NOTES ON GROUP THEORY

GEORGE F. KOSTER

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CHAPTER V

SPACE GROUPS

PREFACE

This Technical Report represents a rough set of notes written in the process of giving a series of lectrues on group theory at M. I. T. during the spring term of 1955. These lectures were attended mainly by members of the Solid-State and Molecular Theory Group and the applications treated in this Report were chosen to be in line with the interests of that group.

There are very few references in the report even though I have used books and articles in the preparation of the notes. I found the following particularly helpful:

E. Wigner, Gruppentheorie (Vieweg, Braunshweig, 1931).

This includes the elementary theory of groups as well as an excellent account of representation theory. Many applications of group theory to quantum mechanics are included in this book.

A. Speiser, Theorie der Gruppen von Endlicher Ordnung (Julius Springer, Berlin, 1927).

An excellent and readable account of the theory of groups and their representations. More thorough than the last reference, but without applications to quantum mechanics.

Eyring, Walter and Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1947).

This book contains a brief account of group and representation theory. It is particularly useful because of the number of character tables in the appendices of the book.

E. Corson, Perturbation Methods in the Quantum Mechanics of n-Electron Systems (Blackie, London, 1951).

This book gives a rather complete treatment of the Dirac vector model.

J. J. Burckhardt, Die Bewegungsgruppen der Kristallographie (Birkhäuser, Basel, 1947).

A complete treatment of space groups in two and three dimensions including an enumeration of these groups, but without a discussion of the irreducible representations of these groups.

F. Seitz, Z. Krist. 88, 433 (1934); 90, 289 (1935); 91, 336 (1935); 94, 100 (1936).

This series of four papers gives an algebraic treatment of space groups in three dimensions and a complete enumeration of these groups.

F. Seitz, Ann. Math. 37, 17 (1936).

This is the pioneer work on the irreducible representations of space groups.

Bouckaert, Smoluchowski, and Wigner, Phys. Rev. 50, 58 (1936).

Application of the theory of Seitz to the face-centered body-centered, and simple-cubic structures.

Further references may be obtained from these articles and books.

I also wish to express my gratitude to Professor J. C. Slater and to the members of the Solid-State and Molecular Theory Group for their interest and encouragement in preparing this Technical Report.

George F. Koster

Cambridge, Mass.
November, 1955

Chapter I

GENERAL PROPERTIES OF GROUPS

1. The Group Postulates and the Multiplication Table

A group $\mathcal{G}$ is a set of distinct elements A, B, C, ... for which an operation of combining is defined, which we shall call multiplication, and which has the following properties:

(a) The product of two elements A and B of the set is itself a member of the set.

(b) The associative law of multiplication holds for products of elements of the set. This means that for any three elements of the set A, B, and C

$$(AB)C \quad A(BC).$$

(c) The set must contain an element E, called the identity, such that for any element A of

$$AE = EA = A.$$

(d) For every element A of the group there must exist an element called A^{-1} which is the inverse of A. This means that for every A there must exist and element A^{-1} in the group such that*

$$A^{-1}A = E$$

The number of elements in $\mathcal{G}$ is called the order of the group. If the number of elements in $\mathcal{G}$ is finite, the group is called a finite group.

We notice that among the group postulates there is none demanding the commuting of elements of the group. Thus the order of the elements in a product is significant and, in general, $AB \neq BA$. If the group is such that $AB = BA$ for all elements A and B in the group, then the group is called Abeleian.

The properties of a group are completely determined if the product of any pair of elements is known. This information about a group is conveniently given in terms of a table which shows the products of pairs of elements and is known as the group multiplication table. This table has the form of Fig. 1-1. The left-hand column lists the elements of the group as does the upper row. The boxes contain the ordered products of an element of the left-hand column and the upper row in that order. The first thing we must show is that in any row of the multiplication table every element of the group occurs once and only once. This is summed up in the first theorem.

	E	A	B	C	·	·	·
E	E	A	B	C	·	·	·
A	A	A^2	AB	AC	·	·	·
B	B	BA	B^2	BC	·	·	·
C	C	CA	CB	C^2	·	·	·
·	·	·	·	·			
·	·	·	·	·			
·	·	·	·	·			

Fig. 1-1

A group multiplication table

*It may be noted here that the inverse of the product of elements is the product of the inverses taken in reverse order. Thus $(ABC)^{-1} = C^{-1} B^{-1} A^{-1}$ since $C^{-1} B^{-1} A^{-1} ABC = E$.

(GENERAL PROPERTIES OF GROUPS)

Theorem 1: For a group $\mathcal{G}$ of order g with elements $E = A_1$, A_2, A_3, ... A_g, the set of products A_nE, A_nA_2, ... A_nA_g, where A_n is an arbitrary member of the group, contains every element of the group once and only once.

Proof: Let us see if an element A_m is contained in this collection. If we can find an element of the group, A_r, such that $A_nA_r = A_m$, the first part of the theorem will be proved. Let us multiply both sides of the equation by A_n^{-1}. We find that $A_r = A_n^{-1} A_m$. Since this product is also a member of the group we have found the desired A_r. We now show that a given element appears only once in the collection of elements. If the same element appeared twice, we would have $A_nA_r = A_nA_s$. By multiplying through from the left by A_n^{-1}, we find that $A_r = A_s$ which means that A_r and A_s were not distinct. The same theorem can, of course, be proved for the collection EA_n, A_2A_n, A_3A_n, ... where we have multiplied through from the right by the element A_n. Having proved this theorem we have shown that multiplying all elements of the group by any given element of the group will cause the products to run over all the elements of the group.

In order that we may have an illustration of a group and its associated multiplication table, let us consider the equilateral triangle and consider all operations which send this triangle into itself. The equilateral triangle is illustrated in Fig. 1-2.

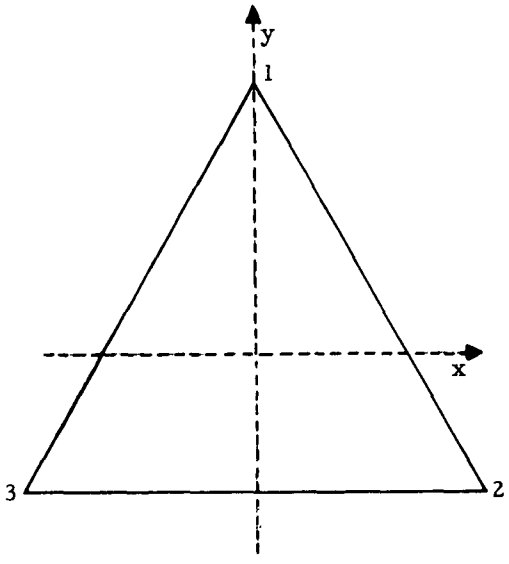


Fig. 1-2
The group C_{3v}

The operations which send this figure into itself are given below.

(1. THE GROUP POSTULATES AND THE MULTIPLICATION TABLE)

E: the identity operation

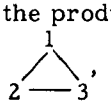
C_3: rotation clockwise through 120° about the center of the triangle

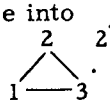
C_3^2: rotation clockwise through 240° about the center of the triangle

σ_1: reflection through the y axis

σ_2: reflection through a line passing through the center of the triangle lying 30° below the x axis (passing through the point 2 as the figure stands)

σ_3: reflection through a line passing through the center of the triangle and lying 30° below the negative x axis (passing through the point 3 as the figure stands).

These operations are considered to move the equilateral triangle and to be defined with respect to the x and y axes which are fixed in space. Let us consider a sequence of two operations and see what the result is. Consider, for example, the operation σ_1 followed by the operation σ_2. This we shall write as $\sigma_2\sigma_1$. The first operation appears on the right in the product and the second on the left. The first operation sends the triangle into 

, this when followed by the second operation σ_2, sends the triangle into 

. This is the same result we would have obtained by using directly the operation C_3^2. In a similar way, we can find the products of all pairs of operations which we have listed. We present these results in the form of a multiplication table which we give in Fig. 1-3.

	E	C_3	C_3^2	σ_1	σ_2	σ_3
E	E	C_3	C_3^2	σ_1	σ_2	σ_3
C_3	C_3	C_3^2	E	σ_3	σ_1	σ_2
C_3^2	C_3^2	E	C_3	σ_2	σ_3	σ_1
σ_1	σ_1	σ_2	σ_3	E	C_3	C_3^2
σ_2	σ_2	σ_3	σ_1	C_3^2	E	C_3
σ_3	σ_3	σ_1	σ_2	C_3	C_3^2	E

Fig. 1-3
Group multiplication table for the group C_{3v}.

From this table we can check the group postulates to see if this set of operations forms a group. It is clear, from the table, that the product of any pair of operations is once again an operation of the set. These operations are associative. The operation which leaves the triangle unmoved is the identity operation for the group. Inspection of the multiplication table also shows us that an inverse exists for every element of the group. Thus

$$E^{-1} = E \qquad \sigma_1^{-1} = \sigma_1$$
$$C_3^{-1} = C_3^2 \qquad \sigma_2^{-1} = \sigma_2$$
$$(C_3^2)^{-1} = C_3 \qquad \sigma_3^{-1} = \sigma_3$$

We can therefore conclude that the set of operations which we have listed forms a

group. We note that this group is not Abelian since all elements do not commute. As an example we note that $\sigma_2\sigma_1 = C_3$ while $\sigma_1\sigma_2 = C_3$. The result of Theorem 1 can also be checked from the group multiplication table. We notice that every element of the group occurs once and only once in a given row or column of the group multiplication table. The group of operations which we have described here is generally known as the group C_{3v} and is the group which leaves the ammonia molecule (NH_3) invariant.

As another example of a group, we shall consider the numbers 1, -1, i, -i and consider all possible products of these numbers. In this case the multiplication is just the ordinary multiplication of complex numbers which is both associative and commutative. The group multiplication table for this group would be:

	1	-1	i	-i
1	1	-1	i	-i
-1	-1	1	-i	i
i	i	-i	-1	1
-i	-i	i	1	-1

Once again we see that the product of any two elements is a member of the set. The number 1 serves as the identity element ment. It is clear from the multiplication table that the inverse of every element exists. This set of numbers, therefore, forms a group under the ordinary multiplication of numbers. As we have mentioned the multiplication of complex numbers is commutative and this means that this group is Abelian.

2. Subgroups, Cosets and Classes

Any collection of elements of a group which themselves obey the group postulates is called a subgroup of the original group. Let $\mathcal{H}$ be a subgroup of order h of a group $\mathcal{G}$ of order g. We shall denote the elements of $\mathcal{H}$ by $B_1 = E, B_2, B_3, \ldots B_h$ and the elements of $\mathcal{G}$ by $A_1 = E, A_2, A_3, \ldots A_g$. We then define the collection of elements $\mathcal{H}A_k = B_1A_k, B_2A_k, \ldots B_hA_k$ (where A_k is not in $\mathcal{H}$) as the right coset of $\mathcal{H}$ with respect to A_k. (We can in a similar way define left cosets by multiplying from the left by A_k.) This right coset of $\mathcal{H}$ is clearly not a group. If it were, it would contain the identity element, E, which in turn would mean that for some element of $\mathcal{H}$, say B_r, $B_rA_k = E$ or $A_k = B_r^{-1}$, which violates the rule that A_k is not in $\mathcal{H}$. We can go further and show that this coset contains no element in common with $\mathcal{H}$. If it did contain an element, B_r, of $\mathcal{H}$ then for some element, B_s, of $\mathcal{H}$ we would have $B_sA_k = B_r$. This in turn means that $A_k = B_rB_s^{-1}$. Since both B_r and B_s^{-1} are in $\mathcal{H}$ this implies that A_k is in $\mathcal{H}$. This again violates the definition of a coset. We can go still further and show any two cosets either contain the same elements or have no element in common. If the two cosets are $\mathcal{H}A_k$ and $\mathcal{H}A_m$ and they were to contain an element in common, we would have $B_rA_k = B_sA_m$ or $A_kA_m^{-1} = B_r^{-1}B_s$. From this we conclude that $A_kA_m^{-1}$ is contained in $\mathcal{H}$. If this is true, the collection of elements $\mathcal{H}A_kA_m^{-1}$ is identical with $\mathcal{H}$ except possibly for order. This means that $\mathcal{H}A_kA_m^{-1}A_m$ which is identical with $\mathcal{H}A_k$ is, except for order, identical with $\mathcal{H}A_m$.

Thus the two cosets $\mathcal{H}A_k$ and $\mathcal{H}A_m$ are completely identical if they have even one element in common. Now let us consider the collection, say n - 1 in number, of distinct cosets. These in addition to $\mathcal{H}$ completely exhaust the group for every element of the group is in either $\mathcal{H}$ or one of the cosets. (It is clear that every element of the group is in one of the cosets since $B_1A_k = A_k$ belongs to one of the cosets for any A_k in $\mathcal{G}$.) From this we can see that g = hn. In other words, the order of any subgroup is a divisor of the order of the group.

As an example of a subgroup of a finite group $\mathcal{G}$ consider the collection of all powers of a given element A of $\mathcal{G}$

$$A^0 = E,\ A,\ A^2,\ \ldots\ A^m,\ \ldots\ A^n,\ \ldots$$

All these are elements of the group $\mathcal{G}$. Since this group is finite, only a finite number of different elements of the group can appear in this sequence. Let n + 1 be the first power for which an element is the same as some earlier power, say the m^{th}. Then we have that $A^{n+1} = A^m$. We can show that m must be 1. If it were not, we would have that $A^n = A^{m-1}$ which contradicts the assumption that n + 1 was the first power for which an element was identical with a preceding element. Therefore $A^{n+1} = A$ from which it follows that $A^n = E$, and $A^{n+k} = A^k$. From this we see that the elements which appear in this series of powers of A are distinct and then, after one of the elements is equal to the identity element, the elements repeat starting with A in the same order. The first power of an element which is equal to the identity element is called the order of the element. The collection of elements A, A^2, ... $A^n = E$ forms a subgroup of the original group $\mathcal{G}$. It is easy to show that this collection of elements satisfies the group postulates and in addition forms an Abelian subgroup of the original group. (Any group which is formed out of powers of a given element is called a cyclic group.) From this argument we see that, since the order of the subgroup formed from powers of an element is equal to the order of the element, that the order of the elements of a group are all divisors of the order of the group $\mathcal{G}$

To illustrate the concepts of subgroups and cosets let us consider the subgroups of C_{3v}. From the multiplication table it is easy to see that the collection $\{E,\ C_3,\ C_3^2\}$ forms a subgroup of the original group. This is a subgroup formed from the powers of the group element C_3 which is an element of order 3. In addition E and σ_1 form a subgroup as do E and σ_2, and E and σ_3. There can be no subgroups of higher order since three is the largest divisor of six. With respect to the subgroup $\{E,\ C_3,\ C_3^2\}$ we can find the right cosets of this subgroup. Let us multiply this subgroup from the right by σ_1. We obtain (from the group multiplication table) the elements σ_1, σ_2, σ_3. This in addition to the original subgroup completely exhaust the group. Multiplication of the subgroup from the right with σ_2 or with σ_3 will merely

reproduce (except for order) the right coset we have written above. Thus the group C_{3v} can be decomposed as into its right cosets as follows:

$$\{E, C_3, C_3^2\} \{\sigma_1, \sigma_2, \sigma_3\}$$

Similarly, if we were to decompose the group C_{3v} into right cosets with respect to the subgroup E, we would obtain:

$$\{E, \sigma_1\} \{C_3, \sigma_2\} \{C_3^2, \sigma_3\}$$

If X is any element of a group $\mathcal{G}$, then X^{-1} A X is called the conjugate of A with respect to X. For any subgroup $\mathcal{H}$ of $\mathcal{G}$, we can define the collection of elements $X^{-1} \mathcal{H} X$. It is simple to show that this collection of elements also forms a group which is called the subgroup conjugate to $\mathcal{H}$ with respect to X are the same as $\mathcal{H}$ for all X in $\mathcal{G}$, then it is said to be an invariant self conjugate, or normal subgroup of $\mathcal{G}$. (We notice that this does not mean that for a given element B of $\mathcal{H}$ that $X^{-1} BX = B$, it only means that the collection $X^{-1} \mathcal{H} X$ is identical with the collection $\mathcal{H}$ even though the order of the elements in the conjugate subgroup may be different.) For invariant subgroups it is clear that the right cosets are the same as the corresponding left cosets. $X^{-1} \mathcal{H} X = \mathcal{H}$ implies that $\mathcal{H} X = X \mathcal{H}$.

