabulated in the literature[9] for a large number of cases.

6.5 Irreducible Tensor Operators

In addition to the transitions of a physical system caused by electric and magnetic dipole radiation, there may be higher order transitions due to electric or magnetic quadrupole, octupole, etc., radiation. Although their intensities are small, they become important when the electric dipole transition is forbidden. The matrix element theorem of Chapter 5 can easily be applied to find the selection rules for the higher order transitions. A theorem due to Wigner and Eckart, to be dealt with in the next section, further gives us the ratios of the various transition probabilities without having to calculate the matrix elements explicitly. These calculations are best performed by using the concept of irreducible tensor operators which is the subject of this section.

The rotational properties of an operator are determined by its commutator with total angular momentum operator $\mathbf{J}$. To see this, let $R(\underline{\phi})$ denote a rotation of the coordinates where the vector $\underline{\phi}$ has the magnitude of the angle of rotation and is parallel to the axis of rotation. Let $U_R(\underline{\phi})$ be the corresponding operator which acts on functions. Let P be any operator before transformation and P' the same operator after the rotation. Then

$$P' = U_R(\underline{\phi})^\dagger \; P \, U_R(\underline{\phi}). \tag{6.58}$$

The rotation operator $U_R(\underline{\phi})$ has the form

$$U_R(\underline{\phi}) = \exp(-i \, \underline{\phi} \cdot \mathbf{J}/\hbar). \tag{6.59}$$

For rotations through infinitesimal angles, (6.58) becomes, to first order in ϕ,

$$\begin{aligned} P' &\simeq (1 + i\underline{\phi} \cdot \mathbf{J}/\hbar) \; P \; (1 - i\underline{\phi} \cdot \mathbf{J}/\hbar) \\ &\simeq P + \frac{i}{\hbar} \; [\underline{\phi} \cdot \mathbf{J}, \; P]. \end{aligned} \tag{6.60}$$

We shall now define scalar and vector operators and then tensor operators in general.

6.5.1 Scalar operators. We say that a quantity is a *scalar* if it is invariant under all rotations. Obvious examples of scalar quantities are mass, length, energy, etc. Similarly, an operator S is said to be a *scalar operator* if it is invariant under all rotations. For example, the Hamil-

[9] Rotenberg et al. (1959).

tonian of an isotropic system such as an atom is a scalar operator. The spin-orbit interaction operator $\mathbf{L}\cdot\mathbf{S}$ is also a scalar operator. A scalar operator thus generates the representation $D^{(0)}$ of the rotation group. By the matrix element theorem, we then see that all the matrix elements of a scalar operator between states belonging to different irreducible representations or to different columns of the same one of $SO(3)$ must vanish. Moreover, it can be shown that the matrix element of a scalar opetator between any two states transforming according to the same column of a certain irreducible representation of $SO(3)$ is independent of the column index.

Thus, if S is a scalar operator, it is invariant under all rotations, so that $S'=S$. By looking at (6.60), with P replaced by S, we see that this is possible if S commutes with all the components of the total angular momentum $\mathbf{J}$ of the system; or

$$[\mathbf{J}, S]=0. \tag{6.61}$$

Let $|Njm\rangle$ be the set of the common eigenfunctions of $\mathbf{J}^2$ and J_z. Our object is to consider the matrix element of S between any two of these eigenstates, i.e., $\langle N'j'm'|S|Njm\rangle$. Since S commutes with $\mathbf{J}$, the operation of $\mathbf{J}^2$ and the components of $\mathbf{J}$ on the vector $S|Njm\rangle$ is the same as their operation on $|Njm\rangle$. The vector $S|Njm\rangle$ thus transforms according to the m-th column of the j-th irreducible representation of the rotation group. By the orthogonality of the basis functions (see Section 5.5.1), we then have

$$\langle N'j'm'|S|Njm\rangle=\delta_{jj'}\delta_{mm'}\langle N'jm|S|Njm\rangle. \tag{6.62}$$

Replacing m by $m-1$ in the first of Eqs. (6.30), we can write

$$|Njm\rangle=[\{j(j+1)-m(m-1)\}\hbar^2]^{-\frac{1}{2}}J_+|Njm-1\rangle. \tag{6.63}$$

By using this, the matrix element on the right-hand side of (6.62) becomes

$$\begin{aligned}&\langle N'jm|S|Njm\rangle\\ &=[\{j(j+1)-m(m-1)\}\hbar^2]^{-\frac{1}{2}}\langle N'jm|SJ_+|Njm-1\rangle\\ &=[\{j(j+1)-m(m-1)\}\hbar^2]^{-\frac{1}{2}}\langle N'jm|J_+S|Njm-1\rangle.\end{aligned} \tag{6.64}$$

Taking the conjugate of the second equation of (6.30), we have

$$\langle Njm|J_+=\langle Njm-1|[j(j+1)-m(m-1)]^{\frac{1}{2}}\hbar. \tag{6.65}$$

Substituting this in (6.64), we finally obtain

$$\langle N'jm|S|Njm\rangle=\langle N'jm-1|S|Njm-1\rangle, \tag{6.66}$$

showing that the matrix element is independent of m and depends only on j and the other quantum numbers. We therefore define the quantity

$$S_{NN'}{}^{(j)}\equiv\langle Njm|S|N'jm\rangle, \tag{6.67}$$

which is called the *reduced matrix element* of the scalar operator S. Eq. (6.62) then becomes

$$< N j m \mid S \mid N' j' m' > = \delta_{jj'} \delta_{mm'} S_{NN'}^{(j)}. \tag{6.68}$$

6.5.2 **Vector operators.** Once again, it is expedient to examine what we understand by a vector. Apart from having a magnitude and a direction, a vector is characterized by its transformation under rotations. If $\mathbf{r}$ is a vector and $\mathbf{r}'$ the vector obtained after an infinitesimal rotation $\underline{\phi}$, it can be seen from vector algebra that

$$\mathbf{r}' \simeq \mathbf{r} + \underline{\phi} \times \mathbf{r}. \tag{6.69}$$

A vector operator is defined in exactly the same way by its transformation properties. An operator $\mathbf{V}$ with three cartesian components (V_x, V_y, V_z) is said to be a *vector operator* if after an infinitesimal rotation $\underline{\phi}$, the transformed operator $\mathbf{V}'$ is given by

$$U_R(\underline{\phi})^\dagger \mathbf{V}\, U_R(\underline{\phi}) \equiv \mathbf{V}' \simeq \mathbf{V} + \underline{\phi} \times \mathbf{V}. \tag{6.70}$$

Comparison with (6.60) shows that a vector operator $\mathbf{V}$ must satisfy the commutation relations

$$\frac{i}{\hbar}[\underline{\phi} . \mathbf{J}, \mathbf{V}] = \underline{\phi} \times \mathbf{V}. \tag{6.71}$$

We note in passing that if $\mathbf{V}$ is replaced by $\mathbf{J}$, the above equation becomes an identity, a proof of which is left to Problem (6.9). The angular momentum operator $\mathbf{J}$ is thus a vector operator. Other examples of vector operators are the quantum mechanical operators for position, linear momentum, orbital angular momentum, spin angular momentum, isotopic spin angular momentum, electric and magnetic dipole moment operators, etc.

It is convenient to work with the *spherical components* (also known as the *standard components*) of the vector operator $\mathbf{V}$ rather than the cartesian components. These are defined by

$$V_1 = -(V_x + iV_y)/\sqrt{2},\ V_0 = V_z,\ V_{-1} = (V_x - iV_y)/\sqrt{2}. \tag{6.72}$$

Using these in (6.71), we finally get the following nine commutators between the components of $\mathbf{J}$ and those of $\mathbf{V}$:

$$\begin{aligned}
&[J_+,\ V_1] = 0, && [J_-, V_1] = \sqrt{2}\,\hbar V_0, && [J_z,\ V_1] = \hbar V_1,\\
&[J_+,\ V_{-1}] = \sqrt{2}\,\hbar V_0, && [J_-,\ V_{-1}] = 0, && [J_z,\ V_{-1}] = -\hbar V_{-1},\\
&[J_+,\ V_0] = \sqrt{2}\,\hbar V_1, && [J_-,\ V_0] = \sqrt{2}\,\hbar V_{-1}, && [J_z,\ V_0] = 0.
\end{aligned} \tag{6.73}$$

These commutation relations can be further condensed to the form

$$\begin{aligned}
&[J_\pm, V_q] = [2 - q(q \pm 1)]^{\frac{1}{2}}\,\hbar\, V_{q\pm 1},\\
&[J_z, V_q] = q\,\hbar\, V_q;\ q = 1, 0, -1.
\end{aligned} \tag{6.74}$$

These equations serve as an alternative definition of a vector operator: **V** is said to be a vector operator if its components satisfy the commutation relations (6.74) with the components of the total angular momentum.

As a third alternative, we can use the fact that the spherical components of a vector **r** transform under a finite rotation $R(\alpha, \beta, \gamma)$ according as

$$R(\alpha, \beta, \gamma)\, r_m \equiv r_m' = \sum_{m'=-1}^{1} r_{m'}\, D_{m'm}^{(1)}(\alpha, \beta, \gamma); \tag{6.75}$$

(see Problem 4.11). We then say that **V** is a vector operator if its components are operators transforming according to

$$U_R(\underline{\phi})^\dagger\, V_m\, U_R(\underline{\phi}) \equiv V_m' = \sum_{m'=-1}^{1} V_{m'}\, D_{m'm}^{(1)}(\alpha, \beta, \gamma), \tag{6.76}$$

where $U_R(\underline{\phi})$ corresponds to the rotation $R(\alpha, \beta, \gamma)$.

For the sake of ready reference, we shall give here the explicit form of the matrix $D^{(1)}(\alpha, \beta, \gamma)$ obtained from (4.88) with $j=1$. It is found to be

$$D^{(1)}(\alpha, \beta, \gamma) = \begin{bmatrix} \cos^2\frac{\beta}{2}\, e^{i(\alpha+\gamma)} & -\frac{1}{\sqrt{2}}\sin\beta\, e^{i\gamma} & \sin^2\frac{\beta}{2}\, e^{i(\gamma-\alpha)} \\ \frac{1}{\sqrt{2}}\sin\beta e^{i\alpha} & \cos\beta & -\frac{1}{\sqrt{2}}\sin\beta\, e^{-i\alpha} \\ \sin^2\frac{\beta}{2} e^{i(\alpha-\gamma)} & \frac{1}{\sqrt{2}}\sin\beta\, e^{-i\gamma} & \cos^2\frac{\beta}{2}\, e^{-i(\alpha+\gamma)} \end{bmatrix}. \tag{6.77}$$

It can be verified that it is a unitary matrix.

We have defined earlier the two types of vectors—polar and axial. Both have the same transformation properties under pure rotations but a polar vector undergoes a change of sign under inversion whereas an axial vector is invariant under inversion. The same definition is taken over for *polar* and *axial vector operators*. Thus, with U_J denoting the inversion operator, we have

$$U_J^\dagger\, \mathbf{V} U_J = \begin{cases} -\mathbf{V} \text{ for a polar vector operator,} \\ +\mathbf{V} \text{ for an axial vector operator.} \end{cases} \tag{6.78}$$

A polar vector (operator) belongs to the representation $D^{(1,-)}$ whereas an axial vector (operator) belongs to $D^{(1,+)}$ of $O(3)$. Among the examples mentioned above in this subsection, the operators for position,

linear momentum and electric dipole moment are polar vector operators while the angular momentum operator (orbital, spin or isotopic spin) and magnetic dipole moment operator are axial vector operators.

6.5.3 Tensor and irreducible tensor operators. If **u** and **v** are two vectors, then it is known from elementary tensor algebra that the nine quantities $u_m v_q$ (where $m, q = -1, 0, 1$) constitute the components of a tensor of rank two and transform under rotations according to

$$R(\alpha, \beta, \gamma)\, u_m v_q \equiv u_{m'}\, v_{q'} = \sum_{n,\, l=-1}^{+1} u_n v_l\, D_{nm}^{(1)}(\alpha, \beta, \gamma)\, D_{lq}^{(1)}(\alpha, \beta, \gamma). \tag{6.79}$$

Similarly, the nine operators $U_m V_q$, where **U** and **V** are vector operators, are said to be the components of the *tensor operator* **UV** of rank two if the transformed components

$$U_{m'}\, V_{q'} \equiv U_R^{+}\, U_m\, V_q\, U_R \tag{6.80}$$

can be expressed in terms of $U_m V_q$ as in (6.79). The tensor operator **UV** is the Kronecker or direct product of the vector operators **U** and **V**.

It is clear that the nine components of the tensor **UV** generate a nine-dimensional representation $D^{(1)} \otimes D^{(1)}$ of $SO(3)$. This representation can be reduced to the form $D^{(0)} \oplus D^{(1)} \oplus D^{(2)}$. It follows that it is possible to construct suitable linear combinations of the nine components of **UV** such that one of these is invariant under all rotations, three of them generate $D^{(1)}$ and the remaining five combinations generate $D^{(2)}$. The invariant linear combination is obviously the trace of the matrix[10] **UV** which is

$$T_0^0 = U_x V_x + U_y V_y + U_z V_z = \sum_{m=-1}^{1} (-1)^m U_m\, V_{-m}. \tag{6.81}$$

T_0^0 is therefore a scalar operator which generates the representation $D^{(0)}$. It is clearly equal to $\mathbf{U} \cdot \mathbf{V}$, the scalar product of the two vector operators **U** and **V**.

The three linear combinations which generate $D^{(1)}$ can be seen to be the components of the vector product $\mathbf{T}^{(1)} = \mathbf{U} \times \mathbf{V}$. This has the cartesian components

$$T_x^{(1)} = U_y V_z - U_z V_y,\ T_y^{(1)} = U_z V_x - U_x V_z,$$
$$T_z^{(1)} = U_x V_y - U_y V_x, \tag{6.82}$$

which transform like x, y and z under rotations. By using (6.72), we

[10] A tensor of rank two such as **UV** can be expressed as a square matrix with elements $U_i V_j$ where $i, j = x, y, z$.

can obtain the spherical components of $\mathbf{T}^{(1)}$ which are

$$T_{\pm 1}^{(1)} = U_{\pm 1} V_0 - U_0 V_{\pm 1}, \quad T_0^{(1)} = U_1 V_{-1} - U_{-1} V_1, \tag{6.83}$$

which transform like $x \pm iy$ and z respectively, or like the spherical harmonics of degree one.

Finally, the five linear combinations which generate $D^{(2)}$ are, apart from constant factors, found to be

$$\begin{aligned} &T_{xy}^{(2)} = U_x V_y + U_y V_x, \; T_{yz}^{(2)} = U_y V_z + U_z V_y, \\ &T_{zx}^{(2)} = U_z V_x + U_x V_z, \; T_{x^2-y^2}^{(2)} = U_x V_x - U_y V_y, \\ &T_{2z^2-x^2-y^2}^{(2)} = 2U_z V_z - U_x V_x - U_y V_y, \end{aligned} \tag{6.84}$$

in terms of the cartesian components of $\mathbf{U}$ and $\mathbf{V}$. They transform like the five independent polynomials of degree two, which is indicated by using suitable subscripts. Once again, converting these into spherical components we get the following components which are proportional to the spherical harmonics of degree two:

$$\begin{aligned} &T_{\pm 2}^{(2)} \sim T_{x^2-y^2}^{(2)} \pm 2i T_{xy}^{(2)} \sim U_{\pm 1} V_{\pm 1} \propto Y_2^{\pm 2}(\theta, \phi), \\ &T_{\pm 1}^{(2)} \sim \mp (T_{zx}^{(2)} \pm i T_{yz}^{(2)}) \sim U_{\pm 1} V_0 + U_0 V_{\pm 1} \propto Y_2^{\pm 1}(\theta, \phi), \\ &T_0^{(2)} \sim T_{2z^2-x^2-y^2}^{(2)} \sim 2U_0 V_0 + U_1 V_{-1} + U_{-1} V_1 \propto Y_2^0(\theta, \phi). \end{aligned} \tag{6.85}$$

The sign $\sim$ is used instead of equality to denote that constant factors have been dropped.

The operators $\mathbf{T}^{(0)}$, $\mathbf{T}^{(1)}$ and $\mathbf{T}^{(2)}$ constructed above are called *irreducible tensor operators*. In general, we define an irreducible tensor operator (or a spherical tensor operator) $\mathbf{T}^{(k)}$ of degree[11] k where $k = 0, \frac{1}{2}, 1, \frac{3}{2}, \ldots$, as an operator having $2k+1$ components $T_q^{(k)}$ with $q = -k, -k+1, \ldots, k-1, k$, called the *spherical* or *standard components* which transform under rotations according to

$$U_R^{\dagger} T_q^{(k)} U_R = \sum_{m=-k}^{k} T_m^{(k)} D_{mq}^{(k)}(R). \tag{6.86}$$

In other words, $\mathbf{T}^{(k)}$ is an irreducible tensor operator if its $2k+1$ components generate the irreducible representation $D^{(k)}$ of $SU(2)$. The $2l+1$ spherical harmonics $Y_l^m(\theta, \phi)$ considered as operators are the standard components of an irreducible tensor operator $\mathbf{Y}^{(l)}$ of degree l. Also, the 2^l electric or magnetic multipole moment operator is an irreducible tensor operator of degree l. For $l = 0, 1, 2, 3, \ldots$, we get the monopole, dipole, quadrupole, octupole, ..., moment operators.

It turns out that all irreducible tensor operators of physical interest

[11] Some authors call this the rank, but this is likely to lead to confusion because the operator $\mathbf{UV}$ is also a tensor of *rank* two.

have integral values of k. Since the components of an irreducible tensor operator $\mathbf{T}^{(k)}$ for integral k have the same transformation properties as the spherical harmonics of degree k, they have the same commutation relations with the components of the total angular momentum operator $\mathbf{J}$ as do the spherical harmonics. This follows from (6.60) which tells that the transformation of an operator under rotations is uniquely determined by its commutators with $\mathbf{J}$. Knowing the commutators[12] of the components of $\mathbf{J}$ with Y_k^m, we can immediately write down the following commutators:

$$[J_z,\ T_q^{(k)}] = q\hbar\ T_q^{(k)},$$
$$[J_\pm,\ T_q^{(k)}] = [k\ (k+1) - q(q\pm 1)]^{\frac{1}{2}}\ \hbar\ T_{q\pm 1}^{(k)}. \qquad (6.87)$$

These equations provide an alternative definition of irreducible tensor operators. This definition, which is due to Racah,[13] states that the $2k+1$ operators $T_q^{(k)}$ are said to be the standard components of an irreducible tensor operator $\mathbf{T}^{(k)}$ if they satisfy the commutation relations (6.87) with the components of the total angular momentum operator. Note that for $k=1$, we have explicitly shown the equivalence of the two definitions (6.86) and (6.87) for vector operators in the previous subsection. In the general case also, it is possible in principle, though laborious, to obtain the commutation relations (6.87) by comparing (6.60) and (6.86).

6.5.4 Direct product of irreducible tensor operators. We have shown in the previous subsection that the direct product of two vector operators can be reduced to a sum of three irreducible tensor operators. We can generalize this concept and show that the direct product of any two irreducible tensor operators can be reduced to a sum of irreducible tensor operators.

Let $\mathbf{S}^{(k)}$ and $\mathbf{T}^{(p)}$ be two irreducible tensor operators of degree k and p, respectively. The direct product of these is defined as a tensor operator having the $(2k+1)(2p+1)$ components $S_q^{(k)}\,T_r^{(p)}$ for $-k \leq q \leq k$ and $-p \leq r \leq p$. To investigate the transformation properties of these components, we consider the effect of a rotation R on one of the components. The transformed component is given by

$$U_R^\dagger\, S_q^{(k)}\ T_r^{(p)}\ U_R = U_R^\dagger\, S_q^{(k)}\ U_R\ U_R^\dagger\, T_r^{(p)}\ U_R$$
$$= \sum_{l,\,n} S_l^{(k)}\ T_n^{(p)}\ D_{lq}^{(k)}(R)\ D_{nr}^{(p)}(R). \qquad (6.88)$$

[12]Schiff (1968), Eqs. (28.16) and (28.17).
[13]Fano and Racah (1959).

This shows that the $(2k+1)(2p+1)$ operators $S_q^{(k)} T_r^{(p)}$ transform according to the direct product representation $D^{(k)} \otimes D^{(p)}$. It follows that the operator $S_q^{(k)} T_r^{(p)}$ can be expressed as a linear combination of irreducible tensor operators $U_t^{(s)}$ for $|k-p| \leq s \leq k+p$ and $-s \leq t \leq s$ with *C-G* coefficients in the form

$$S_q^{(k)} T_r^{(p)} = \sum_s \sum_t U_t^{(s)} <k\ q,\ p\ r | s\ t>. \tag{6.89}$$

Let us invert the above relation to obtain $U_t^{(s)}$. Multiplying both sides of (6.89) by $<k\ q,\ p\ r | s'\ t'>$, summing over q and r and using the orthogonality relation (6.47c), we obtain

$$U_t^{(s)} = \sum_{q=-k}^{k} \sum_{r=-p}^{p} S_q^{(k)} T_r^{(p)} <k\ q,\ p\ r | s\ t>. \tag{6.90}$$

It can be shown explicitly that $U_t^{(s)}$ are the components of an irreducible tensor operator. For this, we obtain the commutation relations of $U_t^{(s)}$ with the angular momentum operator. Using the operator identity $[A, BC] = [A, B]C + B[A, C]$, we find that

$$\begin{aligned}[J_z, U_t^{(s)}] &= \sum_{q,r} \{[J_z, S_q^{(k)}] T_r^{(p)} + S_q^{(k)} [J_z, T_r^{(p)}]\} \\ &\qquad \times <k\ q, p\ r | s\ t> \\ &= \sum_{q,r} (q+r) \hbar\, S_q^{(k)} T_r^{(p)} <k\ q, p\ r | s\ t> \\ &= t \hbar\, U_t^{(s)}, \end{aligned} \tag{6.91}$$

where we have used (6.87) and the fact that the *C-G* coefficient $<k\ q,\ p\ r | s\ t>$ survives only if $q+r=t$ (see (6.44)).

Next, we obtain the commutator of J_+ with $U_t^{(s)}$. Using (6.87), this gives

$$\begin{aligned}[J_+, U_t^{(s)}] = \sum_{q,r} \{&[k(k+1)-q(q+1)]^{\frac{1}{2}} \hbar\, S_{q+1}^{(k)} T_r^{(p)} \\ &+ [p(p+1)-r(r+1)]^{\frac{1}{2}} \hbar S_q^{(k)} T_{r+1}^{(p)}\} <k\ q,\ p\ r | s\ t>. \end{aligned} \tag{6.92}$$

As in obtaining (6.51), we now replace the sum over q in the first term by that over $q'=q+1$. The limits of q' can be taken to be the same as those of q ($-k$ to k). Similarly, in the second term, we replace the sum over r by that over $r'=r+1$. After rearranging the expression, we finally drop the primes in q' and r' to get

$$\begin{aligned}[J_+, U_t^{(s)}] = \sum_{q,r} \{&[k(k+1)-q(q-1)]^{\frac{1}{2}} \hbar <k\ q-1,\ p\ r | s\ t> \\ &+ [p(p+1)-r(r-1)]^{\frac{1}{2}} \hbar <k\ q,\ p\ r-1 | s\ t>\}\, S_q^{(k)} T_r^{(p)}. \end{aligned} \tag{6.93}$$

Using the recursion relation (6.51), this becomes

$$\begin{aligned}[J_+, U_t^{(s)}] = \sum_{q,r} &[s(s+1)-t(t+1)]^{\frac{1}{2}} \hbar\, S_q^{(k)} T_r^{(p)} \\ &\times <k\ q,\ p\ r | s\ t+1>. \end{aligned} \tag{6.94}$$

Substituting from the definition (6.90), we finally get

$$[J_+, U_t^{(s)}]=[s(s+1)-t(t+1)]^{1/2}\hbar\, T_{t+1}^{(s)}. \tag{6.95}$$

A similar treatment shows that

$$[J_-, U_t^{(s)}]=[s(s+1)-t(t-1)]^{1/2}\hbar\, U_{t-1}^{(s)}. \tag{5.96}$$

Eqs. (6.91), (6.95) and (6.96) prove that $\mathbf{U}^{(s)}$ is an irreducible tensor operator of degree s.

6.5.5 Action of a tensor operator on an angular momentum eigenstate. In this subsection, we shall show that the operation of a component of an irreducible tensor operator $\mathbf{T}^{(k)}$ on an angular momentum eigenstate $|j\,m>$ gives a state which can be expanded as a linear combination of the angular momentum eigenstates. For this, we consider the rotational properties of the state $T_q^{(k)}|j\,m>$. Operating on this by $U_R^\dagger$, which corresponds to the rotation R, and using (6.86) and (6.31), we have

$$\begin{aligned} U_R^\dagger T_q^{(k)}|j\,m> &= U_R^\dagger T_q^{(k)}\, U_R U_R^\dagger\, |j\,m> \\ &= \sum_{q',m'} T_{q'}^{(k)}|j\,m'> D_{q'q}^{(k)}(R)\, D_{m'm}^{(j)}(R). \end{aligned} \tag{6.97}$$

This shows that the $(2k+1)(2j+1)$ states $T_q^{(k)}|jm>$ transform according to the direct product representation $D^{(k)} \otimes D^{(j)}$. It immediately follows that they can be written as linear combinations of angular momentum eigenstates $|j'\,m'>$ transforming according to the irreducible representation $D^{(j')}$ for $|k-j| \leq j' \leq k+j$ in the form

$$T_q^{(k)}|j\,m> = \sum_{j',m'} |j'\,m'> <j'\,m'\,|k\,q, j\,m>. \tag{6.98}$$

Inverting the above relation, we find

$$|j'\,m'> = \sum_{q,m} T_q^{(k)}|j\,m> <k\,q, j\,m\,|j'\,m'>. \tag{6.99}$$

It can be explicitly shown that the states constructed in (6.99) are angular momentum eigenstates with quantum numbers j' and m'. This is the converse of the above problem. To this aim, we operate on both sides of (6.99) by J_z and use the first of (6.87) to obtain

$$\begin{aligned} J_z|j'\,m'> &= \sum_{q,m} J_z\, T_q^{(k)}|j\,m> <k\,q, j\,m|j'\,m'> \\ &= \sum_{q,m} (T_q^{(k)} J_z + q\hbar\, T_q^{(k)})|j\,m> <k\,q, j\,m|j'\,m'> \\ &= \sum_{q,m} (m+q)\hbar\, T_q^{(k)}|jm> <k\,q, j\,m|j'\,m'> \\ &= m'\hbar|j'\,m'>. \end{aligned} \tag{6.100}$$

Similarly, we can operate on both sides of (6.99) by $J_\pm$ and, using the

commutation relations (6.87), proceed as before. The reader should be familiar with this method by now. The final result is

$$J_{\pm}\,|j'\,m'\!>=[j'\,(j'+1)-m'\,(m'\pm 1)]^{\frac{1}{2}}\,\hbar\,|j'\,m'\pm 1\!>, \qquad (6.101)$$

which, together with (6.100), shows that (6.99) is an angular momentum eigenstate.

6.6 Matrix Elements of Tensor Operators

The actual transformation properties of the tensor operators and the eigenstates are not of so much importance in themselves as the physically interesting matrix elements of the operators between the eigenstates. There is a theorem due to Wigner and Eckart which gives the ratios of the matrix elements of a tensor operator between angular momentum eigenstates in terms of the *C-G* coefficients. This greatly simplifies the calculation because all the matrix elements of a tensor operator can be related to one particular element which may be chosen to be the simplest one and which is usually determined experimentally.

6.6.1 Wigner-Eckart theorem. On putting in the other quantum numbers explicitly, Eq. (6.98) can be written in the from

$$T_q^{(k)}\,|N\,j\,m\!>=\sum_{j',m'}\,|N\,j'\,m'\!>\,<j'\,m'\,|k\,q,\,j\,m\!>. \qquad (6.102)$$

Let $\mathbf{T}^{(k)}$ be the tensor operator whose matrix elements we are interested in. Owing to the presence of the *C-G* coefficient, only one term in the sum over m' in (6.102) survives, that for which $m'=m+q$. Even this term would vanish if $|m+q|>j'$. Moreover, j' itself is restricted to the range $|k-j|\leq j'\leq k+j$. With these selection rules implicit in the *C-G* coefficients, Eq. (6.102) tells that the state $T_q^{(k)}|\,N\,j\,m\!>$ contains various parts transforming according to the $(m+q)$ column of the irreducible representation $D^{(j')}$ with the coefficients $<j'\,m'\,|\,k\,q.\,j\,m\!>$. The scalar product of $T_q^{(k)}|\,N\,j\,m\!>$ with some angular momentum eigenstate $|\,N_1\,j_1\,m_1\!>$ will survive only if $m_1=m+q$, $|k-j|\leq j_1\leq k+j$ and $|\,m+q|\leq j_1$. When all the three conditions are satisfied, (6.102) shows that the scalar product in question, which is in fact the matrix element $<N_1 j_1\,m_1\,|\,T_q^{(k)}|\,N\,j\,m\!>$, is proportional to $<j_1\,m_1|\,k\,q,\,j\,m\!>$ due to the orthogonality of the states $|\,N\,j\,m\!>$ for different j and m. If any one of the three conditions is violated, the *C-G* coefficient and hence the matrix element under consideration are zero. In either case, therefore, we can write the matrix element $<N_1\,j_1\,m_1\,|\,T_q^{(k)}\,|\,N\,j\,m\!>$ as the product of the coefficient $<j_1\,m_1\,|\,k\,q,\,j\,m\!>$ and some quantity which we write in the form

$$< N_1 j_1 m_1 \mid T_q^{(k)} \mid N j m> = F(N_1 j_1 m_1, T_q^{(k)}, N j m) < j_1 m_1 \mid k\, q, j\, m>. \quad (6.103)$$

It will be our aim now to show that the quantity $F(N_1 j_1 m_1, T_q^{(k)}, N j m)$ is independent of m, m_1 and q.

Taking explicitly the scalar product of $\mid N_1 j_1 m_1>$ with (6.102), we find that

$$< N_1 j_1 m_1 \mid T_q^{(k)} \mid N j m> = < N_1 j_1 m+q \mid N' j_1 m+q>< j_1 m_1 \mid k\, q, j\, m>. \quad (6.104)$$

Similarly, replacing m_1, q and m respectively by m_1', q' and m', we obtain

$$< N_1 j_1 m_1' \mid T_{q'}^{(k)} \mid N j m'> = < N_1 j_1 m'+q' \mid N' j_1 m'+q'>< j_1 m_1' \mid k\, q', j\, m'>. \quad (6.105)$$

We have shown in Section 5.5.1 that the scalar product of two basis functions both transforming according to the same column of the same irreducible representation is independent of the column index (Eq. (5.45b)). We therefore have

$$< N_1 j_1 m+q \mid N' j_1 m+q> = < N_1 j_1 m'+q' \mid N' j_1 m'+q'>. \quad (6.106)$$

Eq. (6.104) then shows that the ratio

$$< N_1 j_1 m_1 \mid T_q^{(k)} \mid N j m> / < j_1 m_1 \mid k\, q, j\, m>$$

is independent of m, q and hence m_1. We can therefore write (6.103) in the form

$$< N_1 j_1 m_1 \mid T_q^{(k)} \mid N j m> = < N_1 j_1 \| \mathbf{T}^{(k)} \| N j>< j_1 m_1 \mid k\, q, j\, m>, \quad (6.107)$$

where the quantity $< N_1 j_1 \| \mathbf{T}^{(k)} \| N j>$ depends only on the nature of the tensor operator and the quantum numbers N, j, N_1 and j_1. It is independent of m, q and m_1. It is known as the *reduced matrix element* or the *double-bar matrix element*.[14]

Eq. (6.107) embodies the *Wigner-Eckart theorem*. Expressed in words, it states that *the matrix element of the q-th standard component of a tensor operator* $\mathbf{T}^{(k)}$ *between the angular momentum eigenstates* $\mid N j m>$ *and* $\mid N_1 j_1 m_1>$ *equals the product of the C-G coefficient* $< j_1 m_1 \mid k\, q, j\, m>$ *with a number which is independent of* m, q *and* m_1.

The matrix element (6.107) has the same selection rules as the *C-G* coefficient appearing in it, i.e., it vanishes unless $\mid k-j \mid \leq j_1 \leq k+j$, $m_1 = m+q$ and $\mid m_1 \mid \leq j_1$. Once the reduced matrix element $< N_1 j_1 \| \mathbf{T}^{(k)} \| N j>$ is determined for given values of j, j_1, N and N_1, all the

[14] It is not a 'matrix element' in the quantum mechanical sense, hence the use of the double bars.

$(2j+1)(2k+1)(2j_1+1)$ matrix elements can be easily obtained from a table of C-G coefficients. Moreover, taking the ratio of any two matrix elements (of the same tensor operator) of the form (6.107), we find that

$$\frac{<N_1 j_1 m_1 \mid T_q^{(k)} \mid N j m>}{<N_1 j_1 m_1' \mid T_{q'}^{(k)} \mid N j m'>} = \frac{<j_1 m_1 \mid k q, j m>}{<j_1 m_1' \mid k q', j m'>}, \tag{6.108}$$

so that the ratios of the matrix elements are determined without any other knowledge.

It is not an easy task to calculate the reduced matrix element theoretically. It is normally determined by calculating one particular matrix element experimentally. This is usually chosen to be the one simplest to observe, that for which $q=0$ and $m=m_1=0$ or $\frac{1}{2}$ depending on whether the system has integral or half-odd-integral angular momentum. The Wigner-Eckart theorem has useful applications in atomic and nuclear physics.