If a group $\mathcal{G}$ of order g is decomposed into cosets with respect to an invariant subgroup $\mathcal{H}$ of order h, then the elements of the group can be collected in the following way

$$\mathcal{G} : \mathcal{H}, A_2\mathcal{H}, A_3\mathcal{H}, \ldots A_n\mathcal{H}$$

$$hn = g$$

Here $A_k (k = 2, 3, \ldots n)$ are the elements of $\mathcal{G}$ which generate distinct cosets. For this decomposition, the original invariant subgroup, $\mathcal{H}$, and the cosets, can be considered as entities which form the elements of an abstract group. This is called the factor group of the invariant subgroup and is denoted by $\mathcal{G}/\mathcal{H}$. This is a group of order n. To check that this is a group, let us see if the cosets together with the subgroup $\mathcal{H}$ satisfy the group postulates. First, we must show that the product of two cosets is itself one of the cosets or $\mathcal{H}$. $(\mathcal{H} A_k)(\mathcal{H} A_m)$, because right cosets are the same as left cosets, is the same as $\mathcal{H} A_k A_m \mathcal{H}$ which in turn is the same as $\mathcal{H}\mathcal{H} A_k A_m$. Since $\mathcal{H}$ is a group this yields $\mathcal{H} A_k A_m$ which is again one of the cosets or $\mathcal{H}$. The associative law of multiplication holds since it holds for the elements of the group $\mathcal{G}$. The subgroup $\mathcal{H}$ considered as an abstract group element serves as the

identity element for the factor group since $\mathcal{H}\mathcal{H}A_k = \mathcal{H}A_k = \mathcal{H}A_k\mathcal{H} = \mathcal{H}A_k$. The inverse of an element $\mathcal{H}A_k$ can be found from the requirement $\mathcal{H}A_k\mathcal{H}A_m = \mathcal{H}$. Taking A_m as A_k^{-1} finds the inverse of $\mathcal{H}A_m$. We have, therefore, shown that the invariant subgroup and the cosets of this subgroup when considered as entities form a group.

Having defined an invariant subgroup, we may define another property of groups which is useful in some applications of group theory. Let us imagine that we have found the largest invariant subgroup, $\mathcal{N}_1$, of $\mathcal{G}$. We might then find the largest invariant subgroup, $\mathcal{N}_2$ of $\mathcal{N}_1$ and carry this process along until we have as the final invariant subgroup, the identity element. This series $\mathcal{G}:\mathcal{N}_1:\mathcal{N}_2:\ \ldots\ :\mathcal{N}_r = E$ is called the composition series for the group.

We might notice in passing that the subgroup $\{E,\ C_3,\ C_3^2\}$ forms an invariant subgroup of the group C_{3v}. From the group multiplication table it is a simple matter to check that if we let $\mathcal{H}$ denote this subgroup

$$E^{-1}\mathcal{H}E = \mathcal{H} \qquad \sigma_1^{-1}\mathcal{H}\sigma_1 = \mathcal{H}$$

$$C_3^{-1}\mathcal{H}C_3 = \mathcal{H} \qquad \sigma_2^{-1}\mathcal{H}\sigma_2 = \mathcal{H}$$

$$\left[C_3^2\right]^{-1}\mathcal{H}C_3^2 = \mathcal{H} \qquad \sigma_3^{-1}\mathcal{H}\sigma_3 = \mathcal{H}$$

The elements of the factor group would then be the coset $\{\sigma_1,\ \sigma_2,\ \sigma_3\}$ and the subgroup $E,\ C_3,\ C_3^2$. The factor group $C_{3v}/\mathcal{H}$ is a group of order 2. We have already seen that the subgroup $\{E,\ C_3,\ C_3^2\}$ is the largest subgroup of C_{3v}. Since it is in addition the largest invariant subgroup of C_{3v} and it has no invariant subgroups outside of the identity element we can write out the composition series for the group C_{3v}. In this case the composition series will be

$$C_{3v}:\ \{E,\ C_3,\ C_3^2\}\ :E$$

The concept of conjugate elements is also useful in breaking up a group in another way than we have previously stated. We define all elements conjugate to a given element in a group $\mathcal{G}$ as belonging to the same class. Thus if we take an element A of a group and form

$$E^{-1}AE = A,\ A_2^{-1}AA_2,\ \ldots\ A_g^{-1}AA_g$$

the elements appearing in this series are said to belong to the same class. We might notice that two elements conjugate to the same element are conjugate to each other. Thus, if $B = X^{-1}AX$ and $C = Y^{-1}AY$, then $A = YCY^{-1}$ and $B = X^{-1}YAY^{-1}X =$

$(Y^{-1}X)^{-1} A(Y^{-1}X)$. From this, we see that an alternative way of defining a class is that collection of elements conjugate to each other. In this way, it can easily be seen that a group can be divided into disjoint classes which will completely exhaust the group. (One class of every group will consist of the identity element which is always in a class by itself. This is clear since $X^{-1} E X = E$ for all X in a group.)

As an example of the decomposition of a group into classes consider an Abelian group. If we fix our attention on an element A of this group and form $X^{-1} AX$ for all X in the group, we notice that, since all elements of an Abelian group commute, $X^{-1} A X = X^{-1} X A = A$. This means that for an Abelian group every element is in a class by itself.

We could also divide the group C_{3v} into classes. The identity element forms a class by itself as we have mentioned above. Let us find all elements conjugate to C_3.

$$E^{-1} C_3 E = C_3 \qquad \sigma_1^{-1} C_3 \sigma_1 = C_3^2$$

$$C_3^{-1} C_3 C_3 = C_3 \qquad \sigma_2^{-1} C_3 \sigma_2 = C_3^2$$

$$\left[C_3^2\right]^{-1} C_3 C_3^2 = C_3 \qquad \sigma_3^{-1} C_3 \sigma_3 = C_3^2$$

Thus we see that the elements C_3 and C_3^2 form a class. We can now find the elements conjugate to σ_1

$$E^{-1} \sigma_1 E = \sigma_1 \qquad \sigma_1^{-1} \sigma_1 \sigma_1 = \sigma_1$$

$$C_3^{-1} \sigma_1 C_3 = \sigma_3 \qquad \sigma_2^{-1} \sigma_1 \sigma_2 = \sigma_3$$

$$\left[C_3^2\right]^{-1} \sigma_1 C_3^2 = \sigma_2 \qquad \sigma_3^{-1} \sigma_1 \sigma_3 = \sigma_2$$

We have now exhausted the group. C_{3v} is therefore divided into classes in the following way:

$$\left\{E\right\} \left\{C_3, C_3^2\right\} \left\{\sigma_1, \sigma_2, \sigma_3\right\}$$

We notice that in this division into classes geometrically similar operations fall into the same class. More precisely if two elements are in the same class we can find a new coordinate system in which the one operation is replaced by the other. Thus if we were to choose our coordinate system so that the x axis pointed in the opposite direction the operation C_3^2 in the old coordinate system would be the same as the operation C_3 in the new coordinate system. With this geometric insight it does not

surprise us to learn that operations in the same class have the same order. If $A' = X^{-1}AX$ and A are in the same class and A is an element of the n^{th} order, then $A'^n = (X^{-1}AX)^n = (X^{-1}AX)(X^{-1}AX)\ldots(X^{-1}AX) = X^{-1}A^nX = X^{-1}EX = E$.

3. Isomorphisms and Homomorphisms

Consider a group $\mathcal{G}$ of order g with elements E, A, B, ... and another group $\mathcal{G}'$ of the same order with elements E', A', B', ... These two groups are said to be isomorphic if the elements of one can be put into one to one correspondence with the elements of the other and if, in addition, A' corresponds to A and B' corresponds to B then AB corresponds to A'B'. ((AB)' = A'B'). This property of isomorphism means that the multiplication tables of the two groups can be put into a one to one correspondence. Two groups which are isomorphic have the same properties and structure and differ only in the labeling of the elements. Isomorphic groups can be thought of as corresponding to the same abstract group.

Sometimes it is possible to make each element of a group $\mathcal{G}$ correspond to one and only one element of another group $\mathcal{G}'$ and in addition make the product of elements of $\mathcal{G}$ correspond to the products of the corresponding elements of $\mathcal{G}'$. In this case, the groups are said to be homomorphic. In this case more than one element of $\mathcal{G}$ may correspond to one element of $\mathcal{G}'$. In other words, the correspondence is not one to one and the group $\mathcal{G}$ must have a larger order than $\mathcal{G}'$. If the orders are the same and the groups are homomorphic, then they are isomorphic. If a group $\mathcal{G}$ is homomorphic to a group $\mathcal{G}'$, then the element E' of $\mathcal{G}'$ which corresponds to the identity element E of $\mathcal{G}$ is the identity element of $\mathcal{G}'$. For groups which are homomorphic we have (XE)' = (EX)' = X' = X'E' = E'X'. The only element of $\mathcal{G}'$ which has this property is the identity element. Therefore, we can conclude that E' is the identity element for the group $\mathcal{G}'$. In a similar manner, we can conclude that the inverse of an element X of $\mathcal{G}$ corresponds to the inverse of the element X' of $\mathcal{G}'$.

We can learn still more about this relation of homomorphism. If $\mathcal{G}$ is homomorphic to $\mathcal{G}'$, then the collection of elements of $\mathcal{G}$ which correspond to the identity element, E', of $\mathcal{G}'$ form an invariant subgroup of $\mathcal{G}$. Let those elements which correspond to E' be denoted by E, E_2, E_3, ... E_n. Since $(E_iE_j)' = E'E' = E'$ the product of any pair of elements of the set belongs to the set. The identity element is in the set. If E_i is in the set E_i^{-1} is also in the set. This is true since from $(E_iE_i^{-1})' = E'$, we conclude that $E'(E_i^{-1})' = E'$. This in turn means that $(E_i^{-1})' = E'$ or that E_i^{-1} is a member of the set. Thus we conclude that the set E, E_2, ... E_n forms a group. Let us call this group $\mathcal{H}$. If we can show that $X^{-1}E_iX$ belongs to $\mathcal{H}$ for any E_i in $\mathcal{H}$ and for any X in $\mathcal{G}$, we will have shown that we have an invariant subgroup. We know that $(X^{-1}E_iX)' = (X^{-1})'E'X' = X'^{-1}E'X' = E'$. Thus $X^{-1}E$ belongs to $\mathcal{H}$, and therefore $\mathcal{H}$ is an invariant subgroup.

More can be shown. We can show that the factor group $\mathcal{G}/\mathcal{H}$ is isomorphic with the group $\mathcal{G}'$. Let us first note that the elements of $\mathcal{G}$ which correspond to the same element A' of $\mathcal{G}'$ belong to the same coset of $\mathcal{G}$ with respect to $\mathcal{H}$. Thus if $A_1, A_2, \ldots A_n$ correspond to A', $(A_i^{-1}A_j)' = A'^{-1}A' = E'$. From this we conclude that $A_i^{-1}A_j = E_k$, where E_k is some member of $\mathcal{H}$. Thus the cosets $A_j\mathcal{H}$ and $A_iE_k\mathcal{H} = A_i\mathcal{H}$ are identical and A_j and A_i lie in the same coset. If we now show that if two elements of $\mathcal{G}$ lie in the same coset they correspond to the same element of the group $\mathcal{G}'$, we will have shown that there is a one to one correspondence between the elements of the factor group $\mathcal{G}/\mathcal{H}$ and the group $\mathcal{G}'$. If two elements A_i and A_j lie in the same coset then $A_iE_k = A_j$ for some E_k in $\mathcal{H}$. Therefore, we have that $(A_j)' = A' = A_i'E' = A_j' = A_i'$. If we show in addition that the product of two elements of the factor group corresponds to the product of the corresponding elements of the group $\mathcal{G}'$, we will have shown that the group $\mathcal{G}'$ is isomorphic with the factor group $\mathcal{G}/\mathcal{H}$. This is clearly so since, if $A\mathcal{H}B\mathcal{H} = C\mathcal{H}$, then $AE_kBE_m = CE_n$ or $A'E'B'E' = CE'$ which means that $A'B' = C'$. From these arguments we also conclude that the order of the group $\mathcal{G}'$ must be a divisor of the order of the group $\mathcal{G}$. It is also clear from the preceding discussion that a group is homomorphic to its own factor group.

We mentioned earlier that any group which has the same multiplication table and whose elements can be put into one to one correspondence with a given group is isomorphic with the given group. We shall illustrate this by giving two groups isomorphic with the group C_{3v} which we have defined above.

Consider the numbers one through three: 1, 2, 3. Any other arrangement of these numbers, for example, 2, 1, 3 is called a permutation of the numbers 1 through 3. The operation which rearranges the numbers is called a permutation. This permutation can be specified by stating which number 1 goes into, which number 2 goes into and which number 3 goes into. The way a permutation is denoted is $\begin{pmatrix} 1 & 2 & 3 \\ a_1 & a_2 & a_3 \end{pmatrix}$. The meaning of this symbol is that 1 is replaced by a_1, 2 is replaced by a_2 and 3 is replaced by a_3, where a_1, a_2, and a_3 are three distinct numbers from 1 through 3. The collection of all operations of this type is called a symmetric group of order 3 and has 3! = 6 members. The fact that these elements form a group can easily be verified; the inverse of $\begin{pmatrix} 1 & 2 & 3 \\ a_1 & a_2 & a_3 \end{pmatrix}$ being $\begin{pmatrix} a_1 & a_2 & a_3 \\ 1 & 2 & 3 \end{pmatrix}$. The six permutations in this group can be written

$$P_1 = E = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix} \qquad P_2 = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \qquad P_3 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix}$$

$$P_4 = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix} \qquad P_5 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \qquad P_6 = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}$$

The product of two permutations $P_n P_m$ means that the permutation P_m is followed by the permutation P_n. (Many authors use the opposite convention.) From this definition we can find, for example, $P_5 P_6$

$$P_5 P_6 = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix} = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} = P_2$$

What we have done in performing this multiplication is to replace 1 by 2 from P_6 and then replace 2 by 2 from P_5. We replace 2 by 1 from P_6 and replace 1 by 3 from P_5. We replace 3 by 3 from P_6 and replace 3 by 1 from P_5 and then identify the resulting arrangement with the permutation P_2. By carrying out all possible multiplications of pairs, it can readily be checked that the set of six permutations form a group and the multiplication table can be constructed. If the identification with the group C_{3v} is made as follows

$$E \longleftrightarrow P_1 \qquad \sigma_1 \longleftrightarrow P_4$$

$$C_3 \longleftrightarrow P_2 \qquad \sigma_2 \longleftrightarrow P_5$$

$$C_3^2 \longleftrightarrow P_3 \qquad \sigma_3 \longleftrightarrow P_6$$

It will be found that the multiplication table for the two groups is the same. The groups are therefore isomorphic and correspond to the same abstract group.

Another group isomorphic with C_{3v} can be found as follows. Imagine the collection of matrices:

$$M_1 = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad M_2 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad M_3 = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

$$M_4 = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad M_5 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \qquad M_6 = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{3} \end{pmatrix}$$

We now take all possible products of two matrices. For example $M_5 M_6$

$$M_5 M_6 = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$$

Therefore, $M_5M_6 = M_2$. Similarly, in taking all possible products of pairs of elements, we would find that the product would always be one of the original six matrices. The second group postulate is satisfied because we are using matrix multiplication. This group of elements contains the identity element, namely: M_1. The multiplication of all pairs would also confirm the existence of the inverse of every element of the set. Thus it is seen that this set of six matrices form a group. If the one to one correspondence

$$E \longleftrightarrow M_1 \qquad \sigma_1 \longleftrightarrow M_4$$

$$C_3 \longleftrightarrow M_2 \qquad \sigma_2 \longleftrightarrow M_5$$

$$C_3^2 \longleftrightarrow M_3 \qquad \sigma_3 \longleftrightarrow M_6$$

is made then it can easily be checked that this collection of matrices forms a group isomorphic with the group C_{3v} of the permutation group of order 3! mentioned in the last paragraph.