6.6.2 Selection rules for multipole transitions. The 2^l electric or magnetic multipole operator is a $(2l+1)$-component irreducible tensor operator of degree l. The electric multipole operator has parity $(-1)^l$ whereas the magnetic multipole operator has parity $(-1)^{l+1}$ under inversion. The case $l=1$ (dipole moment operators) has already been treated in Section 6.2. We shall now obtain the selection rules for electric quadrupole transitions in many- and one-electron atoms.

The electric quadrupole moment operator is an irreducible tensor operator corresponding to $k=2$ and has even parity under inversion. Looking at (6.107), we see that the matrix element of the electric quadrupole moment operator between the states $\mid N L M>$ and $\mid N' L' M'>$ of a many-electron atom will be proportional to the C-G coefficient $<L' M' \mid 2\, q, L M>$ where $-2 \leq q \leq 2$. This immediately gives the selection rules

$$\begin{aligned} &\Delta L = 0, \pm 1, \pm 2 \ (0 \leftarrow/\rightarrow 0,\ 0 \leftarrow/\rightarrow 1); \\ &\Delta M = 0, \pm 1, \pm 2. \end{aligned} \tag{6.109}$$

For transitions between the total angular momentum eigenstates $\mid N J M>$ and $\mid N' J' M'>$, we have similar selection rules. Remembering that J can take integral as well as half-odd-integral values, we have the selection rules

$$\begin{aligned} &\Delta J = 0, \pm 1, \pm 2 \ (0 \leftarrow/\rightarrow 0,\ \tfrac{1}{2} \leftarrow/\rightarrow \tfrac{1}{2},\ 0 \leftarrow/\rightarrow 1); \\ &\Delta M = 0, \pm 1, \pm 2. \end{aligned} \tag{6.110}$$

In one-electron atoms, there is an additional restriction due to

parity. Thus, if there is a state of a one-electron atom belonging to $D^{(l,\sigma)}$, there may be states belonging to $D^{(l+2,\sigma)}$, but there can be no states belonging to $D^{(l+1,\sigma)}$. Since the electric quadrupole moment operator has even parity, we have the following selection rules for a one-electron atom:

$$\Delta l=0, \pm 2 \ (0 \leftarrow/\rightarrow 0). \tag{6.111}$$

As an important corollary of these selection rules, let us consider the expectation value of the 2^l-multipole (electric or magnetic) moment operator in an angular momentum eigenstate; this is $<N\ j\ m \mid T_q^{(l)} \mid N\ j\ m>$. This expectation value vanishes unless $|\ l-j\ | \leq j \leq l+j$, i.e., unless $l \leq 2j$. Thus, a spin-zero particle has zero expectation value for the dipole moment, or, in other words, a spin-zero particle cannot possess any dipole moment. Similarly, a spin-zero or a spin-$\frac{1}{2}$ particle cannot have any quadrupole moment, etc.

PROBLEMS ON CHAPTER 6

(6.1) Show that every class of S_n must contain either all even or all odd permutations.

(6.2) Show that all the classes of S_n are self-inverse classes. (See Problem 3.13 for definition.)

(6.3) For a system of n identical objects, show that

(a) $(j\ k)\ (j\ m)\ (j\ k) = (j\ m)\ (j\ k)\ (j\ m) = (k\ m)$;

(b) $(j\ k)\ (j\ m)\ (j\ k)\ (j\ m) = (j\ m)\ (j\ k)$;

(c) $[(i\ j)\ (l\ k)\ (i\ m)]\ (i\ j) = (i\ m)\ [(i\ j)\ (i\ k)\ (i\ m)]$;

(d) $[(i\ j)\ (i\ k)\ (i\ j)]\ (i\ m) = (i\ m)\ [(i\ j)\ (i\ k)\ (i\ j)]$;

where $l, j, k, m \leq n$.

(6.4) Generate all the permutations of S_4 from the generators (1 2), (1 3), (1, 4) that is, starting with identity, single transpositions ((1 2), (1 3), (1 4)), product of two generators ((1 2) (1 3), (1 3) (1 2), ...), product of three generators, etc. Show that you get exactly 24 distinct elements, [Hint: Use the properties given in Problem (6.3).]

(6.5) Let $\mathbf{J}_1$ and $\mathbf{J}_2$ be two angular momenta.

(a) Show that if $\mathbf{J}_1$ commutes with $\mathbf{J}_2$, the vector $\mathbf{K}=\mathbf{J}_1-\mathbf{J}_2$ (with components $K_x=J_{1x}-J_{2x}$, etc.) is *not* an angular momentum.

(b) Show that $\mathbf{K}=\mathbf{J}_1-\mathbf{J}_2$ is an angular momentum if the components of $\mathbf{J}_1$ and $\mathbf{J}_2$ obey the commutation relations $[J_{1x}, J_{2x}]=0$, $[J_{1x}, J_{2y}]=i\hbar J_{2z}$, $[J_{1z}, J_{2z}]=-i\hbar J_{2y}$, and their cyclic permutations.

(6.6) Let U and V be two vector operators.

(a) Show that

$$\sum_{m=-1}^{+1} (-1)^m U_m V_{-m} = \mathrm{U}.\mathrm{V} \equiv T_0^{(0)}.$$

(b) Show explicitly that the operator $T_0^{(0)}$ constructed above is a scalar

operator. [Hint: On using (6.79) on the left hand side of the above equation, you will get a factor $\sum_m (-1)^m D_{nm}^{(1)} D_{l,-m}^{(1)}$. By looking at the matrix (6.77) you can show that $(-1)^m D_{l,-m}^{(1)} = (-1)^l D_{-l,m}^{(1)*}$. This gives the factor $\sum_m (-1)^l D_{nm}^{(1)} D_{-l,m}^{(1)*}$, which is equal to $(-1)^l \delta_{n,-l}$ owing to the unitarity of $D^{(1)}$. The result follows.]

(6.7) This is the generalization of the above problem. If $\mathbf{U}^{(k)}$ and $\mathbf{V}^{(k)}$ are two tensor operators of the same degree k, show that

$$\sum_{q=-k}^{k} (-1)^q U_q^{(k)} V_{-q}^{(k)}$$

is a scalar operator. (This is known as the *scalar product* of two tensor operators.) [Hint: You will have to show in general from (4.73b) that

$$(-1)^q D_{m,-q}^{(k)} = (-1)^m D_{-m,q}^{(k)*}.]$$

(6.8) Given that one angular momentum is $j_2 = \frac{1}{2}$, obtain the *C-G* coefficients keeping j_1, m_1 and m general. You will have a 2×2 matrix with the row index $m_2 = \pm\frac{1}{2}$ and the column index $j = j_1 \pm \frac{1}{2}$.

(6.9) Show that if $\mathbf{V}$ is replaced by $\mathbf{J}$ in (6.71), it becomes an identity, that is, $i[\underline{\phi} \cdot \mathbf{J}, \mathbf{J}] = \hbar\, \underline{\phi} \times \mathbf{J}$.

Bibliography for Chapter 6

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CHAPTER 7

Crystallographic and Molecular Symmetries

Crystals distinguish themselves by a regular arrangement of the constituent atoms in three dimensions. A crystal can be thought of as made up of a lattice and a basis.[1] A *lattice* is merely a regular pattern of points in one, two or three dimensions. If with each point of the lattice (called a *lattice point*), we associate a *basis* containing a certain number of atoms, the resulting structure is a *crystal.* We assume that the lattice extends to infinity in all the three directions (which may be taken care of by the periodic boundary conditions).

The symmetry of the crystal plays an extremely important role in the study of the properties of crystals such as diffraction of waves from crystals, the electronic structure of crystals, etc. Various other phenomena such as the colours exhibited by crystals having impurities and defects, paramagnetic resonance of impurity atoms and Mössbauer effect studies of an impurity ion in a host crystal also depend on the symmetry of the environment of the impurity atom. It is but natural, therefore, that group theory is an essential and helpful tool in the study of various solid state phenomena.

Owing to the assumption of the infinite extension of a crystal in all directions, there are severe restrictions on the possible rotational symmetries of a crystal. For example, a molecule may have an n-fold

[1] Kittel (1976).

symmetry where n is any positive integer including infinity. However, in crystals, only some values of n are allowed.

The geometrical symmetry transformations of a crystal are of three types: (i) translations, (ii) rotations, reflections and inversion, which are known as *point symmetry operations*, and (iii) combinations of the above two types of operation. When the group of transformations of a certain system consists of operations which leave one point of the system undisplaced in position (i.e., operations of type (ii)), it is called a *point group*. Examples of a point group are C_{4v}, $O(2)$, $O(3)$, etc. Groups containing space translations are not point groups. The crystal symmetry groups can therefore be divided into two categories—the *crystallographic point groups*, which leave at least one point of the crystal undisplaced, and the *crystallographic space groups*, which include the translational symmetry of the crystals. The molecules, on the other hand, possess only point symmetries, except in the case of very long chain polymer molecules which may be thought of as having some translational symmetry and which will not be considered here.

In this chapter, we shall study the crystallographic point and space groups, the molecular point groups, the double groups, and their irreducible representations. The irreducible representations of the space groups will be dealt with in the next chapter.

7.1 Crystallographic Point Groups

The requirement of translational symmetry in the crystals puts a limit on the number of possible crystallographic point groups. This can be easily seen as follows. First we note that all the lattice points in a lattice are equivalent to each other in the sense that the lattice as seen from one lattice point looks exactly the same as viewed from any other lattice point. This means that if the lattice is invariant under a rotation of $2\pi/n$ (n a positive integer) about some axis passing through a lattice point, then a rotation of $2\pi/n$ about a parallel axis passing through any other lattice point is also a symmetry transformation of the lattice. This imposes severe restrictions on the possible point groups. In fact, it is an elementary problem of solid state physics[2] to show that the only n-fold rotations consistent with translational symmetry are $n=1, 2, 3, 4$ and 6. There are altogether 32 crystallographic point groups which we shall enumerate below.

If we choose the point which is invariant under the point group

[2]Azaroff (1960), pp. 16-17.

as the origin of a cartesian coordinate system, then a point group would contain only the following types of operation:

(a) rotations about any axis passing through the origin,
(b) reflections in planes passing through the origin,
(c) inversion.

It should be noted that the operations of the above three types are not independent of each other. Any one of these operations can be constructed by suitably combining the remaining two types of operations. Thus, the inversion can be thought of as a rotation through π about an arbitrary axis passing through the origin followed by a reflection in a plane perpendicular to the axis and passing through the origin.

A rotation followed by a reflection or the inversion is called an *improper rotation* as against a *proper rotation*. We can easily verify that the product of two proper rotations or of two improper rotations is a proper rotation, while the product of a proper rotation with an improper rotation is an improper rotation.[3]

It is also expedient to note that the following pairs of point group operations commute with each other: (a) inversion and any other operation, (b) two rotations about the same axis, (c) rotations through π about two perpendicular axes, (d) a rotation and a reflection in a plane normal to the axis of rotation, (e) a rotation through π and a reflection in a plane passing through the axis of rotation, and (f) two reflections in perpendicular planes. These can be easily verified by performing the operations on a familiar object such as a book.

7.1.1 Enumeration of the thirty-two point groups. We shall now enumerate the 32 crystallographic point groups in three dimensions. In Section 1.1, we have introduced the concept of a group by considering the example of a square. In general, if we have a regular polygon of n sides, a rotation through $2\pi/n$ about an axis normal to the plane of the polygon passing through its centre is a symmetry operation for it. The cyclic group consisting of the n rotations $(C_n, C_n^2, \ldots, C_n^n = E)$ is usually denoted by[4] (the same symbol) C_n.

The only rotational groups consistent with translational symmetry in crystals are C_1, C_2, C_3, C_4 and C_6. The geometrical patterns having these symmetry groups are shown in Fig. (7.1). Such figures, which show the projection of the atoms on a plane, are called *stereographic projections*. In this figure, and in the following figures in this chapter, we

[3] It is exactly analogous to the products of $+1$ and -1 among themselves.

[4] We shall use the Schoenflies notation for the point groups. Another notation known as the international notation is explained at the end of this section.

shall denote a point above the plane by + and a point below the plane by o. The nature of the rotation axis is denoted by a symbol in the

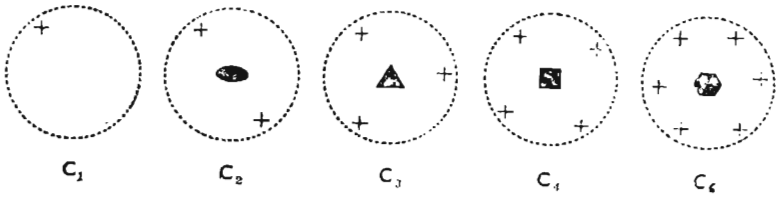

FIGURE 7.1 Stereographic projections for the point groups C_n

centre of the circle. Thus, a filled ellipse denotes a twofold axis, a filled triangle a threefold axis, a filled square a fourfold axis and a filled hexagon a sixfold axis of proper rotations. The corresponding unfilled symbol (see Figs. (7.4) and (7.7)) denotes an n-fold axis of improper rotations.

We can obtain five more point groups by introducing an additional symmetry element—reflection in the horizontal plane denoted by σ_h. We denote the group of order two, (E, σ_h), by C_{1h}. Noting that σ_h commutes with a rotation about the vertical axis, we see that the resulting groups, denoted by C_{nh}, are the direct products of C_n with the group (E, σ_h), or

$$C_{nh} = C_n \otimes C_{1h}. \tag{7.1}$$

The group C_{nh} contains $2n$ elements. The geometrical patterns having these symmetry groups are shown in Fig. (7.2). The presence of a horizontal reflection plane is indicated by drawing a full circle rather than a broken circle.

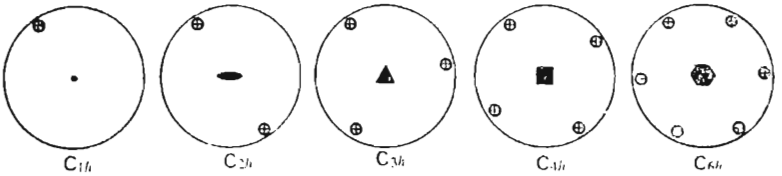

FIGURE 7.2 Stereographic projections for the point groups C_{nh}

Four more point groups can be obtained by adding a vertical reflection plane (passing through the n-fold axis) to the last four groups of Fig. (7.1). Such a reflection plane, passing through the axis of n-fold rotational symmetry, implies the existence of $n-1$ other vertical reflection planes, all passing through the axis of rotation. These groups are denoted by C_{nv} and their stereographs are shown in Fig. (7.3). The reflection planes are shown by solid lines. Although these groups also contain $2n$ elements, they cannot be expressed as

direct products of two smaller groups. This is because a reflection does not commute with a rotation about an axis in the plane of the reflection, as can be readily seen.

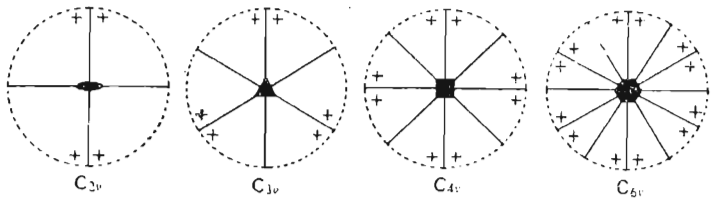

FIGURE 7.3 Stereographic projections for the point groups C_{nv}

In the above case, since the 'vertical' and the 'horizontal' are not distinguishable for C_1, we do not have a new group such as C_{1v}. In other words, the group C_{1v} is identical to C_{1h}.

We may now add the inversion symmetry J to the first five groups. Let us denote the group of order two, (E, J), by the symbol S_2. This group is isomorphic to C_{1h}. Since inversion commutes with all the rotations, we could have five direct-product groups, which may be denoted by

$$S_{2n}=C_n \otimes S_2. \tag{7.2}$$

But not all of these are new groups. In fact, if n is even ($n=2, 4$ or 6), then $C_n \otimes S_2$ is identical to C_{nv}. In the remaining two cases ($n=1$ and 3), we have two new groups S_2 and S_6. A third group S_4, which is distinct from all the point groups hitherto considered, consists of four elements which are powers of the element $JC_4=S_4$, i.e., $S_4=(E, S_4, C_4^2, S_4^3)$, noting that $J^2=E$. These groups are shown in Fig. (7.4). The patterns with the symmetry groups S_2 and S_6 have inversion symmetry, whereas the one with the group S_4 does not. The groups S_2 and S_6, as stated before, are direct products $C_1 \otimes S_2$ and $C_3 \otimes S_2$ respectively, but S_4 is not a direct product of two smaller groups.

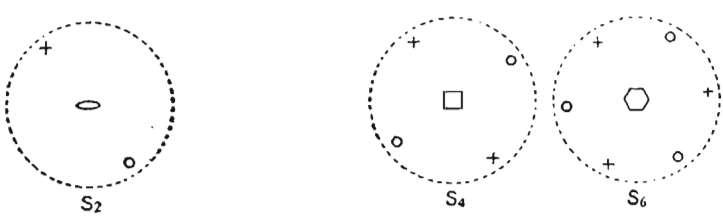

FIGURE 7.4 Stereographic projections for the point groups S_n

The 17 point groups discussed above contain only one axis of n-fold symmerty. We can obtain new point groups by introducing axes

of symmetry in the horizontal plane in addition to the vertical axis. A horizontal axis of n-fold symmetry in conjunction with the vertical axis of n-fold symmetry implies the existence of $n-1$ other horizontal axes of m-fold symmetry. If we take $m=2$, we have four new groups denoted by D_n and shown in Fig. (7.5).

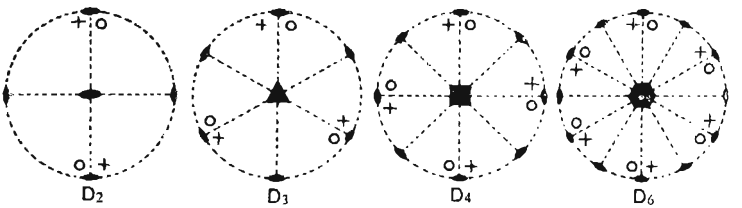

FIGURE 7.5 Stereographic projections for the point groups D_n

Now we add the horizontal twofold axes to the five groups C_{nh} of Fig. (7.2). We get four new groups denoted by D_{nh} and shown in Fig. (7.6). C_{1h} with the horizontal twofold axis is identical to C_{2v}. The group D_{nh} can also be thought of as arising from the groups D_n by the addition of a horizontal mirror plane. This can be easily seen by comparing Fig. (7.5) with Fig. (7.6). The groups D_{nh} have $4n$ elements and have inversion symmetry for even n.

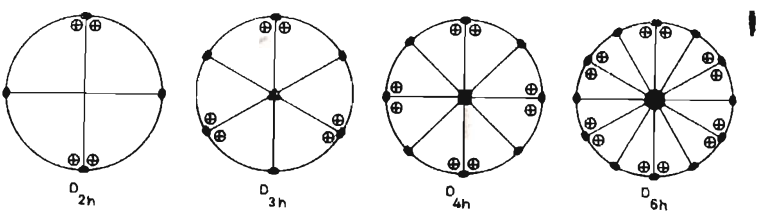

FIGURE 7.6 Stereographic projections for the point groups D_{nh}

Finally, two more groups denoted by D_{nd} for $n=2$ and 3 can be obtained by adding diagonal reflection planes bisecting the angles between the horizontal twofold axes to the groups D_n. This gives us two new groups shown in Fig. (7.7).

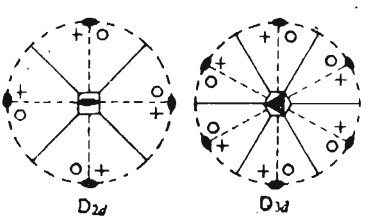

FIGURE 7.7 Stereographic projections for the point groups D_{nd}

The 27 point groups enumerated above have one principal n-fold axis (which we have chosen as the vertical) and may also have n two-fold axes in the horizontal plane. These are known as the *simple point groups* and we have discussed them in increasing order of complexity. These are also the point groups that would occur in two-dimensional crystals. There are five more groups of higher symmetry in which there are more than one axes of higher than twofold symmetry ($m>2$), i e., there is no unique principal axis of higher symmetry. These groups are also characterized by the existence of four threefold axes (e.g., the four diagonals of a cube) making equal angles with three mutually perpendicular directions. In fact, due to these symmetry properties, these groups refer to cubic systems. They are discussed below.

The largest point group, known as O_h, is the full symmetry group of a cube; Fig. (7.8). It has 48 elements among which there are 24 proper rotations and 24 improper rotations. The 24 proper rotations, which

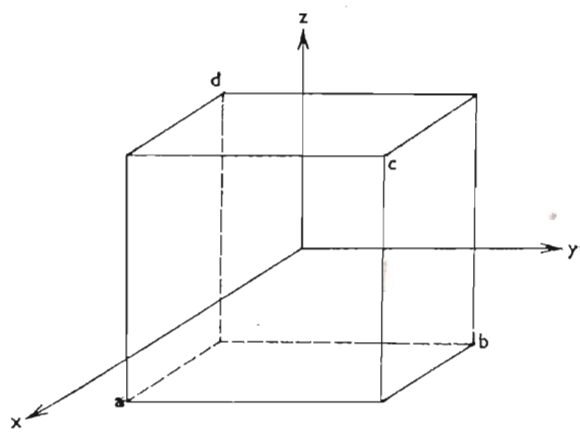

FIGURE 7.8 To illustrate the symmetries of a cube (see text)

themselves constitute a subgroup of O_h denoted by O and called the cubic group of proper rotations, are listed classwise in Table (7.1). Their effect on a cartesian coordinate system (x, y, z) is also indicated in the last column of the table.

The remaining 24 elements of O_h are obtained by combining the 24 elements of O with the inversion operator J, which has the effect of changing (x,y,z) to $(-x,-y,-z)$. The composite operations are denoted by JC_4^2, JC_3, etc. Note that J itself is a symmetry operation of the cube. The additional 24 elements give five new classes, there being 10 classes in O_h in all. It should be clear that

$$O_h = O \otimes (E, J). \tag{7.3}$$

TABLE 7.1 THE ELEMENTS OF THE GROUP O LISTED CLASSWISE ALONG WITH THEIR OPERATION ON A COORDINATE SYSTEM (x,y,z)

Class	Operation	(x, y, z) goes to
(E)	Identity operation (1 element)	(x, y, z)
$(3C_4, 3C_4^3)$ or $(6C_4)$	Rotations through 90° and 270° about x, y and z (6 elements)	$(y, -x, z)$, etc.
$(3C_4^2)$	Rotations through 180° about x, y and z (3 elements)	$(-x, -y, z)$, etc.
$(6C_2)$	Rotations through 180° about a line joining centres of any pair of opposite edges (6 elements)	$(y, x, -z)$, etc.
$(4C_3, 4C_3^2)$ or $(8C_3)$	Rotations through 120° and 240° about the four cube diagonals (8 elements)	(y, z, x), etc.

It is interesting to note that the number of permutations of (x, y, z) among themselves is six, and we can attach a positive or a negative sign to each of them in eight different ways; the total number of arrangements of $\pm x$, $\pm y$ and $\pm z$ is thus 48. In other words, 48 is the number of ways in which we can choose a cartesian coordinate system with axes parallel to the cube edges.

The full symmetry group of a regular octahedron is the same as that of a cube. This can be seen by constructing a regular octahedron with its vertices at the six face centres of a cube. The groups O_h and O are therefore also commonly known as the *full octahedral group* and the *octahedral group of proper rotations*, respectively.

Another important group is the symmetry group of a regular tetrahedron, usually denoted by T_d. This has 24 elements and is also a subgroup of O_h. A regular tetrahedron can be inscribed in a cube by joining the points a, b, c and d marked in Fig. (7.8) with each other. We note that the inversion is not a symmetry operation for the tetrahedron, nor is the four-fold rotation. But the two operations applied one after another leave the tetrahedron invariant, except for a different labeling of the points a, b, c, d. This can be seen from Fig. (7.9), where we have taken C_4 to be a rotation about the z axis of Fig. (7.8). The 24 elements of T_d separated into classes are: (E), $(3C_4^2)$, $(4C_3, 4C_3^2)$, $(3JC_4, 3JC_4^3)$ and $(6JC_2)$. The group T_d is isomorphic to the group O.

The subgroup of T_d containing the 12 proper rotations $(E, 3C_4^2, 4C_3, 4C_3^2)$ is denoted by T. But notice that in the group T, the elements C_3 and C_3^2 belong to different classes, unlike in the larger groups T_d, O

and O_h. The class structure of T is (E), $(3C_4^2)$, $(4C_3)$ and $(4C_3^2)$. This is because there is no operation in T which can reverse the direction of a cube diagonal (see the discussion of rule (ii) for finding classes in Section 1.3).

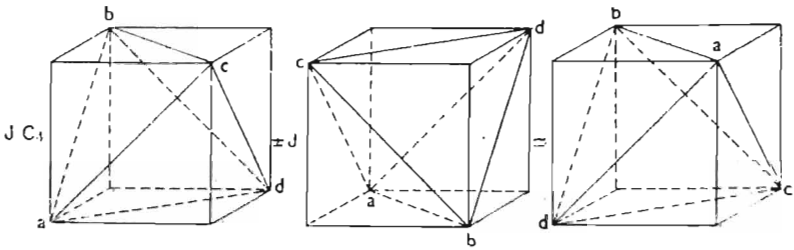

FIGURE 7.9 The improper rotation JC_4 is a symmetry transformation for a regular tetrahedron

Finally, we can construct a group of order 24 by taking the direct product of T with the inversion group (E, J). This group is denoted by T_h and is also a subgroup of O_h. However, it is not the symmetry group of a regular tetrahedron. It is also not isomorphic to O or T_d, since T_h has eight classes.

It will be convenient to list all the 32 crystallographic point groups enumerated above. Although we shall use the Schoenflies notation described above, there is another notation known as the International notation which is often used by crystallographers. In this notation, an n-fold axis of proper rotations is simply denoted by n, while n is used to denote an n-fold axis of improper rotations. A reflection plane is denoted by m and is written in conjunction with n in the form nm or n/m; the latter symbol stands for a horizontal reflection plane. In the list below, the International notation is shown in parentheses after the Schoenflies symbol for point groups:

C_1 (1)	C_2 (2)	C_3 (3)	C_4 (4)	C_6 (6)
C_{1h} (m)	C_{2h} ($2/m$)	C_{3h} ($\bar{6}$)	C_{4h} ($4/m$)	C_{6h} ($6/m$)
	C_{2v} ($2mm$)	C_{3v} ($3m$)	C_{4v} ($4mm$)	C_{6v} ($6mm$)
	S_2 ($\bar{1}$)		S_4 ($\bar{4}$)	S_6 ($\bar{3}$)
	D_2 (222)	D_3 (32)	D_4 (422)	D_6 (622)
	D_{2h} ($\frac{2}{m}\frac{2}{m}\frac{2}{m}$)	D_{3h} ($\bar{6}m2$)	D_{4h} ($4/mmm$)	D_{6h} ($6/mmm$)
	D_{2d} ($\bar{4}2m$)	D_{3d} ($\bar{3}m$)		
T (23)	T_d ($\bar{4}3m$)	T_h ($m3$)	O (432)	O_h ($m3m$)

A number of point groups are isomorphic to each other, as we have mentioned from time to time. The following list of isomorphic

groups will be helpful. The number in the parentheses after each sequence denotes the order of those groups.

(a) C_2, C_{1h} and S_2 (2);

(b) C_4 and S_4 (4);

(c) C_{2v}, C_{2h} and D_2 (4);

(d) C_{3v} and D_3 (6);

(e) C_{4v}, D_4 and D_{2d} (8);

(f) C_{6v}, D_6, D_{3h} and D_{3d} (12);

(g) O and T_d (24).

Before closing this section, we list in Table (7.2) the point groups which can occur in the seven three-dimensional lattice systems in increasing order of symmetry. A system can also have point groups of the systems which have preceded it in Table (7.2). The last entry for each system shows the point group with the highest symmetry for the system.[5]

TABLE 7.2 THE POINT GROUPS CORRESPONDING TO THE SEVEN LATTICE SYSTEMS

System	Point groups
Triclinic	C_1, S_2;
Monoclinic	C_{1h}, C_2, C_{2h};
Orthorhombic	C_{2v}, D_2, D_{2h};
Trigonal	C_3, S_6, C_{3v}, D_3, D_{3d};
Tetragonal	S_4, D_{2d}, C_4, C_{4h}, C_{4v}, D_4, D_{4h};
Hexagonal	C_6, C_{3h}, D_{3h}, C_{6h}, C_{6v}, D_6, D_{6h};
Cubic	T, T_h, T_d, O, O_h.

7.2 Translation Group and the Space Groups

Consider a linear lattice of N lattice points with the lattice constant a. We employ the periodic boundary conditions so that $x-Na\equiv x$, where x is the coordinate measured along the linear lattice. Such a lattice is invariant under translations by multiples of a along the lattice. Let T_1 denote the operator for translation by a and let T_n denote the operator for translation by a distance na. Then

$$T_1x=x-a, \quad T_nx=(T_1)^nx=x-na. \tag{7.4}$$

[5] Landau and Lifshitz (1968), Chapter 13.

Owing to the periodic boundary conditions, we have

$$T_N x=(T_1)^N x=x-Na=x. \tag{7.5}$$

The powers of T_1 clearly generate a cyclic group of order N. We shall denote this group, known as the *translation group*, by

$$T=\{T_N\equiv E,\ T_1,\ T_2,\ \ldots,\ T_{N-1}\}. \tag{7.6}$$

Each element of T is a class by itself since T is an abelian group.

The translation symmetry operators of a three-dimensional lattice also constitute a group. Let the lattice be generated by the three primitive translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$. We use the following periodic boundary conditions:

$$\mathbf{r}-N_1\mathbf{a}_1\equiv\mathbf{r},\ \mathbf{r}-N_2\mathbf{a}_2\equiv\mathbf{r},\ \mathbf{r}-N_3\mathbf{a}_3\equiv\mathbf{r}, \tag{7.7}$$

where $\mathbf{r}$ is the position vector of some point in the lattice and the number of primitive cells is $N_1N_2N_3$.

Let the operator $T(n_1, n_2, n_3)$ denote a translation through a vector $\mathbf{t}(n_1, n_2, n_3)$ given by

$$T(n_1, n_2, n_3)\ \mathbf{r}=\mathbf{r}-n_1\mathbf{a}_1-n_2\mathbf{a}_2-n_3\mathbf{a}_3=\mathbf{r}-\mathbf{t}(n_1, n_2, n_3), \tag{7.8}$$

where $1\leq n_i\leq N_i$. It can be seen that the successive application of two translation operators is equivalent to another translation operator. Thus,

$$T(m_1, m_2, m_3)\ T(n_1, n_2, n_3)\mathbf{r}=T(m_1+n_1, m_2+n_2, m_3+n_3)\mathbf{r}. \tag{7.9}$$

All such operators constitute a group which is of order $N_1N_2N_3$. This is the full translation group T of a three-dimensional lattice. The identity element is $T(0, 0, 0)\equiv T(N_1, N_2, N_3)$. All the translations of the group T commute with each other; the group is therefore again abelian though not cyclic.

An actual three-dimensional lattice will be invariant under the point group transformations as well as the translations. In the case of complex crystals with more than one atom per primitive cell, it may happen that the crystal is invariant under a point group operation followed by a translation, while neither of these individually is a symmetry operation of the crystal. The system shown in Fig. (7.10) provides an example of such a crystal. Here we have a one-dimensional lattice with lattice constant a. Each lattice point, denoted by a dot, has two atoms de-

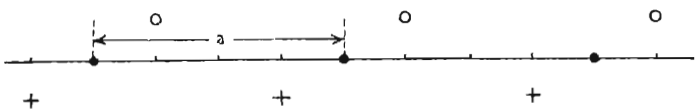

FIGURE 7.10 A one-dimensional system with a twofold screw rotational symmetry

noted by + and o associated with it. The lattice translation vectors are integral multiples of a. In addition, the system is invariant under a translation by $(2n+1)a/2$ followed by a two-fold rotation about the solid line. Such operations are called *screw rotations*. Thus, the system of Fig. (7.10) has a two-fold screw rotation axis as a symmetry element.

Similarly, a crystal is said to possess a glide reflection plane or simply a *glide plane* if it is invariant under a reflection in a plane followed by a translation through a vector lying in the plane.[6] As in the case of the screw rotation axis, the vector itself need not be a symmetry translation vector of the lattice. Note that the two constituent operations of a glide plane, as well as those of a screw axis, commute with each other.

The full symmetry group of a crystal is called its *space group*. It is clear from the above discussion that the elements of the space group are combinations of the point group operations and translations. A general element of a space group may therefore be denoted by $\{A|\underline{\tau}\}$, where A is a point group operation and $\underline{\tau}$ is a translation, which is not necessarily an element of the translation group of the crystal. The operation of $\{A \mid \underline{\tau}\}$ on the position vector is

$$\{A \mid \underline{\tau}\}\ \mathbf{r}=A\mathbf{r}-\underline{\tau}. \tag{7.10}$$

The successive operation of two such elements can be worked out easily as follows:

$$\begin{aligned}\{B \mid \underline{\tau}_2\}\ \{A \mid \underline{\tau}_1\}\ \mathbf{r} &= \{B \mid \underline{\tau}_2\}\ \{A\mathbf{r}-\underline{\tau}_1\} \\ &= BA\mathbf{r}-B\underline{\tau}_1-\underline{\tau}_2,\end{aligned}$$

which gives

$$\{B \mid \underline{\tau}_2\}\ \{A \mid \underline{\tau}_1\}=\{BA \mid B\underline{\tau}_1+\underline{\tau}_2\}. \tag{7.11}$$

The identity element of the space group is clearly $\{E \mid 0\}$ and the inverse of an element is given by

$$\{A \mid \underline{\tau}\}^{-1}=\{A^{-1} \mid -A^{-1}\underline{\tau}\}, \tag{7.12}$$

which can be easily verified by using (7.11).