With this we conclude our general discussion of groups and proceed in the next chapter to a discussion of representation theory. If something more complete than this sketchy treatment of groups is desired the reader is directed to "Die Theorie der Gruppen von Endlicher Ordnung" by Andreas Speiser.

Chapter II

REPRESENTATIONS OF A GROUP

1. Definition and General Properties of a Representation

The concept of a representation of a group forms the basis for much of the application of group theory. By a representation of a group we mean any set of elements which can be put in correspondence to the elements of a group and which have the same multiplication table. A representation is homomorphic to the group that it represents. If the homomorphism is an isomorphism, the representation is said to be true or faithful. It is clear from this definition that any representation of a factor group is a representation of the given group. We merely assign to the element representing a given coset all the elements in the coset and then we have the representation of the total group. In this case the representation is not true. In what follows we shall follow closely "Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren" by Eugene Wigner (Friedr. Vieweg und Sohn Akt. -Ges., Braunschweig, 1931).

A useful form of representation is the representation of a group through square matrices. To each element of the group, A, we have a corresponding matrix* $\Gamma(A)$. These matrices are required to multiply according to the group multiplication table. Thus if AB = C then $\Gamma(A)\ \Gamma(B) = \Gamma(C)$. Here we use the ordinary laws of a matrix multiplication. If $\Gamma(A)_{ij}$ (i, j = 1 . . . n) are the elements of the matrix $\Gamma(A)$ (n is called the dimension of the representation) then by the element of the product $\Gamma(A)\ \Gamma(B)$, we mean

$$\left[\Gamma(C)\right]_{km} = \left[\Gamma(A)\ \Gamma(B)\right]_{km} = \sum_{i=1}^{n} \Gamma(A)_{ki}\, \Gamma(B)_{im} \tag{2-1}$$

We shall restrict ourselves to non singular matrices. (Those which possess an inverse are called non singular.) In this case, the matrix representing the identity operation must be the unit matrix

$$\Gamma(E)_{ij} = \delta_{ij} \tag{2-2}$$

The matrix representing the inverse of an operation A will be the inverse of the matrix representation A. That is

$$\Gamma(A^{-1}) = \left[\Gamma(A)\right]^{-1} \tag{2-3}$$

- - - - - - - - - - - - - - - -

*We denote matrices by bold faced letters: $\Gamma(A)$, $\mathbf{A}$, $\mathbf{B}$ and the elements of these matrices by $\Gamma(A)_{ij}$, A_{ij}, B_{ij}.

(REPRESENTATIONS OF A GROUP)

One can generate many representations of a group from one representation by letting all the matrices in the representation undergo the same similarity transformation. Thus we note that if $\mathbf{S}$ is a non singular matrix and we define $\Gamma'(A) = \mathbf{S}^{-1} \Gamma(A) \mathbf{S}$ for all A in the group, then the multiplication of the primed matrices will follow the same multiplication table that the unprimed ones do. Thus if

$$\Gamma(A)\ \Gamma(B) = \Gamma(C)$$

then

$$\begin{aligned} \Gamma'(A)\ \Gamma'(B) &= \mathbf{S}^{-1}\,\Gamma(A)\mathbf{S}\ \ \mathbf{S}^{-1}\,\Gamma(B)\mathbf{S} \\ &= \mathbf{S}^{-1}\,\Gamma(A)\,\Gamma(B)\mathbf{S} = \mathbf{S}^{-1}\,\Gamma(C)\mathbf{S} \\ &= \Gamma'(C) \end{aligned}$$

Representations related in this way, by a similarity transformation, are called equivalent representations.

Let us illustrate a representation of a group by finding a representation of the group C_{3v}. Imagine that we had two vectors pointing from the center of the triangle, in Fig. 1-2, to the corners 1 and 2. (See Fig. 2-1) Let us denote these vectors by $\vec{a}_1$ and $\vec{a}_2$. These vectors will be sent, by operations of the group C_{3v} into some rotated set of vectors. The rotated vectors can, in turn, be expressed as a linear

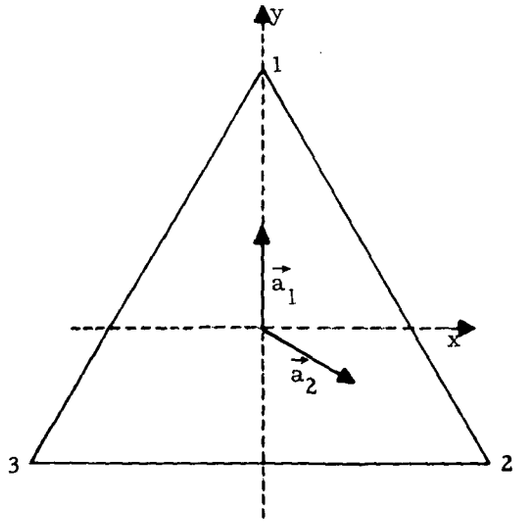


Fig. 2-1

combination of the original vectors. Thus if R is some operation of the group C_{3v}, we can write

$$R\vec{a}_i = \sum_{j=1}^{2} \Gamma(R)_{ji}\, \vec{a}_j \qquad i = 1, 2 \tag{2-4}$$

Here $R\vec{a}_i$ is the vector $\vec{a}_i$ after the operation R has been performed on it. If this operation R is followed by another operation R'

$$R'R\vec{a}_i = \sum_{j=1}^{2} \sum_{k=1}^{2} \Gamma(R')_{kj}\, \Gamma(R)_{ji}\, \vec{a}_k \tag{2-5}$$

Thus we see that the matrix which describes the operation R'R is obtained from the matrices of R and R' by the simple rules of matrix multiplication. Thus

$$\Gamma(R'R) = \Gamma(R')\,\Gamma(R)$$

These matrices which describe the transformations which the vectors $\vec{a}_1$ and $\vec{a}_2$ undergo therefore form a representation of the group. The vectors $\vec{a}_1$ and $\vec{a}_2$ are said to form a basis for this representation.

Let us exhibit these matrices. Consider for example the operation σ_1. This operation sends the vector $\vec{a}_1$ into itself. The vector $\vec{a}_2$ now points in a direction 30^o below the negative x axis. This vector is just the negative of the sum of $\vec{a}_1$ and $\vec{a}_2$. Thus we have

$$\sigma_1\vec{a}_1 = \vec{a}_1$$

$$\sigma_1\vec{a}_2 = -\vec{a}_1 - \vec{a}_2$$

or

$$\Gamma(\sigma_1)_{11} = 1 \qquad \Gamma(\sigma_1)_{12} = -1$$

$$\Gamma(\sigma_1)_{21} = 0 \qquad \Gamma(\sigma_1)_{22} = -1$$

$$(\sigma_1) = \begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}$$

In a similar way, matrices representing all the operators in the group can be found. They are as follows

$$\Gamma(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \Gamma(\sigma_1) = \begin{pmatrix} 1 & -1 \\ 0 & -1 \end{pmatrix}$$

$$\Gamma(C_3) = \begin{pmatrix} 0 & -1 \\ 1 & -1 \end{pmatrix} \qquad \Gamma(\sigma_2) = \begin{pmatrix} -1 & 0 \\ -1 & 1 \end{pmatrix} \tag{2-6}$$

$$\Gamma(C_3^{\,2}) = \begin{pmatrix} -1 & 1 \\ -1 & 0 \end{pmatrix} \qquad \Gamma(\sigma_3) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}$$

We notice that this representation is faithful since there is a one to one correspondence between elements of the group and the matrices.

If we look back at Chapter I we find that we have another two-dimensional representation of the group C_{3v}. In the notation of this chapter we denote

$$\Gamma'(E) = M_1 \qquad \Gamma'(\sigma_1) = M_4$$

$$\Gamma'(C_3) = M_2 \qquad \Gamma'(\sigma_2) = M_5 \tag{2-7}$$

$$\Gamma'(C_3^{\,2}) = M_3 \qquad \Gamma'(\sigma_3) = M_6$$

we see that these matrices also form a representation of the group.

One might wonder if these two matrix representations of the group are related by a similarity transformation and are equivalent. This is indeed the case. The matrices $\Gamma'(R)$ have as a basis a pair of unit vectors $\vec{a}_1'$ pointing along the +x axis and $\vec{a}_2'$ pointing along the +y axis. That the matrices which these vectors generate are the matrices $\Gamma'(R)$ can easily be checked. We are now in a position to find the similarity transformation relating these two two-dimensional representations. The vectors $\vec{a}_1'$ and $\vec{a}_2'$ can be expressed in terms of $\vec{a}_1$ and $\vec{a}_2$.

$$\vec{a}_i = \sum_{j=1}^{2} S_{ji}\, \vec{a}_j \tag{2-8}$$

From the geometry of an equilateral triangle it can easily be seen that

$$\vec{a}_1' = \frac{1}{\sqrt{3}}\, \vec{a}_1 + \frac{2}{\sqrt{3}}\, \vec{a}_2 \tag{2-9}$$

$$\vec{a}_2' = \vec{a}_1$$

or

$$S = \begin{pmatrix} \frac{1}{\sqrt{3}} & 1 \\ \frac{2}{\sqrt{3}} & 0 \end{pmatrix} \tag{2-10}$$

or conversely

$$\begin{aligned} \vec{a}_1 &= \vec{a}_2' \\ \vec{a}_2 &= \frac{\sqrt{3}}{2}\vec{a}_1' - \frac{1}{2}\vec{a}_2' \\ S^{-1} &= \begin{pmatrix} 0 & \frac{\sqrt{3}}{2} \\ 1 & -\frac{1}{2} \end{pmatrix} \end{aligned} \tag{2-11}$$

In this way, we can find the primed matrices in terms of the unprimed matrices

$$\begin{aligned} R\vec{a}_i' &= \sum_{j=1}^{2} S_{ji}\, R\vec{a}_j \\ &= \sum_{j=1}^{2}\sum_{k=1}^{2} S_{ji}\, \Gamma(R)_{kj}\, \vec{a}_k \\ &= \sum_{j=1}^{2}\sum_{k=1}^{2}\sum_{m=1}^{2} S_{ji}\, \Gamma(R)_{kj}\, S^{-1}_{mk}\, \vec{a}_m' \\ &= \sum_{m} \Gamma'(R)_{mi}\, \vec{a}_m' \end{aligned} \tag{2-12}$$

or in matrix notation

$$\Gamma'(R) = S^{-1}\, \Gamma(R) S \tag{2-13}$$

We have seen, therefore, that the two two-dimensional representations $\Gamma(R)$ and $\Gamma'(R)$ are equivalent and the similarity transformation transforming all the matrices in one representation to those in the other is the matrix S representing the transformation of bases.

We might also note that the matrices $\Gamma'(R)$ are unitary. (See Appendix.) In this case, $\Gamma'(R)\dagger = \Gamma'(R^{-1}) = \left[\Gamma'(R)\right]^{-1}$. The matrices $\Gamma(R)$ are not unitary but are related by a similarity transformation to the unitary matrices $\Gamma'(R)$. We shall be interested, primarily, in unitary matrices.

We can find other representations of the group C_{3v}. One trivial representation is obtained by identifying every element of the group with one by one matrices having

+1 as their only element. That is $\Gamma(E) = \Gamma(C_3) = \ldots = \Gamma(\sigma_1) = (1)$. This clearly satisfies the definition of a representation of the group. It is clear that any group can be represented in this manner. This is called the identity representation of the group.

We can also represent the group C_{3v} by one-dimensional matrices in another way. Let us set

$$\Gamma(E) = \Gamma(C_3) = \Gamma(C_3^2) = (1)$$

and (2-14)

$$\Gamma(\sigma_1) = \Gamma(\sigma_2) = \Gamma(\sigma_3) = (-1)$$

Thus, for example

$$\Gamma(C_3)\,\Gamma(\sigma_2) = \Gamma(C_3\sigma_2) = (1)(-1) = (-1) = \Gamma(\sigma_1)$$

It can be easily checked that the remainder of the group multiplication table is checked by this representation. We have now found two one-dimensional representations of C_{3v}. These, however, are not equivalent. There is no one by one matrix which brings the identity representation into the second of the one-dimensional representations through a similarity transformation.

The representation of the group C_{3v} given by Eq. (2-14) affords an example of a representation generated from a representation of a factor group. We remember that in Chapter I we found that the group $\{C_3, C_3^2, E\}$ formed an invariant subgroup of C_{3v}. This subgroup together with the coset $\{\sigma_1, \sigma_2, \sigma_3\}$, when considered as elements of an abstract group, form the elements of the factor group. If we denote the elements of this factor group by E' (corresponding to the invariant subgroup C_3, C_3^2, E) and A' (corresponding to the coset $\{\sigma_1, \sigma_2, \sigma_3\}$), then the multiplication table for this factor group is given in Fig. 2-2. This group can be represented by representing E' by the matrix (1) and A' by the matrix (-1). As we mentioned in the first paragraph of this section, we can generate a representation of the group C_{3v} from this representation of the factor group by letting the matrices corresponding to E, C_3, and C_3^2 be (1) and the matrix corresponding to the remaining elements of the group be (-1). This is the representation of Eq. (2-14).

	E'	A'
E'	E'	A'
A'	A'	E'

Fig. 2-2

We have seen in this section how we can generate from one representation of a group many others through the use of a similarity transformation. There is another method by which we can, from a given representation, generate another. If for two elements of a group we have the relation that AB = C and we have for the matrices

representing these elements $\Gamma(A)\ \Gamma(B) = \Gamma(C)$, then it is possible to generate another representation of the group in the following way. Let us take the transpose of both sides of this multiplication of matrices. This yields $\widetilde{\Gamma(B)}\ \widetilde{\Gamma(A)} = \widetilde{\Gamma(C)}$.* Let us now take the inverse of both sides of the last relation. This yields $\left[\widetilde{\Gamma(A)}\right]^{-1}\left[\widetilde{\Gamma(B)}\right]^{-1} = \left[\widetilde{\Gamma(C)}\right]^{-1}$. Thus the matrices which are the inverses of the transposes of the matrices representing the elements of the group also multiply in the same way as the matrices in the original representation. These new matrices also form a representation of the group. In the case of unitary representations (representations in which all the matrices are unitary) the inverse of the transpose is the same as the complex conjugate of the original matrix. In this event the new representation will just be the complex conjugate of the original representation.