The space group of a crystal will be denoted by S in this and the next chapters. It should be borne in mind that the translations do not in general commute with the point group operations. The apparently complicated notation just developed is therefore inevitable.

The three-dimensional crystals can be divided into seven systems and fourteen types. The translational symmetry of a crystal is completely determined by the type to which it belongs. In other words, each type has its own translation group. It is known that there are altogether

[6]For a lucid exposition of screw rotations and glide planes, see Azaroff (1960), pp. 20–23.

230 crystallographic space groups.[7] We shall not enumerate them here. Suitable references may be found in the bibliography.

We have seen during the discussion of screw axes and glide planes that if $\{A \mid \underline{\tau}\}$ is an element of the space group, it does not necessarily follow that $\{A \mid 0\}$ is also in the space group. In other words, $\{A \mid 0\}$ is not necessarily a symmetry operation of the crystal. A space group S in which all such operations $\{A \mid 0\}$ (for all $A \in G$, the point group) are also elements of S is called a *symmorphic group*. Of all the space groups there are 73 symmorphic groups and 157 nonsymmorphic groups. It should be clear that a space group would be symmorphic if and only if all $\underline{\tau}$'s are equal to $\mathbf{t}$'s, the lattice translation vectors. Thus, a symmorphic space group is one which contains no screw axes or glide planes.

In a given space group, every point group operation A has associated with it a characteristic *smallest* translation vector $\underline{\delta}$ of the form $\underline{\delta}=\xi\mathbf{a}_1+\eta\mathbf{a}_2+\zeta\mathbf{a}_3$ with $0\leq\xi, \eta, \zeta<1$. The point group element A always appears in the space group in the form $\{A \mid \underline{\delta}+\mathbf{t}\}$ where $\mathbf{t}$ is a lattice translation vector. If $\underline{\delta}$ is zero for all the point group elements, we have a symmorphic space group, for then operations of the form $\{A \mid 0\}$ are elements of the space group for all $A \in G$. However, if $\underline{\delta}$ is nonzero for some point group elements, we have a nonsymmorphic space group. Consider a crystal of diamond as an example. The lattice is face centred cubic, so that the point group is the full octahedral group O_h. However, the crystal has a basis of two atoms per lattice point, one at (0, 0, 0) and another at (1/4, 1/4, 1/4) in terms of the orthogonal translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ of the associated simple cubic lattice. Now it should be properly understood that although the *lattice* is invariant under the octahedral group O_h, not all the operations of O_h leave the *crystal* invariant. In other words, the diamond crystal which has a tetrahedral symmetry is invariant only under the operations of the tetrahedral group T_d. This subgroup of O_h has 24 elements and all of these appear in the space group in the form $\{A \mid \mathbf{t}\}$ with $\underline{\delta}=0$, where $A \in T_d$. As for the remaining 24 elements, it can be verified by looking at the crystal structure of diamond that an operation by one of these followed by a translation through one-fourth of the cube diagonal leaves the crystal invariant. These elements therefore appear in the space group in the form $\{B \mid \underline{\delta}+\mathbf{t}\}$ where $\underline{\delta}=(\mathbf{a}_1+\mathbf{a}_2+\mathbf{a}_3)/4$ for all B in O_h but not in T_d. In either case, $\mathbf{t}$ is any translation vector of the face centred cubic lattice.

[7] Buerger (1967).

Even in the case of symmorphic groups, the space group is not a direct product of the point group and the translation group because of the noncommutativity of the operations. It can, however, be shown that the translation group T is a normal subgroup of any space group (symmorphic or nonsymmorphic). Let us denote by $\{\{A \mid \underline{\delta}+\mathbf{t}\}\}$ the set of operations generated by giving all possible values to the lattice translation vector $\mathbf{t}$ while keeping A and $\underline{\delta}$ fixed. Consider, then, the right and the left cosets of the translation group $T=\{\{E \mid \mathbf{t}\}\}$ with respect to a particular element $\{A \mid \underline{\delta}\}$ of S:

$$\{\{E \mid \mathbf{t}\}\}\{A \mid \underline{\delta}\}=\{\{A \mid \underline{\delta}+\mathbf{t}\}\},$$
$$\{A \mid \underline{\delta}\}\{\{E \mid \mathbf{t}\}\}=\{\{A \mid \underline{\delta}+A\mathbf{t}\}\}. \tag{7.13}$$

As $\mathbf{t}$ runs over all the translation vectors of the lattice, the two sets on the right of (7.13) are clearly seen to be identical, whether $\underline{\delta}$ is a translation vector or not. The translation group is thus an invariant subgroup of symmorphic as well as nonsymmorphic space groups. It can be further shown that the factor group S/T is isomorphic to the point group G.

7.3 Molecular Point Groups

Molecules may possess any of the crystallographic point group symmetries enumerated in Section 7.1. In addition, they may belong to other symmetry groups containing, for example, fivefold rotational symmetry or the full rotational symmetry about an axis. Because molecules have no restrictions of translational symmetry, they can, in principle, possess an n-fold axis of symmetry where n is any positive integer or infinite. We shall discuss below a few of these additional point symmetry groups which occur in molecules.

C_∞, $C_{\infty v}$. A diatomic molecule such as that shown in Fig. (7.11) or, in fact, any linear molecule, has the full rotational symmetry about the line joining the atoms. Examples of such molecules are LiH, NH,

FIGURE 7.11 A diatomic molecule containing two distinct atoms A and B has the symmetry group $C_{\infty v}$

CO, etc., and, in general, MX where M is an alkali or hydrogen atom and X is a halide atom. The rotation group which is denoted by C_∞ in the present notation is just the axial rotation group denoted by $SO(2)$ in Chapter 4. Moreover, when a system has axial rotational symmetry, it also has reflection symmetry in any vertical plane passing through the line AB. This makes the full symmetry group of the molecule AB $C_{\infty v}$ rather than C_∞. It should be noted that a reflection in a plane passing through AB does not commute with a rotation about the line AB: $C_{\infty v}$ is therefore not an abelian group.

The class structure of $C_{\infty v}$ is such that reflections in all vertical planes belong to a class. Moreover, rotations through ϕ and $-\phi$ about AB belong to a class. This can be easily verified by looking at Fig. (7.12). with reference to the figure, let $R(\phi)$ denote an anticlockwise rotation about a vertical axis passing through the centre of the circle shown and let σ_v denote a reflection in the vertical plane $\phi=0$. The operation of $\sigma_v^{-1} R(\phi)\sigma_v$ on an atom at position 1 with azimuthal angular co-ordinate α takes the atom successively to the positions 2, 3 and 4 shown in Fig. (7.12). The combined operation taking an atom at α to one at

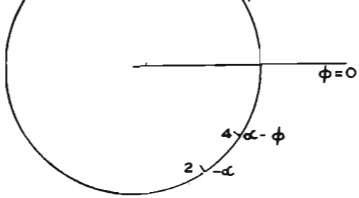

FIGURE 7.12 The rotations $R(\phi)$ and $R(-\phi)$ are conjugate to each other in the group $C_{\infty v}$

$\alpha-\phi$ is equivalent to the rotation $R(-\phi)$. Hence $\sigma_v^{-1} R(\phi) \sigma_v = R(-\phi)$, showing that $R(\phi)$ and $R(-\phi)$ belong to a class.

$D_{\infty h}$. If the diatomic molecule of Fig. (7.11) has both identical atoms as in Fig. (7.13a), then it has other symmetry elements also. This is also true of linear molecules such as ABA and ABBA shown in Figs (7.13b) and (7.13c). In addition to the axial rotational symmetry about the line of atoms, we notice that the molecule has a reflection symmetry in a 'horizontal' plane passing through the centre of the molecule denoted by σ_h. It also has a two-fold rotational symmetry C_2' about any horizontal axis[8] passing through the centre of the molecule. A

[8]The prime is used in C_2' to denote that the axis of rotation here is different from the main symmetry axis which is the line of atoms.

rotation through π about the vertical axis together with σ_h gives the inversion symmetry J. The inversion together with C_2' gives reflection

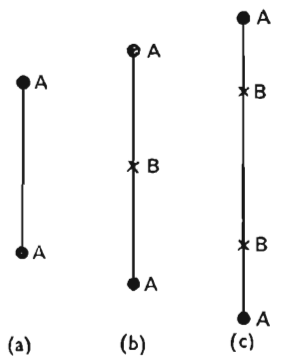

FIGURE 7.13 Molecules having the symmetry group $D_{\infty h}$. Examples of type (a) are H_2, N_2, O_2, Cl_2, etc.; an example of type (b) is CO_2 while C_2H_2 is a molecule of type (c).

in a vertical plane, σ_v. The class structure of $D_{\infty h}$ is therefore as follows: the two rotations $R(\phi)$ and $R(-\phi)$ belong to a class; $JR(\phi)$ and $JR(-\phi)$ belong to a class; E and J constitute separate classes as they commute with all the other elements; all vertical reflections σ_v belong to a class; finally, all $J\sigma_v = C_2'$ belong to a class.

The group D_∞ (without the horizontal reflection plane) indicates axial rotational symmetry about the line of atoms and twofold symmetry about any horizontal axis passing through the centre of the molecule. It is then clear that

$$D_{\infty h} = D_\infty \otimes (E, J). \tag{7.14}$$

Complex molecules may also possess other symmetries such as fivefold, sevenfold, etc. It is easy to obtain all point groups containing a principal axis of a given n-fold symmetry. For example, there are altogether five point groups each having a five-fold rotation axis. These are C_5, C_{5v}, C_{5h}, D_5, and D_{5h}. It is left as an exercise to obtain their stereographic projections.

7.4 Irreducible Representations of Point Groups

The general method of obtaining the character table and the irreducible representations of point groups has been discussed fairly in detail by considering the example of C_{4v} and C_{3v} in Sec. 3.6. We shall therefore not consider the character tables of all point groups separately. However, as a general principle, we note that when a group can be expressed as the direct product of two smaller groups, its character table can be obtained from those of the smaller groups as discussed in Section 3.11. We shall illustrate this by considering two examples here,

one for the cubic groups O and O_h and other for the continuous groups $C_{\infty v}$ or D_∞ and $D_{\infty h}$. The character table of O is worked out in the following example.

Example : Here we shall work out the character table of the group O. This group has five classes given in Table 7.1. It has five irreducible representations whose dimensions are found from the equation

$$l_1^2 + l_2^2 + l_3^2 + l_4^2 + l_5^2 = 24, \tag{7.15}$$

which gives $l_1 = l_2 = 1$, $l_3 = 2$, $l_4 = l_5 = 3$. By convention, we denote the one-dimensional representations by Γ_1 and Γ_2, the two-dimensional one by Γ_{12}, and the three-dimensional representations by Γ'_{15}, and Γ''_{25}. We take Γ_1 to be the identity representation.

We note that all the classes of O are self-inverse, so that the characters in all the irreducible representations will be real.

In the second one-dimensional representation Γ_2, the class $(6C_4)$ can have characters ± 1, $\pm i$, the classes $(3C_4^2)$ and $(6C_2)$ can have characters ± 1, and the class $(8C_3)$ can have characters 1, ω, ω^2, where $\omega = \exp(2\pi i/3)$. But we can exclude the complex numbers as noted above, so that the class $(8C_3)$ must have character 1, while the other three classes may have characters ± 1. To make Γ_2 orthogonal to Γ_1, the only possibility now remains that the class $(3C_4^2)$ should have character 1 and the classes $(6C_4)$ and $(6C_2)$ should have characters -1.

We now come to the two-dimensional irreducible representation Γ_{12} and denote the characters of the five classes to be $(2\ a\ b\ c\ d)$. Orthogonality of Γ_{12} with Γ_1 and Γ_2, and normalization of Γ_{12} gives the equations

$$2 + 6a + 3b + 6c + 8d = 0, \tag{7.16a}$$

$$2 - 6a + 3b - 6c + 8d = 0, \tag{7.16b}$$

$$4 + 6a^2 + 3b^2 + 6c^2 + 8d^2 = 24. \tag{7.16c}$$

The first two of the above equations give

$$2 + 3b + 8d = 0, \qquad a + c = 0. \tag{7.17}$$

We need one more equation to determine the four constants. With this view, we wish to use (3.65) involving products of classes. The simplest class to deal with in the present group is $(3C_4^2)$ or explicitly $(C_{4x}^2, C_{4y}^2, C_{4z}^2)$. We consider the product of this class with itself. Noting that $C_{4x}^2 C_{4y}^2 = C_{4y}^2 C_{4x}^2 = C_{4z}^2$, we get

$$(3C_4^2)(3C_4^2) = 3(E) + 2\,(3C_4^2). \tag{7.18}$$

Using (3.65) with $i = j = 3$, and $a_{331} = 3$, $a_{333} = 2$, $a_{332} = a_{334} = a_{335} = 0$, we find

$$3b^2 = 4 + 4b \Rightarrow b = 2 \text{ or } -2/3. \tag{7.19}$$

When this is used in (7.16c) and (7.17), the choice $b = -2/3$ gives an absurdity, while $b = 2$ gives $d = -1$, $a = c = 0$. Thus we have the characters for Γ_{12}.

Now we have two three-dimensional irreducible representations Γ'_{15} and Γ'_{25}. Assuming, for any of them, the characters to be $(3\ p\ q\ r\ s)$, the orthogonality with the first three representations and the normalization give the four equations

$$\begin{aligned} 3+6p+3q+6r+8s &= 0, \\ 3-6p+3q-6r+8s &= 0, \\ 6+6q-8s &= 0, \\ 9+6p^2+3q^2+6r^2+8s^2 &= 24. \end{aligned} \tag{7.20}$$

These give the solution $q = -1$, $s = 0$, $p = \pm 1$, $r = \mp 1$. There is apparently two-fold arbitrariness, but it is consistent with the fact that there are two three-dimensional representations to be worked out. Thus at one stroke, we get both the characters by choosing $p = -r = 1$ for Γ'_{15} and $p = -r = -1$ for Γ'_{25}. The complete character table for the group O as obtained above, together with the basis functions for the irreducible representations, is given in Table 7.3. Various notations are in vogue for the irreducible representations; the notation used in Table (7.3) and throughout this book is due to Bouckaert, Smoluchowski and Wigner.[9]

TABLE 7.3 THE CHARACTER TABLE OF THE CUBIC GROUP O

Basis functions	Irr. repr.	E	$6C_4$	$3C_4^2$	$6C_2$	$8C_3$
$x^n+y^n+z^n$ (n even)	Γ_1	1	1	1	1	1
xyz	Γ_2	1	−1	1	−1	1
$\{x^2-y^2,\ 2z^2-x^2-y^2\}$	Γ_{12}	2	0	2	0	−1
$\{x,\ y,\ z\}$	Γ'_{15}	3	1	−1	−1	0
$\{xy,\ yz,\ zx\}$	Γ'_{25}	3	−1	−1	1	0

[9] Bouckaert, Smoluchowski and Wigner (1936).

TABLE 7.4 THE CHARACTER TABLE OF O_h

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

Having obtained the irreducible representations of O, it is easy to obtain those of O_h. Since $O_h = O \otimes (E, J)$, O_h will have ten irreducible representations which are direct products of the irreducible representations of O and those of the inversion group (E, J). The character table of O_h is given in Table (7.4). Notice that each irreducible representation of O gives two irreducible representations of O_h, one of which is even and the other odd under inversion.

As a second example, we take the case of the groups $C_{\infty v}$ or D_∞. These are nonabelian continuous groups and have the following classes: $C_{\infty v} = (E, 2R_\phi, \sigma_v)$ and $D_\infty = (E, 2R_\phi, C_2')$. Each has two one-dimensional irreducible representations, one of which is the identity representation and the other is orthogonal to the identity representation. Further, each group has an infinite number of two-dimensional irreducible representations. For this we notice that the real and the imaginary parts of $(x+iy)^n$ for any positive integer n generate a two-dimensional irreducible representation of both $C_{\infty v}$ and D_∞. The complete character table of these two groups is given in Table (7.5). These groups have no irreducible representations of dimensions larger than two. The notation for the irreducible representations which we have used here and in Table (7.6) is the conventional one used by molecular physicists and chemists.

Finally, we consider the group $D_{\infty h}$ which can be expressed as a direct product in several different ways. Thus,

$$D_{\infty h} = D_\infty \otimes (E, \sigma_h) = C_{\infty v} \otimes (E, \sigma_h) = C_{\infty v} \otimes (E, J). \qquad (7.21)$$

The classes of $D_{\infty h}$ are E, $2R_\phi$, C_2', J, $2JC_\phi$ and $JC_2' = \sigma_v$. Once again, each irreducible representation of $C_{\infty v}$ or D_∞ gives two irredu-

TABLE 7.5 THE CHARACTER TABLE OF $C_{\infty v}$ AND D_{∞}

Irr. repr.	E	$2R_\phi$	σ_v or C_2'	Basis functions	
				$C_{\infty v}$	D_{∞}
A_1	1	1	1	x^2+y^2	
A_2	1	1	−1	—— |	z
E_1	2	$2\cos\phi$	0	(x, y)	
E_2	2	$2\cos 2\phi$	0	$(x^2-y^2, 2xy)$	
E_3	2	$2\cos 3\phi$	0	$(x^3-3xy^2, 3x^2y-y^3)$	
.	.	.	.		
.	.	.	.		

cible representations of $D_{\infty h}$, one of which is even under inversion and the other odd. These are designated by the subscripts g and u standing for the German words *gerade* (meaning even) and *ungerade* (meaning odd) respectively. The character table of $D_{\infty h}$ is given in Table (7.6).

TABLE 7.6 THE CHARACTER TABLE OF $D_{\infty h}$

	E	$2R_\phi$	C_2'	J	$2JR_\phi$	JC_2'
A_{1g}	1	1	1	1	1	1
A_{1u}	1	1	1	−1	−1	−1
A_{2g}	1	1	−1	1	1	−1
A_{2u}	1	1	−1	−1	−1	1
E_{1g}	2	$2\cos\phi$	0	2	$2\cos\phi$	0
E_{1u}	2	$2\cos\phi$	0	−2	$-2\cos\phi$	0
E_{2g}	2	$2\cos 2\phi$	0	2	$2\cos 2\phi$	0
E_{2u}	2	$2\cos 2\phi$	0	−2	$-2\cos 2\phi$	0
.	.	.	.	.	.	.
.	.	.	.	.	.	.
.	.	.	.	.	.	.

The irreducible representations of all the crystallographic point groups and some molecular point groups are listed in Table (7.7). Wherever available, the notation of Bouckaert et al.[10] for the irreducible representations has been shown on the left. This notation is generally

[10]Bouckaert, Smoluchowski and Wigner (1936); Koster (1957).

TABLE 7.7 THE CHARACTER TABLES OF CRYSTALLOGRAPHIC AND SOME MOLECULAR POINT GROUPS

C_1	E
	1

C_2	E	C_2
	1	1
	1	−1

C_3	E	C_3	C_3^2	
	1	1	1	
	1	w	w^2	$w=\exp(2\pi i/3)$
	1	w^2	w	

C_4	E	C_4	C_4^2	C_4^3
	1	1	1	1
	1	−1	1	−1
	1	$-i$	−1	i
	1	i	−1	$-i$

C_5	E	C_5	C_5^2	C_5^3	C_5^4	
	1	1	1	1	1	
	1	w	w^2	w^3	w^4	
	1	w^4	w^3	w^2	w	$w=\exp(2\pi i/5)$
	1	w^2	w^4	w	w^3	
	1	w^3	w	w^4	w^2	

TABLE 7.7 (continued)

C_6	E	C_6	C_6^2	C_6^3	C_6^4	C_6^5	
	1	1	1	1	1	1	
	1	−1	1	−1	1	−1	
{	1	w	w^2	w^3	w^4	w^5	$w=\exp(2\pi i/6)$
{	1	w^5	w^4	w^3	w^2	w	
{	1	w^2	w^4	1	w^2	w^4	
{	1	w^4	w^2	1	w^4	w^2	

C_{2v}	E	C_2	σ_v	σ_v'	
$D_1\ G_1\ S_1\ Z_1\ \Sigma_1$	1	1	1	1	X_1
$D_2\ G_2\ S_2\ Z_2\ \Sigma_2$	1	1	−1	−1	X_2
$D_3\ G_3\ S_3\ Z_3\ \Sigma_3$	1	−1	1	−1	X_3
$D_4\ G_4\ S_4\ Z_4\ \Sigma_4$	1	−1	−1	1	X_4

C_{3v}	E	$2C_3$	$3\sigma_v$
$F_1\ \Lambda_1$	1	1	1
$F_2\ \Lambda_2$	1	1	−1
$F_3\ \Lambda_3$	2	−1	0

C_{4v}	E	$2C_4$	C_4^2	$2m$	2σ	
$W_1\ T_1\ \Delta_1$	1	1	1	1	1	$M_1\ \Gamma_1$
$W_1'\ T_1'\ \Delta_1'$	1	1	1	−1	−1	$M_2\ \Gamma_2$
$W_2\ T_2\ \Delta_2$	1	−1	1	1	−1	$M_3\ \Gamma_3$
$W_2'\ T_2'\ \Delta_2'$	1	−1	1	−1	1	$M_4\ \Gamma_4$
$W_3\ T_5\ \Delta_5$	2	0	−2	0	0	$M_5\ \Gamma_5$

TABLE 7.7 (continued)

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$
	1	1	1	1
	1	1	1	−1
	2	$2\cos x$	$2\cos 2x$	0
	2	$2\cos 2x$	$2\cos 4x$	0

$x=2\pi/5$

C_{6v}	E	$2C_6$	$2C_6^2$	C_6^3	$3\sigma_d$	$3\sigma_v$
	1	1	1	1	1	1
	1	1	1	1	−1	−1
	1	−1	1	−1	−1	1
	1	−1	1	−1	1	−1
	2	1	−1	−2	0	0
	2	−1	−1	2	0	0

C_{1h}	E	σ_h	
Q_1	1	1	$Z_1\ \Sigma_1\ \Delta_1$
Q_2	1	−1	$Z_2\ \Sigma_2\ \Delta_2$

$C_{nh}=C_n \otimes C_{1h}$.

S_2	E	J
	1	1
	1	−1

S_4	E	S_4	C_4^2	S_4^3
	1	1	1	1
	1	−1	1	−1
{	1	i	−1	$-i$
{	1	$-i$	−1	i

TABLE 7.7 (continued)

$S_6 = C_3 \otimes S_2$.

D_2	E	C_{2x}	C_{2y}	C_{2z}
N_1	1	1	1	1
N_2	1	1	−1	−1
N_3	1	−1	1	−1
N_4	1	−1	−1	1

D_3	E	$2C_3$	$3C_2'$
L_1	1	1	1
L_2	1	1	−1
L_3	2	−1	0

D_4	E	$2C_4$	C_4^2	$2C_2'$	$2C_2''$
X_1 M_1	1	1	1	1	1
X_2 M_2	1	1	1	−1	−1
X_3 M_3	1	−1	1	1	−1
X_4 M_4	1	−1	1	−1	1
X_5 M_5	2	0	−2	0	0

D_5	E	$2C_5$	$2C_5^2$	$5C_2'$	
	1	1	1	1	
	1	1	1	−1	
	2	$2\cos x$	$2\cos 2x$	0	$x = 2\pi/5$
	2	$2\cos 2x$	$2\cos 4x$	0	

TABLE 7.7 (continued)

D_6	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2'$	$3C_2''$
	1	1	1	1	1	1
	1	1	1	1	−1	−1
	1	−1	1	−1	1	−1
	1	−1	1	−1	−1	1
	2	1	−1	−2	0	0
	2	−1	−1	2	0	0

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$
W_1	1	1	1	1	1
W_1'	1	1	1	−1	−1
W_2	1	−1	1	1	−1
W_2'	1	−1	1	−1	1
W_3	2	0	−2	0	0

$D_{3d}=D_3 \otimes S_2$;
$D_{nh}=D_n \otimes S_2$, $n=2, 4, 6$;
$D_{nh}=D_n \otimes (E, \sigma_h)$, $n=3, 5$.

T	E	$3C_2$	$4C_3$	$4C_3^2$
	1	1	1	1
{	1	1	w	w^2
	1	1	w^2	w
	3	−1	0	0

$w=\exp(2\pi i/3)$

$T_h=T \otimes S_2$;

TABLE 7.7 (continued)

O: see Table (7.3)
$O_h = O \otimes S_2$ (see Table (7.4))

T_d	E	$8C_3$	$3C_2$	$6\sigma_d$	$6S_4$
P_1	1	1	1	1	1
P_2	1	1	1	−1	−1
P_3	2	−1	2	0	0
P_4	3	0	−1	1	−1
P_5	3	0	−1	−1	1

used for labeling the energy bands in cubic lattices. The labels used for the energy bands of the two-dimensional square lattice are shown on the ... et. There is no standard notation for the irreducible representations of many point groups. Pairs of complex conjugate representations will be degenerate in the case of time-reversal symmetry.[11] This is indicated by bracketing them together. Groups which are direct products of smaller groups are indicated as such and their character tables are not listed. For the groups which are direct products of smaller groups with (E, J) or (E, σ_h), the additional representations are denoted by primes. For example, the five irreducible representations fo D_4 are labeled M_i or X_i; the ten irreducible representations of D_{4h} will be denoted by M_i and M_i' or X_i and X_i' with $1 \leq i \leq 5$. For a comprehensive list of the various notations in use, the reader is referred to the literature.[12]

7.5 The Double Group

We have seen in Chapter 4 in connection with the discussion of $SO(2)$ and $SO(3)$ that they have single-valued as well as double-valued representations. We remarked that if, when the system has an integral angular momentum, its symmetry group is, say, $SO(2)$ or $SO(3)$, then ... half-odd-integral angular momenta, the proper symmetry group would be the corresponding double group $SO'(2)$ or $SO'(3)$. The above statement holds good even for systems with symmetries less than $SO(3)$ or $SO(2)$, such as molecules or crystals. For integral angular momenta, if the symmetry group of a system is some point group G, then with half-odd-integral angular momenta, the symmetry group would be the corresponding double group G'.

[11] See Appendix C.
[12] Tinkham (1964); Rosenthal and Murphy (1936); Koster (1957).

The concept of a double group arises from the fact that certain systems do not return to their original states after undergoing a rotation of 2π about any axis. This was the need to introduce the element $\bar{E}$ (see page 138) which denotes a rotation through 2π about any axis. It is important to distinguish here the effect of a rotation through 2π on a coordinate system and that on a physical wave function. A coordinate system *does* return to its original state after a rotation of 2π about any axis passing through the origin. However, spinor wave functions of particles with half-odd-integral spin angular momenta get multiplied by -1 after a rotation through 2π and return to their original values only after a rotation through 4π. Regarded as an operation on the spinor wave functions, therefore, $\bar{E}$ is not the identity element.

7.5.1 Classes of a double group. The double group G', in general, contains all the operations of G plus the operations of G combined with the element $\bar{E}$ denoting a rotation through 2π about some axis with the property $(\bar{E})^2=E$, the identity element. If A is an element of G, we shall denote the product $\bar{E}A=A\bar{E}$ by $\bar{A}$ and call it the barred operation. The order of G' is double that of G but the number of classes in G' is not necessarily twice that in G. The element $\bar{E}$ commutes with all the point group operations of G and hence in the particular case when A and $\bar{A}$ belong to different classes for all $A \in G$, the number of classes of G' is certainly double that of G. For every class of G such as $(A, B, C, \ldots)$, we have two classes in G', $(A, B, C, \ldots)$ and $(\bar{A}, \bar{B}, \bar{C}, \ldots)$. On the other hand, if the group G is such that A and $\bar{A}$ belong to the same class for some $A \in G$, the number of classes of G' will be less than twice that of G. The following rules have been found[13] for determining whether A and $\bar{A}$ belong to a class or not.

(i) The identity E and the operator $\bar{E}$ constitute two separate classes. In groups containing inversion symmetry, the inversion J and $\bar{E}J\equiv\bar{J}$ also constitute separate classes.

(ii) If A is a twofold rotation about some axis, A and $\bar{A}$ belong to one class *if and only if* there is either another twofold rotation in G about an axis normal to the axis of A or a reflection in a plane through the axis of A. For example, the group D_2 contains two-fold rotations about three mutually perpendicular axes; these may be denoted by C_{2x}, C_{2y} and C_{2z}. In the corresponding double group D_2', C_{2x} and $\bar{C}_{2x}$ are in the same class and similarly $(C_{2y}, \bar{C}_{2y})$ and $(C_{2z}, \bar{C}_{2z})$ are two

[13]Koster (1957).

other classes of D_2'. The group C_{4v} has reflection planes passing through the fourfold axis, so that C_4^2 and $\bar{C}_4^2$ belong to one class in the double group C_{4v}'. However, in the double groups C_{2h}', C_{4h}' and C_{6h}', C_2 and $\bar{C}_2$ would belong to separate classes for obvious reasons (here C_2 denotes a twofold rotation about the axis of symmetry).

(iii) For all other rotations (i.e., rotations through $2\pi/n$ where $n>2$), the classes of the barred and the unbarred operations are different. Thus, in the group C_{3v}, the two threefold rotations are in a class $(2C_3)$. In the double group C_{3v}', this gives rise to two classes $(2C_3)$ and $(2\bar{C}_3)$. The number of classes *corresponding to these elements* is doubled.

(iv) If A is a reflection in some plane, A and $\bar{A}$ belong to a class *if and only if* there is either another reflection in a plane normal to that of the first or a twofold rotation about an axis in the plane of A. For example, the groups C_{2v}, C_{4v} and C_{6v} have perpendicular reflection planes, so that σ_v and $\bar{\sigma}_v$ belong to a class in the corresponding double groups. In the group C_{3v}, however, the reflection planes are not perpendicular to each other; σ_v and $\bar{\sigma}_v$ therefore belong to separate classes in the double group C_{3v}'. For similar reasons, the horizontal reflection σ_h and $\bar{\sigma}_h$ belong to one class in the double groups D_{nh}' but σ_v and $\bar{\sigma}_v$ belong to separate classes in D_{3d}'.

(v) Finally, if the group G contains improper rotations, these rotations of the form JC_n are subject to the same rules (ii) and (iii).

These rules enable us to decompose any double group into its classes once the classes of the corresponding point group have been obtained. We shall illustrate the use of these rules below by considering a few double groups to familiarize the reader with their application.

C_n. This has the n elements C_n, C_n^2, ..., $C_n^n=E$, each in a class by itself. The double groups C_n' are also cyclic groups of order $2n$ with the elements $(C_n, C_n^2, \ldots, C_n^n=\bar{E}, \bar{C}_n, \bar{C}_n^2, \ldots, \bar{C}_n^n=E)$.

C_{nv}. For even n, these groups have a two-fold rotation about the main n-fold axis. Since there are reflection planes passing through this axis, the two-fold rotation $C_2\equiv C_n^{n/2}$ and $\bar{C}_2$ belong to one class in the double group according to rule (ii). According to rule (iv), a vertical reflection σ_v and the corresponding barred operation $\bar{\sigma}_v$ belong to the same class. For odd n, neither rule (ii) nor (iv) is applicable so that in C_{nv}' for n odd, all the barred and the corresponding unbarred operations belong to separate classes. The number of classes in this case is doubled. For example, the classes of C_{3v}' are (E), $(\bar{E})$, $(2C_3)$, $(2\bar{C}_3)$, $(3\sigma_v)$ and $(3\bar{\sigma}_v)$. The classes of C_{1v}' are (E), $(\bar{E})$, $(2C_4)$, $(2\bar{C}_4)$, $(C_4^2, \bar{C}_4^2)$, $(2m, 2\bar{m})$ and $(2\sigma, 2\bar{\sigma})$. Here we have used the notation

$(2C_4)$ for (C_4, C_4^3), $(2m)$ for (m_x, m_y), etc.

C_{nh}. In all the corresponding double groups, the number of classes is doubled, each class of C_{nh} giving rise to two classes of C_{nh}' The double groups are abelian for all values of n just as the groups C_{nh} are.

D_2. This abelian group has four elements $(E, C_{2x}, C_{2y}, C_{2z})$. The last three elements come under rule (ii). The double group D_2' of order 8 thus has the following 5 classes: (E), $(\bar{E})$, $(C_{2x}, \bar{C}_{2x})$, $(C_{2y}, \bar{C}_{2y})$ and $(C_{2z}, \bar{C}_{2z})$.

It is then clear that the classes of the double groups corresponding to all the simple point groups can be obtained quite easily. Let us now consider two groups typical of cubic systems and one continuous group.

T. As discussed before, this group of order 12 has the 4 classes (E), $(3C_4^2)$, $(4C_3)$ and $(4C_3^2)$. Since there are three mutually perpendicular two-fold axes, the second class comes under rule (ii) and in the double group T', there will be a class $(3C_4^2, 3\bar{C}_4^2)$. The last two classes of T come under rule (iii) and will give rise to four classes of T'. The classes of T' are then: (E), $(\bar{E})$, $(3C_4^2, 3\bar{C}_4^2)$, $(4C_3)$, $(4\bar{C}_3)$, $(4C_3^2)$, $(4\bar{C}_3^2)$.

O. This group with 24 elements has the 5 classes (E), $(3C_4, 3C_4^3)$, $(3C_4^2)$, $(6C_2)$ and $(4C_3, 4C_3^2)$. The third and the fourth classes come under rule (ii) while the second and the fifth classes under rule (iii). The double group O' is then found to have the classes (E), $(\bar{E})$, $(3C_4, 3C_4^3)$, $(3\bar{C}_4, 3\bar{C}_4^3)$, $(3C_4^2, 3\bar{C}_4^2)$, $(6C_2, 6\bar{C}_2)$, $(4C_3, 4C_3^2)$ and $(4\bar{C}_3, 4\bar{C}_3^2)$.

$C_{\infty v}$. This group has the classes (E), $(2R_\phi)$ and (σ_v). The class $(2R_\phi)$ contains two elements for $\phi \neq \pi$ (excluding $\phi = 0$, which is the identity) and only one element C_2 for $\phi = \pi$. The corresponding double group $C_{\infty v}'$ has the classes (E), $(\bar{E})$, $(2R_\phi)$, $(2\bar{R}_\phi)$, $(C_2, \bar{C}_2)$, and $(\sigma_v, \bar{\sigma}_v)$, with $\phi \neq 0$ or π.

7.5.2 Irreducible representations of a double group. A double group G' is homomorphic to the group G whose double group it is. This can be easily seen by choosing the two-to-one mapping as $A, \bar{A} \rightarrow A$; $B, \bar{B} \rightarrow B$; etc. Now let $AB = C$ in the group G. The product of elements from the set $(A, \bar{A})$ with those of the set $(B, \bar{B})$ of G' then gives the set $(C, \bar{C})$ whose elements are mapped onto C of G, proving the homomorphism.

Let G be a finite group having c classes and let the corresponding double group G' have c' classes. The group G' then has c' irreducible representations all of which are single-valued. These can be used to obtain the irreducible representations of G. We shall see that of these,

there are c single-valued and $c'-c$ double-valued representations of G.

The effect of $\bar{E}$ on any basis function is clearly to give the same function or the negative of the function depending on whether the system has integral or half-odd-integral angular momentum. This shows that the matrix representing $\bar{E}$ in any representation is either the unit matrix or the negative unit matrix. The character is therefore $\pm l_i$ where l_i is the dimension of the representation. Similarly, for all $A \in G, \chi(\bar{A}) = \pm\chi(A)$ in any representation. The first c irreducible representations of G' can be written down simply from those of the smaller group G by using $\chi(\bar{A}) = \chi(A)$. It is easy to see that these c irreducible representations of G' satisfy the orthonormality relations for rows. For the remaining $c'-c$ irreducible representations, we see that each of these can be made orthogonal to each of the first c rows by choosing $\chi(\bar{A}) = -\chi(A)$ (because half the elements of G' are unbarred operations and the other half are barred operations). These give the double-valued representations of the group G. In the particular case when A and $\bar{A}$ belong to the same class for some $A, \chi(\bar{A}) = \chi(A)$, so that in all the double-valued representations, we must have $\chi(\bar{A}) = -\chi(A) = 0$.

Coming to some particular examples, let us start with the simple case of C_2 with elements (E, C_2) in two classes. This has two irreducible representations. The double group C_2' has the four elements $(E, C_2, \bar{E}, \bar{C}_2)$ and is a cyclic group. Its irreducible representations are shown in Table (7.8). It should be clear that the first two of these are single-valued representations while the last two are double-valued representations of C_2.

TABLE 7.8 THE CHARACTER TABLE OF C_2'

C_2'	E	C_2	$\bar{E}$	$\bar{C}_2$
Γ_1	1	1	1	1
Γ_2	1	−1	1	−1
Γ_3	1	i	−1	$-i$
Γ_4	1	$-i$	−1	i

Next, we consider the group D_2 which has four classes and four irreducible representations. The double group D_2' has 8 elements in 5 classes so that the additional irreducible representation of D_2' must be of order 2. Moreover, since C_{2x} and $\bar{C}_{2x}$ belong to one class, their characters in this fifth representation must be zero. The same holds

good for C_{2y}, $\bar{C}_{2y}$, C_{2z} and $\bar{C}_{2z}$. The character table of D_2' is shown in Table (7.9).

TABLE 7.9 THE CHARACTER TABLE OF D_2'

D_2'	E	$\bar{E}$	$(C_{2x}, \bar{C}_{2x})$	$(C_{2y}, \bar{C}_{2y})$	$(C_{2z}, \bar{C}_{2z})$
Γ_1	1	1	1	1	1
Γ_2	1	1	1	−1	−1
Γ_3	1	1	−1	1	−1
Γ_4	1	1	−1	−1	1
Γ_5	2	−2	0	0	0

It can be verified that D_2' is not isomorphic to C_{4v} or D_4. However, it is isomorphic to the group of the eight matrices generated in Problem (1.7) where we have emphasized that two groups having the same number of elements and classes need not be isomorphic. In fact, these are just the eight matrices of the irreducible representation Γ_5 of D_2'.

The double group C_{4v}' has 16 elements in 7 classes whereas C_{4v} has 8 elements in 5 classes. If the additional irreducible representations of C_{4v}' are denoted by $\Gamma^{(6)}$ and $\Gamma^{(7)}$, their dimensions l_6 and l_7 must satisfy the relation

$$\sum_{i=1}^{7} l_i^2 = 16.$$

But the dimensions of the first five irreducible representations are known because they satisfy the relation

$$\sum_{i=1}^{5} l_i^2 = 8.$$

Hence $l_6^2 + l_7^2 = 8$, giving $l_6 = l_7 = 2$. The characters of the classes $(C_4^2, \bar{C}_4^2)$, $(2m, 2\bar{m})$ and $(2\sigma, 2\bar{\sigma})$ in both of these additional representations must be zero because, as just mentioned, the barred and the unbarred operations belong to the same class. The characters of E in both $\Gamma^{(6)}$ and $\Gamma^{(7)}$ must be 2 and those of $\bar{E}$ −2. Finally, the characters of C_4 and of $\bar{C}_4$ in both of these representations must be negative of each other. It is then a fairly simple matter to obtain the full character table of C_{4v}'. In Table (7.10), we have shown the two additional characters of C_{4v}'.

Lastly, we consider the double group O' of the cubic group O. The group O has 24 elements in 5 classes whereas O' has 48 elements in 8

TABLE 7.10 THE ADDITIONAL CHARACTERS OF C_{4v}'

	(E)	$(\bar{E})$	$(2C_4)$	$(2\bar{C}_4)$	$(C_4^2, \bar{C}_4^2)$	$(2m, 2\bar{m})$	$(2\sigma, 2\bar{\sigma})$
$\Gamma^{(6)}$	2	−2	$\sqrt{2}$	$-\sqrt{2}$	0	0	0
$\Gamma^{(7)}$	2	−2	$-\sqrt{2}$	$\sqrt{2}$	0	0	0

classes. Denoting the additional irreducible representations of O' by Γ_6, Γ_7 and Γ_8, we see that their dimensions are given by $l_6^2+l_7^2+l_8^2=24$, or $l_6=l_7=2$, $l_8=4$. Once again, the characters of the classes $(3C_4^2, 3\bar{C}_4^2)$ and $(6C_2, 6\bar{C}_2)$ must be zero in all the three additional representations. The characters can be worked out without much difficulty by methods already discussed in Chapter 3. The additional characters of O' are listed in Table (7.11).

TABLE 7.11 THE ADDITIONAL CHARACTERS OF O'

	(E)	$(\bar{E})$	$(6C_4)$	$(6\bar{C}_4)$	$(3C_4^2, 3\bar{C}_4^2)$	$(6C_2, 6\bar{C}_2)$	$(8C_3)$	$(8\bar{C}_3)$
Γ^6	2	−2	$\sqrt{2}$	$-\sqrt{2}$	0	0	1	−1
Γ^7	2	−2	$-\sqrt{2}$	$\sqrt{2}$	0	0	1	−1
Γ^8	4	−4	0	0	0	0	−1	1

Koster[14] has listed the characters of the double groups corresponding to all the crystallographic point groups.

7.6 Crystal Field Splitting of Atomic Levels

When an atom is placed in a molecule or a crystal, the symmetry of the atom is reduced. An isolated atom has the symmetry of the full rotation-inversion group $O(3)$, whereas in a molecule or a crystal it has the symmetry of the point group to which the molecule or the crystal belongs. All the point groups are subgroups of $O(3)$. The $(2l+1)$-fold degeneracy of the electronic levels of an isolated atom therefore splits in accordance with the irreducible representations of the point group. This is one of the most important applications of the theory of Section 5.6. We shall consider below the splitting of levels in the octahedral groups O and O_h.

[14]Koster (1957), Section IV.

To begin with, we shall disregard the spin of the electrons and consider only the (integral) orbital angular momentum. The splitting of levels in double groups will be taken up later in this section.

Let us first consider the octahedral group O. This group consists of twofold, threefold and fourfold rotations. We can work out the characters of these elements in the representation $D^{(L)}$ of $SO(3)$ by using the formula(4.50). These are given in Table (7.12) for the first few values of L. Comparing this with Table (7.3) for the characters of O, we find that the levels with $L=0$ and $L=1$ are unsplit. The S function of $D^{(0)}$ now generates the identity representation Γ_1 of O, while the three P functions of $D^{(1)}$ generate Γ_{15}' of O. The atomic levels with $L>1$ must split under the octahedral field because there is no irreducible representation of O with dimensions greater than 3. Once again, comparing the characters of $D^{(2)}$ and $D^{(3)}$ with those in Table (7.3), we get the

TABLE 7.12 THE CHARACTERS OF THE ELEMENTS OF THE POINT GROUP O IN THE IRREDUCIBLE REPRESENTATIONS OF $SO(3)$

	E	$6C_4$	$3C_4^2$	$6C_2$	$8C_3$
$D^{(0)}$	1	1	1	1	1
$D^{(1)}$	3	1	−1	−1	0
$D^{(2)}$	5	−1	1	1	−1
$D^{(3)}$	7	−1	−1	−1	1

following scheme for the splitting of $D^{(2)}$ and $D^{(3)}$:

$$D^{(2)}=\Gamma_{12}\oplus\Gamma_{25}',\ D^{(3)}=\Gamma_2\oplus\Gamma_{15}'\oplus\Gamma_{25}'. \tag{7.22}$$

This shows that the five degenerate atomic D functions split into two levels in cubic symmetry, one twofold degenerate level whose basis functions transform like $(x^2-y^2,\ 2z^2-x^2-y^2)$ and one threefold degenerate level with basis functions transforming like $(yz,\ zx,\ xy)$. Similarly, the sevenfold degenerate F level splits into one nondegenerate level and two triply degenerate levels. The nondegenerate level has the basis function xyz while the two triply degenerate levels have basis functions transforming respectively like $(x,\ y,\ z)$ and $(yz,\ zx,\ xy)$, all the seven functions being linear combinations of the spherical harmonics Y_3^m of degree 3.

The above analysis presents no difficulties in extending to the case when inversion symmetry is present, i.e., to the group O_h. The $L=0$ and $L=1$ levels are still unsplit but the three P functions for $L=1$

TABLE 7.13 THE CHARACTERS OF THE ELEMENTS OF THE DOUBLE GROUP O' IN THE IRREDUCIBLE REPRESENTATIONS $D^{(J)}$ FOR HALF-ODD-INTEGRAL J; n TAKES ALL NONNEGATIVE INTEGRAL VALUES

	(E)	$(\bar{E})$	$(6C_4)$	$(6\bar{C}_4)$	$(3C_4^2, 3\bar{C}_4^2)$	$(6C_2, 6\bar{C}_2)$	$(8C_3)$	$(8\bar{C}_3)$
$D^{(J)}$	$2J+1$	$-(2J+1)$	$\sqrt{2}$	$-\sqrt{2}\,(J=(8n+1)/2)$			1	$-1\,\left(J=\frac{6n+1}{2}\right)$
			0	$0\,(J=(4n+3)/2)$	0	0	-1	$1\,\left(J=\frac{6n+3}{2}\right)$
			$-\sqrt{2}$	$\sqrt{2}\,(J=(8n+5)/2)$			0	$0\,\left(J=\frac{6n+5}{2}\right)$

now belong to Γ_{15} owing to their odd parity under inversion (see Table (7.4)). The splitting of the D level is still as in (7.22) due to even parity of the D functions, whereas the splitting of the F level becomes

$$D^{(3)}=\Gamma_2' \oplus \Gamma_{15} \oplus \Gamma_{25}. \tag{7.23}$$

Let us now consider the spin angular momenta of the electrons. If the atom has an even number of electrons in the unfilled shell, the net angular momentum is integral. The levels belonging to $D^{(J)}$ then split exactly according to the schemes just obtained. But if there is an odd number of electrons, the corresponding functions will generate some double-valued representation $D^{(J)}$ with J half-odd-integral. The basis functions (which will now be the products of the orbital and the spin functions), will get multiplied by -1 on a rotation through 2π. We should therefore work with the double group O'. If we work out the characters of the $(2J+1)$-dimensional representation of O' generated by these basis functions, we shall find that $\chi^{(J)}(\bar{A})=-\chi^{(J)}(A)$ for all $A \in O'$. Such a representation will be orthogonal to all the single-valued representations of O' and hence, on reduction, will be found to contain only the double-valued representations of O'.

We shall work out the reduction of $D^{(J)}$ for a few half-odd-integral values of J. Using (4.89) for the characters of $D^{(J)}$, we can obtain the characters of the elements of O' in $D^{(J)}$. These are given in a comprehensive form in Table (7.13). Comparing this with the double-valued representations of O' given in Table (7.11), we get the following scheme for the splitting of the total angular momentum levels:

$$\begin{aligned} D^{(1/2)}&=\Gamma_6, \\ D^{(3/2)}&=\Gamma_8, \\ D^{(5/2)}&=\Gamma_7 \oplus \Gamma_8, \\ D^{(7/2)}&=\Gamma_6 \oplus \Gamma_7 \oplus \Gamma_8, \text{ etc.} \end{aligned} \tag{7.24}$$

We notice that the degeneracies of all the decomposed levels in (7.24) are even-fold. This is just the consequence of the Kramers' theorem discussed in Section 5.9.4 which tells that for systems with half-odd-integral angular momenta, all the levels must have even-fold degeneracies owing to the time-reversal symmetry.

PROBLEMS ON CHAPTER 7

(7.1) Draw the stereographic projections for the point groups C_{3}, C_{3v}, C_{3h}, D_3 and D_{3h}.

(7.2) What are the point symmetry groups of the molecules NH_3, CH_4, C_6H_6, H_2O and NaCl?

(7.3) Show that the three functions (x, y, z) generate the representations Γ_{15}' of O and Γ_{15} of O_h.

(7.4) Write down the multiplication tables of the double groups C_2', C_{2h}', D_2', C_{3v}' and D_3'.

(7.5) Obtain the additional characters for the double groups C_{3v}', D_3', S_4', D_4' and C_5'.

(7.6) Consider a ligand such as $Ni(CN)_4^{2-}$ which has the symmetry of the point group D_{4h} (with Ni at the centre). In isolated Ni, the five d orbitals (yz, zx, xy, x^2-y^2, $2z^2-x^2-y^2$) are degenerate. Obtain the characters of the representation of D_{4h} generated by these five functions and reduce this representation. Obtain the symmetrized linear combinations of these d orbitals transforming according to the irreducible representations of D_{4h}.

(7.7) Prove the statement made at the end of Section 7.2 that the factor group S/T is isomorphic to the point group G. Proceed along the following lines: (a) Obtain the various cosets of the translation group with respect to the space group elements as in (7.13). (b) Show that the number of distinct cosets of T is equal to the order of G. (c) Work out the law of composition for the coset multiplication and hence prove the isomorphism of S/T with G.

(7.8) Show that

(a) $\{A|\underline{\tau}\}^{-1}\{E|\mathbf{t}\}\{A|\underline{\tau}\}=\{E|A^{-1}\mathbf{t}\}$,

(b) $\{A|\underline{\tau}\}^{-1}\{B|\underline{\sigma}\}\{A|\underline{\tau}\}=\{A^{-1}BA|A^{-1}(B\underline{\tau}+\underline{\sigma}-\underline{\tau})\}$.

(7.9) Obtain the splitting of the atomic levels in the tetrahedral group T_d.

(7.10) Determine the point group symmetry of all the two-dimensional lattice types.

(7.11) Determine the point group of the lattice and the subgroup of the point group which leaves the crystal invariant in the following cases: (i) NaCl, (ii) CsCl, (iii) Zn (hexagonal phase), (iv) Cu_3Au (a cubic structure with Au atoms at the corners and Cu atoms at the face centres), and (v) $MgAl_2O_4$ (the cubic spinel structure).

(7.12) If $\underline{\delta}_A$ and $\underline{\delta}_B$ are the characteristic nonprimitive translations associated respectively with two point group elements A and B in a certain space group, show that the characteristic nonprimitive translation associated with the element AB is $A\underline{\delta}_B+\underline{\delta}_A$.

(7.13) Work out the splitting of the levels $D^{(4)}$ and $D^{(5)}$ of an isolated atom in the cubic group O_h.

(7.14) Work out the splitting of the levels $D^{(9/2)}$ and $D^{(11/2)}$ of an isolated atom in the double group O'.

Bibliography for Chapter 7

Azaroff (1960); Ballhausen (1962); Bell (1954); Bhagavantam (1966); Bloss (1971); Bradley and Cracknell (1972); Buerger (1967); Cracknell (1968); Falicov (1967); Koster (1957); Koster, Dimmock and Wheeler (1963); Kovalev (1965); Loebl (1968); Nussbaum (1966); Phillips (1963); Slater (1965); Tinkham (1964); Zak, Casher, Gluck and Gur (1970).

CHAPTER 8

Group Theory in Solid State Physics

Having discussed the thirty two crystallographic point groups in sufficient detail and the elementary concepts of translation groups and space groups in the previous chapter, we shall come to proper solid state physics in the present one. Since it is beyond the scope of the present book to consider the various applications of the theory of groups to the physics of solids, we shall, in fact, deal with only one major problem, that of the electronic structure of crystals. We expect that this will help the student to establish a firm grasp on the group theoretical methods in solid state physics. Moreover, although a few more applications are discussed briefly in the appendices, we believe that a detailed discussion of the problem of electronic structure, together with the crystal field splitting of atomic levels treated in the previous chapter, will pave the way for any other application of group theory in solid state physics, such as impurity states and colour centres, crystal field theory and paramagnetic resonance, lattice dynamics, etc. For example, the role of group theory in lattice dynamics is exactly the same as its role in the band structure problem.

8.1 The Problem of the Electronic Structure of Crystals

The energies and the wave functions of an electron in a crystal are the solutions of the Schroedinger equation

$$\mathcal{H}\phi(\mathbf{r}) = \left\{ -\frac{\hbar^2\nabla^2}{2m} + V(\mathbf{r}) \right\} \phi(\mathbf{r}) = E\phi(\mathbf{r}), \tag{8.1}$$

where $V(\mathbf{r})$ is the potential experienced by the electron in the periodic lattice. The full symmetry group of the crystal Hamiltonian is the space group to which the crystal belongs. As we shall show in the next section, the solutions of this equation appear in the form of Bloch functions $\phi_{\mathbf{k}}(\mathbf{r})$ with the corresponding energy eigenvalues $E(\mathbf{k})$. The functional relation $E \equiv E(\mathbf{k})$ is known as the *electronic band structure* or simply the *electronic structure* of the crystal. A knowledge of $E(\mathbf{k})$ allows us to determine a number of observable properties of the crystal such as, in particular, the transport properties and the optical properties. The simplest inference that can be drawn from the electronic structure is whether the crystal is a metal, a semimetal, a semiconductor or an insulator.

It must be emphasized at the beginning that we shall be working in the single-particle approximation already discussed in Chapter 6. We shall neglect the vibrations of the nuclei and assume that they are fixed at their respective lattice sites. We shall also neglect all the interactions of the electrons among themselves and assume that they behave as a gas of free electrons. We shall later discuss the perturbation caused by the periodic potential. The eigenstates obtained under these approximations are called the *single-particle states* and will represent the stationary states of the electrons. The electrons fill these states in accordance with the Pauli exclusion principle; each state can accommodate at most two electrons, one with spin up and one with spin down.

Apart from the above assumptions, there is no restriction on the potential $V(\mathbf{r})$ except that it be periodic with the periodicity of the lattice. As should be amply clear by now, group theory will be a great help in simplifying the secular equations, in classifying the eigenstates of the problem and in labeling the energy bands. It will, however, not give us any quantitative estimates of the energies involved.

Since we are concerned only with the group theoretical aspect of the electronic structure, the exact analytical form of the potential $V(\mathbf{r})$ need not worry us. For the sake of simplicity, we shall often consider the case $V(\mathbf{r})=0$, i.e., the case of a constant potential. This is the elementary quantum mechanical problem of electrons in a box and the solutions of (8.1) are then just the plane waves

$$\phi_{\mathbf{k}}(\mathbf{r}) = \exp(i\mathbf{k}.\mathbf{r}) \tag{8·2a}$$

with energies

$$E(\mathbf{k}) = \hbar^2\mathbf{k}^2/2m. \tag{8.2b}$$

This is known as the *free electron approximation*. This simple case serves to give a considerable insight into the problem of the electronic band structure of crystals.

8.2 Translation Group and the Reciprocal Lattice

Owing to the translational symmetry of the crystal, the eigenfunctions of the Hamiltonian in (8.1) with a periodic potential have a specific form given by the Bloch theorem. According to this theorem, the eigenfunctions have definite translational properties determined by a wave vector $\mathbf{k}$ and the values of an eigenfunction at equivalent points in different unit cells are simply related by a phase factor. Although the proof of the Bloch theorem is fairly elementary,[1] we shall consider in this section its proof based on group theoretical arguments followed by a discussion on the nature of the wave vector $\mathbf{k}$ and the reciprocal lattice.

8.2.1 Bloch theorem. The elements of the translation group of a crystal with periodic boundary conditions can be denoted, as in Section 7.2, by $T(n_1, n_2, n_3)$. We have seen that the translation group is an abelian group. Each element of the translation group T is therefore a class by itself. It follows that all the irreducible representations of T must be one-dimensional.

Let $\phi(\mathbf{r})$ be an eigenfunction of the Hamiltonian in (8.1). Since the Hamiltonian is invariant under the translation group, we may use $\phi(\mathbf{r})$ to generate an irreducible representation of T. The operation of any element of T on $\phi(\mathbf{r})$ is then just to multiply it by a scalar which is its representation with $\phi(\mathbf{r})$ as the basis. Let us denote by $P_{n_1 n_2 n_3}$ an operator corresponding to the translation $T(n_1, n_2, n_3)$ and acting on functions of $\mathbf{r}$. Then, choosing a general element of T (which is also an element of the space group S), we have

$$P_{n_1 n_2 n_3}\,\phi(\mathbf{r}) = c(n_1, n_2, n_3)\,\phi(\mathbf{r}), \tag{8.3}$$

where $c(n_1, n_2, n_3)$ is a constant to be determined. However, by definition, the operation of the translation operator has the effect

$$P_{n_1 n_2 n_3}\,\phi(\mathbf{r}) = \phi(\mathbf{r} + n_1\mathbf{a}_1 + n_2\mathbf{a}_2 + n_3\mathbf{a}_3), \tag{8.4}$$

where $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$ are the fundamental lattice translation vectors, as in Section 7.2. In particular, we must have

$$P_{100}\,\phi(\mathbf{r}) = \phi(\mathbf{r} + \mathbf{a}_1) = c(1, 0, 0)\,\phi(\mathbf{r}). \tag{8.5}$$

Operating by P_{100} on $\phi(\mathbf{r})$ N_1 times and using the periodic boundary conditions $\phi(\mathbf{r} + N_1\mathbf{a}_1) \equiv \phi(\mathbf{r})$, we find that

$$P_{N100}\,\phi(\mathbf{r}) = \phi(\mathbf{r}) = c(N_1, 0, 0)\,\phi(\mathbf{r}) = [c(1, 0, 0)]^{N_1}\,\phi(\mathbf{r}). \tag{8.6}$$

[1] Kittel (1976), p. 195.

This shows that

$$c(1, 0, 0)=\exp(2\pi i m_1/N_1),\ -N_1/2\leq m_1\leq N_1/2, \tag{8.7a}$$

and

$$c(n_1, 0, 0)=\exp(2\pi i m_1 n_1/N_1). \tag{8.7b}$$

We could obtain similar expressions for $c(0, n_2, 0)$ and $c(0, 0, n_3)$. Multiplying these together, we have

$$c(n_1, n_2, n_3)=\exp\left[2\pi i\left(\frac{m_1 n_1}{N_1}+\frac{m_2 n_2}{N_2}+\frac{m_3 n_3}{N_3}\right)\right]. \tag{8.8}$$

Let us now define the fundamental translation vectors of the reciprocal lattice by

$$\mathbf{b}_1=2\pi\,(\mathbf{a}_2\times\mathbf{a}_3)/v_c,\ \mathbf{b}_2=2\pi\,(\mathbf{a}_3\times\mathbf{a}_1)/v_c,$$
$$\mathbf{b}_3=2\pi\,(\mathbf{a}_1\times\mathbf{a}_2)/v_c,\ v_c=\mathbf{a}_1\cdot(\mathbf{a}_2\times\mathbf{a}_3). \tag{8.9}$$

It can be verified that these have the following properties:

$$\mathbf{b}_i\cdot\mathbf{a}_j=2\pi\,\delta_{ij},\ i,j=1, 2, 3. \tag{8.10}$$

A general vector $\mathbf{k}$ of the reciprocal space can then be written as a linear combination of $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ in the form

$$\mathbf{k}=(m_1/N_1)\,\mathbf{b}_1+(m_2/N_2)\,\mathbf{b}_2+(m_3/N_3)\,\mathbf{b}_3, \tag{8.11}$$

where m_i are any integers. If all the m_i's are integral multiples of the respective N_i's, we have a linear combination of $\mathbf{b}_1$, $\mathbf{b}_2$ and $\mathbf{b}_3$ with integral coefficients. Such vectors are called *reciprocal lattice vectors* and may be denoted by

$$\mathbf{G}(h, k, l)=h\mathbf{b}_1+k\mathbf{b}_2+l\mathbf{b}_3. \tag{8.12}$$

where h, k and l are integers. The lattice generated by the end points of all the reciprocal lattice vectors is called the *reciprocal lattice* and the end points themselves are called *reciprocal lattice points*. The scalar product of a vector $\mathbf{k}$ of the reciprocal space and a direct lattice translation vector $\mathbf{t}(n_1, n_2, n_3)$ can be worked out by using (8.10) and is found to be

$$\mathbf{k}\cdot\mathbf{t}(n_1, n_2, n_3)=2\pi\left(\frac{m_1 n_1}{N_1}+\frac{m_2 n_2}{N_2}+\frac{m_3 n_3}{N_3}\right). \tag{8.13a}$$

As a special case, if we replace $\mathbf{k}$ by $\mathbf{G}$, we have, by using (8.12),

$$\mathbf{G}\cdot\mathbf{t}=2\pi\,(hn_1+kn_2+ln_3)=2\pi\times\text{integer}. \tag{8.13b}$$

Using this back in (8.8), we have

$$c(n_1, n_2, n_3)=\exp[i\,\mathbf{k}\cdot\mathbf{t}(n_1, n_2, n_3)]. \tag{8.14}$$

Combining this with (8.3) and (8.4), we find that the eigenfunction $\phi(\mathbf{r})$ has the property

$$\phi(\mathbf{r}+\mathbf{t})=\exp(i\,\mathbf{k}\cdot\mathbf{t})\ \phi(\mathbf{r}). \tag{8.15}$$

This can be satisfied if and only if $\phi(\mathbf{r})$ is of the form

$$\phi(\mathbf{r})=\exp(i\,\mathbf{k}\cdot\mathbf{r})\;u_{\mathbf{k}}(\mathbf{r}), \tag{8.16}$$

where the function $u_{\mathbf{k}}(\mathbf{r})$ is periodic in $\mathbf{r}$ with the periodicity of the lattice, i.e., $u_{\mathbf{k}}(\mathbf{r}+\mathbf{t})=u_{\mathbf{k}}(\mathbf{r})$ for all the direct lattice translation vectors $\mathbf{t}$. This is the *Bloch theorem: the eigenfunctions of the Hamiltonian of an electron in a periodic potential must be of the form* (8.16), or *have the property* (8.15). Note that the two statements (8.15) and (8.16) of the Bloch theorem are equivalent.

The vector $\mathbf{k}$ is called the *wave vector* of an electron in the state $\phi_{\mathbf{k}}(\mathbf{r})$ and is *defined by the behaviour of the function* $\phi_{\mathbf{k}}(\mathbf{r})$ *under the translation operators*, i.e., by (8.15). Thus we see that the eigenfunctions and the eigenvalues of the Schroedinger equation (8.1) can be labeled by the wave vector $\mathbf{k}$. From our discussion of Section 5.4, it is clear that the wave vector $\mathbf{k}$ is a good quantum number of an electron in a crystal so long as the translational symmetry of the Hamiltonian is not disturbed. The wave vector $\mathbf{k}$ manifests itself in various scattering phenomena of the electron with other excitations in the crystal, the quantity $\hbar\,\mathbf{k}$ appearing as the linear momentum of the electron. This linear momentum should not, however, be taken in the classical sense because it is not necessarily parallel to the electron group velocity.

We shall write (8.1) in the form

$$\mathcal{H}\phi_{\mathbf{k}}(\mathbf{r})=E(\mathbf{k})\;\phi_{\mathbf{k}}(\mathbf{r}). \tag{8.17}$$

The function $u_{\mathbf{k}}(\mathbf{r})$ of (8.16) is not an arbitrary function. In order that the Bloch function (8.16) satisfy the Schroedinger equation (8.1). it can be shown by substituting (8.16) in (8.1) that $u_{\mathbf{k}}(\mathbf{r})$ must be a solution of the eigenvalue equation

$$\left\{\frac{1}{2m}(-\hbar^2\,\underline{\nabla}^2-i\,\hbar\,\mathbf{k}\cdot\underline{\nabla}+\mathbf{k}^2)+V(\mathbf{r})\right\}u_{\mathbf{k}}(\mathbf{r})=E(\mathbf{k})\,u_{\mathbf{k}}(\mathbf{r}). \tag{8.18}$$

8.2.2 Symmetry of the reciprocal lattice. We shall first show that the reciprocal lattice has the same point group symmetry as the direct lattice, i.e., if the direct lattice is invariant under a certain point group operation performed about one of its lattice sites, then the corresponding reciprocal lattice is also invariant under the same operation performed about one of its lattice points and vice versa.

Let A be any element of the point group of the direct lattice and $\mathbf{G}$ be a reciprocal lattice vector. For any translation vector $\mathbf{t}$ of the direct lattice, $A\mathbf{t}$ is also a translation vector. From (8.13b), we then have

$$\mathbf{G}\cdot A\mathbf{t}=2\pi\times\text{integer, for all } \mathbf{t}. \tag{8.19}$$

Since the operations of the point group are orthogonal transformations, the scalar product of two vectors remains invariant under their action, i.e., $A^{-1}\mathbf{G}\cdot A^{-1}(A\mathbf{t})=\mathbf{G}\cdot A\mathbf{t}$, so that (8.19) gives

$$A^{-1}\mathbf{G}\cdot\mathbf{t}=2\pi\times\text{integer, for all } \mathbf{t}. \tag{8.20}$$

Since this is true for all lattice vectors $\mathbf{t}$, (8.20) shows that $A^{-1}\mathbf{G}$ must be of the form $q_1\mathbf{b}_1+q_2\mathbf{b}_2+q_3\mathbf{b}_3$ with integral q_i. In other words, $A^{-1}\mathbf{G}$ must be a reciprocal lattice vector.

As this holds for any element A of the point group, it is evident that any symmetry operation of the direct lattice is also a symmetry operation of the reciprocal lattice. Now the converse can also be easily proved either by following the above line of argument or simply by noting that the direct lattice is the reciprocal of the reciprocal lattice. Thus the reciprocal lattice has no other symmetry elements in addition to those of the direct lattice. It follows that *the reciprocal lattice has the same point group symmetry as the direct lattice.*

This result has an important consequence in terms of the seven systems into which lattices are divided. It follows that *the reciprocal lattice belongs to the same system as the direct lattice*, although it may not belong to the same *type*. For example, if the direct lattice is cubic, the reciprocal lattice is also cubic. However, talking of types, the reciprocal lattice of a body centred lattice is face centred and vice versa.

8.2.3 Brillouin zone. Eq. (8.15) shows that every value of $\mathbf{k}$ gives us an irreducible representation of the translation group. However, not all of these are distinct representations. For, consider two $\mathbf{k}$ vectors related to each other by a reciprocal lattice vector $\mathbf{G}$, such as $\mathbf{k}'=\mathbf{k}+\mathbf{G}$. It is then evident from (8.13b) that $\exp(i\mathbf{k}'\cdot\mathbf{t})=\exp(i\mathbf{k}\cdot\mathbf{t})$ for all $\mathbf{t}$'s. This shows that there is a whole host of points in the reciprocal space of the form $\mathbf{k}+\mathbf{G}$ (with fixed $\mathbf{k}$ and $\mathbf{G}$ running over all the reciprocal lattice vectors) which correspond to one irreducible representation of T. In other words, the $\mathbf{k}$ vector of a Bloch function is not unique; a Bloch function may be characterized by any wave vector from the set $\mathbf{k}+\mathbf{G}$.