2. Reducible and Irreducible Representations of a Group

A representation $\Gamma(R)$ of a group (where R is an element of the group) is called reducible if all the matrices in the group can be put in the form of (2-15) by a single similarity transformation

$$\Gamma'(R) = S^{-1}\Gamma(R)S = \left(\begin{array}{c|c} \Gamma_1(R) & Q(R) \\ \hline 0 & \Gamma_2(R) \end{array}\right) \qquad (2\text{-}15)$$

if n were the dimension of the representation $\Gamma(R)$, and $\Gamma_1(R)$ were a square matrix with n_1 rows and columns, $\Gamma_2(R)$ would be a square matrix with $n_2 = n - n_1$ rows and columns. $Q(R)$ is a rectangular matrix with n_1 rows and n_2 columns. The 0 in (2-15) represents a matrix with n_1 columns and n_2 rows having all elements zero. If there exists no similarity transformation which can bring all the matrices of a representation to the form (2-15), then the representation is called irreducible. We can also notice that for a reducible representation the portions $\Gamma_1(R)$ and $\Gamma_2(R)$ also form a representation of the group. This is most easily seen by taking the product of two matrices in the representation. Thus

$$\Gamma'(RR') = \Gamma'(R)\ \Gamma'(R') = \left(\begin{array}{c|c} \Gamma_1(R) & Q(R) \\ \hline 0 & \Gamma_2(R) \end{array}\right)\left(\begin{array}{c|c} \Gamma_1(R) & Q(R') \\ \hline 0 & \Gamma_2(R') \end{array}\right) \qquad (2\text{-}16)$$

---

*We make use here of the fact that the transpose of the product of two matrices is just the product of the transposes in the reverse order. This is easily seen since the i, j^{th} element of $\left[\widetilde{AB}\right]$ is $\sum_k A_{jk}B_{ki}$. The i, j^{th} element of $\widetilde{B}\widetilde{A}$ is $\sum_k B_{ik}A_{jk}$. Thus we have shown $\left[\widetilde{AB}\right] = \widetilde{B}\widetilde{A}$

$$= \left(\begin{array}{c|c} \Gamma_1(R)\ \Gamma_1(R') & \Gamma_1(R)\ Q(R') + Q(R)\ \Gamma_2(R') \\ \hline 0 & \Gamma_2(R)\ \Gamma_2(R') \end{array}\right) \qquad \text{(2-16 con'd)}$$

$$= \left(\begin{array}{c|c} \Gamma_1(RR') & Q(RR') \\ \hline 0 & \Gamma_2(RR') \end{array}\right)$$

Therefore we have that

$$\begin{aligned} \Gamma_1(RR') &= \Gamma_1(R)\ \Gamma_1(R') \\ \Gamma_2(RR') &= \Gamma_2(R)\ \Gamma_2(R') \end{aligned} \qquad (2\text{-}17)$$

Thus $\Gamma_1(R)$ and $\Gamma_2(R)$ form representations of a group. These two new representations may or may not be reducible themselves.

If this reduced matrix $\Gamma'(R)$ is unitary, we can show that the $Q(R)$ portion of the matrix must be zero. Since the matrix for the inverse of a group element R, in the case of a unitary representation, is the complex conjugate transpose of the matrix representation R, the matrix for $\Gamma'(R^{-1})$ would have the form

$$\left(\begin{array}{c|c} \left[\Gamma_1(R)\right]\dagger & 0 \\ \hline \left[Q(R)\right]\dagger & \left[\Gamma_2(R)\right]\dagger \end{array}\right) \qquad (2\text{-}18)$$

since all matrices in the representation of the group must have the form (2-15), we see at once that $\left[Q(R)\right]\dagger = 0$ or $Q(R) = 0$. Thus unitary matrices in reduced form will have square unitary matrices down the diagonal and zeros elsewhere. In this case, the reducible nature of $\Gamma(R)$ can be expressed in the equation

$$\Gamma(R) = \Gamma_1(R) + \Gamma_2(R) \qquad (2\text{-}19)$$

This equation does not mean the addition of the matrices in the ordinary sense but merely expresses the fact that $\Gamma(R)$ can be put in the form (2-15) by a similarity transformation.

In the example of the two two-dimensional representations of the group C_{3v},

we saw that one was unitary and the other was not. We were able, in this case, to find a similarity transformation which sent the non unitary representation into the unitary one. This is actually a general result and we shall now show this.

Theorem 2: Any representation of a group consisting of non singular matrices can be transformed by a suitable similarity transformation into a unitary representation (is equivalent to a unitary representation.

Proof: Consider a group $\mathcal{G}$ with elements which we denote by R. We assume we have a representation of this group $\Gamma(R)$ which consists of non singular square matrices. (A necessary and sufficient condition that a matrix is non singular is that its determinant does not vanish.) Let us construct the matrix

$$H = \sum_R \Gamma(R)\ \Gamma(R)\dagger \tag{2-20}$$

Here the summation goes over all elements R in $\mathcal{G}$ and $\Gamma(R)\dagger$ is the adjoint (complex conjugate transpose) of $\Gamma(R)$. This matrix H is Hermitian as can easily be seen. If we take the transpose of (2-20) we obtain

$$\begin{aligned} \tilde{H} &= \sum_R \tilde{\Gamma}(R)\dagger\ \tilde{\Gamma}(R) \\ &= \sum_R \Gamma(R)^*\ \Gamma(R)\dagger^* \end{aligned} \tag{2-21}$$

This shows that the transpose of H is just the complex conjugate of H which is just another way of saying the matrix is Hermitian. A well known matrix theorem states that a Hermitian matrix can be brought to diagonal form* by a unitary transformation. Let us bring H to diagonal form by the unitary transformation U. That is

$$U^{-1}\ HU = D;\ U\dagger = U^{-1} \tag{2-22}$$

where D is a diagonal matrix.

We have therefore

$$\begin{aligned} D &= \sum_R U^{-1}\ \Gamma(R)\ \Gamma(R)\dagger\ U \\ &= \sum_R U^{-1}\ \Gamma(R)\ U \left[U^{-1}\ \Gamma(R) U\right]\dagger \\ &= \sum_R \Gamma'(R)\ \Gamma'(R)\dagger \end{aligned} \tag{2-23}$$

*A matrix D is said to be diagonal when it has nothing but zeros off the main diagonal. That is $D_{ij} = 0$ for $i \neq j$.

where

$$\Gamma'(R) = U^{-1} \Gamma(R) U \tag{2-24}$$

The diagonal elements of D, namely D_{jj}, are given by

$$D_{jj} = \sum_k \sum_R \Gamma'(R)_{jk} \Gamma'(R)^*_{jk} \tag{2-25}$$

and are, therefore, all real and $D_{jj} \geq 0$. They cannot be equal to zero unless $\Gamma'(R)_{jk} = 0$ for all R and k. This is impossible since this would mean that the determinant of $\Gamma'(R)$ would vanish since all the elements in one row would be equal to zero. This contradicts the hypothesis that $\Gamma(R)$ is non singular. Since the diagonal elements of D are all real and positive, we can define matrices $D^{1/2}$ and $D^{-1/2}$ having all positive diagonal elements by taking the positive square root of all the diagonal elements of D. We now see that

$$1 = D^{-1/2} \sum_R \Gamma'(R) \Gamma'(R)\dagger D^{-1/2} \tag{2-26}$$

Let us now define

$$\Gamma''(R) = D^{-1/2} \Gamma'(R) D^{1/2} \tag{2-27}$$

We are now in a position to show that the matrices $\Gamma''(R)$ are unitary. Consider

$$\Gamma''(R) \Gamma''(R)\dagger = \left[D^{-1/2} \Gamma'(R) D^{1/2}\right] \left[D^{-1/2} \Gamma'(R) D^{1/2}\right]^\dagger \tag{2-28}$$

Let us now insert the matrix 1 in the form of Eq. (2-26) between the square brackets in Eq. (2-28)

$$\begin{aligned}
\Gamma''(R) \Gamma''(R)\dagger &= \left[D^{-1/2} \Gamma'(R) D^{1/2}\right] \left[D^{-1/2} \Gamma'(R) D^{1/2}\right]\dagger \\
&= D^{-1/2} \Gamma'(R) D^{1/2} \left[D^{-1/2} \sum_{R'} \Gamma'(R') \Gamma'(R')\dagger D^{-1/2}\right] D^{1/2} \Gamma'(R)\dagger D^{-1/2} \\
&= D^{-1/2} \left[\sum_{R'} \Gamma'(R) \Gamma'(R') \Gamma'(R')\dagger \Gamma'(R)\dagger\right] D^{-1/2} \\
&= D^{-1/2} \left\{\sum_{R'} \Gamma'(R) \Gamma'(R') \left[\Gamma'(R) \Gamma(R')\right]\dagger\right\} D^{-1/2} \\
&= D^{-1/2} \sum_{R'} \Gamma'(RR') \Gamma'(RR')\dagger D^{-1/2}
\end{aligned} \tag{2-29}$$

(2. REDUCIBLE AND IRREDUCIBLE REPRESENTATIONS OF A GROUP)

We have noticed from Theorem 1 in the first chapter that if R' runs over all the elements in the group the product RR' runs over all the elements of the group once more. Therefore, we have that

$$\Gamma''(R)\ \Gamma''(R)^{\dagger} = D^{-1/2} \sum_{R} \Gamma'(R)\ \Gamma'(R)^{\dagger}\ D^{-1/2} = 1 \tag{2-30}$$

This is just the condition that makes a matrix unitary. Thus the representation $\Gamma''(R)$ is a unitary representation. The similarity transformation which brings the non unitary representation into the unitary representation is through the matrix $UD^{1/2}$

$$\Gamma''(R) = \left[UD^{1/2}\right]^{-1}\ \Gamma(R)\ UD^{1/2} = D^{-1/2}\ U^{-1}\ \Gamma(R)\ UD^{1/2} \tag{2-31}$$

is the desired unitary matrix.

From the result of this theorem it can be seen that unitary representations of a group are particularly interesting to study. In this connection there is another property of unitary representation which is important. It turns out to be the case that equivalent unitary representations are related by a similarity transformation using a unitary matrix. This result is summed up in the next theorem.

> Theorem 3: If two unitary representations of a group $\mathcal{G}$ are equivalent through the use of a matrix S, then a unitary matrix U can be found which, when used in a similarity transformation, sends the matrices in one representation into those of the other. Thus if $\Gamma'(R)$ and $\Gamma(R)$ are the two representations and we have
>
> $$\Gamma'(R) = S^{-1}\ \Gamma(R) S \tag{2-32}$$
>
> then a unitary matrix U can be found such that
>
> $$\Gamma'(R) = U^{-1}\ \Gamma(R) U = U^{\dagger}\ \Gamma(R) U \tag{2-33}$$

Proof: From Eq. (2-32) we have that

$$S\Gamma'(R) = \Gamma(R) S \tag{2-34}$$

for all R in $\mathcal{G}$. Let us take the adjoint of both sides of this expression

$$\Gamma'(R)^{\dagger}\ S^{\dagger} = S^{\dagger}\Gamma(R)^{\dagger} \tag{2-35}$$

or

$$\Gamma'(R^{-1})\, S^{\dagger} = S^{\dagger}\Gamma(R^{-1}) \tag{2-36}$$

for all R in $\mathcal{G}$. The latter relation is true because of the unitary nature of the two representations. Since (2-36) is valid for all operators R in the group and since for every element of the group there is a corresponding inverse, we have

$$\Gamma'(R)\; S^{\dagger} = S^{\dagger}\Gamma(R) \tag{2-37}$$

If we multiply (2-34) through from the right by $S^{\dagger}$ and make use of (2-37), we obtain

$$\begin{aligned} \Gamma(R)\; SS^{\dagger} &= S\Gamma'(R)\, S^{\dagger} \\ &= SS^{\dagger}\Gamma(R) \end{aligned} \tag{2-38}$$

By methods similar to those used in the proof of the last theorem, we see that $SS^{\dagger}$ is a Hermitian matrix. Under some unitary transformation V it can be brought to diagonal form D.

$$\begin{aligned} V^{-1}\, SS^{\dagger}\, V &= D \\ SS^{\dagger} &= VDV^{-1} \end{aligned} \tag{2-39}$$

In analogy to the previous theorem we can show that D will have positive diagonal elements and we can, therefore, define a matrix $D^{-1/2}$ which is diagonal with real diagonal elements. If we denote $K = VD^{-1/2}V^{-1}$ then $U = KS$ will be shown to be the matrix which we are looking for. In order to do this, we must show that U is unitary and that $\Gamma'(R) = U^{-1}\,\Gamma(R)U$. In order to show that U is unitary we show that $UU^{\dagger} = 1$.

$$UU^{\dagger} = KSS^{\dagger}K^{\dagger} = VD^{-1/2}V^{-1}\; SS^{\dagger}\; VD^{-1/2}V^{-1} \tag{2-40}$$

In (2-40) we have made use of the fact that V is unitary and that $D^{-1/2}$ has nothing but real diagonal elements. Therefore

$$UU^{\dagger} = VD^{-1/2}\, DD^{-1/2}\, V^{-1} = VV^{-1} = 1 \tag{2-41}$$

In (2-41) we have made use of Eq. (2-39). Having shown that U is unitary all that remains is to show that $\Gamma'(R) = U^{-1}\,\Gamma(R)U$.

$$U^{-1}\,\Gamma(R)\,U = S^{-1}\,VD^{1/2}\,V^{-1}\,\Gamma(R)\,VD^{-1/2}\,V^{-1}S \tag{2-42}$$

If in Eq. (2-42), we could commute the matrix $D^{1/2}$ through $V^{-1}\Gamma(R)V$ we could then prove the theorem. From Eqs. (2-38) and (2-39) we have

$$\Gamma(R)\,VDV^{-1} = VDV^{-1}\,\Gamma(R) \tag{2-43}$$

Multiplying from the right by V and from the left by V^{-1} yields

$$V^{-1}\,\Gamma(R)\,VD = DV^{-1}\,\Gamma(R)\,V \tag{2-44}$$

From this last equation we see that D commutes with $V^{-1}\Gamma(R)V$. If we call the matrix elements of $V^{-1}\,\Gamma(R)V$, A_{ij}, then in terms of components we have

$$A_{ij}(D_{jj} - D_{ii}) = 0 \text{ for all } i, j \tag{2-45}$$

This means that if D_{ii} is different from D_{jj} for some i and j A_{ij} must vanish. From this, it is clear that

$$A_{ij}(D_{jj}^{1/2} - D_{ii}^{1/2}) \text{ for all } i, j \tag{2-46}$$

Thus we see that $D^{1/2}$ commutes with $V^{-1}\,\Gamma(R)V$. Using this fact in Eq. (2-42) yields

$$\begin{aligned} U^{-1}\,\Gamma(R)\,U &= S^{-1}V\;V^{-1}\Gamma(R)V\;D^{1/2}D^{-1/2}V^{-1}S \\ &= S^{-1}\,\Gamma(R)S \end{aligned} \tag{2-47}$$

This completes the proof of the theorem.

We have now seen that every representation of a group through non singular matrices is equivalent to a unitary representation and that equivalent unitary representation and that equivalent unitary representations can be obtained from one another through the use of a unitary transformation. We have also seen that a reduced unitary representation can be written in the form

$$\Gamma(R) = \Gamma_1(R) + \Gamma_2(R) \tag{2-48}$$

In order to complete our discussion of reducibility we shall need to show that a representation reduced in the form (2-15) can, by a similarity transformation, be put in the

form (2-48). (In other words the Q portion of (2-15) will vanish.) This result is summed up in Theorem 4.

Theorem 4: If a representation is in its reduced from (2-15), a similarity transformation will bring it to a unitary reduced form. (That is, in (2-15), $\Gamma_1(R)$ and $\Gamma_2(R)$ are unitary and $Q(R) = 0$.)

Proof: Let us assume that we have a representation $\Gamma(R)$ where $\Gamma(R)$ has the form

$$\Gamma(R) = \left(\begin{array}{c|c} \Gamma_1(R) & Q(R) \\ \hline 0 & \Gamma_2(R) \end{array}\right) \tag{2-49}$$

Let us form the Hermitian matrix

$$H = \sum_R \Gamma(R)\ \Gamma(R)^\dagger \tag{2-50}$$

This matrix, as we have seen from the proof of Theorem 2 when diagonalized by a unitary transformation, has nothing but positive non zero diagonal elements. This defines a positive definite Hermitian matrix. A well known matrix theorem* states that for a positive definite Hermitian matrix a non singular matrix S can be found such that

$$SHS^\dagger = 1 \tag{2-51}$$

In addition, this matrix can be chosen to have the form

$$S = \begin{pmatrix} S_{11} & S_{12} & \cdot & \cdot & \cdot & \cdot \\ 0 & S_{22} & \cdot & \cdot & \cdot & \cdot \\ 0 & 0 & S_{33} & & & \\ \cdot & \cdot & & \cdot & & \\ \cdot & \cdot & & & \cdot & \\ 0 & 0 & \cdot & \cdot & \cdot & S_{nn} \end{pmatrix} \tag{2-52}$$

In other words, all the matrix elements below the main diagonal vanish. With this matrix S let us form $\Gamma'(R) = S\Gamma(R)\ S^{-1}$. In order to show that S is the desired matrix all we need do is show that $\Gamma'(R)$ is unitary.