To avoid this ambiguity and to be able to characterize every Bloch function and every irreducible representation of T by a unique $\mathbf{k}$ vector, we choose a unit cell in the reciprocal lattice. From the set of equivalent points $\mathbf{k}+\mathbf{G}$, we choose that point which lies in the chosen unit cell. Any point of the reciprocal space may be reduced to an equivalent point in this unit cell and the ambiguity mentioned above

can be removed. Every allowed value of $\mathbf{k}$ in the unit cell then gives a unique irreducible representation of T. As we shall see below, there are as many of these as the elements of the translation group T which in turn are equal to the number $N_1N_2N_3$ of primitive cells of the direct lattice.

In a given lattice, whether direct or reciprocal, a unit cell may be chosen in an infinite number of ways. As an example, we have shown in Fig. (8.1) three different ways of choosing the fundamental translation vectors and the corresponding unit cells for a two-dimensional oblique lattice. Fig. (8.2) shows three different sets of fundamental translation vectors corresponding to those of Fig. (8.1) in the reciprocal lattice of the oblique lattice. In each of Figs. (8.2a), (8.2b) and (8.2c), we have shown two different unit cells These differ only in choosing the independent values of $\mathbf{k}$ defined in (8.11). The first unit cell in each of these three figures corresponds to the choice $0 \leq m_i < N_i$, while the second to $-N_i/2 \leq m_i < N_i/2$. For a two-dimensional lattice, note that $\mathbf{a}_3$ is infinite and consequently, $\mathbf{b}_3=0$. Fig. (8.2d)

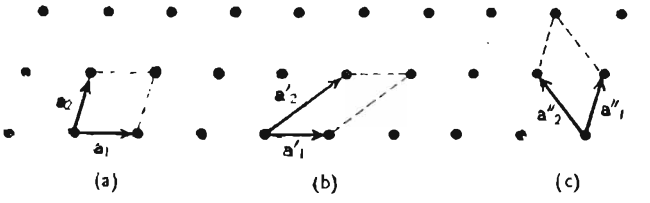

FIGURE 8.1 (a), (b) and (c) show three of the infinite number of ways in which a unit cell may be chosen in a two-dimensional oblique lattice. The unit cell in each case is the parallelogram completed with the fundamental translation vectors shown. Each unit cell has the same area.

shows an altogether different way of constructing a unit cell. A hexagon shown in this figure is known as the *Wigner-Seitz cell*. For a three-dimensional lattice, in general, it is defined as follows. We choose a certain lattice point in the given lattice (direct or reciprocal). The Wigner-Seitz cell is then the volume containing points nearer, or at most equidistant, to the chosen lattice point than to any other lattice point. It is evident that it is the volume enclosed by the perpendicular bisectors of the vectors from the chosen lattice point to all its neighbours.

There is a particular advantage in choosing such a unit cell—*the Wigner-Seitz cell has the full point group symmetry of the lattice*, which

is fairly easy to prove on the basis of its definition. Finally, the Wigner-Seitz cell of the reciprocal lattice is known as the *Brillouin zone*. Owing to its full point group symmetry, the Brillouin zone is a particularly convenient choice for a unit cell in the reciprocal lattice

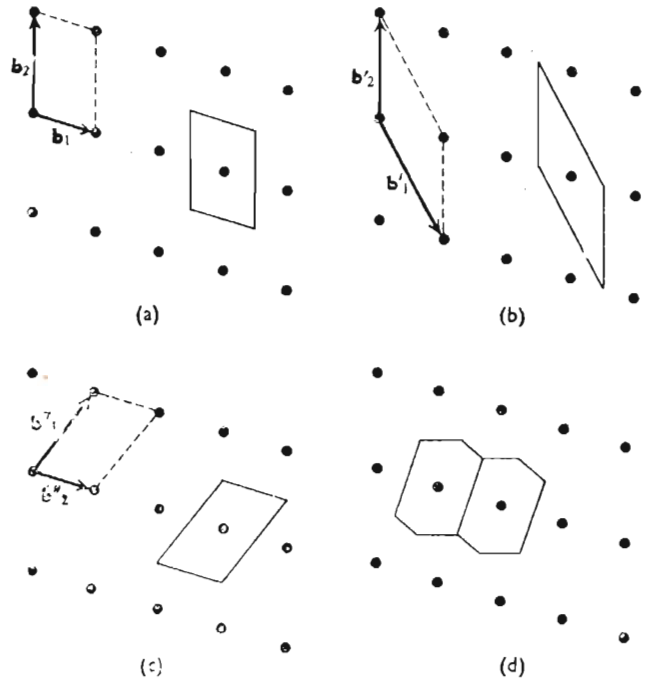

FIGURE 8.2 (a) The primitive translation vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ of the reciprocal lattice corresponding to the lattice translation vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ of Fig. (8.1a). The unit cell is shown in two ways for this choice of $\mathbf{b}_1$ and $\mathbf{b}_2$. Note that $\mathbf{b}_1$ is normal to $\mathbf{a}_2$ and $\mathbf{b}_2$ to $\mathbf{a}_1$. Moreover, the lengths of $\mathbf{b}_1$ and $\mathbf{b}_2$ are inversely proportional to those of $\mathbf{a}_1$ and $\mathbf{a}_2$, respectively. (b) and (c) similarly correspond respectively to Figs. (8.1b) and (8.1c). (d) The Wigner-Seitz cell or the Brillouin zone as a unit cell of the reciprocal lattice. This is independent of the choice of the primitive translation vectors. Again, each unit cell has the same area in the reciprocal space.

in the study of the electronic structure of crystals. It should be clear that for every point of the boundary (face, edge or corner) of the Brillouin zone, there is at least one other point on the boundary which differs from the first by a reciprocal lattice vector. All such points on the Brillouin zone boundary must therefore be treated as equivalent and may be designated by the same value of $\mathbf{k}$.

8.3 Irreducible Representations of a Space Group

The group of the Schroedinger equation (8.1) is the space group to which the crystal belongs. The electronic energy levels and their degeneracies are therefore determined by the irreducible representations of the space group and not by those of the translation group or the point group alone. In discussing the irreducible representations of a space group below, we shall closely follow the treatment of Koster.[2]

Suppose we have an irreducible representation of the space group S by the matrices $D(\{A \mid \underline{\tau}\})$ of order n, where A is an element of the point group G and $\underline{\tau}$ is of the form $\underline{\delta}+\mathbf{t}$, as discussed in Section 7.2. Owing to the finite order of the group S, we can assume that these matrices are unitary.

For any space group S, the group T of pure translations $\{E \mid \mathbf{t}\}$ is a subgroup of S. Let us pick out those matrices of the representation D which correspond to the pure translations. Since T has only one-dimensional irreducible representations, it is possible to find a unitary transformation which brings all the matrices of the form $D(\{E \mid \mathbf{t}\})$ to a fully diagonal form. In other words, *given an irreducible representation of a space group S, there exists an equivalent representation in which all the elements of T are represented by fully diagonal matrices.*

Now the diagonal elements of a matrix representing $\{E \mid \mathbf{t}\}$ can only be of the form $\exp(i\mathbf{k}\cdot\mathbf{t})$ because these are the only irreducible representations of T. Let us suppose that altogether q distinct wave vectors $\mathbf{k}_1$, $\mathbf{k}_2, \ldots, \mathbf{k}_q$ appear in the diagonal elements of $D(\{E \mid \mathbf{t}\})$. We may also assume, without loss of generality, that all the diagonal elements having $\mathbf{k}_1$ are grouped together, and so on. The matrices of our irreducible representation corresponding to elements of T then take the form

$$D(\{E \mid \mathbf{t}\}) = \begin{bmatrix} \exp(i\mathbf{k}_1\cdot\mathbf{t}) & & & & \mathbf{O} \\ & \exp(i\mathbf{k}_1\cdot\mathbf{t}) & & & \\ & & \ddots & & \\ & & & \exp(i\mathbf{k}_j\cdot\mathbf{t}) & \\ & & & & \ddots \\ \mathbf{O} & & & & \exp(i\mathbf{k}_q\cdot\mathbf{t}) \end{bmatrix} \tag{8.21}$$

Since we know that (see Problem 7.8)

$$\{A \mid \underline{\tau}\}^{-1}\{E \mid \mathbf{t}\}\{A \mid \underline{\tau}\} = \{E \mid A^{-1}\mathbf{t}\},$$

[2] Koster (1957).

the corresponding matrices must satisfy the relation

$$[D(\{A \mid \underline{\tau}\})]^{-1} D(\{E \mid \mathbf{t}\}) D(\{A \mid \underline{\tau}\}) = D(\{E \mid A^{-1}\mathbf{t}\}). \tag{8.22}$$

Making use of the fact that $\mathbf{k} \cdot A^{-1}\mathbf{t} = A\mathbf{k} \cdot \mathbf{t}$, we see that the matrix representing $\{E \mid A^{-1}\mathbf{t}\}$ will be

$$D(\{E \mid A^{-1}\mathbf{t}\}) = \begin{bmatrix} \exp(iA\mathbf{k}_1 \cdot \mathbf{t}) & & & \mathbf{O} \\ & \exp(iA\mathbf{k}_1 \cdot \mathbf{t}) & & \\ & & \exp(iA\mathbf{k}_j \cdot \mathbf{t}) & \\ \mathbf{O} & & & \exp(iA\mathbf{k}_q \cdot \mathbf{t}) \end{bmatrix}. \tag{8.23}$$

If two diagonal matrices are related by a unitary transformation as in (8.22), they must contain the same diagonal elements except possibly in a different order. It follows that the diagonal elements of (8.21) and (8.23) are the same except for order, perhaps. Thus, if $\exp(iA\mathbf{k}_j \cdot \mathbf{t})$ occurs in (8.23), it must also appear in (8.21). Moreover, $\exp(iA\mathbf{k}_1 \cdot \mathbf{t})$ must appear as often in (8.23) as $\exp(i\mathbf{k}_1 \cdot \mathbf{t})$ appears in (8.21). Now A is arbitrary and we could take any elements of the point group G for A. This means that elements such as $\exp(iA\mathbf{k}_1 \cdot \mathbf{t})$ for *all* $A \in G$ must appear in (8.21).

We can further show that no element of the form $\exp(i\mathbf{k}' \cdot \mathbf{t})$, where $\mathbf{k}'$ is not equal to $A\mathbf{k}_1$ for any element of G, can appear in (8.21). For, if it does, we shall show that the representation of the space group under consideration is reducible. In this case, in the matrix (8.21), we can gather all terms of the type $\exp(iA\mathbf{k}_1 \cdot \mathbf{t})$ for all $A \in G$ first and write the remaining terms of the form $\exp(i\mathbf{k}' \cdot \mathbf{t})$ later, bringing it in the form

$$D(\{E \mid \mathbf{t}\}) = \left[\begin{array}{c|c} \begin{array}{l}\text{terms of the type} \\ \exp(iA\mathbf{k}_1 \cdot \mathbf{t})\end{array} & \mathbf{O} \\ \hline \mathbf{O} & \begin{array}{l}\text{remaining terms such} \\ \text{as } \exp(i\mathbf{k}' \cdot \mathbf{t})\end{array} \end{array}\right]. \tag{8.24}$$

Let us write (8.22) in the form

$$D(\{A \mid \underline{\tau}\})\, D(\{E \mid A^{-1}\mathbf{t}\}) = D(\{E \mid \mathbf{t}\})\, D(\{A \mid \underline{\tau}\}), \tag{8.25}$$

and assume for $D(\{A \mid \underline{\tau}\})$ a martix of the form

$$D(\{A \mid \tau\}) = \left[\begin{array}{c|c} D'(\{A \mid \underline{\tau}\}) & X \\ \hline Y & D''(\{A \mid \underline{\tau}\}) \end{array}\right], \tag{8.26}$$

where D' and D'' are square matrices of the same order as the first and the second diagonal blocks of (8.24) respectively. Using (8.24), (8.25) and (8.26), it can then be shown that the block matrices X and Y must be identically null matrices. But then (8.26) shows that the representation is reducible, contrary to our assumption that we have started with an irreducible representation.

The discussion hitherto leads to the conclusion that the matrix (8.21) contains diagonal elements only of the form $\exp(iA\mathbf{k}_1\cdot\mathbf{t})$ for all $A\in G$ and that each distinct element appears an equal number of times. If there are q distinct wave vectors in the set $A\mathbf{k}_1$ for all $A\in G$, as we have assumed, and if each appears, say, d times, then (8.21) becomes

$$D(\{E\mid\mathbf{t}\})=\begin{bmatrix} \exp(i\mathbf{k}_1\cdot\mathbf{t})E_d & & \\ & \exp(iA_2\mathbf{k}_1\cdot\mathbf{t})\,E_d & \mathbf{O} \\ & & \ddots \\ \mathbf{O} & & \exp(iA_q\mathbf{k}_1\cdot\mathbf{t})\,E_d \end{bmatrix}, \tag{8.27}$$

where E_d is a unit matrix of order d and we have divided the $n\times n$ matrix into q blocks each of order d so that $n=qd$. Moreover, $A_1\equiv E$ (the identity), $A_2,\ldots,A_q$ are *selected* elements of the point group which when acting on $\mathbf{k}_1$ give the q distinct wave vectors, i.e.,

$$A_i\mathbf{k}_1=\mathbf{k}_i,\quad 1\leq i\leq q. \tag{8.28}$$

Note that each $\mathbf{k}_i$ corresponds to a distinct representation of T.

At this stage, we shall defer our discussion of the irreducible representations of a space group and come back to it after the next two subsections.

8.3.1 Bloch functions as basis for irreducible representations. The form of the matrix (8.27) corresponding to a pure translation suggests that the basis functions for the representation D are Bloch functions. This is evident because only a Bloch function has the property of being multiplied by $\exp(i\mathbf{k}_j\cdot\mathbf{t})$ under a translation through $\mathbf{t}$.

Suppose we have d orthogonal Bloch functions ϕ_{1j} $(1\leq j\leq d)$, each corresponding to the wave vector $\mathbf{k}$. Let us construct the following n functions from these :

$$\phi_{ij}=P(\{A_i\mid\underline{\delta}_i\})\,\phi_{1j},\ 1\leq i\leq q, \tag{8.29}$$

where $\underline{\delta}_i$ is the characteristic translation associated with the point group element A_i (see Section 7.2), $P(\{A \mid \underline{\delta}\})$ is the operator corresponding to the element $\{A \mid \underline{\delta}\}$ and acting on functions, and A_i are the selected elements of the point group defined previously in this section. We shall show that the functions ϕ_{ij} are Bloch functions with the wave vector $A_i\mathbf{k}$.

We can write ϕ_{1j} in the form

$$\phi_{1j}(\mathbf{r})=\exp(i\mathbf{k}\cdot\mathbf{r})\, u_{\mathbf{k}}{}^{j}(\mathbf{r}), \tag{8.30}$$

where $u_{\mathbf{k}}{}^{j}(\mathbf{r})$ has the periodicity of the lattice. Operating on this by the space group element $\{A_i \mid \underline{\delta}_i\}$, we get

$$\begin{aligned}\phi_{ij}(\mathbf{r})&=P(\{A_i \mid \underline{\delta}_i\})\ [\exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}{}^{j}(\mathbf{r})]\\ &=\exp[i\mathbf{k}\cdot A_i^{-1}\ (\mathbf{r}+\underline{\delta}_i)]u_{\mathbf{k}}{}^{j}(A_i^{-1}\ (\mathbf{r}+\underline{\delta}_i))\\ &=\exp(i\mathbf{k}\cdot A_i^{-1}\mathbf{r})\ [\exp(i\mathbf{k}\cdot A_i^{-1}\underline{\delta}_i)u_{\mathbf{k}}{}^{j}(A_i^{-1}\mathbf{r}+A_i^{-1}\underline{\delta}_i)].\end{aligned} \tag{8.31}$$

We can now show that the function in the square brackets in the above equation has the periodicity of the lattice. Thus, replacing $\mathbf{r}$ by $\mathbf{r}+\mathbf{t}$ we find that

$$u_{\mathbf{k}}{}^{j}(A_i^{-1}(\mathbf{r}+\mathbf{t})+A_i^{-1}\underline{\delta}_i)=u_{\mathbf{k}}{}^{j}(A_i^{-1}\mathbf{r}+A_i^{-1}\underline{\delta}_i), \tag{8.32}$$

because $A_i^{-1}\mathbf{t}$ is also a lattice translation vector if $\mathbf{t}$ is and $u_{\mathbf{k}}{}^{j}$ is a periodic function. Replacing $\mathbf{r}$ by $\mathbf{r}+\mathbf{t}$ in ϕ_{ij} of (8.31), we therefore find

$$\phi_{ij}(\mathbf{r}+\mathbf{t})=\exp(i\mathbf{k}\cdot A_i^{-1}\mathbf{t})\phi_{ij}(\mathbf{r}). \tag{8.33}$$

Now, since $\mathbf{k}\cdot A_i^{-1}\mathbf{t}=A_i\mathbf{k}\cdot\mathbf{t}$, we have finally

$$\phi_{ij}(\mathbf{r}+\mathbf{t})=\exp(iA_i\mathbf{k}\cdot\mathbf{t})\phi_{ij}(\mathbf{r}), \tag{8.34}$$

showing that ϕ_{ij} is a Bloch function with the wave vector $A_i\mathbf{k}$. Since $\{A_i \mid \underline{\delta}_i\}$ are symmetry operations for the Hamiltonian of (8.1), it follows that all the n Bloch functions of (8.29) are degenerate. In other words, we have $E(A\mathbf{k})=E(\mathbf{k})$ for all $A\in G$, showing that *the constant energy surfaces in the reciprocal space have the full point group symmetry of the lattice.*

These n Bloch functions clearly generate the irreducible representation D of the space group which we have discussed so far because the pure translations would have the form (8.27) with these Bloch functions as basis. The significance of the number d of orthogonal Bloch functions for a given value of the wave vector $\mathbf{k}$ will be explained in subsection 8.3.3.

8.3.2 The star and the group of the wave vector. Let us pick up a certain $\mathbf{k}$ vector in or on the Brillouin zone of the lattice. Let us apply

all the transformations of the point group of the lattice on **k**. This will give us, in general, g wave vectors where g is the order of the point group G. However, not all of these may be distinct, remembering that wave vectors differing by reciprocal lattice vectors are to be treated as identical. It may give us, say, q distinct wave vectors where q will turn out to be a divisor of g. The set of these q wave vectors is called the *star of the wave vector.*

If $q=g$, which means that every element of the point group gives a distinct **k** vector, we say that we have a *general* **k** vector. If $q<g$, on the other hand, the end point of the **k** vector must be on a *plane of symmetry* or on a *line of symmetry* or must itself be a *special point* in the Brillouin zone.

To illustrate the situation, we have shown in Fig. (8.3) the Brillouin zone of a plane square lattice of lattice constant a. The Brillouin zone is a square of side $2\pi/a$. The special points and the lines of symmetry for this structure are labeled with special symbols which have

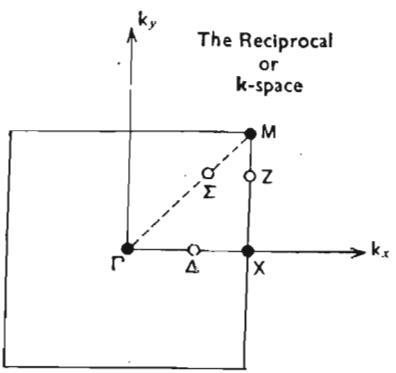

FIGURE 8.3 The special points and the lines of symmetry for a plane square lattice

become an established convention over the years. There are three special points denoted by Γ: $\mathbf{k}=(0, 0)$, X: $\mathbf{k}=(\frac{1}{2}, 0)$ and M: $\mathbf{k}=(\frac{1}{2}, \frac{1}{2})$ in units[3] of $2\pi/a$. There are also three lines of symmetry, a general point on which is denoted respectively by Δ: $\mathbf{k}=(k_x, 0)$, Z: $\mathbf{k}=(k_x, \frac{1}{2})$ and Σ: $\mathbf{k}=(k_x, k_x)$ with $0<k_x<\frac{1}{2}$. Fig. (8.4) shows the stars of various **k** vectors for the same case of a plane square lattice.

Let us now consider the symmetry of the **k** vector. Let us think of all the point group elements which leave a **k** vector unchanged to within

[3] We shall use the unit of $2\pi/a$ for the cartesian components of the **k** vector for square and cubic lattices throughout this chapter.

a reciprocal lattice vector, i.e., elements which have the property

$$B\mathbf{k}=\mathbf{k}+\mathbf{G}, \tag{8.35}$$

where $\mathbf{G}$ is any reciprocal lattice vector, including zero. The set of such transformations is clearly a group, for, if two operators separately leave

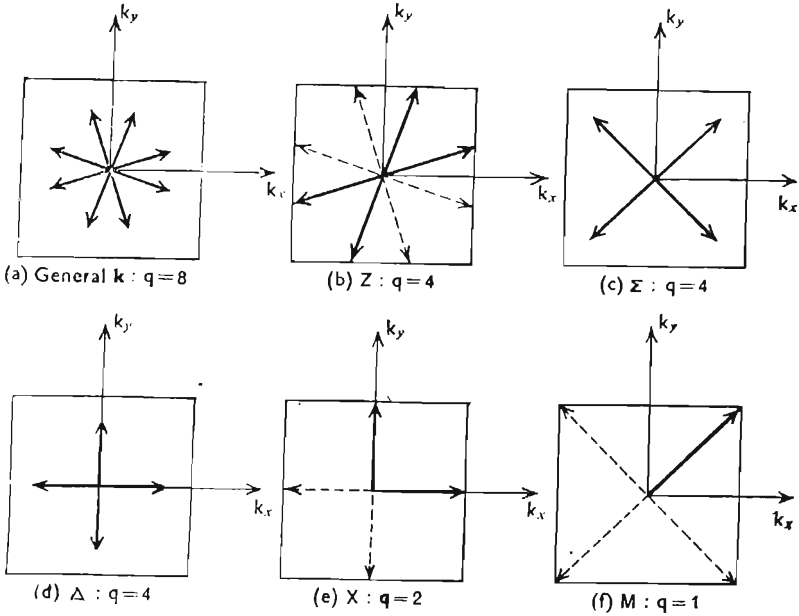

FIGURE 8.4 The stars of various $\mathbf{k}$ vectors for a plane square lattice. Every dashed vector is related to one solid vector by a reciprocal lattice vector and is therefore not counted separately; q denotes the number of distinct vectors in the star.

$\mathbf{k}$ invariant, their product also leaves $\mathbf{k}$ unchanged. The inverse of an operator and the identity are included in the same set. This group is called the *group of the wave vector* and will be denoted by K in this chapter. It is clearly a subgroup of the point group G.

For a general $\mathbf{k}$ vector in the Brillouin zone, the group of $\mathbf{k}$ consists only of the identity element. For a special point or a point on a line or a plane of symmetry, the order of K will be larger than one. In fact, it is easy to verify the following rule:

The order of the point group = The order of the group of $\mathbf{k}$ $\times$ *the number of vectors in the star of* $\mathbf{k}$. (8.36)

This can be easily checked with reference to Fig. (8.4). Consider the point Z in Fig. (8.3). Remembering that the point group for a square

lattice is C_{4v}, we see that the elements of C_{4v} which leave this particular $\mathbf{k}$ vector invariant are E and m_y. The group K for the point Z is thus $(E, m_y)=C_{1h}$. The $\mathbf{k}$ vector at the point X has four symmetry elements, E, m_x, m_y, C_4^2 (see Fig. (8.4e)). The group K for the point X is therefore C_{2v}. In Table (8.1), we have listed the various special points and the lines of symmetry along with their notations and the group of $\mathbf{k}$. Note that the point M has the full point group symmetry

TABLE 8.1 THE SPECIAL POINTS AND THE LINES OF SYMMETRY IN THE BRILLOUIN ZONE OF A PLANE SQUARE LATTICE. WE HAVE $0<k_x, k_y<\frac{1}{2}$ AND $k_x \neq k_y$

k	Symbol	q	K, the group of k	Order of K
(k_x, k_y)	general	8	C_1	1
(k_x, k_x)	Σ	4	C_{1h}	2
$(k_x, \frac{1}{2})$	Z	4	C_{1h}	2
$(k_x, 0)$	Δ	4	C_{1h}	2
$(\frac{1}{2}, 0)$	X	2	C_{2v}	4
$(\frac{1}{2}, \frac{1}{2})$	M	1	C_{4v}	8
$(0, 0)$	Γ	1	C_{4v}	8

because all the corners of the Brillouin zone are connected to each other by reciprocal lattice vectors (see Fig. (8.4f)).

We have previously defined $A_1, A_2, \ldots, A_q$ as selected elements of the point group G which when acting on $\mathbf{k}_1$ give q distinct vectors. These are just the q point group elements which generate the star of the vector $\mathbf{k}_1$. Since K is a subgroup of G, we can decompose G into cosets of K with respect to the elements A_i as follows:

$$G=K\cup A_2K\cup A_3K\cup \ldots \cup A_qK. \tag{8.37}$$

It can be verified that the elements of the coset A_iK take $\mathbf{k}_1$ to $\mathbf{k}_i$.

8.3.3 Irreducible representations of a space group (continued). Let us come back to our discussion of the representations of space groups which we left at Eq. (8.28). We shall not go into the details here, but be satisfied with the important results without proofs. For a rigorous treatment, the reader is once again referred to Koster.[4]

The most important result is that *all the irreducible representations*

[4] Koster (1957). See also Heine (1960).

of a space group can be obtained from those of the group K of the **k** *vector on letting* **k** *run throughout* (*inside and on the surface of*) *the Brillouin zone.* We shall point out the main steps in obtaining the irreducible representations of a space group.

Assuming that we have an n-dimensional irreducible representation of the space group, we have shown in (8.27) that the matrices corresponding to pure translations have a special form in which the first $n/q=d$ diagonal elements are $\exp(i\mathbf{k}_1\cdot\mathbf{t})$, the next d elements are $\exp(iA_2\mathbf{k}_1\cdot\mathbf{t})=\exp(i\mathbf{k}_2\cdot\mathbf{t})$, etc. Considering a general element $\{A\,|\,\tau\}$ of the space group, let us partition the matrices $D(\{A\,|\,\tau\})$ in the following way:

$$D(\{A\,|\,\tau\})=\begin{bmatrix} D_{11}(\{A\,|\,\tau\}) & \cdots & D_{1q}(\{A\,|\,\tau\}) \\ \vdots & & \\ D_{q1}(\{A\,|\,\tau\}) & \cdots & D_{qq}(\{A\,|\,\tau\}) \end{bmatrix} \tag{8.38}$$

Here, each block $D_{lm}(\{A\,|\,\tau\})$ with $1\leq l,\ m\leq q$ is a square matrix of order d. The basis functions for this representation are n Bloch functions, d of which have the wave vector $\mathbf{k}_1$, d have the wave vector $\mathbf{k}_2$, etc. It turns out that in this representation, which is said to be in the *standard form*, each row in (8.38) contains only one nonvanishing block. It will be our object to specify this block.

Suppose we are considering the l-th row of the matrix (8.38). Let us pick up the l-th vector in the star of $\mathbf{k}_1$, which is $\mathbf{k}_l$, and operate on it by A. The effect will be to give some vector of the star of $\mathbf{k}_1$, say,

$$A\mathbf{k}_l=\mathbf{k}_m. \tag{8.39}$$

The only nonvanishing block in the l-th row of (8.38) is then the m-th block, that is,

$$D_{lj}(\{A\,|\,\tau\})=D_{lm}(\{A\,|\,\tau\})\,\delta_{jm},\quad 1\leq j\leq q. \tag{8.40}$$

The nonvanishing block $D_{lm}(\{A\,|\,\tau\})$ can be obtained in terms of the irreducible representations of the group K of $\mathbf{k}_1$. This can be easily done for all **k** vectors *inside* and *on* the Brillouin zone of a crystal whose space group is symmorphic and for **k** vectors *inside* the Brillouin zone of a crystal whose space group is nonsymmorphic. For the remaining case of **k** vectors *on* the Brillouin zone of a crystal whose space group is nonsymmorphic, there exists no general method of obtaining the block D_{lm} for a general element $\{A\,|\,\tau\}$ of the space group. It is still possible to obtain the block D_{lm}, of course, by making use of the special properties of the nonsymmorphic group under consideration. We shall, however, not describe this here.

For *all* **k** vectors in the case of symmorphic groups and for **k** vectors *inside* the Brillouin zone for nonsymmorphic groups, the method for obtaining $D_{lm}(\{A\,|\,\underline{\tau}\})$ is as follows. Having chosen a particular **k** vector, we denote it by $\mathbf{k}_1$ and find the other vectors of the star of $\mathbf{k}_1$, which we denote by $\mathbf{k}_2, \mathbf{k}_3, \ldots, \mathbf{k}_q$. We then select q point group elements A_i which satisfy (8.28). To obtain the (l, m)-th block of the matrix D, consider the elements A_l and A_m. Let $\underline{\delta}_l$ and $\underline{\delta}_m$ be the characteristic translations associated with A_l and A_m respectively. Define the space group element $\{B\,|\,\underline{\sigma}\}$ by

$$\{B\,|\,\underline{\sigma}\}=\{A_m\,|\,\underline{\delta}_m\}^{-1}\,\{A\,|\,\underline{\tau}\}\,\{A_l\,|\,\underline{\delta}_l\}. \tag{8.41}$$

Working out the product on the right-hand side, we obtain

$$B=A_m^{-1}\,AA_l,\quad \underline{\sigma}=A_m^{-1}\,(A\underline{\delta}_l+\underline{\tau}-\underline{\delta}_m). \tag{8.42}$$

It can be verified that B is an element in the group K of the vector $\mathbf{k}_1$. Let us choose a particular d-dimensional irreducible representation, say Γ, of K and define

$$D(B,\,\underline{\sigma})=\exp(i\mathbf{k}_1\cdot\underline{\sigma})\,\Gamma(B). \tag{8.43}$$

The (l, m)-th block of $D(\{A\,|\,\underline{\tau}\})$ is then the above matrix, that is

$$D_{lm}(\{A\,|\,\underline{\tau}\})=D(B,\,\underline{\sigma}). \tag{8.44}$$

The procedure can be repeated for all the space group elements by letting $\{A\,|\,\underline{\tau}\}$ run over the space group S. The representation obtained is clearly of dimension qd. Each irreducible representation of K for every value of **k** gives us an irreducible representation of S. However, not all of these are distinct representations. To obtain all the distinct irreducible representations of S, we must let **k** run through a suitably selected $1/g$-th part of the Brillouin zone (g=order of the point group G) so as to include only one vector from a given star of **k**.

To summarize the results obtained in this chapter so far, we first found that the energy eigenstates of the Hamiltonian with a periodic potential are Bloch functions. The dispersion relation $E=E(\mathbf{k})$ is a multivalued function in the first Brillouin zone and the constant energy surfaces represented by $E(\mathbf{k})=constant$ have the full point group symmetry of the lattice. Owing to the Bloch form of the eigenfunctions, we need to solve the Schroedinger equation only in one unit cell rather than throughout the crystal. The Bloch functions can be used to generate the irreducible representations of the space group S. Finally, the degeneracies for any value of **k** can be simply inferred from the irreducible representations of the group of **k** and the number of vectors in the star of **k**.

8.4 Free Electron Energy Bands: One- and Two-Dimensional Lattices

We have mentioned in Section 8.1 that under the free electron approximation, the energy is a quadratic function of the magnitude of the wave vector in the extended zone scheme. It is more convenient to show and to study the energy bands in the reduced zone scheme. In this section, we shall consider the examples of a one-dimensional lattice and a square lattice.

8.4.1 One-dimensional lattice. In the extended zone scheme, the energy versus the wave vector relation will be just a parabola $E=\hbar^2k^2/2m$ as shown in Fig. (8.5). For representing the energy in the reduced zone scheme, we note that the first Brillouin zone of the lattice is the region $-\pi/a \leq k < \pi/a$ of the reciprocal space and that the reciprocal lattice vectors are $G=2\pi m/a$, where a is the direct lattice constant and m is any integer. To draw the energy bands in this scheme, we imagine a parabola such as that shown in Fig. (8.5)

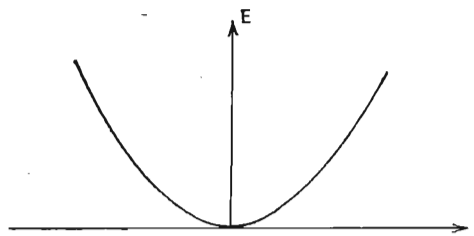

FIGURE 8.5 The energy versus wave vector relation for a one-dimensional lattice in the extended zone scheme under the free electron approximation

drawn with its vertex at each of the reciprocal lattice points and consider only that part of each parabola which is in the first Brillouin zone. This is shown in Fig. (8.6). The various parts of the parabola in this figure (i.e., the various *bands*) are clearly represented by the equations

$$E=(\hbar^2/2m)\,(k-G)^2, \tag{8.45}$$

where G takes the successive values 0, $\pm 2\pi/a$, $\pm 4\pi/a$, etc.