- - - - - - - - - - - - - - - -

*See, for example, "The Mathematics of Physics and Chemistry" by H. Margenau and G. M. Murphy (D. Van Nostrand Company, Inc., New York, 1943. This theorem is also contained in "Die Theorie der Gruppen von Endlicher Ordnung" by Andreas Speiser.

$$\Gamma'(R)\,\Gamma'(R)^\dagger = \left\{S\Gamma(R)S^{-1}\right\}\left\{S^{\dagger-1}\Gamma(R)^\dagger S^\dagger\right\} \tag{2-53}$$

Between the curly brackets let us put $\mathbf{1}$ in the form of Eq. (2-51). This yields

$$\Gamma'(R)\;\Gamma'(R)^\dagger = S\Gamma(R)\,H\Gamma(R)^\dagger S^\dagger \tag{2-54}$$

From the proof of Theorem 3, we see that this is the same as

$$\Gamma'(R)\;\Gamma'(R)^\dagger = SHS^\dagger = \mathbf{1} \tag{2-55}$$

From this we see that, $\Gamma'(R) = S\Gamma(R)S^{-1}$ is unitary. Now let us notice that both S and S^{-1} have the form (2-52). (That S^{-1} has this form can be seen by expressing S^{-1} in terms of the determinant of S and the cofactors of S.) Thus we see at once, from the block multiplication of the three matrices that form $\Gamma'(R)$, that $\Gamma'(R)$ must have the reduced form

$$\Gamma'(R) = \left(\begin{array}{c|c} \Gamma_1'(R) & Q'(R) \\ \hline 0 & \Gamma_2'(R) \end{array}\right) \tag{2-56}$$

Since $\Gamma'(R)$ is unitary, we have seen that $Q'(R) = 0$, and that $\Gamma_1'(R)$ and $\Gamma_2'(R)$ are unitary matrices.

$$\Gamma'(R) = \left(\begin{array}{c|c} \Gamma_1'(R) & 0 \\ \hline 0 & \Gamma_2'(R) \end{array}\right) = \Gamma_1'(R) + \Gamma_2'(R) \tag{2-57}$$

This completes the proof of this theorem.

From the theorems of this section, we see that if a representation is reducible to the form (2-15) by a similarity transformation, it is reducible to the form (2-57) by a similarity transformation where $\Gamma_1'(R)$ and $\Gamma_2'(R)$ are unitary. If the original reducible representation were unitary, then the reduction to the form (2-57) can be carried out through a unitary transformation (Theorem 3).

We may write a reducible representation in the form

$$\Gamma(R) = \Gamma_1(R) + \Gamma_2(R)$$

It may be that $\Gamma_1(R)$ and $\Gamma_2(R)$ can be further reduced. We can keep on reducing the blocks which appear in this process. Eventually this process must cease when all the

blocks which appear are irreducible. Thus we see that a representation is either irreducible, or can be expressed as a "sum" of irreducible expressions.

$$\Gamma(R) = n_1 \Gamma_1(R) + n_2 \Gamma_2(R) + \ldots n_r \Gamma_r(R) \tag{2-58}$$

By a sum of irreducible representations (2-58) we mean that $\Gamma(R)$ can be written in the form (through a similarity transformation)

$$\begin{pmatrix} \boxed{\Gamma_1(R)} & & & 0 \\ & \boxed{\Gamma_1(R)} & & \\ & & \ddots & \\ 0 & & & \boxed{\Gamma_r(R)} \end{pmatrix} \tag{2-59}$$

Here n_k is the number of times the irreducible representation $\Gamma_k(R)$, or something equivalent to it, appears. The irreducible representations of a group appear as the fundamental entities out of which all representations are built. We see from this that the properties of irreducible representations will be important to us in our later work.

One of the most important theorems concerning irreducible representations of a group is Schur's Lemma. This theorem plays such a central role in the further development and its applications are so numerous that we shall devote the next section to the proof of this theorem.

3. Schur's Lemma

Before going on to the proof of a Schur's Lemma we shall need a closely related theorem.

Theorem 5: The only matrix which commutes with all the matrices in an irreducible representation is a constant times the unit matrix.

Proof: We have, by hypothesis, that a matrix commutes with all the matrices of an irreducible representation. Let us call this matrix $\mathbf{C}$ and the matrices in the irreducible representation $\Gamma(R)$. (We assume that the matrices $\Gamma(R)$ are unitary and of dimension n.)

$$\mathbf{C}\Gamma(R) = \Gamma(R)\,\mathbf{C} \text{ for all } R \tag{2-60}$$

If we take the adjoint of this expression, we find that

$$\Gamma(R)^\dagger C^\dagger = C^\dagger \Gamma(R)^\dagger \text{ for all } R \tag{2-61}$$

or

$$\Gamma(R^{-1}) C^\dagger = C^\dagger \Gamma(R^{-1}) \tag{2-62}$$

This last relation means that $C^\dagger$ commutes with all the matrices representing the group since as R runs over the elements of the group so does R^{-1}. Therefore, $C + C^\dagger$ and $i(C - C^\dagger)$ commute with all $\Gamma(R)$. These matrices are Hermitian. It is, therefore, sufficient to show that any Hermitian matrix which commutes with all $\Gamma(R)$ is a constant times the unit matrix since C is expressible as a linear combination of these Hermitian forms. We shall therefore assume that C is Hermitian. If this is the case, it can be brought to diagonal form D by a unitary transformation U ($D = U^{-1} C U$). If the same unitary transformation is applied to $\Gamma(R)$, we can define

$$\Gamma'(R) = U^{-1} \Gamma(R) U \tag{2-63}$$

$\Gamma'(R)$ commutes with D since

$$\begin{aligned} \Gamma'(R) D - D\Gamma'(R) &= U^{-1}\Gamma(R)U\ U^{-1}CU - U^{-1}CU\ U^{-1}\Gamma(R)U \\ &= U^{-1}\left[\Gamma(R)C - C\Gamma(R)\right]U \\ &= 0 \end{aligned} \tag{2-64}$$

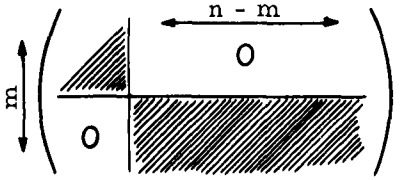
If D is not a constant times the unit matrix, then it must have unequal diagonal elements. Let us assume that m of the diagonal elements are equal but distinct from the remaining n - m. Our unitary transformation U can be arranged so that the m equal diagonal elements are the first m diagonal elements. Our commutation relation (2-64) states that

$$\Gamma'(R)_{sr} D_{rr} = D_{ss} \Gamma'(R)_{sr} \quad s, r = 1 \ldots n \tag{2-65}$$

If D_{ss} is taken to be one of the first m diagonal elements and D_{rr} is taken from the n - m remaining elements, then we obtain

$$\begin{aligned} \Gamma'(R)_{sr}\left[D_{rr} - D_{ss}\right] &= 0 \qquad s = 1 \ldots m \\ \Gamma'(R)_{sr} &= 0 \qquad r = m+1 \ldots n \end{aligned} \tag{2-66}$$

In other words $\Gamma'(R)$ is a matrix of the form



This means that $\Gamma(R)$ has been reduced. This contradicts the hypothesis. We have therefore shown that D is a diagonal matrix with equal diagonal elements or $D = c\,1$. If D has this form then

$$C = UDU^{-1} = U1U^{-1} = c\,1 \tag{2-68}$$

has the same diagonal form. This completes the proof of this theorem. Even though we have only proved this theorem for unitary representations we can easily extend the result to cover the case of non unitary irreducible representations. If $\Gamma(R)$ were not unitary it could be made unitary through a similarity transformation. (See Theorem 2.) If we denote $\Gamma'(R)$ as the matrices in the unitary representation and S as the matrix which makes $\Gamma(R)$ unitary, then

$$\Gamma'(R) = S^{-1}\Gamma(R)S \tag{2-69}$$

We notice at once that if $\Gamma(R)$ is irreducible so is the unitary representation $\Gamma'(R)$. If a matrix C commutes with all $\Gamma(R)$ then the matrix $S^{-1}CS$ commutes with $\Gamma'(R) = S^{-1}\Gamma(R)S$. This means that $S^{-1}CS$ is a constant times the unit matrix. This means in turn that C is a constant times the unit matrix which is what we desired to show.

The converse of Theorem 5 also provides a useful theorem. This converse provides the first method which we have for testing whether or not a representation is irreducible short of trying all possible similarity transformations on the representation to see if any will result in the form (2-15).

Theorem 6: If the only matrix which commutes with all the matrices of a given representation is a constant times the unit matrix, then the representation is irreducible.

Proof: Let $\Gamma(R)$ be the matrices in the representation. Let us assume the conclusion were false, that is, let us assume $\Gamma(R)$ is reducible. We know, from the results of Theorem 4, that a reducible representation can be brought to the form (2-57) by a similarity transformation. Let us put the representation $\Gamma(R)$ in its reduced form (2-57) by the use of a similarity transformation S.

$$\Gamma'(R) = S^{-1}\,\Gamma(R)S = \left(\begin{array}{c|c} \overset{m}{\Gamma_1(R)} & \overset{n-m}{0} \\ \hline 0 & \Gamma_2(R) \end{array}\right) \tag{2-70}$$

It is clear that the matrix

$$C = \left(\begin{array}{c|c} \overset{m}{c_1 1} & \overset{n-m}{0} \\ \hline 0 & c_2 1 \end{array}\right) \tag{2-71}$$

where $c_1 \neq c_2$ commutes with $\Gamma'(R)$.

$$\begin{aligned} \Gamma'(R)C - C\Gamma'(R) &= 0 \\ S^{-1}\,\Gamma(R)\,SC - CS^{-1}\,\Gamma(R)S &= 0 \end{aligned} \tag{2-72}$$

Multiplying from the right by S^{-1} and from the left by S yields

$$\Gamma(R)\,SCS^{-1} - SCS^{-1}\,\Gamma(R) = 0 \tag{2-73}$$

We know from the hypothesis that SCS^{-1} must be a constant times the unit matrix. Therefore

$$\begin{aligned} SCS^{-1} &= c1 \\ C &= c1 \end{aligned} \tag{2-74}$$

This cannot be since $c_1 \neq c_2$. We have been led to a contradiction and this proves that $\Gamma(R)$ is irreducible.

We are now in a position to prove Schur's Lemma.

Theorem 7: (Schur's Lemma) If $\Gamma_1(R)$ and $\Gamma_2(R)$ are two irreducible representations of a group with dimensions n_1 and n_2 respectively ($n_1 \leq n_2$) and we have found a matrix A with n_1 rows and n_2 columns such that

$$A\Gamma_2(R) = \Gamma_1(R)A \text{ for all } R \tag{2-75}$$

then either A is a zero n_1 by n_2 matrix or $n_1 = n_2$, A is square, non singular, and the representations $\Gamma_1(R)$ and $\Gamma_2(R)$ are equivalent.

Proof: We assume from the outset that $\Gamma_1(R)$ and $\Gamma_2(R)$ are unitary. Let us take the adjoint of Eq. (2-75).

$$\Gamma_2(R)^\dagger \mathbf{A}^\dagger = \mathbf{A}^\dagger \Gamma_1(R)^\dagger \text{ for all } R \tag{2-76}$$

or

$$\begin{aligned} \Gamma_2(R^{-1})\,\mathbf{A}^\dagger &= \mathbf{A}^\dagger \Gamma_1(R^{-1}) \text{ for all } R \\ \Gamma_2(R)\,\mathbf{A}^\dagger &= \mathbf{A}^\dagger \Gamma_1(R) \end{aligned} \tag{2-77}$$

Multiply (2-77) from the right by $\mathbf{A}$ and (2-75) from the left by $\mathbf{A}^\dagger$ and subtract. From this we see that

$$\mathbf{A}^\dagger \mathbf{A}\Gamma_2(R) = \Gamma_2(R)\,\mathbf{A}^\dagger\mathbf{A} \text{ for all } R \tag{2-78}$$

We know from the result of Theorem 5 that the only matrix which commutes with all the matrices of an irreducible representation is a scalar times the unit matrix. Therefore

$$\mathbf{A}^\dagger\mathbf{A} = c\mathbf{1} \tag{2-79}$$

Now if c is not equal to zero and $n_1 = n_2$, then the determinant of $\mathbf{A}\mathbf{A}^\dagger$ does not vanish. From this we conclude that the determinant of $\mathbf{A}$ does not vanish. This means that the inverse of $\mathbf{A}$ exists and from (2-75)

$$\mathbf{A}^{-1}\ \Gamma_1(R)\mathbf{A} = \Gamma_2(R) \tag{2-80}$$

In this case the representations are equivalent. If c vanishes, then

$$\mathbf{A}^\dagger\mathbf{A} = 0 \tag{2-81}$$

which means, when written out for the diagonal elements

$$\sum_{k=1}^{n_2} A_{jk}^* A_{jk} = 0 \quad (j = 1 \ldots n_1) \tag{2-82}$$

From this we conclude that $A_{jk} = 0$ for all j and k. Thus $\mathbf{A}$ is a zero matrix.

If $n_1 < n_2$ then $\mathbf{A}$ is a rectangular matrix. We can form a square matrix by adding $n_2 - n_1$ rows of zeros to $\mathbf{A}$ forming a matrix $\mathbf{B}$.

$$\mathbf{B} = \begin{pmatrix} A_{11} & \cdots & A_{1n_2} \\ \vdots & & \vdots \\ A_{n_1 1} & \cdots & A_{n_1 n_2} \\ 0 & \cdots & 0 \\ \vdots & & \vdots \\ 0 & \cdots & 0 \end{pmatrix} \tag{2-83}$$

It is clear that

$$\mathbf{A}^\dagger \mathbf{A} = \mathbf{B}^\dagger \mathbf{B} \tag{2-84}$$

Since $\mathbf{B}$ has some all zero rows, the determinant of $\mathbf{B}$ vanishes. Therefore the determinant of $\mathbf{A}\mathbf{A}^\dagger$ vanishes which means in turn that the c defined above vanishes. We have again that

$$\sum_{k=1}^{n_2} A_{jk}^* A_{jk} = 0 \quad (j = 1, \ldots, n_1)$$

From this we conclude that $A_{jk} = 0$ for all j and k. Thus we have shown for the case $n_1 < n_2$ that $\mathbf{A}$ vanishes. This completes the proof of the theorem.

The case for $n_2 < n_1$ can be handled in an analogous manner. Schur's Lemma is also valid for non unitary representations. We shall not complete the proof in detail for this case but merely indicate the method. Suppose $\Gamma_1(R)$ and $\Gamma_2(R)$ were not unitary. Matrices $\mathbf{S}$ and $\mathbf{R}$ can be found such that

$$\begin{aligned} \Gamma_1'(R) &= \mathbf{S}^{-1} \Gamma_1(R) \mathbf{S} \\ \Gamma_2'(R) &= \mathbf{R}^{-1} \Gamma_2(R) \mathbf{R} \end{aligned} \tag{2-85}$$

form unitary representations of the group. They are, of course, also irreducible. By hypothesis, we have that

$$\begin{aligned} \mathbf{A}\Gamma_2(R) &= \Gamma_1(R)\mathbf{A} \\ \mathbf{A}\mathbf{R}\Gamma_2'(R)\mathbf{R}^{-1} &= \mathbf{S}\Gamma_1'(R)\mathbf{S}^{-1}\mathbf{A} \end{aligned} \tag{2-86}$$

or

$$S^{-1} A R \Gamma_2'(R) = \Gamma_1'(R) S^{-1} A R$$

From the result of the proof of Schur's Lemma for the case of unitary representations, we know that either $S^{-1} A R$ is a zero matrix or else $n_2 = n_1$ and $S^{-1} A R$ is square non singular and the representations $\Gamma_1'(R)$ and $\Gamma_2'(R)$ are equivalent. From these facts we can conclude that either A is a zero matrix or else $n_2 = n_1$ and A is square non singular and the representations $\Gamma_1(R)$ and $\Gamma_2(R)$ are equivalent. This indicates the completion of the proof for the non unitary case.