8.4.2 Square lattice. The energy versus wave vector relation for a two-dimensional lattice may be represented by a surface in three dimensions with two dimensions standing for k_x and k_y and the third for the energy E. For *any* two-dimensional lattice, this surface in the

extended zone scheme and under the free electron approximation would be a paraboloid of revolution obtained by revolving the parabola of Fig. (8.5) about the E axis. In the reduced zone scheme, the same surface

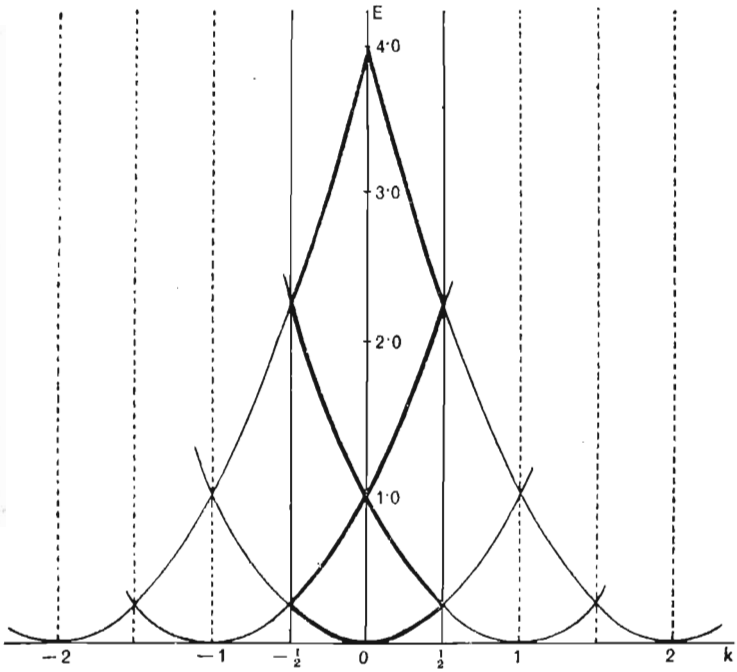

FIGURE 8.6 The free electron energy bands for a one-dimensional lattice in the reduced zone scheme; k in units of $2\pi/a$ and E in units of $2\hbar^2\pi^2/ma^2$, which is the free electron energy at $k=2\pi/a$

would assume a rather complicated form depending on the lattice. We can, nevertheless, show the cross-sections of this surface along various lines of symmetry in the first Brillouin zone. This will be illustrated here for a square lattice with the point symmetry group C_{4v}.

The reciprocal lattice of the square lattice is again a square lattice. The reciprocal lattice vectors are

$$\mathbf{G}=m\,\hat{k}_x+n\hat{k}_y, \tag{8.46}$$

where $\hat{k}_x$ and $\hat{k}_y$ are orthonormal vectors in the reciprocal space, and m and n are any integers. Imagine a set of paraboloids, such as mentioned above, with their vertices at each of the reciprocal lattice points. The part of the surface of each paraboloid contained in the first Brillouin zone ($-\frac{1}{2}\leq k_x, k_y<\frac{1}{2}$) will constitute a branch of the function $E=E(\mathbf{k})$

in the reduced zone scheme. It is however, not possible to show this surface in a diagram with any ease. The problem would be still more complex for three-dimensional lattices because $E=E(\mathbf{k})$ will then be a surface in the four-dimensional space (k_x, k_y, k_z, E).

We may considerably simplify the matter by considering the various cross-sections of the multivalued function $E=E(\mathbf{k})$ along different lines of symmetry in the Brillouin zone. For example, we may start from the point Γ at the centre of the Brillouin zone and go along the line Δ to the point X. Along the line ΓX, we would have $k_y=0, 0\leq k_x\leq \frac{1}{2}$. We may next go from X to M along the line Z where $k_x=\frac{1}{2}$ and $0\leq k_y \leq \frac{1}{2}$. Finally, we may show the variation of energy with respect to the magnitude of $\mathbf{k}$ from M to Γ along the line Σ where $k_x=k_y=k/\sqrt{2}$. The free electron bands along these lines of symmetry are shown in Fig. (8.7) for a square lattice. The method of obtaining the bands

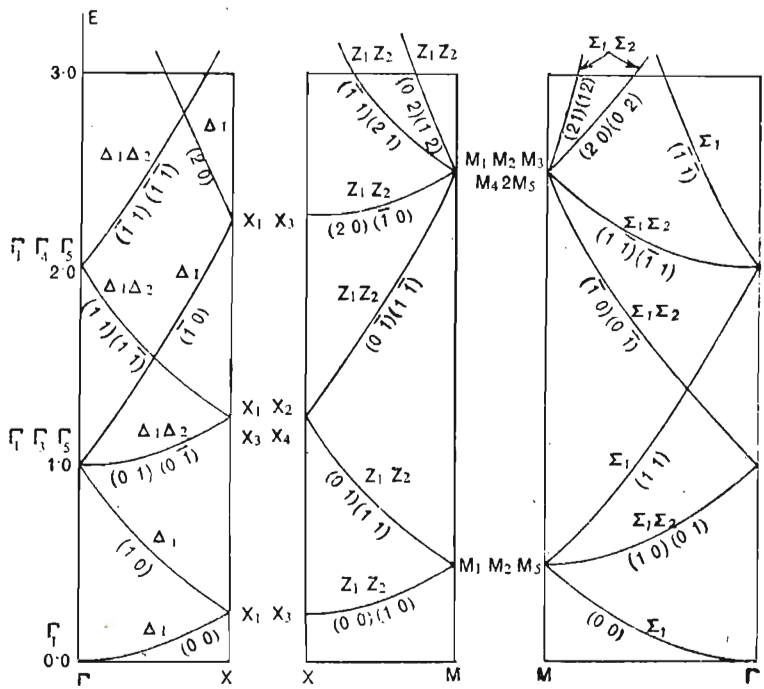

FIGURE 8.7 The free electron energy bands of a square lattice along the lines of symmetry and their labeling by the irreducible representations of the group of the wave vector. The plane waves corresponding to the bands are indicated below each band (see Section 8.4.3).

and the labeling of the various bands by the irreducible representations of the group of the wave vector will be explained in the following subsection.

8.4.3 Method of obtaining free electron bands and their labeling. It is clear that the equation of a free electron paraboloid with its vertex at the reciprocal lattice point $\mathbf{G}(m, n)$ is

$$E=\hbar^2[(G_x-k_x)^2+(G_y-k_y)^2]/2m, \tag{8.47}$$

where G_x and G_y are the cartesian components of $\mathbf{G}$. Converting E and k to the reduced units (k in units of $2\pi/a$ and E in units of $2\hbar^2\pi^2/ma^2$), the above equation becomes

$$E=(m-k_x)^2+(n-k_y)^2, -\tfrac{1}{2}\leq k_x, k_y\leq \tfrac{1}{2}. \tag{8.48}$$

The corresponding plane wave solution of the Schroedinger equation is

$$(m\ n)\equiv\phi_k(m, n)=\exp[i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}]$$
$$=\exp[i\{(k_x-m)x+(k_y-n)y\}]. \tag{8.49}$$

We shall now consider below the three lines of symmetry Δ, Z and Σ.

Δ. Along the line ΓX, we have $k_y = 0$ and may restrict k_x to the open interval $(0, \frac{1}{2})$ since the other part $(-\frac{1}{2}, 0)$ of the interval gives symmetrical bands. The cross-section of the paraboloid (8.48) along the line Δ is then

$$E(\Delta)=(m-k_x)^2+n^2,\ 0<k_x<\tfrac{1}{2}. \tag{8.50}$$

The corresponding plane wave is

$$(m\ n)_\Delta=\exp[i\{(k_x-m)x-ny\}]. \tag{8.51}$$

Each set of values of the integers m and n gives us a band. It is also evident from (8.50) that smaller absolute values of m and n will correspond to lower bands. We start considering the successive reciprocal lattice vectors in increasing order of magnitude.

The shortest reciprocal lattice vector is (0 0), which from (8.50), gives the band

$$E_{0,0}(\Delta)=k_x^2,\ 0<k_x<\tfrac{1}{2}. \tag{8.52}$$

The corresponding plane wave is $(0\ 0)_\Delta=\exp(ik_xx)$. This is the lowest band along the line ΓX shown in Fig. (8.7).

The group of the $\mathbf{k}$ vector along the line Δ, excluding the end-points Γ and X, is the subgroup (E, m_x) of C_{4v}. The two irreducible representations of this group will be denoted by Δ_1 and Δ_2 for points on the line Δ. It is then clear that the plane wave $(0\,0)_\Delta$ transforms according to Δ_1 under the group (E, m_x).

The next set of reciprocal lattice vectors is (1 0), $(\bar{1}\ 0)$, (0 1) and (0 $\bar{1}$). Substituting these values of m and n one by one in (8.50), we get

three bands, two of which are nondegenerate and are generated by the plane waves $(1\ 0)_\Delta$ and $(\bar{1}\ 0)_\Delta$ respectively, and the third is a doubly degenerate band generated by the plane wave $(0\ 1)_\Delta$ and $(0\ \bar{1})_\Delta$. Each of the plane waves $(1\ 0)_\Delta$ and $(\bar{1}\ 0)_\Delta$ transforms according to Δ_1. The two plane waves $(0\ 1)_\Delta$ and $(0\ \bar{1})_\Delta$, on the other hand, have the explicit forms

$$\begin{aligned}(0\ 1)_\Delta &= \exp[\,i(k_x x - y)],\\ (0\ \bar{1})_\Delta &= \exp[\,i(k_x x + y)].\end{aligned} \tag{8.53}$$

It is clear that they go into each other under m_x, which has the effect of changing y to $-y$. They therefore generate the representation $\Delta_1 \oplus \Delta_2$ of (E, m_x). It is easy to see that the two linear combinations

$$(0\ 1)_\Delta \pm (0\ \bar{1})_\Delta \propto \exp(ik_x x) \times \begin{cases}\cos y\\ \sin y\end{cases} \tag{8.54}$$

transform respectively according to Δ_1 and Δ_2.

The next sets of reciprocal lattice vectors are $\{(1\ 1), (1\ \bar{1}), (\bar{1}\ 1), (\bar{1}\ \bar{1})\}$, $\{(2\ 0), (\bar{2}\ 0), (0\ 2), (0\ \bar{2})\}$, etc. The bands corresponding to all of these plane waves can be obtained by following the same procedure and as many bands as we please may be obtained. Fig. (8.7) shows all the bands upto $E=3$.

Z. The group of the **k** vector for a general point on the line XM (excluding both X and M) is (E, m_y). Its irreducible representations will be denoted by Z_1 and Z_2. The **k** vector is of the form $(\frac{1}{2}, k_y)$ with $0 < k_y < \frac{1}{2}$. The energy and the plane waves are therefore given by

$$\begin{aligned}E(Z) &= (m-\tfrac{1}{2})^2 + (n-k_y)^2,\ 0 < k_y < \tfrac{1}{2};\\ (m\ n)_z &= \exp\, i[(\tfrac{1}{2}-m)\,x + (k_y - n)\,y].\end{aligned} \tag{8.55}$$

Considering successive plane waves, once again, we can obtain the various bands along Z. It is found that each band along XM is doubly degenerate because the two sets $(-m, n)$ and $(m+1, n)$ for $m = 0, 1, 2, 3, \ldots$ give the same energy. The two plane waves corresponding to each band transform according to the representation $Z_1 \oplus Z_2$.

Σ. The group of the **k** vector for a general point along ΓM (excluding both Γ and M) is (E, σ_v). Its irreducible representations will be denoted by Σ_1 and Σ_2. The **k** vector has the from (k_x, k_x). The energy and the plane waves are given by

$$\begin{aligned}E(\Sigma) &= (m-k_x)^2 + (n-k_x)^2,\ 0 < k_x < \tfrac{1}{2};\\ (m\ n)_\Sigma &= \exp\,[\,i\{(k_x - m)x + (k_x - n)y\}].\end{aligned} \tag{8.56}$$

The energy bands and the symmetries of the plane waves are easily obtained by the method outlined above for Δ.

The labeling of the plane wave states at the special points

Γ, X and M is obtained as follows.

Γ. The group of the $\mathbf{k}$ vector at Γ is the full point group C_{4v}. Its irreducible representations (for the square lattice) will be denoted by Γ_i, $1 \leq i \leq 5$ (see table for C_{4v} in Table 7.7).

The plane wave corresponding to the lowest energy is $(0\ 0)_\Gamma$ which has $E=0$. This plane wave at $\mathbf{k}=0$ is, in fact, a constant which belongs to the representation Γ_1.

The next four plane waves $(1\ 0)_\Gamma$, $(\bar{1}\ 0)_\Gamma$, $(0\ 1)_\Gamma$ and $(0\ \bar{1})_\Gamma$ are degenerate at Γ with energy $E=1$. The explicit forms of these plane waves at $\mathbf{k}=0$ are

$$(1\ 0)_\Gamma = \exp(-ix),\ (\bar{1}\ 0)_\Gamma = \exp(ix),$$
$$(0\ 1)_\Gamma = \exp(-iy),\ (0\ \bar{1})_\Gamma = \exp(iy). \tag{8.57}$$

By working out the characters, it can be shown that they generate the representation $\Gamma_1 \oplus \Gamma_3 \oplus \Gamma_5$ of C_{4v}. The next four plane waves $(1\ 1)_\Gamma$, $(1\ \bar{1})_\Gamma$, $(\bar{1}\ 1)_\Gamma$ and $(\bar{1}\ \bar{1})_\Gamma$, are degenerate at Γ with energy $E=2$, and transform according to the representation $\Gamma_1 \oplus \Gamma_4 \oplus \Gamma_5$ under C_{4v}.

X. The group of the $\mathbf{k}$ vector at X is the subgroup (E, m_x, m_y, C_4^2) of C_{4v} and its irreducible representations (for the square lattice) will be denoted by X_i, $1 \leq i \leq 4$ (see table for C_{2v} in Table 7.7). We get the following sets of degenerate plane waves at the point X: (i) the set $\{(0\ 0)_X, (1\ 0)_X\}$ corresponding to the representation $X_1 \oplus X_3$ with $E=0.25$; (ii) the set $\{(0\ 1)_X, (0\ \bar{1})_X, (1\ \bar{1})_X, (1\ 1)_X\}$ transforming according to $X_1 \oplus X_2 \oplus X_3 \oplus X_4$ with $E=1.25$; (iii) the set $\{(\bar{1}\ 0)_X, (2\ 0)_X\}$ again belonging to $X_1 \oplus X_3$ and with $E=2.25$, etc.

M. The group of the $\mathbf{k}$ vector at M is the full group C_{4v}. Its irreducible representations are denoted by M_i $(1 \leq i \leq 5)$, which are respectively equivalent to Γ_i. The following sets of degenerate plane waves can be obtained: (i) the set $\{(0\ 0)_M, (1\ 0)_M, (0\ 1)_M, (1\ 1)_M\}$ with $E=0.5$ and belonging to the representation $M_1 \oplus M_2 \oplus M_5$, (ii) the set $\{(0\ \bar{1})_M, (1\ \bar{1})_M, (2\ 0)_M, (\bar{1}\ 0)_M, (\bar{1}\ 1)_M, (2\ 1)_M, (0\ 2)_M, (1\ 2)_M\}$ with $E=2.5$ and belonging to the regular representation of C_{4v}, etc.

8.4.4 Compatibility relations. We see from Fig. (8.7) that, in general, there is more degeneracy at the special points than on the lines of symmetry. Further, if we move away from the lines of symmetry to a general point in the Brillouin zone, where the group of the $\mathbf{k}$ vector consists only of the identity element, the degeneracy of all the bands will be completely lifted.

Consider a point of high symmetry such as Γ where the group of the wave vector is C_{4v}. As we move away from Γ along a line of symmetry, say Δ, the group of symmetry reduces to C_{1h}. Consider an irreducible representation Γ_i at the point Γ. As the symmetry is reduced from C_{4v} to C_{1h}, the representation Γ_i may, in general, split into a (direct) sum of the irreducible representations Δ_1 and Δ_2. The reduction can be obtained by the method described in Chapter 3 simply by inspecting the character tables of C_{4v} and C_{1h} and is independent of the basis functions generating the particular representation Γ_i. It depends, however, on which elements of the larger group (C_{4v} here) are contained in the smaller group (C_{1h} here).

For example, we get the following relations between the representations at Γ and those at Δ :

$$\Gamma_1 \to \Delta_1,\ \Gamma_2 \to \Delta_2,\ \Gamma_3 \to \Delta_1,\ \Gamma_4 \to \Delta_2,\ \Gamma_5 \to \Delta_1 \oplus \Delta_2. \qquad (8.58)$$

We then say that the representation Δ_1 is *compatible with* Γ_1 and Γ_3. Δ_2 is compatible with Γ_2 and Γ_4 and Δ_1 and Δ_2 are both compatible with Γ_5. Similar relations can be established between Γ_i and Σ_1 and Σ_2, and also at the special points X and M. It is convenient to express the *compatibility relations* between the irreducible representations at the special points and those along the various lines of symmetry meeting at that point in a tabular form for a given point group. These provide a simple check on the correctness of the labeling of the bands in a diagram of the electronic structure of a crystal. The compatibility relations for a square lattice with the point group C_{4v} are given in Table (8.2).

TABLE 8.2 THE COMPATIBILITY RELATIONS FOR A SQUARE LATTICE

Γ_1	Γ_2	Γ_3	Γ_4	Γ_5
Δ_1	Δ_2	Δ_1	Δ_2	$\Delta_1\Delta_2$
Σ_1	Σ_2	Σ_2	Σ_1	$\Sigma_1\Sigma_2$

M_1	M_2	M_3	M_4	M_5
Z_1	Z_2	Z_1	Z_2	Z_1Z_2
Σ_1	Σ_2	Σ_2	Σ_1	$\Sigma_1\Sigma_2$

X_1	X_2	X_3	X_4
Δ_1	Δ_2	Δ_1	Δ_2
Z_1	Z_2	Z_2	Z_1

8.5 Free Electron Energy Bands. Three-Dimensional Lattices

In continuation of our study of the previous section, we shall discuss in this section the free electron energy bands of the three types of cubic lattices. The method of obtaining the free electron bands and their labeling has already been described for a square lattice. Since the same procedure applies to three-dimensional lattices, it will not be mentioned here in much detail.

8.5.1 Simple cubic lattice. The reciprocal lattice of a simple cubic lattice is also simple cubic and the reciprocal lattice vectors are given by

$$\mathbf{G}(m\ n\ p)=m\hat{k}_x+n\hat{k}_y+p\hat{k}_z.$$

where $\hat{k}_x$, $\hat{k}_y$ and $\hat{k}_z$ are orthonormal vectors in the reciprocal space, and m, n and p can take all integral values. The first Brillouin zone is a cube with edge length unity. The special points and the lines of symmetry in the Brillouin zone are shown in Fig. (8.8). Table (8.3) lists the special points, the lines and the planes of symmetry, their stars of $\mathbf{k}$ vectors and the groups of $\mathbf{k}$ vectors. The tetrahedron ΓXMR is the suitable 1/48th part of the Brillouin zone since the operation of the 48 elements of the point group O_h on this tetrahedron fills the Brillouin zone completely without any gaps or overlap.

For obtaining the free electron bands in the reduced zone scheme, we note that the equation of a free electron hyper-paraboloid with its vertex at the reciprocal lattice point $\mathbf{G}(m\ n\ p)$ will be

$$E=[\mathbf{G}(m\ n\ p)-\mathbf{k}]^2=(m-k_x)^2+(n-k_y)^2+(p-k_z)^2. \qquad (8.59)$$

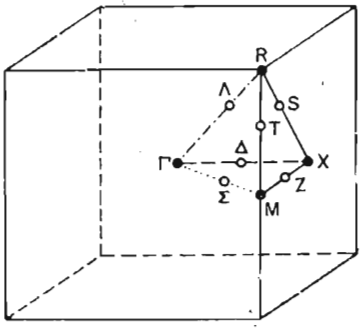

FIGURE 8.8 The special points and the lines of symmetry in the Brillouin zone of a simple cubic lattice

Fig. (8.9) shows the free electron bands for a simple cubic lattice along the lines ΓX and ΓR. Table (8.4) lists the compatibility relations

between the special points Γ, X, M and R and the lines of symmetry emanating from them.

8.5.2 Body-centred cubic lattice. The reciprocal lattice of a body-centred cubic (bcc) lattice is a face-centred cubic (fcc) lattice and the reciprocal lattice vectors are

$$\mathbf{G}(m\ n\ p)=m\mathbf{b}_1+n\mathbf{b}_2+p\mathbf{b}_3, \tag{8.60}$$

with

$$\mathbf{b}_1=\hat{k}_y+\hat{k}_z,\ \mathbf{b}_2=\hat{k}_z+\hat{k}_x,\ \mathbf{b}_3=\hat{k}_x+\hat{k}_y. \tag{8.61}$$

The shortest nonzero reciprocal lattice vectors are the twelve vectors $\pm\hat{k}_x\pm\hat{k}_y$, $\pm\hat{k}_y\pm\hat{k}_z$ and $\pm\hat{k}_z\pm\hat{k}_x$. The first Brillouin zone is the volume enclosed by the twelve perpendicular bisectors of these vectors and is a regular rhombic dodecahedron (12 faces). Fig. (8.10) shows the first Brillouin zone along with the special points and the lines of symmetry

TABLE 8.3 THE STARS AND THE GROUPS OF THE WAVE VECTORS FOR THE SPECIAL POINTS, LINES AND PLANES OF SYMMETRY FOR A SIMPLE CUBIC LATTICE. WE HAVE $0<k_x, k_y, k_z<\frac{1}{2}$ AND $k_x\neq k_y\neq k_z\neq k_x$

k	Symbol	No. of vectors in star of k	K, the group of k	Order of K
(k_x, k_y, k_z)	none	48	C_1	1
(k_x, k_x, k_z)	none	24	C_{1h}	2
$(k_x, k_y, 0)$	none	24	C_{1h}	2
$(k_x, k_y, \frac{1}{2})$	none	24	C_{1h}	2
$(k_x, k_x, 0)$	Σ	12	C_{2v}	4
$(k_x, \frac{1}{2}, 0)$	Z	12	C_{2v}	4
$(k_x, k_x, \frac{1}{2})$	S	12	C_{2v}	4
(k_x, k_x, k_x)	Λ	8	C_{3v}	6
$(k_x, \frac{1}{2}, \frac{1}{2})$	T	6	C_{4v}	8
$(k_x, 0, 0)$	Δ	6	C_{4v}	8
$(\frac{1}{2}, \frac{1}{2}, 0)$	M	3	D_{4h}	16
$(\frac{1}{2}, 0, 0)$	X	3	D_{4h}	16
$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	R	1	O_h	48
$(0, 0, 0)$	Γ	1	O_h	48

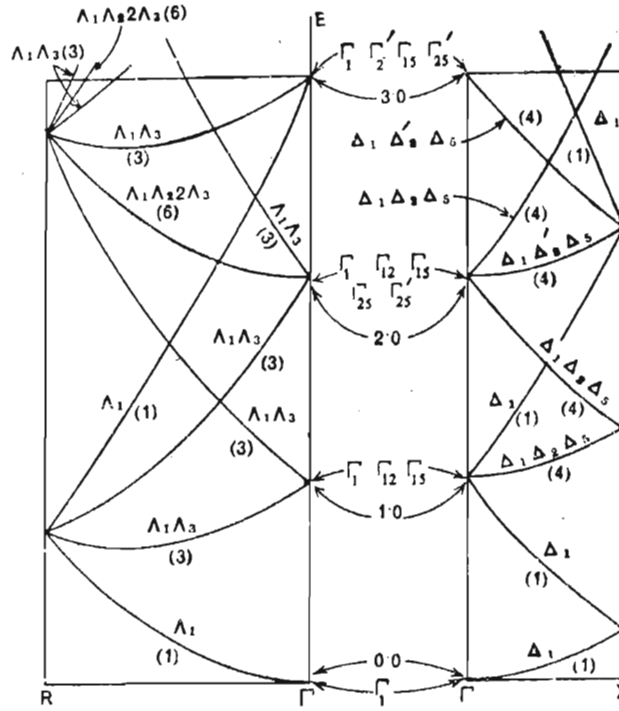

FIGURE 8.9 The free electron energy bands for a simple cubic lattice along ΓX and ΓR upto $E=3$. The labeling of the bands at Γ and along Δ and Λ is also shown. The degeneracy of each band is the number in the parantheses

TABLE 8.4 THE COMPATIBILITY RELATIONS FOR A SIMPLE CUBIC LATTICE

Γ_1	Γ_2	Γ_{12}	Γ_{15}'	Γ_{25}'	Γ_1'	Γ_2'	Γ_{12}'	Γ_{15}	Γ_{25}
Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$	Δ_1'	Δ_2'	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_2\Delta_5$
Λ_1	Λ_2	Λ_3	$\Lambda_2\Lambda_3$	$\Lambda_1\Lambda_3$	Λ_2	Λ_1	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$
Σ_1	Σ_4	$\Sigma_1\Sigma_4$	$\Sigma_2\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_3$	Σ_2	Σ_3	$\Sigma_2\Sigma_3$	$\Sigma_1\Sigma_3\Sigma_4$	$\Sigma_1\Sigma_2\Sigma_4$

X_1	X_2	X_3	X_4	X_5	X_1'	X_2'	X_3	X_4'	X_5'
Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_5	Δ_1'	Δ_2'	Δ_2	Δ_1	Δ_5
Z_1	Z_1	Z_4	Z_4	Z_2Z_3	Z_2	Z_2	Z_3	Z_3	Z_1Z_4
S_1	S_4	S_1	S_4	S_2S_3	S_2	S_2	S_2	S_3	S_1S_4

TABLE 8.4 (continued)

M_1	M_2	M_3	M_4	M_5	M_1'	M_2'	M_3'	M_4'	M_5'
Σ_1	Σ_4	Σ_1	Σ_4	$\Sigma_2\Sigma_3$	Σ_2	Σ_3	Σ_2	Σ_3	$\Sigma_1\Sigma_4$
Z_1	Z_1	Z_3	Z_3	Z_2Z_4	Z_2	Z_2	Z_4	Z_4	Z_1Z_3
T_1	T_2	T_2'	T_1'	T_5	T_1'	T_2'	T_2	T_1	T_5

R_1	R_2	R_{12}	R_{15}'	R_{25}'	R_1'	R_2'	R_{12}'	R_{15}	R_{25}
Λ_1	Λ_2	Λ_3	$\Lambda_2\Lambda_3$	$\Lambda_1\Lambda_3$	Λ_2	Λ_1	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$
S_1	S_4	S_1S_4	$S_2S_3S_4$	$S_1S_2S_3$	S_2	S_3	S_2S_3	$S_1S_3S_4$	$S_1S_2S_4$
T_1	T_2	T_1T_2	$T_1'T_5$	$T_2'T_5$	T_1'	T_2'	$T_1'T_2'$	T_1T_5	T_2T_5

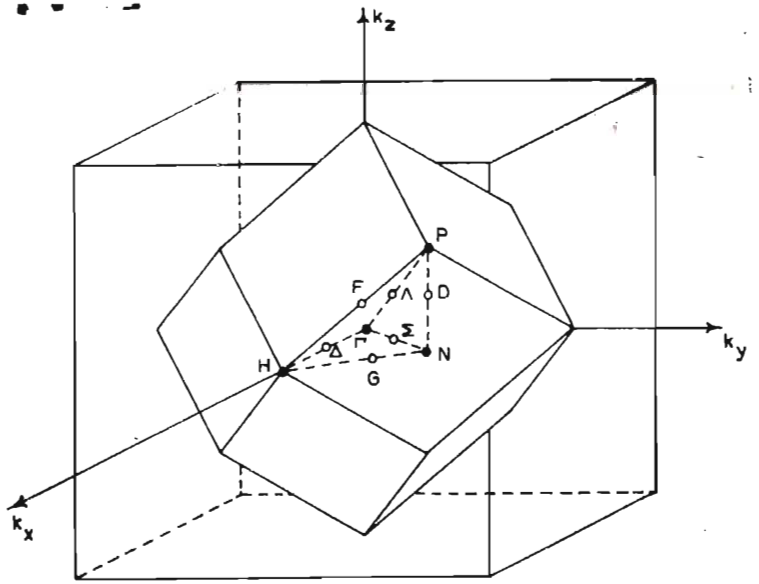

FIGURE 8.10 The special points and the lines of symmetry in the Brillouin zone of a bcc lattice. The reciprocal lattice points are at the centre of the cube and at the mid-points of the edges of the cube shown. The length of the cube edge is 2.

for a bcc lattice. The electronic structure needs to be calculated only in the tetrahedron ΓHNP which is a 1/48th part of the Brillouin zone. Fig. (8.11) shows the free electron band structure of a crystal having bcc structure with one atom per lattice point along the lines ΓH and ΓP. The compatibility relations for the bcc lattice are listed in Table (8.5).

8.5.3 Face-centred cubic lattice. The reciprocal lattice of an fcc lattice is a bcc lattice and the fundamental translation vectors of the reciprocal lattice are

$$\mathbf{b}_1=\hat{k}_x+\hat{k}_y-\hat{k}_z,\ \mathbf{b}_2=\hat{k}_x-\hat{k}_y+\hat{k}_z,\ \mathbf{b}_3=-\hat{k}_x+\hat{k}_y+\hat{k}_z. \quad (8.62)$$

There are eight shortest nonzero reciprocal lattice vectors which are

$$\pm\hat{k}_x\pm\hat{k}_y\pm\hat{k}_z. \quad (8.63)$$

If we construct the perpendicular bisectors of these eight vectors, we

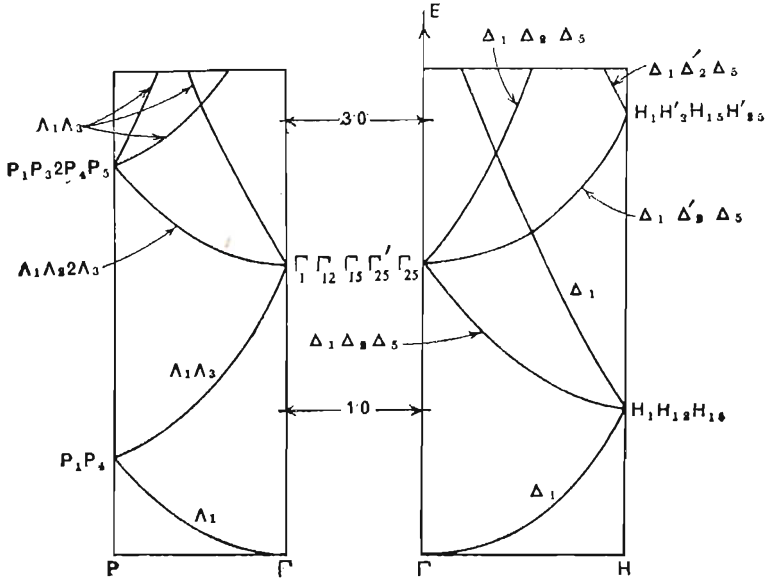

FIGURE 8.11 The free electron energy bands for a bcc lattice along ΓH and ΓP up to just above $E=3$

obtain an octahedron. However, this octahedron is not the Brillouin zone of the fcc lattice because the regions near its corners are closer to other reciprocal lattice points than to the central one. The six corners of the octahedron therefore need to be truncated by perpendicular bisectors of the vectors to the six second-neighbour reciprocal lattice points which are

$$\pm 2\hat{k}_x,\ \pm 2\hat{k}_y,\ \pm 2\hat{k}_z. \quad (8.64)$$

The Brillouin zone of an fcc lattice is thus a truncated octahedron with 14 faces which is shown in Fig. (8.12) along with the symmetry points and lines. The pentahedron $\Gamma XULKW$ (5 faces, 6 vertices) is the suitable 1/48th part of the Brillouin zone in which the electronic structure need be calculated.

TABLE 8.5 THE COMPATIBILITY RELATIONS FOR A BODY CENTRED CUBIC LATTICE. THE FIRST COLUMN DENOTES THE GROUP OF THE WAVE VECTOR

Γ : same as in Table (8.4).

O_h	H_1	H_2	H_{12}	H_{15}'	H_{25}'	H_1'	H_2'	H_{12}'	H_{15}	H_{25}
C_{4v}	Δ_1	Δ_2	$\Delta_1\Delta_2$	$\Delta_1'\Delta_5$	$\Delta_2'\Delta_5$	Δ_1'	Δ_2'	$\Delta_1'\Delta_2'$	$\Delta_1\Delta_5$	$\Delta_2\Delta_5$
C_{3v}	F_1	F_2	F_3	F_2F_3	F_1F_3	F_2	F_1	F_3	F_1F_3	F_2F_3
C_{2v}	G_1	G_4	G_1G_4	$G_2G_3G_4$	$G_1G_2G_3$	G_2	G_3	G_2G_3	$G_1G_3G_4$	$G_1G_2G_4$

T_d	P_1	P_2	P_3	P_4	P_5
C_{3v}	Λ_1	Λ_2	Λ_3	$\Lambda_1\Lambda_3$	$\Lambda_2\Lambda_3$
C_{3v}	F_1	F_2	F_3	F_1F_3	F_2F_3
C_{2v}	D_1	D_2	D_1D_2	$D_1D_3D_4$	$D_2D_3D_4$

D_{2h}	N_1	N_2	N_3	N_4	N_1'	N_2'	N_3'	N_4'
C_{2v}	Σ_1	Σ_2	Σ_3	Σ_4	Σ_1	Σ_2	Σ_3	Σ_4
C_{2v}	D_1	D_3	D_4	D_2	D_4	D_2	D_1	D_3
C_{2v}	G_1	G_3	G_2	G_4	G_4	G_2	G_3	G_1

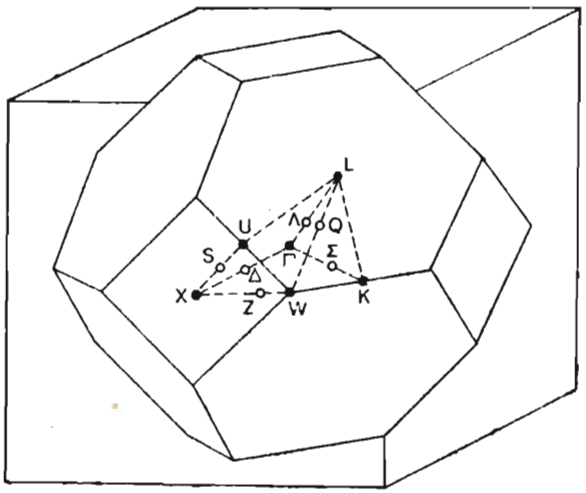

FIGURE 8.12 The special points and the lines of symmetry in the Brillouin zone of an fcc lattice. The reciprocal lattice points are at the centre and the corners of the cube shown. The length of the cube edge is 2.