In the next section we shall apply Schur's Lemma to the proof of the orthogonality relations for irreducible representations of a group. These relations form one of the most useful of all properties of irreducible representations.

4. The Orthogonality Relations

The orthogonality relations for irreducible unitary representations of a group state that for two distinct inequivalent unitary representations $\Gamma_1(R)$ and $\Gamma_2(R)$

$$\sum_R \Gamma_1(R)^*_{ij} \Gamma_2(R)_{k\ell} = 0 \text{ for all } i, j, k, \ell \tag{2-87}$$

The summation extends over all R in the group $\mathcal{G}$ which we shall assume to be of order g. For the coefficients of the same unitary irreducible representations of the group

$$\sum_R \Gamma_1(R)^*_{ij} \Gamma_1(R)_{k\ell} = \frac{g}{n_1} \delta_{ik} \delta_{j\ell} \tag{2-88}$$

Here n_1 is the dimension of the irreducible representation. We can put these two relations into a single relation

$$\sum_R \Gamma_\alpha(R)^*_{ij} \Gamma_\beta(R)_{k\ell} = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{ik} \delta_{j\ell} \tag{2-89}$$

n_α is the dimension of the α^{th} irreducible representation and the sum as written vanishes unless we have the same irreducible representation and the same row and column of that irreducible representation.

We shall prove this useful theorem by the use of Schur's Lemma. Let us construct for a pair of representations (we shall not at this point assume they are unitary) the matrix A with n_2 rows and n_1 columns

$$A = \sum_R \Gamma_2(R) X \left[\Gamma_1(R)\right]^{-1} \tag{2-90}$$

here $\Gamma_2(R)$ is of dimension n_2, $\Gamma_1(R)$ is of dimension n_1, and X is an arbitrary rectangular matrix with n_2 rows and n_1 columns. We first note that

$$\Gamma_2(R')A = A\Gamma_1(R') \tag{2-91}$$

We can see this easily since

$$\begin{aligned}\Gamma_2(R')A &= \sum_R \Gamma_2(R'R)X\left[\Gamma_1(R)\right]^{-1} \\ &= \sum_R \Gamma_2(R'R)X\left[\Gamma_1(R'R)\right]^{-1}\Gamma_1(R')\end{aligned} \tag{2-92}$$

We notice that as R runs over the group $\mathcal{G}$ so does $R'R$. Therefore

$$\sum_R \Gamma_2(R'R)X\left[\Gamma_1(R'R)\right]^{-1} = A \tag{2-93}$$

which proves our assertion. We notice now, from Schur's Lemma, that if $\Gamma_2(R)$ and $\Gamma_1(R)$ are inequivalent A must vanish. We have, therefore, for arbitrary X

$$\sum_R \Gamma_2(R)X\left[\Gamma_1(R)\right]^{-1} = 0 \tag{2-94}$$

Writing out the matrix elements of A this becomes

$$\sum_{j'\ell'}\sum_R \Gamma_2(R)_{ij'}X_{j'\ell'}\Gamma_1(R^{-1})_{\ell'k} = 0 \tag{2-95}$$

Let us let $X_{j'\ell'}$ vanish except for the element $X_{j\ell}$ which we take to be unity. From this we get

$$\sum_R \Gamma_2(R)_{ij}\Gamma_1(R^{-1})_{\ell k} = 0 \tag{2-96}$$

For a unitary representation $\Gamma_1(R^{-1})_{\ell k} = \Gamma_1(R)^*_{k\ell}$. Therefore for two inequivalent unitary representations we have proved the theorem, namely

$$\sum_R \Gamma_2(R)_{ij}\Gamma_1(R)^*_{k\ell} = 0$$

If the representation $\Gamma_2(R)$ is the same as $\Gamma_1(R)$, then we have

$$\Gamma_1(R)A = A\Gamma_1(R) \tag{2-97}$$

This in turn means, from the result of Theorem 5, that A is a scalar times the unit

matrix

$$\mathbf{A} = \sum_R \Gamma_l(R)\mathbf{X}\ \Gamma_l(R^{-1}) = c\mathbf{1} \tag{2-98}$$

where c, of course, depends on $\mathbf{X}$. Let us once again choose $\mathbf{X}$ in such a manner that the only non vanishing elements is $X_{j\ell}$ which is unity and call the corresponding c, $c_{j\ell}$.

$$\sum_R \Gamma_l(R)_{ij}\, \Gamma_l(R^{-1})_{\ell k} = c_{j\ell}\, \delta_{ik} \tag{2-99}$$

We must now determine $c_{j\ell}$. Let us set i = k and sum over i (i = 1, ... n_l)

$$\sum_i \sum_R \Gamma_l(R)_{ij}\, \Gamma_l(R^{-1})_{\ell i} = n_l\, c_{j\ell} \tag{2-100}$$

But

$$\sum_i \Gamma_l(R)_{ij}\, \Gamma_l(R^{-1})_{\ell i} = \Gamma_l(R^{-1}R)_{\ell j} = \delta_{\ell j}$$

Therefore

$$\sum_R \delta_{j\ell} = n_l\, c_{j\ell}$$

or

$$g\, \delta_{j\ell} = n_l\, c_{j\ell}$$

$$c_{j\ell} = \frac{g}{n_l}\, \delta_{j\ell}$$

which finally means that

$$\sum_R \Gamma_l(R)_{ij}\, \Gamma_l(R^{-1})_{\ell k} = \frac{g}{n_l}\, \delta_{j\ell}\, \delta_{ik} \tag{2-102}$$

For a unitary representation, we have

$$\sum_R \Gamma_l(R)^*_{k\ell}\ \Gamma_l(R)_{ij} = \frac{g}{n_l}\, \delta_{ik}\, \delta_{\ell j} \tag{2-103}$$

This proves the second portion of our orthogonality theorem for group representations.

Before leaving these general orthogonality relations it will be useful to write the orthogonality relations for non unitary representations of the group in a slightly different form. The orthogonality relations for non unitary representations are summed

up in Eqs. (2-96) and (2-102). These two relations can be combined into a single orthogonality relation for non unitary representations which takes the form

$$\sum_R \Gamma_\alpha(R)_{ij} \Gamma_\beta(R^{-1})_{\ell k} = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{ik} \delta_{j\ell} \tag{2-104}$$

We saw in the first section of this chapter that if we had a representation $\Gamma(R)$ we could form a new representation of the group by using the matrices $\Gamma(R)^{-1}$. Let us define $\Gamma(R)^t$ as

$$\Gamma(R)^t = \Gamma(R)^{-1} = \Gamma(R^{-1}) \tag{2-105}$$

With this definition we can rewrite the orthogonality relations (2-104) in the form

$$\sum_R \Gamma_\alpha(R)_{ij} \Gamma_\beta(R)^t_{k\ell} = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{ik} \delta_{j\ell} \tag{2-106}$$

When written in this form, for non unitary representations, the orthogonality relations involve the matrix elements of the representation $\Gamma_\alpha(R)$ with those of $\Gamma_\beta(R)^t$. For the case of unitary representations $\Gamma_\beta(R)^t = \Gamma_\beta(R)^*$ and our relations (2-106) become the ordinary orthogonality relations between the elements of a unitary irreducible representation.

As an example of these orthogonality relations we may consider the group C_{3v}. We have found two one-dimensional representations. One is the identity representation and the other is the representation given in Eq. (2-14). These are clearly irreducible representations. (A one-dimensional representation of any group is irreducible. It cannot be put in the form (2-15) by a similarity transformation.) We also had a two-dimensional unitary representation using the matrices $M_1 \ldots M_6$ which we introduced in the first chapter. We can see that this is an irreducible representation of the group in the following way. If it were reducible, since it is two-dimensional, it could be reduced so that every element of the group were represented by a diagonal matrix. Diagonal matrices commute. The group elements in general do not commute. Since we had a faithful representation we have encountered a contradiction and therefore this two-dimensional representation is irreducible.

Let us write out these three irreducible representations

R	E	C_3	C_3^2	σ_1	σ_2	σ_3
$\Gamma_1(R)$	1	1	1	1	1	1
$\Gamma_2(R)$	1	1	1	-1	-1	-1
$\Gamma_3(R)$	$\begin{matrix}1 & 0\\ 0 & 1\end{matrix}$	$\begin{matrix}-\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{-\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}$	$\begin{matrix}-\frac{1}{2} & \frac{-\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}$	$\begin{matrix}-1 & 0\\ 0 & 1\end{matrix}$	$\begin{matrix}\frac{1}{2} & \frac{-\sqrt{3}}{2}\\ \frac{-\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}$	$\begin{matrix}\frac{1}{2} & \frac{\sqrt{3}}{2}\\ \frac{\sqrt{3}}{2} & -\frac{1}{2}\end{matrix}$

We can now easily check a few of the orthogonality relations. For example

$$\sum_R \Gamma_1(R)_{11}\,\Gamma_2(R)_{11} = (1)(1) + (1)(1) + (1)(1) + (1)(-1) + (1)(-1) + (1)(-1)$$
$$= 0$$

$$\sum_R \Gamma_1(R)\,\Gamma_3(R)_{12} = (1)(0) + (1)\frac{\sqrt{3}}{2} + (1)(\tfrac{-\sqrt{3}}{2}) + (1)(0) + (1)(\tfrac{-\sqrt{3}}{2}) + (1)(\tfrac{\sqrt{3}}{2})$$
$$= 0$$

$$\sum_R \Gamma_3(R)_{12}\,\Gamma_3(R)_{21} = (0)(0) + \frac{\sqrt{3}}{2}(\tfrac{-\sqrt{3}}{2}) + (\tfrac{-\sqrt{3}}{2})(\tfrac{\sqrt{3}}{2}) + (0)(0) + (\tfrac{-\sqrt{3}}{2})(\tfrac{-\sqrt{3}}{2}) + (\tfrac{\sqrt{3}}{2})(\tfrac{\sqrt{3}}{2})$$
$$= 0$$

$$\sum_R \Gamma_3(R)_{11}\,\Gamma_3(R)_{11} = (1)(1) + (-\tfrac{1}{2})(-\tfrac{1}{2}) + (-\tfrac{1}{2})(-\tfrac{1}{2}) + (-1)(-1) + (\tfrac{1}{2})(\tfrac{1}{2}) + (\tfrac{1}{2})(\tfrac{1}{2})$$
$$= 3 = \frac{6}{2}$$

$$\sum_R \Gamma_2(R)_{11}\,\Gamma_2(R)_{11} = (1)(1) + (1)(1) + (1)(1) + (-1)(-1) + (-1)(-1) + (-1)(-1)$$
$$= 6 = \frac{6}{1}$$

5. Group Characters

In the last sections, we have studied representations of group. We noticed that if we had a representation of a group we could generate a great many more from it by using a similarity transformation. If a representation were reducible, all representations equivalent to it were also reducible. If a representation were irreducible all representations equivalent to it were also irreducible. In this way, we see that we can assign properties to a representation and all those equivalent to it. We would like to have some specification of a representation which is unchanged if the representation undergoes a similarity transformation. The character of a rep-

resentation provides such a specification.

Before going into this let us notice that the trace of a matrix (sum of the diagonal elements) is unchanged if the matrix undergoes a similarity transformation. Consider a matrix $\mathbf{A}$ and a matrix $\mathbf{A}' = \mathbf{S}^{-1}\mathbf{A}\mathbf{S}$. The latter matrix is related to the former through a similarity transformation. By the trace of $\mathbf{A}$ we mean

$$\text{trace}\,(\mathbf{A}) = \sum_i A_{ii} \tag{2-108}$$

If we calculated the trace of $\mathbf{A}'$, we obtain

$$\begin{aligned}
\text{trace}\,(\mathbf{A}') &= \text{trace}\,(\mathbf{S}^{-1}\mathbf{A}\mathbf{S}) \\
&= \sum_i A'_{ii} \\
&= \sum_{ijk} S^{-1}_{ij} A_{jk} S_{ki} \\
&= \sum_{jk} \left[\mathbf{S}\,\mathbf{S}^{-1}\right]_{kj} A_{jk} \\
&= \sum_{jk} \delta_{kj} A_{jk} = \sum_j A_{jj} \\
&= \text{trace}\,(\mathbf{A})
\end{aligned} \tag{2-109}$$

If we were to calculate the trace of every matrix $\Gamma(R)$ in a representation of a group, this collection of numbers would be the same for every representation equivalent to $\Gamma(R)$. The traces of matrices representing a group are denoted by $\chi(R)$ and are called the character system of the representation

$$\chi(R) = \sum_j \Gamma(R)_{jj} \tag{2-110}$$

If the group is of order g then the character system of the representation consists of the g numbers $\chi(R)$.

From the invariance of the character under a similarity transformation, we can also conclude that the characters of group elements in the same class are equal. This is clear since if R and R' belong to the same class $R = X^{-1}R'X$. For the matrices in the representation $\Gamma(R)$

$$\Gamma(R) = \left[\Gamma(X)\right]^{-1} \Gamma(R')\,\Gamma(X) \tag{2-111}$$

From this we conclude that if R and R' are in the same class $\chi(R) = \chi(R')$. Thus if the group $\mathcal{G}$ had r classes $C_1 = E, C_2, C_3, \ldots, C_r$ with $h_1 = 1, h_2, h_3, \ldots, h_r$ elements respectively and if we denote the i^{th} class of elements by $R_1^i, \ldots, R_{h_i}^i$, we

have that

$$\chi(R_1^i) = \chi(R_2^i) \ldots = \chi(R_{h_i}^i) \tag{2-112}$$

Thus, it is seen that for a given representation the characters are only a function of which class the group elements belong. We could, therefore, specify the character system of a given representation by giving the characters of elements belonging to the same class. In this way, we see that we could denote the character by $\chi(C_i)$, where $\chi(C_i)$ is the character of all elements in the i^{th} class.

In the last section we noticed that there were orthogonality relations between the matrix elements in irreducible representations. These were summed up for irreducible representations in Eq. (2-106)

$$\sum_R \Gamma_\alpha(R)_{ij} \Gamma_\beta(R)^t_{k\ell} = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{ik} \delta_{j\ell} \tag{2-113}$$

If we set i = j and k = ℓ and sum i from 1 to n_α and k from 1 to n_β, we obtain

$$\begin{aligned} \sum_R \chi_\alpha(R) \chi_\beta(R)^t &= \frac{g}{n_\alpha} \delta_{\alpha\beta} \sum_{i=1}^{n_\alpha} \sum_{k=1}^{n_\beta} \delta_{ik} \delta_{ik} \\ &= \frac{g}{n_\alpha} \delta_{\alpha\beta} \sum_{k=1}^{n_\alpha} 1 \\ &= g \, \delta_{\alpha\beta} \end{aligned} \tag{2-114}$$

Thus, we have an orthogonality theorem between group characters. Here $\chi_\alpha(R)$ is the character system for $\Gamma_\alpha(R)$ and $\chi_\beta(R)^t$ is the character system for $\Gamma_\beta(R)^t = \Gamma_\beta\widetilde{(R^{-1})}$.

We may write this orthogonality relation somewhat differently by noticing that if $\chi(R)$ is the trace of the matrix $\Gamma(R)$ in a group representation, then $\chi(R)^t = \chi(R)^*$ is the trace of the matrix $\Gamma(R)^t$. This can most easily be seen by noticing that if the representation $\Gamma(R)$ is made unitary by a similarity transformation using a matrix S, then we have for the unitary representation

$$\Gamma'(R) = S^{-1} \Gamma(R) S \tag{2-115}$$

and therefore

$$\widetilde{\Gamma'(R)}^{-1} = \Gamma'(R)^* = \widetilde{S}(R)^t \widetilde{S}^{-1} \tag{2-116}$$

Thus $\Gamma(R)^t$ is equivalent to the representation $\Gamma'(R)^*$ using the matrix $\widetilde{S}^{-1}$. The trace of $\Gamma'(R)^*$ is just the complex conjugate of the trace of $\Gamma'(R)$. From the in-

variance of traces under a similarity transformation we see at once that

$$\begin{aligned}\chi(R)^t = \text{trace}\,(\Gamma(R)^t) &= \text{trace}\,(\Gamma'(R)^*) \\ &= \left[\text{trace}\,(\Gamma'(R))\right]^* \\ &= \left[\text{trace}\,(\Gamma(R))\right]^* \\ &= \chi(R)^*\end{aligned} \tag{2-117}$$

From the preceding paragraph, we can rewrite the orthogonality relations in the form

$$\sum_R \chi_\alpha(R)\,\chi_\beta(R)^* = g\,\delta_{\alpha\beta} \tag{2-118}$$

We have also noticed that the characters associated with elements in the same class are equal. Our orthogonality relations can, therefore, be written in the form

$$\sum_{i=1}^{r} h_i\,\chi_\alpha(C_i)\,\chi_\beta(C_i)^* = g\,\delta_{\alpha\beta} \tag{2-119}$$

From the preceding discussion we can conclude

Theorem 8: A necessary and sufficient condition for the equivalence of two irreducible representations is the equality of their character systems.

Proof: It is clear from the invariance of characters under a similarity transformation that we have a necessary condition. To show the sufficiency, we must show that if the characters of two irreducible representations are identical, then the representations are equivalent. If we call $\Gamma(R)$ and $\Gamma'(R)$ the two irreducible representations and they have characters $\chi(R)$ and $\chi'(R)$ $(\chi(R) = \chi'(R))$. If they were inequivalent,

$$\sum_R \chi(R)\,\chi'(R)^* = 0 \tag{2-120}$$

from Eq. (2-118). But we know that for a representation $\Gamma(R)$ from Eq. (2-118)

$$\sum_R \chi(R)\,\chi(R)^* = g \tag{2-121}$$

Since $\chi(R) = \chi'(R)$ we have been led to a contradiction. From this we see that all we need do to check the equivalence of two irreducible representations is to compare their character systems. It is the case that the same theorem holds for reducible representations. Before we prove this, we must analyze the relation between a re-

ducible representation and its reduced form more fully.

We saw in Section 2 of this chapter that every reducible representation could be reduced to the form (2-59) through a similarity transformation. This reducibility was expressed by Eq. (2-58)

$$\Gamma(R) = c_1 \Gamma_1(R) + c_2 \Gamma_2(R) + c_a \Gamma_a(R) + \ldots \tag{2-122}$$

c_a is the number of times the a^{th} irreducible representation or a representation equivalent to it appears in the diagonal blocks of (2-59). By taking traces we see that, if we call $\chi(R)$ the character of $\Gamma(R)$,

$$\chi(R) = c_1\chi_1(R) + c_2\chi_2(R) + \ldots + c_a\chi_a(R) + \ldots \tag{2-123}$$

We can find the numbers c_a of the following theorem.

Theorem 9: The number of times an irreducible representation $\Gamma_a(R)$ or a representation equivalent to it appears in a reducible representation $\Gamma(R)$ is given by

$$c_a = \frac{1}{g} \sum_R \chi(R)\, \chi_a{}^*(R) \tag{2-124}$$

Proof: Let us multiply both sides of Eq. (2-123) by $\chi_a(R)^*$ and sum over R. Using the orthogonality relations for group characters, we have that

$$\sum_R \chi(R)\, \chi_a{}^*(R) = c_a\, g \tag{2-125}$$

This proves the theorem.

From Theorem 9 we see that the reduction of a reducible representation into its irreducible parts is unique. By being unique we mean that the number of times that an irreducible representation appears along the diagonal in (2-59) when added to the number of times an equivalent irreducible representation appears is a unique number. The order in which the irreducible representations appear need not be unique nor need the individual blocks equivalent to a particular irreducible representation be the same in both decompositions. In order to show that the decomposition is unique, in this sense, let us assume that there were two possible decompositions.

$$\begin{aligned} \Gamma(R) &= c_1 \Gamma_1(R) + \ldots\, c_a \Gamma_a(R) + \ldots \\ \Gamma(R) &= c_1'\Gamma_1(R) + \ldots\, c_a'\Gamma_a(R) + \ldots \end{aligned} \tag{2-126}$$

From Theorem 9 we see that

$$c_a = \frac{1}{g} \sum_R \chi(R)\, \chi_a{}^*(R)$$
$$c_a{}' = \frac{1}{g} \sum_R \chi(R)\, \chi_a{}^*(R) \qquad (2\text{-}127)$$

We have, therefore, that $c_a = c_a{}'$ and the decomposition into irreducible representations is unique.

From this it is clear that if two representations (reducible or irreducible) have the same character system they are equivalent. We see, from Theorem 9, that they can, by a similarity transformation, be brought to the same reduced form if there character systems are the same. Since they both can be brought to the same form by a similarity transformation they are equivalent. To see if two representations are equivalent all we need do is see if their character systems are identical.

From these facts we get another interesting piece of information about the characters. Consider, for a reducible representation (2-123)

$$\sum_R |\chi(R)|^2 = \sum_R \chi(R)\, \chi(R)^* = \sum_R \sum_{ij} a_i\, \chi_i(R)\, a_j\, \chi_j(R)^* \qquad (2\text{-}128)$$

Because of the orthogonality theorem

$$\sum_R |\chi(R)|^2 = g \sum_{ij} g\, \delta_{ij}\, a_i\, a_j$$
$$= g \sum_i a_i{}^2 \qquad (2\text{-}129)$$

Thus, for a reducible representation $\sum |\chi(R)|^2$ is the order of the group multiplied by the sum of the squares of the number of times the various irreducible representations appear in the reducible representation. If a representation is irreducible, we have

$$\sum_R |\chi(R)|^2 = g(1) = g$$

From this we conclude

Theorem 10: A necessary and sufficient condition for a representation to be irreducible is

$$\sum_R |\chi(R)|^2 = g \qquad (2\text{-}130)$$

Proof: The necessity we have already shown. That the representation is irreducible if the relation (2-130) is satisfied is also clear. If it were reducible, then

$$\sum_R |\chi(R)|^2 > g$$

which contradicts the hypothesis

$$\sum_R |\chi(R)|^2 = g$$

This theorem gives a convenient test for the irreducibility of a given representation. For the two-dimensional representation of the group C_{3v} given in Eq. (2-107) we have

$$\chi(E) = 2;\ \chi(C_3) = \chi(C_3^{\,2}) = -1;\ \chi(\sigma_1) = \chi(\sigma_2) = \chi(\sigma_3) = 0$$
$$(2)^2 + (1)^2 + (1)^2 + (0)^2 + (0)^2 + (0)^2 = 6 \qquad (2\text{-}131)$$

Thus, for this representation the sum of the squares of the characters is equal to the order of the group and we again check that the representation is irreducible.

6. Class Multiplication, The Regular Representation, and Representation Multiplication

In this section, we shall introduce three new concepts which will prove useful in the applications of group theory. We shall not make extensive use of them in this section but merely employ them to determine the number of irreducible representations which a group has and, in addition, prove that the sums of the squares of the orders of the irreducible representations is equal to the order of the group.

A. Class Multiplication

Let us denote by $C_i (i = 1 \ldots r)$ the classes of a group $\mathcal{G}$ of order g. We shall call h_i the number of elements in the i^{th} class and we shall denote these elements by $R_1^i \ldots R_{h_i}^i$. We can define a quantity

$$C_i = R_1^i + R_2^i + \ldots R_{h_i}^i \qquad (2\text{-}132)$$

where we add all the elements in the i^{th} class. We have not previously introduced the sum of elements of a group. We shall not, at this point, go into the properties of such a sum, but shall discuss this point in detail later on in another connection. With the definition (2-132) we can define

$$C_i C_j = (R_1^i + \ldots + R_{h_i}^i)(R_1^j + \ldots + R_{h_j}^j) = \sum_{p=1}^{h_i} \sum_{q=1}^{h_j} R_p^i R_q^j \tag{2-133}$$

The sum on the right-hand side of (2-133) consists again of a sum over group elements. We notice that $X^{-1} C_i C_j X = X^{-1} C_i X X^{-1} C_j X = C_i C_j$ for any X in $\mathcal{G}$. From this we conclude that the right-hand side of (2-133) consists of a sum of classes since if it contains one element in a class it must contain all elements in that class. The sum of the right of (2-133) might contain a class more than once. In any case, we may write

$$C_i C_j = \sum_{k=1}^{r} c_{ijk} C_k \tag{2-134}$$

Here c_{ijk} is the number of times the class sum C_k is contained in the product $C_i C_j$ and is some integers > 0.

The quantities c_{ijk} have a number of properties. First, we note that for any X in the group $X^{-1} C_i X = C_i$. It is clear that for any R in C_i, $X^{-1} R X$ is a number of the sum C_i since $X^{-1} R X$ is in the same class as R. We can, from this, conclude that as R runs over the members of a class C_i so does $X^{-1} R X$. This yields the first property of c_{ijk}. Since $C_i C_j = C_j C_i$ we conclude

$$c_{ijk} = c_{jik} \tag{2-135}$$

We also notice that $C_1 C_j = E C_j = C_j$. Therefore we have the relation

$$c_{1jk} = c_{j1k} = \delta_{jk} \tag{2-136}$$

Let us also notice that if C_i is a class then there is another class consisting of the same number of elements containing the inverses of all the elements in C_i. This is clear since if R is a member of the class C_i, then consider $X^{-1} R^{-1} X = \left[X^{-1} R X\right]^{-1}$. The latter quantity is also the inverse of a member of the class C_i. Let us denote by C_i' the class consisting of the inverses of the class C_i. It may be that $C_i = C_i'$. Consider, for example, the class $\{\sigma_1, \sigma_2, \sigma_3\}$ of the group C_{3v}. As we have mentioned the number of elements in the class C_i' is the same as the number of elements in the class C_i, namely h_i. From this we conclude that $C_i C_j$ either contains the identity class $C_1 = E$ h_i times if $j = i'$ or not at all if $j \neq i'$. In other words

$$c_{ij1} = h_i \delta_{ji'} \tag{2-137}$$

The concept of class multiplication enables us to derive a new set of relations between the group characters. Suppose we formed for an irreducible representation $\Gamma_a(R)$ the class sums corresponding to (2-132)

$$C_a^i = \sum_{p=1}^{h_i} \Gamma_a(R_p^i) \tag{2-138}$$

Since matrices in a representation multiply just like the corresponding group elements, we conclude from this that for any group element X

$$\Gamma_a(X)\, C_a^i = C_a^i\, \Gamma_a(X) \tag{2-139}$$

This allows us to conclude, from Theorem 5, that C_a^i must be a constant times the unit matrix

$$C_a^i = \eta_a^i 1 \tag{2-140}$$

Let us now determine the constant η_a^i. We can take the trace of both sides of Eq, (2-138) yields $\eta_a^i\, n_a$. If we take the trace of the right-hand side of Eq. (2-138), we get (since the characters of all elements in the same class is the same) $h_i\, \chi_a(C_i)$. From this we conclude that

$$\eta_a^i = \frac{h_i\, \chi_a(C_i)}{n_a} \tag{2-141}$$

We notice from relation (2-134) and (2-140) that

$$C_a^i\, C_a^j = \sum_{k=1}^{r} c_{ijk}\, C_a^k \tag{2-142}$$

and

$$\eta_a^i\, \eta_a^j = \sum_{k=1}^{r} c_{ijk}\, \eta_a^k \tag{2-143}$$

Using (2-141) we obtain as a new relation between group characters

$$\frac{h_i h_j\, \chi_a(C_i)\, \chi_a(C_j)}{n_a n_a} = \sum_{k=1}^{r} c_{ijk}\, \frac{h_k\, \chi_a(C_k)}{n_a}$$

or (2-144)

$$h_i\, \chi_a(C_i)\, h_j\, \chi_a(C_j) = n_a \sum_{k=1}^{r} c_{ijk}\, h_k\, \chi_a(C_k)$$

B. Regular Representation

We can generate on particularly useful representation of a group in the following way. Consider a group $\mathcal{G}$ of order g with elements $R_1 = E, R_2, \ldots, R_g$. We can consider these group elements themselves as the basis vectors which generate a representation much as we consider the vectors in Section 1 of this chapter as generating a representation. Thus, if we were to consider some element X of the group we may write

$$X R_\ell = \sum_{k=1}^{g} A_{k\ell}(X)\, R_k \tag{2-145}$$

From the group postulates, we know that XR_ℓ is a member of the group. Thus, we see that $A_{k\ell}(X) = 0$ unless $XR_\ell = R_k$ in which case it is unity. This representation $\mathbf{A}(X)$ will be of dimensions g and have a single 1 in each column and all the rest of the elements zero. This is called the regular representation. It is clear that the only group element which will have a matrix with non vanishing elements along the diagonal is $\mathbf{A}(E)$. In this g 1's will appear along the diagonal. Therefore we conclude that $\chi(E) = g$; $\chi(R) = 0$.

In order to fix this representation in our minds, let us calculate the matrix representing the operator C_3 for the group C_{3v}. Let $R_1 = E$, $R_2 = C_3$, $R_3 = C_3^2$, $R_4 = \sigma_1$, $R_5 = \sigma_2$, $R_6 = \sigma_3$. Then

$$R_2 R_1 = R_2$$

$$R_2 R_2 = R_3$$

$$R_2 R_4 = R_6$$

$$R_2 R_5 = R_4$$

$$R_2 R_6 = R_5$$

Therefore, the matrix $\mathbf{A}(C_3)$ in the regular representation is given by

$$\mathbf{A}(C_3) = \begin{pmatrix} 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 \end{pmatrix} \tag{2-146}$$

Knowing the characters of the regular representation, we can by the procedure of the last section, determine how many times each irreducible representation occurs in the regular representation. The number of times the a^{th} irreducible representation occurs is given by

$$\begin{aligned} c_a &= \frac{1}{g} \sum_R \chi(R)\, \chi_a(R)^* \\ &= \frac{1}{g}\, \chi(E)\, \chi_a(E)^* \end{aligned} \tag{2-147}$$

We know that $\chi_a(E)$ is equal to the dimension of the a^{th} irreducible representation

$$c_a = \frac{1}{g}\, g\, n_a = n_a \tag{2-148}$$

From this we learn that the a^{th} irreducible representation occurs as often as its dimension. This allows us to conclude, since the order of the regular representation is g, that

$$g = \sum_a n_a^{\,2} \tag{2-149}$$

In this manner we have shown that the number of irreducible representations of a finite group is finite and in addition

Theorem 11: The sum of the squares of the dimensions of the irreducible representations is equal to the order of the group.