TABLE 8.6 THE COMPATIBILITY RELATIONS FOR AN FCC LATTICE. THE FIRST COLUMN DENOTES THE GROUP OF THE WAVE VECTOR

Γ : same as in Table (8.4).

D_{4h}	X_1	X_2	X_3	X_4	X_5	X_1'	X_2'	X_3'	X_4'	X_5'
C_{4v}	Δ_1	Δ_2	Δ_2'	Δ_1'	Δ_5	Δ_1'	Δ_2'	Δ_2	Δ_1	Δ_5
C_{2v}	Z_1	Z_1	Z_4	Z_4	Z_2Z_3	Z_2	Z_2	Z_3	Z_3	Z_1Z_4
C_{2h}	S_1	S_4	S_1	S_4	S_2S_3	S_2	S_3	S_2	S_3	S_1S_4

D_{3h}	L_1	L_2	L_3	L_1'	L_2'	L_3'
C_{3v}	Λ_1	Λ_2	Λ_3	Λ_2	Λ_1	Λ_3
C_{1h}	Q_1	Q_2	Q_1Q_2	Q_1	Q_2	Q_1Q_2

C_{4v}	W_1	W_2	W_1'	W_2'	W_3
C_{2v}	Z_1	Z_2	Z_2	Z_1	Z_3Z_4
C_{1h}	Q_1	Q_2	Q_1	Q_2	Q_1Q_2

Fig. (8.13) shows the free electron band structure of a crystal having fcc structure with one atom per lattice point along the lines ΓX and ΓL. The compatibility relations for the fcc lattice are listed in Table (8.6).

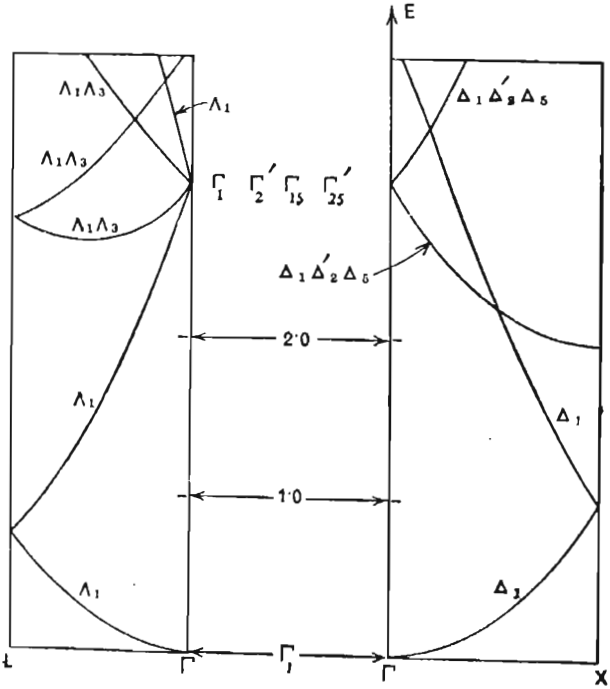

FIGURE 8.13 The free electron energy bands of an fcc lattice along ΓX and ΓL upto just above $E=3$

8.6 Energy Bands of Real Crystals

In the previous two sections, we have been discussing the free electron energy bands of crystals. In this approximation, we completely disregard the complicated crystal potential arising from the ions and the electrons and assume that a single electron is moving in a constant potential inside the lattice. Although very far from truth, this model has helped us to gain a considerable insight into the nature of the electronic bands. It turns out that the energy bands of many metals, particularly the one-electron metals (alkalies), are not significantly different from the free electron bands. There are a few changes as we go from the free electron model to a real crystal with its periodic potential of which we note the following: (a) splitting of the high degeneracy characteristic of the free electron model, and (b) hybridization of bands having the same symmetry. We shall discuss these effects in this section at proper places. We shall discuss only one and perhaps the simplest method for determining the energy bands of real crystals—the plane wave expansion method.

8.6.1 Plane wave expansion method. We have seen that in the free electron approximation, the electronic wave functions are just the plane waves $\exp[i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}]$. As $\mathbf{k}$ runs over the first Brillouin zone and $\mathbf{G}$ runs over the set of all reciprocal lattice vectors, the plane waves constitute a complete set for the expansion of the one-electron wave functions in real crystals. Considering the complete Schroedinger equation (8.1) with the potential $V(\mathbf{r})$, we can express the eigenfunction $\phi(\mathbf{r})$ as a linear combination of the plane waves. Moreover, the potential $V(\mathbf{r})$, being periodic, can be represented by its Fourier series with summation on the reciprocal lattice vectors. It is further known that a periodic potential mixes only plane waves whose wave vectors differ by reciprocal lattice vectors. We therefore have

$$\phi(\mathbf{r}) = \sum_{\mathbf{G}} c(\mathbf{k}-\mathbf{G}) \exp[i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}], \tag{8.65a}$$

$$V(\mathbf{r}) = \sum_{\mathbf{G}} V_G \exp(i\mathbf{G}\cdot\mathbf{r}). \tag{8.65b}$$

Substituting these in (8.1) and rearranging terms, we have

$$\sum_{\mathbf{G}}[(\lambda_{\mathbf{k}-\mathbf{G}}-E)\, c(\mathbf{k}-\mathbf{G}) + \sum_{\mathbf{G}'} V_{\mathbf{G}'}\, c(\mathbf{k}-\mathbf{G}-\mathbf{G}')] \exp[i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r}] = 0, \tag{8.66}$$

where $\lambda_{\mathbf{k}-\mathbf{G}} = \hbar^2(\mathbf{k}-\mathbf{G})^2/2m$ is the free electron energy. Since all the plane waves constitute a set of independent functions for different $\mathbf{G}$'s, the coefficient of each term in the above equation must be separately

zero. This gives

$$(\lambda_{\mathbf{k}-\mathbf{G}}-E)\,c(\mathbf{k}-\mathbf{G})+\sum_{\mathbf{G}'} V_{\mathbf{G}'}\,c(\mathbf{k}-\mathbf{G}-\mathbf{G}')=0, \tag{8.67}$$

for all $\mathbf{G}$'s. The unknown coefficients $c(\mathbf{k}-\mathbf{G})$ for a particular value of $\mathbf{k}$ and different values of $\mathbf{G}$ as well as the unknown energy eigenvalue of $E=E(\mathbf{k})$ can be determined from (8.67). We can obviously write down one equation such as (8.67) for every value of $\mathbf{G}$. This gives us a set of linear homogeneous equations in the unknown coefficients $c(\mathbf{k}-\mathbf{G})$. The condition for the existence of a nontrivial solution for these coefficients is that the determinant of the elements multiplying $c(\mathbf{k}-\mathbf{G}-\mathbf{G}')$ in (8.67) be zero. This is expressed in a shorthand notation as

$$\det\left|(\lambda_{\mathbf{k}-\mathbf{G}}-E)\delta_{\mathbf{G}\mathbf{G}'}+V_{\mathbf{G}'-\mathbf{G}}\right|=0. \tag{8.68}$$

Eq. (8.67) or (8.68) is known as the *secular equation* of the problem.

As an illustration, consider a monatomic one-dimensional crystal and suppose that only three Fourier coefficients for $G=0$ and $\pm G_1$ in (8.65b), where G_1 is the shortest nonzero reciprocal lattice vector, have appreciable magnitude while the rest can be neglected. Since the potential is real, we have $V_{-G_1}=V_{G_1}^*$. V_0 is an additive constant potential and may be dropped from consideration (in other words, we take $V_0\equiv 0$). In the wave function (8.65a), we similarly assume that only the three coefficients $c(k)$, $c(k-G_1)$ and $c(k+G_1)$ predominate and the rest can be neglected. We now write (8.67) for the three values $G=0$ and $\pm G_1$, and obtain three linear homogeneous equations for the three unknown coefficients. The condition for them to have nontrivial solutions is that

$$\begin{vmatrix} (\lambda_{k-G_1}-E) & V_1^* & 0 \\ V_1^* & (\lambda_k-E) & V_1 \\ 0 & V_1 & (\lambda_{k+G_1}-E) \end{vmatrix}=0, \tag{8.69}$$

where $V_1\equiv V_{G_1}$. On solving, this gives us three eigenvalues (probably the lowest) and substituting these back in the three homogeneous equations, we can solve for the three coefficients, upto a normalization constant, to obtain the wave function

$$\phi_k(x)=c(k)\exp(ikx)+c(k-G_1)\exp[i(k-G_1)x] + c(k+G_1)\exp[i(k+G_1)x]. \tag{8.70}$$

If we wish to improve the accuracy of the calculation, the obvious procedure within the framework of this method is to include a large number of terms, say n, in the Fourier expansion (8.65b) of the periodic

potential. We must then include the corresponding terms in the wave function (8.65a). The secular determinant will then be of order n which will give us n eigenvalues, at least the lowest few of which will be fairly accurate.

The problem is obvious. The more the accuracy one desires, the larger is the order of the determinant that must be solved. Even with the present-day computers, it is a fairly difficult task to solve, say, a 30×30 or a 50×50 determinant. Group theory comes to our rescue with its familiar technique of block-diagonalization so that determinants as large as 300×300 or 500×500 can be solved.[5] We shall discuss this in the next subsection.

8.6.2 Factorization of the secular determinant. Consider a three-dimensional simple cubic monatomic crystal. The reciprocal lattice vectors can be divided into sets according to their magnitudes. Thus, there is one reciprocal lattice vector with length zero, six vectors with length unity, twelve with length $\sqrt{2}$, and so on. In the expansion of the potential, it is reasonable to expect that the magnitude of the Fourier coefficients corresponding to large reciprocal lattice vectors will be small. We may therefore decide to include the first few terms in the expansion (8.65b). However, since the potential $V(\mathbf{r})$ has the symmetry of the lattice, *we must include either none or all the vectors of a set of equivalent reciprocal lattice vectors.* Table (8.7) lists a number of sets of reciprocal lattice vectors for a simple cubic lattice in increasing order of length. We shall illustrate the procedure below by considering the expansion of the wave function in 33 plane waves (the first five sets of Table 8.7).

Consider the point Γ where the group of the wave vector is O_h. The plane waves are of the form $\exp(-i\mathbf{G}\cdot\mathbf{r})$. Each set of plane waves listed in Table (8.7) can be used to generate a representation of O_h. Table (8.8) shows the characters of the representations generated by the first five sets and their decomposition into the irreducible representations. From each set of plane waves, we can then construct the symmetrized linear combinations transforming according to the irreducible representations of O_h. For example, the symmetrized combi-

[5] Although more rapidly convergent methods than the plane wave expansion are nowadays available, all of them are essentially based on the solution of a secular equation. Our purpose is merely to illustrate the use of group theory in reduction of the secular determinant and this is served well by the simple plane wave expansion method.

nations of the six plane waves of the set $\{100\}_\Gamma$ are

$$\Gamma_1 : (100)_\Gamma + (\bar{1}00)_\Gamma + (010)_\Gamma + (0\bar{1}0)_\Gamma + (001)_\Gamma + (00\bar{1})_\Gamma \sim 1;$$

$$\Gamma_{12} : \begin{cases} (100)_\Gamma + (\bar{1}00)_\Gamma - (010)_\Gamma - (0\bar{1}0)_\Gamma \sim x^2 - y^2, \\ (100)_\Gamma + (\bar{1}00)_\Gamma + (010)_\Gamma + (0\bar{1}0)_\Gamma - 2(001)_\Gamma \\ \qquad - 2(00\bar{1})_\Gamma \sim x^2 + y^2 - 2z^2; \end{cases}$$

$$\Gamma_{15} : \begin{cases} (100)_\Gamma - (\bar{1}00)_\Gamma \sim x, \\ (010)_\Gamma - (0\bar{1}0)_\Gamma \sim y, \\ (001)_\Gamma - (00\bar{1})_\Gamma \sim z. \end{cases}$$

TABLE 8.7 SOME SETS OF SHORTEST RECIPROCAL LATTICE VECTORS FOR A SIMPLE CUBIC LATTICE

Set	Length	Number	Cumulative total
{0 0 0}	0	1	1
{1 0 0}	1	6	7
{1 1 0}	$\sqrt{2}$	12	19
{1 1 1}	$\sqrt{3}$	8	27
{2 0 0}	2	6	33
{2 1 0}	$\sqrt{5}$	24	57
{2 1 1}	$\sqrt{6}$	24	81
{2 2 0}	$\sqrt{8}$	12	93
{2 2 1}	3	24	117
{3 0 0}	3	6	123
{3 1 0}	$\sqrt{10}$	24	147
{3 1 1}	$\sqrt{11}$	24	171
{2 2 2}	$\sqrt{12}$	8	179
{3 2 0}	$\sqrt{13}$	24	203
{3 2 1}	$\sqrt{14}$	48	251
{4 0 0}	4	6	257

TABLE 8.8 THE CHARACTERS OF THE REPRESENTATIONS OF O_h GENERATED BY THE FIRST FIVE SETS OF TABLE (8.7) AND THEIR REDUCTION

Set	E	$6C_4$	$3C_4^2$	$6C_2$	$8C_3$	J	$6JC_4$	$3JC_4^2$	$6JC_2$	$8JC_3$	Representation
$\{000\}_\Gamma$	1	1	1	1	1	1	1	1	1	1	Γ_1
$\{100\}_\Gamma$	6	2	2	0	0	0	0	4	2	0	$\Gamma_1\oplus\Gamma_{12}\oplus\Gamma_{15}$
$\{110\}_\Gamma$	12	0	0	2	0	0	0	4	2	0	$\Gamma_1\oplus\Gamma_{12}\oplus\Gamma_{15}\oplus\Gamma_{25}\oplus\Gamma_{25}'$
$\{111\}_\Gamma$	8	0	0	0	2	0	0	0	4	0	$\Gamma_1\oplus\Gamma_2'\oplus\Gamma_{15}\oplus\Gamma_{25}'$
$\{200\}_\Gamma$	6	2	2	0	0	0	0	4	2	0	$\Gamma_1\oplus\Gamma_{12}\oplus\Gamma_{15}$

The required block-diagonalization is then immediately obtained if we expand the wave function not in plane waves but in the symmetrized plane waves. If we express these in the notation of Chapters 3 and 5 by $\psi_{pm}{}^\alpha$, we can express the wave function as

$$\phi_{\mathbf{k}}(\mathbf{r})=\sum_{\alpha,\,p,\,m} a_{\alpha pm}\,\psi_{pm}{}^\alpha. \tag{8.71}$$

Using this expansion in the Schroedinger equation (8.1), we have

$$[\mathcal{H}_0-E+V(\mathbf{r})]\sum_{\alpha,\,p,\,m} a_{\alpha pm}\,\psi_{pm}{}^\alpha=0, \tag{8.72}$$

where $\mathcal{H}_0$ denotes the kinetic energy operator. Taking the scalar product of this with some symmetrized plane wave $\psi_{qn}{}^\beta$ and noting that $\mathcal{H}_0$, E and $V(\mathbf{r})$ are invariant under O_h, we have

$$(\psi_{qn}{}^\beta,\ \sum_{\alpha,\,p,\,m} a_{\alpha pm}\,[\mathcal{H}_0-E+V(\mathbf{r})]\,\psi_{pm}{}^\alpha)=0,$$

or

$$\sum_p a_{\beta pn}\,(\psi_{qn}{}^\beta,\,[\mathcal{H}_0-E+V(\mathbf{r})]\,\psi_{pn}{}^\beta)=0, \tag{8.73}$$

for all β, q and n. This is again a set of linear homogeneous equations in the unknown coefficients $a_{\beta pn}$ and the eigenvalue E and the coefficients $a_{\beta pn}$ can be obtained by solving the determinant of the elements $(\psi_{qn}{}^\beta,\,[\mathcal{H}_0-E+V(\mathbf{r})]\,\psi_{pn}{}^\beta)$. The significant difference, however, is that the order of this determinant is considerably smaller—it is equal to the number of values of p (or q) for fixed values of β and n.

Coming to the example which we have taken up, we see from Table (8.8) that the representation Γ_1 occurs five times in the scheme. Thus $1\leq p\leq 5$ in this case and we have a 5×5 determinant to solve which will give us five eigenvalues corresponding to Γ_1. The representations Γ_2' and Γ_{25} occur only once each. These give us the corresponding 1×1 blocks which are the eigenvalues themselves. The

representation Γ_{25}' occurs twice and is three-dimensional. Corresponding to the three columns of Γ_{25}' ($n=1, 2, 3$; $p, q=1, 2$), we have three 2×2 determinants. Solving any one of these, we get two eigenvalues, each of which will be threefold degenerate. The representation Γ_{12} occurs thrice and is two-dimensional. Corresponding to the two columns of Γ_{12} ($n=1, 2$; $p, q=1, 2, 3$), we have two 3×3 determinants. But only one of them need be solved to obtain three eigenvalues and each of these will be twofold degenerate. Finally, Γ_{15} occurs four times so that we have three 4×4 determinants only one of which may be solved to obtain the four threefold degenerate eigenvalues. The problem of solving a 33×33 determinant has thus been reduced to one of solving two one-dimensional determinants and one determinant each of order 2, 3, 4 and 5. The result is the 33 electronic energy levels at $\mathbf{k}=0$. Additional sets of plane waves can easily be included without much increase in the labour and the convergence of the eigenvalues can be studied. The transition from the case of the free electron approximation to that of the nearly free electron model is schematically illustrated in Fig. (8.14). As has been emphasized in this book, group theory gives only the splitting of the degeneracies. The exact ordering of the levels depends on the actual potential and must be obtained by solving the secular equation. It is possible that a 'strong' potential may have a drastic effect on the ordering of the levels as shown in Figs. (8.14c) and (8.14d) for Si and Ge. In the

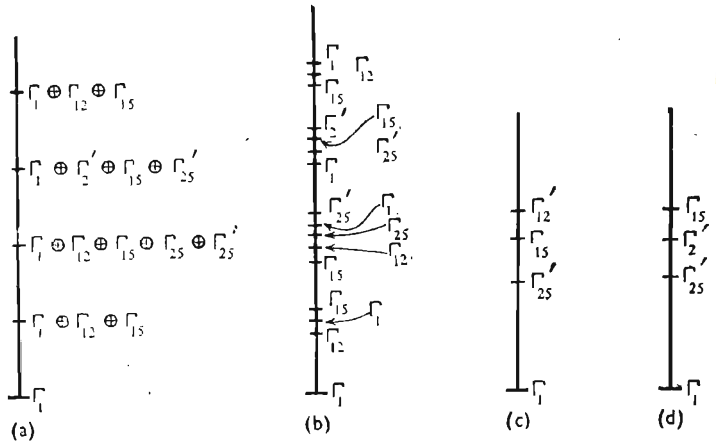

FIGURE 8.14 The high degeneracy of the electronic levels in the free electron model (a) splits under the action of a periodic potential (b) (schematic) ; (c) and (d) show the first few levels at $\mathbf{k}=0$ in Si and Ge, respectively (not to scale).

case of Si, the ordering is $\Gamma_1, \Gamma_{25}', \Gamma_{15}, \Gamma_{12}', \Gamma_2', \Gamma_1, \ldots$, while for Ge, it is $\Gamma_1, \Gamma_{25}', \Gamma_2', \Gamma_{15}, \ldots$.

At any other point in the Brillouin zone with less than full cubic symmetry, the reduction of the secular equation is not so effective. Although, in principle, the procedure is the same, the labour therefore increases. For example, the group of the wave vector along the line Δ is C_{4v} which has one- and two-dimensional irreducible representations. We may again consider a number of plane waves of the form $\exp(i(\mathbf{k}-\mathbf{G})\cdot\mathbf{r})$, obtain suitable symmetrized combinations transforming according to the irreducible representations of C_{4v} and take up the problem of solving the secular determinant. The blocks will, however, be in general of larger dimensions than at Γ. At a general point where the group of the wave vector is only the identity element, we have to solve the complete determinant without any factorization (33×33 in the above example). In other words, the larger the group of the wave vector, the larger is the accuracy of the eigenvalues with a given amount of labour. It is obviously easier to obtain the eigenvalues at symmetry points and along symmetry lines in the Brillouin zone.

One effect of the crystal potential on the energy bands which we have mentioned at the beginning of this section is the hybridization of bands having the same symmetry. In the free electron model, bands

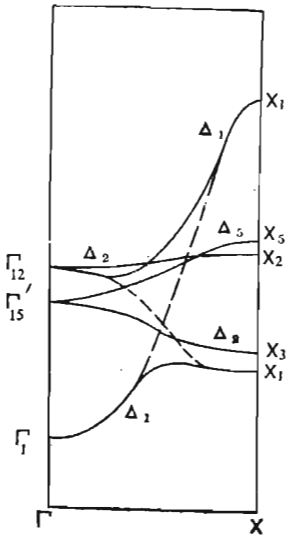

FIGURE 8.15 The band structure of copper along ΓX showing the hybridization of two bands having the symmetry Δ_1. The dotted curves are hypothetical bands in the absence of hybridization

having the same symmetry may cross. Thus, there are a number of crossings of bands of symmetry Δ_1 along ΓX in Fig. (8.13). With the

introduction of the periodic potential, such degeneracies are lifted and we get new bands.

Consider, for example, the two bands with symmetries Δ_1 and $\Delta_1 \oplus \Delta_2 \oplus \Delta_3$ in the range $1 < E < 2$ of Fig. (8.9). The plane wave generating the first of these bands is $(\bar{1}00)_\Delta = \exp[i(k_x + 1)x]$ while the other band is generated by the four plane waves $(110)_\Delta$, $(1\bar{1}0)_\Delta$, $(101)_\Delta$ and $(10\bar{1})_\Delta$. The linear combination of these which transforms according to Δ_1 is the sum of the four plane waves which gives $\exp(ik_x x)(\cos y + \cos z)$. These two symmetrized functions transform according to Δ_1 and are degenerate at $k = 1/4$ with $E = 25/16$ in the free electron model. When the crystal potential is taken into account, there will be nonvanishing matrix elements of the potential between these functions having the same symmetry and the solutions will be the roots of the corresponding blocks in the secular equation. This means that the proper eigenfunctions must be constructed by taking linear combinations of as many functions having the same symmetry as possible. This phenomenon is known as *hybridization* and has the obvious effect of lifting the degeneracy between bands having the same symmetry. Fig. (8.15) shows the energy bands of copper (fcc structure) along ΓX obtained by Segall.[6] The hybridization of two bands having symmetry Δ_1 should be obvious. We can therefore take it as a general rule that *bands having the same symmetry do not cross.*

PROBLEMS ON CHAPTER 8

(8.1) Show that the Wigner-Seitz cell has the full point group symmetry of the lattice.

(8.2) If the group of a certain vector $\mathbf{k}$ is K, show that the group of any vector in the star of $\mathbf{k}$ is also K.

(8.3) Obtain the compatibility relations for the double-valued representations of the cubic group O between the points Γ and the lines Δ, Λ and Σ.

(8.4) Verify the compatibility relations given in Tables (8.4), (8.5) and (8.6).

(8.5) Obtain the free electron energy bands of bcc and fcc lattices shown in Figs. (8.11) and (8.13) and verify the labeling of the various bands.

(8.6) Construct tables such as Table (8.3) for bcc and fcc lattices listing the groups of the wave vector at various special points and on lines and planes of symmetry in the respective Brillouin zones. Check your results with the groups of the wave vector given in Tables (8.5) and (8.6).

(8.7) Determine the groups of the wave vector at the following points for

[6] Segall (1962). Figure reproduced with permission of the author.

an fcc lattice: (ii) U, (ii) K, a general point along (iii) WK, (iv) UL, (v) WU, (vi) KL. Obtain the compatibility relations for the representations at W and a general point along WU.

(8.8) Determine the groups of the wave vector for a general point on the planes ΓXP, ΓHN and ΓNP for a bcc lattice. Do the same for a general point on the planes ΓXM, ΓMR, ΓXR and MXR for a simple cubic lattice.

(8.9) Obtain the free electron energy bands along the various lines of symmetry in the reduced zone scheme for a two-dimensional rectangular lattice and a hexagonal lattice. Obtain the labeling of the various bands.

(8.10) Draw the free electron energy bands for a simple cubic lattice along ΓM, MR, XM and XR and label them by the proper irreducible representations. Verify that the compatibility relations of Table (8.4) are satisfied.

(8.11) In spite of the rule that bands having the same symmetry do not cross, explain why many bands apparently having the same symmetry cross each other in the free electron model.

(8.12) Construct tables such as Table (8.7) for bcc and fcc lattices listing the various sets of reciprocal lattice vectors.

Bibliography for Chapter 8

Azaroff (1960); Bell (1954); Bhagavantam (1966); Bhagavantam and Venkatarayudu (1969); Callaway (1964); Falicov (1967); Hamermesh (1964); Harrison (1970); Jones (1960); Kittel (1963); Koster (1957); Koster, Dimmock and Wheeler (1963); Loebl (1968); Mariot (1962); Meijer and Bauer (1962); Nussbaum (1966); Slater (1965); Tinkham (1964).

APPENDIX A

Elastic Constants of Crystals

We expect the reader of this book to be familiar with the elementary considerations of the elastic properties of crystals.[1] The stress, which is defined as the force acting on a unit area of the solid, is a second rank nine-component tensor whose components may be denoted by X_x, Y_y, Z_z, Y_z, Z_x, X_y, Y_x, Z_y and X_z. The first three are the components of the tensile stress while the last six denote the shear stress. The notation is such that the capital letter denotes the direction of the force while the subscript denotes the normal to the plane on which the force acts. Thus, for example, Y_z denotes the component of force acting along the y direction on a unit area of the solid normal to the z direction. When the solid is in static equilibrium (that is, has no resultant force or torque acting on it), it can be shown that the stress tensor is a symmetric tensor, so that

$$X_y = Y_x, \quad Y_z = Z_y, \quad Z_x = X_z. \tag{A.1}$$

We thus have only six independent elastic stress components.

The elastic strain tensor is similarly a symmetric second rank tensor with the six independent dimensionless components e_{xx}, e_{yy}, e_{zz}, $e_{yz} = e_{zy}, e_{zx} = e_{xz}, e_{xy} = e_{yx}$. Let us denote the stress and the strain components by the six-dimensional *column vectors*

$$\begin{aligned} x &\equiv \{e_{xx}, e_{yy}, e_{zz}, e_{yz}, e_{zx}, e_{xy}\}, \\ X &\equiv \{X_x, Y_y, Z_z, Y_z, Z_x, X_y\}, \end{aligned} \tag{A.2}$$

where we have used the curly brackets to denote a column vector. To the first order in stresses and strains, the Hooke's law is obeyed and the components are linearly dependent on each other. This is a good approximation for small deformations and we can write the cause-effect relationship in the form

$$x=SX,\ X=Cx, \tag{A.3}$$

where S and C are square matrices[1] of order six and it is obvious that C is the inverse of S. The elements S_{ij} $(1\leq i,j\leq 6)$ of S are called the *elastic compliance constants* or simply *elastic compliances*, while the elements C_{ij} of C are called the *elastic stiffness constants*. Together, they are just called the *elastic constants* of the solid. Although there are 36 elastic constants involved in (A.3), they can be chosen to be symmetric, so that $C_{ij}=C_{ji}$ $(S_{ij}=S_{ji})$. This reduces the number of independent elastic constants to 21 even for a system with no symmetry at all. A crystal with the lowest possible symmetry (triclinic system) has all the 21 independent elastic constants.

The number of independent elastic constants further reduces if the crystal possesses higher symmetry. This result can be deduced as follows. The *elastic energy density* of a solid can be expressed as a bilinear function of the strain components with coefficients which are the elastic stiffness constants in the form

$$U=\sum_{l=1}^{6}\ \sum_{k=1}^{l}\ (1-\tfrac{1}{2}\delta_{kl})\,C_{kl}\,e_k\,e_l, \tag{A.4}$$

where we have identified the subscripts on the strain components as

$$xx\equiv 1,\ yy\equiv 2,\ zz\equiv 3,\ yz\equiv 4,\ zx\equiv 5,\ xy\equiv 6. \tag{A.5}$$

The general matrix is therefore of the form

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{bmatrix} \tag{A.6}$$

Now, the elastic energy density should remain invariant under any symmetry transformation of the crystal. For example, if a strained cubic crystal is under consideration, its elastic energy density should not change by a mere relabeling of the x, y and z axes. We shall show

[1]Note that S and C are really fourth rank tensors because they transform one second rank tensor into another second rank tensor.

explicitly by taking up a couple of examples that such a condition on the elastic energy density is equivalent to conditions on the elastic constants. The result is that some of these constants identically vanish while some of the remaining ones become equal to each other, reducing considerably the number of independent elastic constants.

Cubic Crystals

Cubic crystals are characterized by a threefold rotational symmetry about each of the four cube diagonals. The effect of these rotations on the cartesian coordinates is illustrated in Table (A.1).

TABLE A.1 THE EFFECT OF THE THREE-FOLD ROTATIONS ABOUT THE CUBE DIAGONALS ON THE CARTESIAN COORDINATES

No.	A clockwise rotation through $2\pi/3$ about the axis	has the effect
1	$[1\ \ 1\ \ 1]$	$x\to y\to z\to x$
2	$[1\ \ 1\ \ \bar{1}]$	$x\to -z\to y\to x$
3	$[1\ \ \bar{1}\ \ 1]$	$x\to z\to -y\to x$
4	$[\bar{1}\ \ 1\ \ 1]$	$x\to -z\to -y\to x$

Consider the first operation of Table (A.1) applied on the crystal so that the elastic energy density of (A.4) takes the form

$$\begin{aligned}U=&\tfrac{1}{2}C_{11}e_{yy}^2+C_{12}e_{yy}e_{zz}+C_{13}e_{yy}e_{xx}+C_{14}e_{yy}e_{zx}+C_{15}e_{yy}e_{xy}\\&+C_{16}e_{yy}e_{yz}+\tfrac{1}{2}C_{22}e_{zz}^2+C_{23}e_{zz}e_{xx}+C_{24}e_{zz}e_{zx}+C_{25}e_{zz}e_{xy}\\&+C_{26}e_{zz}e_{yz}+\tfrac{1}{2}C_{33}e_{xx}^2+C_{34}e_{xx}e_{zx}+C_{35}e_{xx}e_{xy}+C_{36}e_{xx}e_{yz}\\&+\tfrac{1}{2}C_{44}e_{zx}^2+C_{45}e_{zx}e_{xy}+C_{46}e_{zx}e_{yz}+\tfrac{1}{2}C_{55}e_{xy}^2\\&+C_{56}e_{xy}e_{yz}+\tfrac{1}{2}C_{66}e_{yz}^2.\end{aligned}\qquad(A.7)$$

If the elastic energy density is to remain invariant under such a transformation, it follows that (A.7) must be identically equal to (A.4) for all values of the strain components. This is possible only if the coefficients of the corresponding terms in (A.4) and (A.7) are identically equal to each other. On comparing (A.4) and (A.7), and remembering that $e_{xy}=e_{yx}$, etc., this gives

$$\begin{aligned}&C_{11}=C_{22}=C_{33},\quad C_{12}=C_{23}=C_{13},\quad C_{14}=C_{25}=C_{36},\\&C_{15}=C_{26}=C_{34},\quad C_{16}=C_{24}=C_{35},\quad C_{44}=C_{55}=C_{66},\\&C_{45}=C_{56}=C_{46}.\end{aligned}\qquad(A.8)$$

Thus, a single symmetry transformation has reduced the number of independent elastic constants from 21 to 7. The elastic energy density

then takes the form

$$U=\tfrac{1}{2}C_{11}(e_{xx}^2+e_{yy}^2+e_{zz}^2)+C_{12}(e_{xx}e_{yy}+e_{yy}e_{zz}+e_{zz}e_{xx})+C_{14}(e_{xx}e_{yz}+e_{yy}e_{zx}+e_{zz}e_{xy})+C_{15}(e_{xx}e_{zx}+e_{yy}e_{xy}+e_{zz}e_{yz})+C_{16}(e_{xx}e_{xy}+e_{yy}e_{yz}+e_{zz}e_{zx})+\tfrac{1}{2}C_{44}(e_{yz}^2+e_{zx}^2+e_{xy}^2)+C_{45}(e_{yz}e_{zx}+e_{zx}e_{xy}+e_{xy}e_{yz}). \tag{A.9}$$

Consider now another transformation, say the second one in Table (A.1). We note that by the definition of the strain components, $e_{y(-z)}=e_{(-y)z}=-e_{yz}$, $e_{(-y)(-z)}=e_{yz}$, etc. The same procedure is repeated, that is, we work out the effect of the transformation on the elastic energy density (A.9), and equate the coefficients of the corresponding terms in (A.9) and in the new expression to obtain

$$C_{14}=-C_{14},\quad C_{15}=-C_{15},\quad C_{16}=-C_{16},\quad C_{45}=-C_{45}. \tag{A.10}$$

This reduces the elastic energy density to

$$U=\tfrac{1}{2}C_{11}(e_{xx}^2+e_{yy}^2+e_{zz}^2)+C_{12}(e_{xx}e_{yy}+e_{yy}e_{zz}+e_{zz}e_{xx})+\tfrac{1}{2}C_{44}(e_{yz}^2+e_{zx}^2+e_{xy}^2). \tag{A.11}$$

The remaining two operations listed in Table (A.1), or, in fact, all the other operations of the point group O_h, leave the energy density (A.11) invariant and therefore produce no further reduction. This shows that the cubic crystals have only three independent elastic constants, which are conventionally chosen to be C_{11}, C_{12} and C_{44}. The use of the relations (A.8) and (A.10) reduces the matrix (A.6) of the elastic coefficients to the form

$$\begin{bmatrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\ C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{44} \end{bmatrix}. \tag{A.12}$$

Note that we have used the invariance of the elastic energy density only under the threefold rotations about the cube diagonals without referring to the fourfold symmetry about the coordinate axes. The result of the above analysis is therefore valid for any cubic crystal whose point group may be any one of the five cubic point groups T, T_d, T_h, O or O_h.

Alternatively, we could also have derived the same result by applying the various transformations on the stress-strain relation itself, without going to the elastic energy density. To illustrate this, let us write Eqs. (A.3) in full:

$$X_x=C_{11}e_{xx}+C_{12}e_{yy}+C_{13}e_{zz}+C_{14}e_{yz}+C_{15}e_{zx}+C_{16}e_{xy},$$
$$Y_y=C_{12}e_{xx}+C_{22}e_{yy}+C_{23}e_{zz}+C_{24}e_{yz}+C_{25}e_{zx}+C_{26}e_{xy},$$
$$Z_z=C_{13}e_{xx}+C_{23}e_{yy}+C_{33}e_{zz}+C_{34}e_{yz}+C_{35}e_{zx}+C_{36}e_{xy},$$
$$Y_z=C_{14}e_{xx}+C_{24}e_{yy}+C_{34}e_{zz}+C_{44}e_{yz}+C_{45}e_{zx}+C_{46}e_{xy},$$
$$Z_x=C_{15}e_{xx}+C_{25}e_{yy}+C_{35}e_{zz}+C_{45}e_{yz}+C_{55}e_{zx}+C_{56}e_{xy},$$
$$X_y=C_{16}e_{xx}+C_{26}e_{yy}+C_{36}e_{zz}+C_{46}e_{yz}+C_{56}e_{zx}+C_{66}e_{xy}. \quad (A.13)$$

We now apply the first transformation ($x\to y\to z\to x$) of Table (A.1) on the above equations. This brings them to the form

$$Y_y=C_{11}e_{yy}+C_{12}e_{zz}+C_{13}e_{xx}+C_{14}e_{zx}+C_{15}e_{xy}+C_{16}e_{yz},$$
$$Z_z=C_{12}e_{yy}+C_{22}e_{zz}+C_{23}e_{xx}+C_{24}e_{zx}+C_{25}e_{xy}+C_{26}e_{yz},$$
$$X_x=C_{13}e_{yy}+C_{23}e_{zz}+C_{33}e_{xx}+C_{34}e_{zx}+C_{35}e_{xy}+C_{36}e_{yz},$$
$$Z_x=C_{14}e_{yy}+C_{24}e_{zz}+C_{34}e_{xx}+C_{44}e_{zx}+C_{45}e_{xy}+C_{46}e_{yz},$$
$$X_y=C_{15}e_{yy}+C_{25}e_{zz}+C_{35}e_{xx}+C_{45}e_{zx}+C_{55}e_{xy}+C_{56}e_{yz},$$
$$Y_z=C_{16}e_{yy}+C_{26}e_{zz}+C_{36}e_{xx}+C_{46}e_{zx}+C_{56}e_{xy}+C_{66}e_{yz}. \quad (A.14)$$

On comparing these with (A.13) and equating coefficients of the corresponding terms, we get the same conditions as (A.8). Similarly, applying the second transformation of Table (A.1) and using the invariance of the stress-strain relationship, we would get the conditions (A.10). In applying these transformations, use must be made of the fact that, like the strain components, the stress components satisfy the relations $X_{(-y)}=(-X)_{(y)}=-(X_y)$, while $(-X)_{(-y)}=X_y$, etc. We thus finally arrive at the form (A.12) for the matrix of elastic constants.

Tetragonal Crystals

Tetragonal crystals are characterized by the relations $a_1=a_2\neq a_3$ and $\alpha=\beta=\gamma=90°$. The point symmetry group of the *lattice* is D_{4h}. We shall take the x and the y axes along $\mathbf{a}_1$ and $\mathbf{a}_2$ respectively and z along $\mathbf{a}_3$, so that the lattice has a four-fold symmetry about the z axis. A rotation through 90° about z has the effect $x\to y\to -x$, $z\to z$. Applying this operation on the elastic energy density (A.4), and equating the coefficients of the corresponding terms in (A.4) and in the transformed expression, we find the following conditions on the elastic constants:

$$C_{11}=C_{22},\ C_{44}=C_{55},\ C_{13}=C_{23},\ C_{16}=-C_{26},\ C_{34}=-C_{35},$$
$$C_{14}=C_{25},=C_{15}=C_{24}=C_{36}=C_{45}=C_{46}=C_{56}=0. \quad (A.15)$$

This reduces the number of independent elastic constants to 8 and the elastic energy density becomes

$$U=\tfrac{1}{2}C_{11}(e_{xx}^2+e_{yy}^2)+\tfrac{1}{2}C_{33}e_{zz}^2+C_{12}e_{xx}e_{yy}+C_{13}(e_{xx}+e_{yy})e_{zz}$$
$$+C_{16}(e_{xx}-e_{yy})e_{xy}+C_{24}(e_{yz}-e_{zx})e_{zz}$$
$$+\tfrac{1}{2}C_{44}(e_{yz}^2+e_{zx}^2)+\tfrac{1}{2}C_{66}e_{xy}^2. \quad (A.16)$$

The group D_{4h} also includes a two-fold symmetry about the x or the y axis. Consider a rotation through π about the x axis, which has the effect $y \to -y$, $z \to -z$, $x \to x$. Applying this on the energy density (A.16), we find that all terms remain invariant except the two involving coefficients C_{16} and C_{34}, which must vanish. The final form of the energy density is then

$$U = \tfrac{1}{2}C_{11}(e_{xx}^2 + e_{yy}^2) + \tfrac{1}{2}C_{33}\,e_{zz}^2 + C_{12}\,e_{xx}\,e_{yy} + C_{13}(e_{xx} + e_{yy})\,e_{zz} + \tfrac{1}{2}C_{44}(e_{yz}^2 + e_{zx}^2) + \tfrac{1}{2}C_{66}\,e_{xy}^2. \quad \text{(A.17)}$$

It can be seen that any other transformation of D_{4h} leaves the bilinear form (A.17) invariant so that there is no further simplification. A tetragonal crystal thus has six independent elastic constants and the matrix of elastic constants reduces to the form

$$\begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \quad \text{(A.18)}$$

The forms of the matrices of elastic constants for various crystal systems are listed below.[2] Only the coefficients on one side of the principal diagonal are shown, since the martix is symmetric.

1. Triclinic system: 21 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ & & C_{33} & C_{34} & C_{35} & C_{36} \\ & & & C_{44} & C_{45} & C_{46} \\ & & & & C_{55} & C_{56} \\ & & & & & C_{66} \end{matrix}$$

2. Monoclinic system: 13 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{22} & C_{23} & 0 & 0 & C_{26} \\ & & C_{33} & 0 & 0 & C_{36} \\ & & & C_{44} & C_{45} & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{matrix}$$

[2] Bhagavantam (1966), Chapter 11. Tables reproduced with permission of Academic Press, Inc., London, and the author.

3. Orthorhombic system: 9 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{22} & C_{23} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{11} & 0 & 0 \\ & & & & C_{55} & 0 \\ & & & & & C_{66} \end{matrix}$$

4. Tetragonal system:

(i) Point groups C_4, S_4, C_{4h}: 7 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & C_{16} \\ & C_{11} & C_{13} & 0 & 0 & -C_{16} \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & C_{66} \end{matrix}$$

(ii) Point groups C_{4v}, D_{2d}, D_4, D_{4h}: 6 independent constants. See Eq. (A.18).

5. Trigonal system:

(i) Point groups C_3, S_6: 7 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & 0 \\ & C_{11} & C_{13} & -C_{14} & -C_{15} & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & -C_{15} \\ & & & & C_{14} & C_{11} \\ & & & & & \tfrac{1}{2}(C_{11}-C_{12}) \end{matrix}$$

(ii) Point groups C_{3v}, D_3, D_{3d}: 6 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{14} & C_{14} \\ & & & & & \tfrac{1}{2}(C_{11}-C_{12}) \end{matrix}$$

6. Hexagonal system: 5 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ & C_{11} & C_{13} & 0 & 0 & 0 \\ & & C_{33} & 0 & 0 & 0 \\ & & & C_{44} & 0 & 0 \\ & & & & C_{44} & 0 \\ & & & & & \tfrac{1}{2}(C_{11}-C_{12}) \end{matrix}$$

7. Cubic system : 3 independent constants. See Eq. (A.12).
8. Isotropic medium: 2 independent constants.

$$\begin{matrix} C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\ & C_{11} & C_{12} & 0 & 0 & 0 \\ & & C_{11} & 0 & 0 & 0 \\ & & & \tfrac{1}{2}(C_{11}-C_{12}) & 0 & 0 \\ & & & & \tfrac{1}{2}(C_{11}-C_{12}) & 0 \\ & & & & & \tfrac{1}{2}(C_{11}-C_{12}) \end{matrix}$$

APPENDIX B

Piezoelectricity and Dielectric Susceptibility

Some crystals have the property of deveolping an electric dipole moment under the action of an applied electric field. Some of these crystals possess an additional property of developing an electric dipole moment under an applied mechanical stress even in the absence of an electric field. The crystals of the latter type are called *piezoelectric* and quartz is an excellent example of such crystals. Other examples are Rochelle salt (sodium-potassium-tartrate-tetrahydrate, $NaKC_4H_4O_6 \cdot 4H_2O$), and ferroelectrics of the type of potassium dihydrogen phosphate (KH_2PO_4).

The electric dipole moment is a result of strain produced in the crystal by the external electric field. The various quantities are thus related to each other. If we define P to be the electric polarization (the electric dipole moment per unit volume), x the elastic strain, E the applied electric field and X the applied mechanical stress, then any two variables of the set (P, E, x, X) may be taken as the independent variables and the remaining two as the dependent variables. For low fields and stresses, the polarization and strain are found to depend linearly on E and X by the relations[1]

$$P = -dX + \chi E, \quad x = -S^E X + \tilde{d} E. \tag{B.1}$$

Here d is the piezoelectric strain coefficient tensor, χ the dielectric

[1]Bhagavantam (1966), Chapter 14; Fatuzzo and Merz (1967), p. 44; Kaenzig (1957), p. 71.

susceptibility tensor and S^E is the elastic compliance tensor, the superscript E being used to denote that the elastic compliances depend on the electric field and are to be evaluated at constant electric field.

Eqs. (B.1) are not as simple as they look. This is because the electric field E and the electric polarization P are vectors, whereas the stress X and the strain x are second rank tensors. It therefore follows that χ is a second rank tensor (since it relates two vectors), d is a third rank tensor (since it relates a vector with a second rank tensor) and S^E, as discussed in Appendix A, is a fourth rank tensor. However, since x and X have only six independent components rather than nine, we can write them as column vectors (matrices of order 6×1) as we have done in Appendix A. Then, since E and P are also column vectors of order 3×1, it follows that the independent components of the piezoelectric strain coefficient tensor d can be written in the form of a 3×6 matrix

$$d=\begin{bmatrix} d_{11} & d_{12} & d_{13} & d_{14} & d_{15} & d_{16} \\ d_{21} & d_{22} & d_{23} & d_{24} & d_{25} & d_{26} \\ d_{31} & d_{32} & d_{33} & d_{34} & d_{35} & d_{36} \end{bmatrix}. \tag{B.2}$$

χ is similarly a 3×3 matrix while S^E is a 6×6 matrix; $\tilde{d}$ in (B.1) denotes the transposed matrix of d and will be of order 6×3. Thus, expressed explicitly, the first of Eqs. (B.1) becomes

$$\begin{aligned} P_x=&-d_{11}X_x-d_{12}Y_y-d_{13}Z_z-d_{14}Y_z-d_{15}Z_x-d_{16}X_y \\ &+\chi_{11}E_x+\chi_{12}E_y+\chi_{13}E_z, \\ P_y=&-d_{21}X_x-d_{22}Y_y-d_{23}Z_z-d_{24}Y_z-d_{25}Z_x-d_{26}X_y \\ &+\chi_{21}E_x+\chi_{22}E_y+\chi_{23}E_z, \\ P_z=&-d_{31}X_x-d_{32}Y_y-d_{33}Z_z-d_{34}Y_z-d_{35}Z_x-d_{36}X_y \\ &+\chi_{31}E_x+\chi_{32}E_y+\chi_{33}E_z. \end{aligned} \tag{B.3}$$

A case of fairly general interest arises when a crystal has inversion symmetry. The polarization P is a polar vector and goes to $-P$ under inversion. However, the mechanical stress is invariant under the operation of inversion so that the linear relationship between P and X implies that P must identically vanish for crystals having a centre of symmetry. Thus, we arrive at the conclusion that crystals having inversion symmetry cannot be piezoelectric. This excludes 12 point groups and leaves only 20 point groups as the possible point groups of piezoelectric crystals. We shall explicitly evaluate the nonvanishing piezoelectric strain coefficients for a couple of cases.

Cubic Crystals (Point groups T and T_d)

Crystals having point groups T_h, O and O_h are invariant under inversion and from the discussion of the preceding paragraph, it follows that $d_{ij}=0$ for $1\leq i\leq 3$, $1\leq j\leq 6$ for crystals having point groups T_h, O and O_h. We are left with the two cubic groups T and T_d.

Applying the three-fold rotation $x\to y\to z\to x$ on Eqs. (B.3), we find the following equations (it is sufficient to consider only two of the three equations):

$$\begin{aligned} P_y=&-d_{11}Y_y-d_{12}Z_z-d_{13}X_x-d_{14}Z_x-d_{15}X_y-d_{16}Y_z\\ &+\chi_{11}E_y+\chi_{12}E_z+\chi_{13}E_x,\\ P_z=&-d_{21}Y_y-d_{22}Z_z-d_{23}X_x-d_{24}Z_x-d_{25}X_y-d_{26}Y_z\\ &+\chi_{21}E_y+\chi_{22}E_z+\chi_{23}E_x. \end{aligned} \tag{B.4}$$

Comparing these respectively with the second and the third equations of (B.3), we find the conditions

$$\begin{aligned} &d_{11}=d_{22}=d_{33},\ d_{12}=d_{23}=d_{31},\ d_{13}=d_{21}=d_{32},\\ &d_{14}=d_{25}=d_{36},\ d_{15}=d_{26}=d_{34},\ d_{16}=d_{24}=d_{35},\\ &\chi_{11}=\chi_{22}=\chi_{33},\ \chi_{12}=\chi_{23}=\chi_{31},\ \chi_{13}=\chi_{21}=\chi_{32}. \end{aligned} \tag{B.5}$$

Next, we apply the three-fold rotation $x\to -z\to y\to x$ on Eqs. (B.3). Remembering that E and P are polar vectors so that $P_{(-x)}=-P_x$ and $E_{(-x)}=-E_x$, etc., we get the following equations (again, only two equations are written):

$$\begin{aligned} -P_z=&-d_{11}Z_z-d_{12}X_x-d_{13}Y_y+d_{14}X_y-d_{15}Y_z+d_{16}Z_x\\ &-\chi_{11}E_z+\chi_{12}E_x-\chi_{13}E_y,\\ P_x=&-d_{21}Z_z-d_{22}X_x-d_{23}Y_y+d_{24}X_y-d_{25}Y_z+d_{26}Z_x\\ &-\chi_{21}E_z+\chi_{22}E_x-\chi_{23}E_y. \end{aligned} \tag{B.6}$$

Once again, comparing these respectively with the third and the first of Eqs. (B.3), we find in addition to (B.5) the following conditions:

$$\begin{aligned} &d_{11}=-d_{33},\ d_{12}=-d_{31},\ d_{13}=-d_{32},\ d_{15}=-d_{34},\\ &d_{24}=-d_{16},\ \chi_{12}=-\chi_{31},\ \chi_{13}=-\chi_{21}. \end{aligned} \tag{B.7}$$

Together with (B.5), these equations leave only three nonvanishing piezoelectric strain coefficients only one of which is independent ($d_{14}=d_{25}=d_{36}$) and three nonvanishing dielectric susceptibility components, again, only one of which is independent ($\chi_{11}=\chi_{22}=\chi_{33}$). For cubic crystals having the point groups T and T_d, we therefore have

$$d=\begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & 0\\ 0 & 0 & 0 & 0 & d_{14} & 0\\ 0 & 0 & 0 & 0 & 0 & d_{14} \end{bmatrix}, \tag{B.8a}$$

$$\chi=\begin{bmatrix} \chi_{11} & 0 & 0\\ 0 & \chi_{11} & 0\\ 0 & 0 & \chi_{11} \end{bmatrix}. \tag{B.8b}$$

Eqs. (B.3) then reduce to

$$\begin{aligned} P_x &= -d_{14} Y_z + \chi_{11} E_x, \\ P_y &= -d_{14} Z_x + \chi_{11} E_y, \\ P_z &= -d_{14} X_y + \chi_{11} E_z. \end{aligned} \tag{B.9}$$

Tetragonal Crystals (Point group C_{4v})

Tetragonal crystals can have one of the seven point groups C_4, S_4, C_{4h}, D_{2d}, C_{4v}, D_4 and D_{4h}. Of these, C_{4h} and D_{4h} contain inversion symmetry and hence are excluded from the piezoelectric classes. Each of the remaining five groups leads to a different set of nonvanishing piezoelectric strain coefficients. We shall treat only one case as an illustrative example—that of the group C_{4v}.

Let us take the z axis to be the axis of four-fold symmetry. A four-fold rotation about the z axis then has the effect $x \to y \to -x$, $z \to z$. Applying this on Eqs. (B.3), we have

$$\begin{aligned} P_y &= -d_{11} Y_y - d_{12} X_x - d_{13} Z_z + d_{14} X_z - d_{15} Z_y + d_{16} Y_x \\ &\qquad + \chi_{11} E_y - \chi_{12} E_x + \chi_{13} E_z, \\ -P_x &= -d_{21} Y_y - d_{22} X_x - d_{23} Z_z + d_{24} X_z - d_{25} Z_y + d_{26} Y_x \\ &\qquad + \chi_{21} E_y - \chi_{22} E_x + \chi_{23} E_z, \\ P_z &= -d_{31} Y_y - d_{32} X_x - d_{33} Z_z + d_{34} X_z - d_{35} Z_y + d_{36} Y_x \\ &\qquad + \chi_{31} E_y - \chi_{32} E_x + \chi_{33} E_z. \end{aligned} \tag{B.10}$$

Comparing these with (B.3), we find

$$\begin{aligned} &d_{11} = \pm d_{22} \equiv 0,\ d_{12} = \pm d_{21} \equiv 0,\ d_{13} = \pm d_{23} \equiv 0, \\ &d_{16} = \pm d_{26} \equiv 0,\ d_{34} = \pm d_{35} \equiv 0,\ \chi_{13} = \pm \chi_{23} \equiv 0, \\ &\chi_{31} = \pm \chi_{32} \equiv 0,\ d_{36} = -d_{36} \equiv 0,\ d_{14} = -d_{25}, \\ &d_{15} = d_{24},\ d_{31} = d_{32},\ \chi_{11} = \chi_{22},\ \chi_{12} = -\chi_{21}. \end{aligned} \tag{B.11}$$

Eqs. (B.3) then reduce to

$$\begin{aligned} P_x &= -d_{14} Y_z - d_{15} Z_x + \chi_{11} E_x + \chi_{12} E_y, \\ P_y &= -d_{15} Y_z + d_{14} Z_x - \chi_{12} E_x + \chi_{11} E_y, \\ P_z &= -d_{31} X_x - d_{31} Y_y - d_{33} Z_z + \chi_{33} E_z. \end{aligned} \tag{B.12}$$

Now we apply on (B.12) a reflection in the xz plane which takes y to $-y$. It can be seen that this makes two of the above coefficients vanish:

$$d_{14} = 0,\ \chi_{12} = 0. \tag{B.13}$$

Other operations of the group C_{4v} produce no further reduction. Thus, in a tetragonal piezoelectric crystal having the point group C_{4v}, the electric polarization is related to the applied stress and the applied electric field by the relations

$$P_x = -d_{15} Z_x + \chi_{11} E_x,$$
$$P_y = -d_{15} Y_z + \chi_{11} E_y,$$
$$P_z = -d_{31} X_x - d_{31} Y_y - d_{33} Z_z + \chi_{33} E_z. \qquad \text{(B.14)}$$

The piezoelectric strain coefficient matrix and the dielectric susceptibility matrix take the forms

$$d = \begin{bmatrix} 0 & 0 & 0 & 0 & d_{15} & 0 \\ 0 & 0 & 0 & d_{15} & 0 & 0 \\ d_{31} & d_{31} & d_{33} & 0 & 0 & 0 \end{bmatrix}, \qquad \text{(B.15a)}$$

$$\chi = \begin{bmatrix} \chi_{11} & 0 & 0 \\ 0 & \chi_{11} & 0 \\ 0 & 0 & \chi_{33} \end{bmatrix}. \qquad \text{(B.15b)}$$

A complete list of the nonvanishing piezoelectric strain coefficients for all the 20 allowed point groups can be found in the book by Bhagavantam.[2]

Bhagavantam (1966). p. 161.

APPENDIX C

Time-Reversal Symmetry and Degeneracy

We have seen in Chapter 5 that symmetry is normally connected with degeneracy. This is because a larger symmetry group usually has irreducible representations of larger dimensions which immediately determine the degeneracies. However, when the symmetry group of a system also contains the time-reversal symmetry, the full symmetry group has operators some of which are unitary while some are anti-unitary. It is then not possible to define a matrix representation of the group in the usual sense. This can be seen as follows.

Let us denote by G the symmetry group of a system without time-reversal. With the inclusion of the time-reversal symmetry T, which commutes with all the operations of G, the full symmetry group is $G \otimes (E, T)$. Let $\{\phi_i\}$ be a set of functions generating a representation Γ of G and let A and B be some elements of G. Then we have

$$B\phi_i = \sum_j \phi_j \, \Gamma_{ji}(B). \tag{C.1}$$

Operating on this by the operator TA, we find

$$\begin{aligned} TA(B\phi_i) &= \sum_j (TA) \, [\phi_j \, \Gamma_{ji}(B)] \\ &= \sum_j (TA\phi_j) \, \Gamma_{ji}^*(B), \end{aligned} \tag{C.2}$$

where we have used the property (2.55) of antilinear operators. Now the operation of TA on ϕ_j must also be expressible as a linear combination of the ϕ_i's, so that

$$TA\phi_j = \sum_k \phi_k \, \Gamma_{kj}(TA), \tag{C.3}$$

where $\Gamma_{kj}(TA)$ are the elements of a matrix which corresponds to the operator TA. Using this in (C.2), we have

$$TAB\phi_l = \sum_{j,\,k} \phi_k \, \Gamma_{kj}(TA) \, \Gamma_{jl}^*(B). \tag{C.4}$$

But considering the effect of the operator TAB on ϕ_l directly, we must have

$$TAB\phi_l = \sum_k \phi_k \, \Gamma_{kl}(TAB). \tag{C.5}$$

Comparing (C.4) and (C.5) and remembering that ϕ_k are independent functions, we get the matrix relation

$$\Gamma(TAB) = \Gamma(TA)\Gamma^*(B) \neq \Gamma(TA)\Gamma(B). \tag{C.6}$$

This shows that the matrices of the representation here do not satisfy the property (3.1) of the usual representations defined at the beginning of Chapter 3. These matrices therefore do not constitute a representation of the group in the usual sense. Wigner calls such a set of matrices a *corepresentation* of the group containing unitary as well as antiunitary operators.

In case of groups containing unitary operators only, we have discussed the connection between symmetry and degeneracy in Chapter 5 and have shown that the various degeneracies are equal to the dimensions of the irreducible representations of the symmetry group. However, when the group contains antiunitary operators, the representation theory of Chapter 3 does not hold good. Nevertheless, it was shown by Wigner that the question whether time-reversal symmetry introduces additional degeneracy in the system or not can be answered by a consideration of the representation matrices corresponding only to the unitary operators of the symmetry group, that is, the symmetry group G disregarding the time-reversal symmetry.

Let Γ be a representation of the group G. Problem (3.3) then tells us that Γ^* is also a representation of G. Now the following three cases arise: (a) Γ and Γ^* are equivalent to the same real irreducible representation, that is, have the same real characters; (b) Γ and Γ^* are inequivalent, that is, have distinct characters; (c) Γ and Γ^* are equivalent but cannot be made real, that is, have the same characters which are, however, complex.

In order to apply the Wigner's result, we must separately consider systems with (i) integral spin, and (ii) half-odd-integral spin. Combining the above three cases (a), (b) and (c) with the two cases (i) and (ii) according to spin, we have altogether six possibilities. Wigner's result

regarding the additional degeneracy can then be expressed as follows:

No extra degeneracy in cases a(i) and c(ii);

Doubled degeneracy in cases b(i), b(ii), a(ii) and c(i). (C.7)

To determine whether a given representation of a group belongs to the case (a), (b) or (c), Frobenius and Schur have devised a simple test which depends only on the characters χ of the representation Γ. The test is given by

$$\sum_{A\in G} \chi(A^2)=\begin{cases} g & - \text{ case (a)}, \\ 0 & - \text{ case (b)}, \\ -g & - \text{ case (c)}, \end{cases} \tag{C.8}$$

where g is the order of the group G.

We note from the test (C.7) that in case the representations Γ and Γ^* are inequivalent (case (b)) the degeneracy is doubled irrespective of whether the spin is integral or half-odd-integral. It is for this reason that complex conjugate representations have been bracketted together in Table (7.7) for the irreducible representations of the point groups. Consider the basis functions for the irreducible representations Γ and Γ^*. Although there exists no operator in G which mixes the basis functions of Γ with those of Γ^*, the time-reversal operator will mix these functions and hence Γ and Γ^* would be degenerate in the presence of time-reversal symmetry.

Time-Reversal in Band Theory

The symmetry group of a crystal is its space group. Since a space group contains a very large number of elements (practically infinite), the Frobenius-Schur test (C.8) is not convenient. Herring has worked out a simpler test which requires only the characters of the irreducible representations of the group of the wave vector $\mathbf{k}$. This test is

$$\sum_{B} \chi(B^2)=\begin{cases} n & - \text{ case (a)}, \\ 0 & - \text{ case (b)}, \\ -n & - \text{ case (c)}, \end{cases} \tag{C.9}$$

where the sum is over those point group elements which take $\mathbf{k}$ to $-\mathbf{k}$ and n is the number of such elements. It should be clear that B^2 will leave $\mathbf{k}$ invariant and will therefore belong to the group of the wave vector $\mathbf{k}$.

An important result of time-reversal symmetry on the electronic band structure is that

$$E(\mathbf{k}\uparrow)=E(-\mathbf{k}\downarrow), \tag{C.10}$$

where $E(\mathbf{k}\uparrow)$ is the energy of an electron with wave vector $\mathbf{k}$ and spin up, etc. To prove this, we write the Schroedinger equation in the form

$$\mathcal{H}\psi_{\mathbf{k}\uparrow} = E(\mathbf{k}\uparrow)\,\psi_{\mathbf{k}\uparrow}, \tag{C.11}$$

where $\psi_{\mathbf{k}\uparrow}$ is the product of a Bloch function with wave vector $\mathbf{k}$ and a spin-up function:

$$\psi_{\mathbf{k}\uparrow} = \exp(i\mathbf{k}\cdot\mathbf{r})u_{\mathbf{k}}(\mathbf{r}) \times \text{spin-up function}. \tag{C.12}$$

If the crystal possesses time-reversal symmetry, the Hamiltonian $\mathcal{H}$ commutes with the time-reversal operator T and the function $T\psi_{\mathbf{k}\uparrow}$ must be degenerate with $\psi_{\mathbf{k}\uparrow}$. Remember that $T = i\sigma_y K$, where K is the complex conjugation operator. If we operate by T on $\psi_{\mathbf{k}\uparrow}$ of (C.12), the Pauli spin operator σ_y will operate only on the spin function and will turn the spin-up function into a spin-down function. We have

$$\begin{aligned} T\psi_{\mathbf{k}\uparrow} &= i\sigma_y K\psi_{\mathbf{k}\uparrow} \\ &= i\exp(-i\mathbf{k}\cdot\mathbf{r})\,u_{\mathbf{k}}{}^*(\mathbf{r}) \times \text{spin-down function}. \end{aligned} \tag{C.13}$$

This is clearly the product of a Bloch function with wave vector $-\mathbf{k}$ and a spin-down function and can be denoted by $\phi_{-\mathbf{k}\downarrow}$. But we must have

$$\mathcal{H}\phi_{-\mathbf{k}\downarrow} = E(-\mathbf{k}\downarrow)\,\phi_{-\mathbf{k}\downarrow}. \tag{C.14}$$

Comparing this with (C.11) and noting that $\psi_{\mathbf{k}\uparrow}$ and $\phi_{-\mathbf{k}\downarrow}$ must be degenerate owing to time-reversal symmetry, we immediately arrive at the result (C.10). *This result is valid irrespective of the spatial symmetry of the crystal.*

If, in addition, the crystal has an inversion symmetry, it can be easily seen that we would have

$$E(\mathbf{k}\uparrow) = E(-\mathbf{k}\uparrow), \tag{C.15}$$

because the space-inversion operator takes $\mathbf{k}$ to $-\mathbf{k}$ but does not operate on the spin. If time-reversal and space-inversion symmetries exist simultaneously, we can combine (C.10) and (C.15) and simply write

$$E(\mathbf{k}) = E(-\mathbf{k}), \tag{C.16}$$

for any spin.

APPENDIX D

Functions and Mappings

Let $X = \{x_1, x_2, \ldots, x_m\}$ and $Y = \{y_1, y_2, \ldots, y_n\}$ be two nonempty sets. The set C containing all ordered pairs (x_i, y_j), $1 \leqslant i \leqslant m$, $1 \leqslant j \leqslant n$, is called the cartesian product of X and Y, and is denoted by $C = X \times Y$. The elements of C are thus (x_1, y_1), (x_1, y_2), $\ldots$, (x_1, y_n), (x_2, y_1), $\ldots$, (x_2, y_n), etc., mn elements altogether. In the ordered pair (x_i, y_j), we shall refer to x_i as the first coordinate and y_j as the second coordinate.

Let f be a nonempty subset of C such that no two distinct elements of f have the same first coordinate. That is, if (x_i, y_j) is an element of the subset f, then no element of the form (x_i, y_k) with $k \neq j$ can be in f. In other words, if (x_i, y_j) and (x_i, y_l) are elements of f, then we must have $j = l$ Any such set is called a *function*[1] *from* X *to* Y.

The *domain* of the function f from X to Y is the subset of X containing all the first coordinates of the elements of f, while the *range* of the function f is the subset of Y containing all the second coordinates of the elements of f.

Example : Let $X = \{a, b, c\}$ and $Y = \{p, q, r, s\}$ be two sets. Their cartesian product is

$$C = X \times Y = \{(a, p), (a, q), (a, r), (a, s), (b, p), (b, q), (b, r), (b, s), (c, p), (c, q), (c, r), (c, s)\}. \quad \text{(D. 1)}$$

To define a function from X to Y, we may choose any subset of C

[1]The reader will realize that this condition implies, in the ordinary sense, that f is a single-valued function.

with the restriction that no two elements of the subset having different second coordinates may have the same first coordinate. For example, we can choose the following functions from X to Y:

$$f = \{(a, q), (c, s)\},$$
$$g = \{(a, p), (b, p), (c, q)\},$$
$$h = \{(a, r), (b, r), (c, r)\}. \qquad \text{(D. 2)}$$

The function f has the domain $\{a, c\}$ and range $\{q, s\}$, the function g has the domain $\{a, b, c\}$, that is the entire set X, and range $\{p, q\}$, while the function h again has X for its domain but $\{r\}$ as its range.

A function f from X to Y is said to be a *mapping* if the domain of f is the entire set X. Thus among the functions defined in (D. 2), g and h are mappings. A mapping is further divided into two categories : f is said to be a *mapping of X into Y* if the range of f if a proper subset of Y, and is denoted by

$$f : X \to Y, \qquad \text{(D. 3)}$$

while f is called a *mapping of X onto Y* if the range of f is the entire set Y, which is denoted by

$$f : X \xrightarrow{\text{onto}} Y \qquad \text{(D. 4)}$$

If (x, y) is an element of a function f from X to Y, where $x \in X$ and $y \in Y$, then y is said to be the *image* of x under f, and is denoted by $y = f(x)$. Thus in the example of functions defined in (D. 2), we have $q = f(a)$, $p = g(b)$, $r = h(b)$, etc. A function f from X to Y is said to be *one-to-one* if distinct elements of X have distinct images in Y under f. In the above example, f is a one-to-one function from X to Y while g and h are not one-to-one.

Coming to groups, let $G = \{E, A, B, C \ldots\}$ be a group of order g with E as the identity element and let $G' = \{E_1, E_2, \ldots, E_n, A_1, A_2, \ldots A_n, \ldots\}$ be a group of order ng, with E_1 as the identity element. Let us define a mapping from G' onto G such that $f(E_i) = E$, $f(A_i) = A$, etc., for $1 \leqslant i \leqslant n$. If G and G' follow multiplication tables such that $A_iB_j = C_k$ in G' (for some values of i, j, k) implies $f(A_i)f(B_j) = f(C_k)$, that is $AB = C$, in G, then the group G' is said to be *homomorphic* to G. Compare with Section 1.6.

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