We still cannot say how many irreducible representations there are for a finite group. We now have at our disposal sufficient information to answer this question. Let us say there are r' irreducible representations. Let us take the trace of the matrices in the regular representation. From (2-148) we can write

$$\begin{aligned} \mathbf{A}(R) &= \sum_{a=1}^{r'} n_a\, \Gamma_a(R) \\ &= \sum_{a=1}^{r'} n_a \chi_a(R) = 0 \text{ if } R \neq E \\ &\qquad\qquad = g \text{ if } R = E \end{aligned} \tag{2-150}$$

or since $n_a = \chi_a(E)$

$$\begin{aligned} \sum_{a=1}^{r'} \chi_a(E)\, \chi_a(R) &= 0 \text{ if } R \neq E \\ &= g \text{ if } R = E \end{aligned} \tag{2-151}$$

Now let us sum Eq. (2-144) over all α

$$\sum_{\alpha=1}^{r'} h_i \chi_\alpha(C_i)\, h_j \chi_\alpha(C_j) = \sum_{\alpha=1}^{r'} n_\alpha \sum_{k=1}^{r} c_{ijk}\, h_k \chi_\alpha(C_k) \tag{2-152}$$

Since $n_\alpha = \chi_\alpha(E)$, using Eq. (2-151), we obtain

$$\begin{aligned} h_i h_j \sum_{\alpha=1}^{r'} \chi_\alpha(C_i)\, \chi_\alpha(C_j) &= \sum_{k=1}^{r} c_{ijk}\, h_k\, \delta_{k1}\, g \\ &= c_{ij1}\, h_1\, g = c_{ij1}\, g \end{aligned} \tag{2-153}$$

We know from relation (2-137) that $c_{ij1} = h_i\, \delta_{ji'}$. Therefore,

$$h_i h_j \sum_{\alpha=1}^{r'} \chi_\alpha(C_i)\, \chi_\alpha(C_j) = g\, h_i\, \delta_{ji'} \tag{2-154}$$

Dividing out the factor $h_i h_j$, we obtain

$$\sum_{\alpha=1}^{r'} \chi_\alpha(C_i)\, \chi_\alpha(C_j) = \frac{g}{h_i}\, \delta_{ji'} \tag{2-155}$$

One need only consider the unitary representations of a group to convince oneself that $\chi_\alpha(C_{i'}) = \chi_\alpha(C_i)^*$. This leads to

$$\sum_{\alpha=1}^{r'} \chi_\alpha(C_i)\, \chi_\alpha(C_j)^* = \frac{g}{h_i}\, \delta_{ij} \tag{2-156}$$

This is a new orthogonality relation for the characters. In it we hold the classes fixed and sum over the representations. We now rewrite our orthogonality relations (2-156) and (2-119) slightly differently so that their similarity can be seen

$$\sum_{\alpha=1}^{r'} \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i) \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_j)^* = \delta_{ij} \tag{2-157}$$

$$\sum_{i=1}^{r'} \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i) \sqrt{\frac{h_i}{g}}\, \chi_\beta(C_i)^* = \delta_{\alpha\beta} \tag{2-158}$$

If we now set $i = j$ in (2-157) and sum over i and set $\alpha = \beta$ in (2-158) and sum over α, we obtain

$$\begin{aligned} \sum_{i=1}^{r} \sum_{\alpha=1}^{r'} \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i) \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i)^* &= r' \\ \sum_{\alpha=1}^{r'} \sum_{i=1}^{r} \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i) \sqrt{\frac{h_i}{g}}\, \chi_\alpha(C_i)^* &= r \end{aligned} \tag{2-159}$$

This allows us to conclude that r = r' or

Theorem 12: The number of irreducible representations of a group is equal to the number of classes of that group.

The character systems of a group are generally presented in the form of a character table. In this table the classes are listed across the top of the table and the irreducible representations are listed down the left-hand side of the table. In general a character table has the form of (2-160)

	$C_1 = E$	C_2	. . . . .	C_r
Γ_1	$\chi_1(E)$	$\chi_1(C_2)$		$\chi_1(C_r)$
Γ_2	$\chi_2(E)$	$\chi_2(C_2)$		$\chi_2(C_r)$
.				
.				
.				
.				
.				
Γ_r	$\chi_r(E)$	$\chi_r(C_2)$		$\chi_r(C_r)$

(2-160)

For the group C_{3v}, we can now construct the character table from the information in (2-107). We have presented in that table three non equivalent irreducible representations of the group C_{3v}. Since there are only three classes to the group C_{3v}, this must represent the complete set of no equivalent irreducible representations. The character table for this group is then

C_{3v}

	E	C_3, C_3^2	$\sigma_1, \sigma_2, \sigma_3$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-1	0

C. Representation Multiplication

From two representations of a group $\Gamma'(R)$ and $\Gamma''(R)$ it is possible to construct a new representation of the group by the following procedure. Let us define a matrix $\Gamma(R)$ which is written as $\Gamma'(R) \times \Gamma''(R)$, and is called the Kronecker or direct product of the representations $\Gamma'(R)$ and $\Gamma''(R)$. The matrix elements of $\Gamma(R)$ are obtained by taking all possible products of the matrix elements of $\Gamma'(R)$ and $\Gamma''(R)$.

$$\Gamma(R)_{(ij)(k\ell)} = \Gamma'(R)_{ik}\,\Gamma''(R)_{j\ell} \tag{2-162}$$

This is the element in the ij^{th} row of $\Gamma(R)$ and the $k\ell^{th}$ column. The index (ij) is generally taken in dictionary order so that (ij) precedes (ij') when $i < i'$ or if $i = i'$ when $j < j'$. If $\Gamma'(R)$ was of dimension m and $\Gamma''(R)$ was of dimension n, then $\Gamma(R) = \Gamma'(R) \times \Gamma''(R)$ is of dimension mn. Let us first notice that if $\Gamma'(R)$ and $\Gamma''(R)$ form a representation of the group then $\Gamma(R)$ forms a representation of the group. In other words we must show that $\Gamma(RR') = \Gamma(R)\ \Gamma(R')$.

$$\begin{aligned}\Gamma(RR')_{(ij)(k\ell)} &= \Gamma'(RR')_{ik}\,\Gamma''(RR')_{j\ell} \\ &= \sum_{p,\,q} \Gamma'(R)_{ip}\,\Gamma'(R')_{pk}\quad (R)_{jq}\quad ''(R)_{q\ell} \\ &= \sum_{(pq)} \Gamma(R)_{(ij)(pq)}\,\Gamma(R)_{(pq)(k\ell)}\end{aligned} \tag{2-163}$$

This proves our assertion, and we see that $\Gamma(R)$ forms a representation for the group.

We can find the relation between the character systems of $\Gamma(R)$ and those of $\Gamma'(R)$ and $\Gamma''(R)$. Let us denote these characters by $\chi(R)$, $\chi'(R)$, and $\chi''(R)$, respectively.

$$\chi(R) = \sum_{(ij)} \Gamma(R)_{(ij)(ij)} = \sum_{ij} \Gamma'(R)_{ii}\,\Gamma''(R)_{jj} = \chi'(R)\,\chi''(R) \tag{2-164}$$

Thus the character corresponding to R in the direct product representation is just given by the products of the characters of the representations entering into the direct product.

A particularly useful set of direct products are the products of the irreducible representations. If $\Gamma_\alpha(R)$ and $\Gamma_\beta(R)$ are irreducible representations of a group, we may define $\Gamma_\alpha(R) \times \Gamma_\beta(R)$. This may of course be reducible. If it is we may write

$$\Gamma_\alpha(R) \times \Gamma_\beta(R) = \sum_{\lambda=1}^{r} g_{\alpha\beta\lambda}\ \Gamma_\lambda(R) \tag{2-165}$$

$g_{\alpha\beta\lambda}$ represents the number of times the λ irreducible representation occurs in the product of the α and β irreducible representations. From the relation (2-164) and Theorem 9, we see that

$$g_{\alpha\beta\lambda} = \frac{1}{g} \sum_{R} \chi_\alpha(R)\,\chi_\beta(R)\,\chi_\lambda(R)^* \tag{2-166}$$

These quantities have many of the properties which the quantities c_{ijk} had above. From the definition it can be seen at once, using (2-118), that

$$\begin{aligned} g_{\alpha\beta\lambda} &= g_{\beta\alpha\lambda} \\ g_{1\beta\lambda} &= g_{\beta 1\lambda} = \delta_{\beta\lambda} \\ g_{\alpha\beta 1} &= g_{\beta\alpha 1} = 0 \text{ unless } \Gamma_\beta \text{ is equivalent to } \Gamma_\alpha{}^t \\ &= 1 \text{ if } \Gamma_\beta \text{ is equivalent to } \Gamma_\alpha{}^t \end{aligned} \tag{2-167}$$

We see that we have expressed the quantities $g_{\alpha\beta\lambda}$ in terms of the group characters. We can in a similar manner express the quantities c_{ijk} (Eq. (2-134) in terms of the group characters. Let us take the Eq. (2-144) and multiply by

$$\frac{1}{n_\alpha}\ \chi_\alpha(C_m)^*$$

and sum over α. Using relation (2-155) we obtain

$$\begin{aligned} \sum_{\alpha=1}^{r} \frac{h_i\ \chi_\alpha(C_i)\ h_j\ \chi_\alpha(C_j)}{n_\alpha}\ \chi_\alpha(C_m)^* &= g\ c_{ijm} \\ c_{ijm} &= \frac{h_i\ h_j}{g} \sum_{\alpha=1}^{r} \frac{\chi_\alpha(C_i)\ \chi_\alpha(C_j)\ \chi_\alpha(C_m)^*}{\chi_\alpha(E)} \end{aligned} \tag{2-168}$$

Appendix

If we have a matrix $\mathbf{A}$ with elements A_{ij} we may define a number of matrices in terms of the elements of this given matrix.

We call $\mathbf{A}^*$ the complex conjugate of $\mathbf{A}$. Its i, j^{th} element is A^*_{ij}.

$\tilde{\mathbf{A}}$ is the transpose of $\mathbf{A}$. Its i, j^{th} element is A_{ji}.

$\mathbf{A}^\dagger = \tilde{\mathbf{A}}^*$ is the adjoint of $\mathbf{A}$ (complex conjugate transpose).
Its i, j^{th} element is A^*_{ji}.

In this notation we may define some properties which a matrix may possess.

A matrix $\mathbf{A}$ is said to be Hermitian if $\mathbf{A}^\dagger = \mathbf{A}$.

A matrix is symmetric if $\tilde{\mathbf{A}} = \mathbf{A}$.

A matrix is skew symmetric if $\tilde{\mathbf{A}} = -\mathbf{A}$.

Unitary matrices have the property that $\mathbf{A}^\dagger = \mathbf{A}^{-1}$.

Chapter III

RELATION OF GROUP THEORY AND QUANTUM MECHANICS

In the preceding chapters we have concerned ourselves with the abstract properties of groups and their representations. This theory of groups finds wide application in quantum theory. In order to proceed with this, we must study the effects of coordinate transformations on functions of these coordinates.

1. Operators for Coordinate Transformations

Let us imagine that in an n dimensional space we have defined a function $f(x_1, x_2, \ldots, x_n)$. Here $x_1, x_2, \ldots, x_n$ are the coordinates of a point in this space. We may, from the outset, denote $f(x_1, x_2, \ldots x_n)$ as $f(\vec{x})$ where $\vec{x}$ is a vector from the origin to the point whose coordinates are $x_1, x_2, \ldots, x_n$. We now let our coordinate system undergo a real linear orthogonal transformation* of the coordinates to a new coordinate system $x_1', x_2', x_3', \ldots x_n'$

$$\begin{aligned} x_1' &= R'_{11} x_1 + R'_{12} x_2 + \ldots + R'_{1n} x_n \\ &\vdots \qquad\qquad\qquad\qquad \vdots \\ x_n' &= R'_{n1} x_1 + R'_{n2} x_2 + \ldots + R'_{nn} x_n \end{aligned} \tag{3-1}$$

In vector notation, we have

$$\vec{x}' = R' \vec{x} \tag{3-2}$$

The function $f(\vec{x})$ can be described in terms of the new coordinate system. Of course in this new coordinate system we must describe it by a new function of these coordinates. Let us call this new function $Rf(x_1', x_2' \ldots x_n')$.

$$Rf(x_1', x_2', \ldots, x_n') = f(x_1, x_2, \ldots, x_n) \tag{3-3}$$

or

$$Rf(\vec{x}') = Rf(\ 'x) = f(\vec{x}) \tag{3-4}$$

We can look upon R as an operator which changes the function f in such a way that Rf

---

*By a real orthogonal transformation we mean that R is real and unitary or $R^{-1} = \tilde{R} = R^{\dagger}$.

evaluated at the point $\vec{x}'$ is the same as f evaluated at the point $\vec{x}$. We can rewrite (3-4) in a different manner.

$$f(\vec{x}') = f(R'\vec{x}) = R^{-1} f(\vec{x}) \tag{3-5}$$

Here R^{-1} is defined by

$$R^{-1} f(R'^{-1}\vec{x}) = f(\vec{x}) \tag{3-6}$$

From (3-5) it is seen that the original function f when evaluated at the point $\vec{x}'$ is the same as the function, f operated on by the inverse transformation R^{-1}, and evaluated at the original point $\vec{x}$.

This is a concept most easily illustrated by a simple example. Imagine, in two dimensions, the function $f(x_1, x_2) = ax_1^2 + bx_2^2$. The contours of constant value for this function are ellipses and are illustrated in Fig. 3-1. We might imagine the coordinate transformation which represents a rotation clockwise through 90^o.

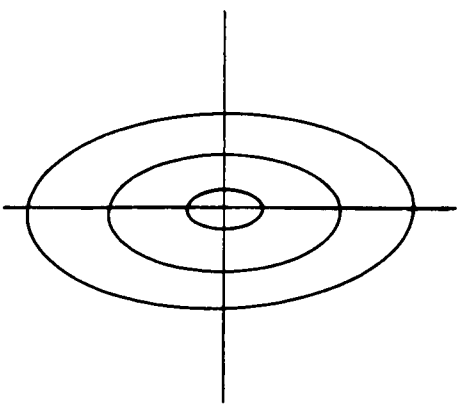


Fig. 3-1

$$x_1' = -x_2$$

$$x_2' = x_1$$

The original function $f(x_1 x_2)$ described in terms of the rotated coordinate system is $Rf(x_1', x_2') = ax_2'^2 + bx_1'^2 = ax_1^2 + bx_2^2$ (Eq. 3-3). Eq. (3-5) can be easily interpreted. This says that we have the same physical situation if we rotate the function (contour lines) counter clockwise through 90^o and describe this function in terms of the old coordinate system as we get if we rotate the coordinate system clockwise through 90^o and leave the function (contour lines) stationary, evaluating it at the point $\vec{x}' = R'\vec{x}$. (See Figs. 3-2a and 3-2b.) Thus, in a manner of speaking, rotating the function is the same as rotating the coordinate system in the opposite direction.

In this way for every coordinate transformation R' we can define a corresponding operator R through the use of Eq. (3-4). These operators which act on the functions multiply in the same way that the coordinate transformations multiply. Thus if $R'\vec{x} = \vec{x}'$ and $S\vec{x}' = \vec{x}''$, then

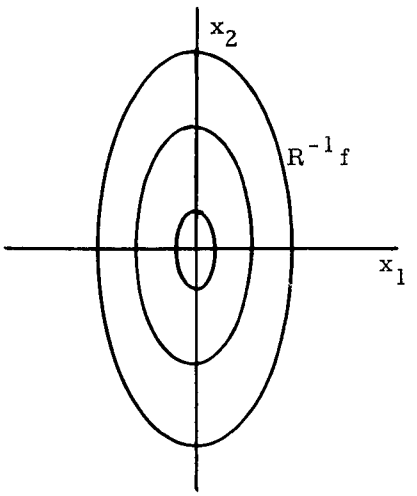


Fig. 3-2a

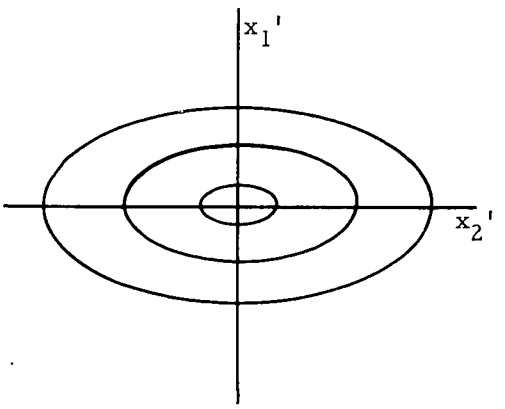


Fig. 3-2b

$$Rf(\vec{x}) = Rf(\mathbf{R}'\vec{x}) = f(\vec{r})$$

$$SR\, f(\vec{x}'') = SR\, f(\mathbf{S}'\mathbf{R}'\vec{x}) = f(\vec{x})$$

We also have that

$$(SR)\, f(x'') = f(x)$$

Therefore, the combined operations (SR) is the same as the product of S and R. It is obvious that the operators R are the linear operators

$$R(af + bg) = aRf + bRg$$

This is merely an expression of the fact that in changing variables in the sum of two functions we can change the variables in each independently and then add.

In addition to this, the operators R are unitary. Thus if we have the integral

$$(f, g) = \int f^*(\vec{x})\, g(\vec{x})\, dx_1 \ldots dx_n$$

the value of this integral is unchanged if we change the variables of integration. Thus

$$(b, g) = \int f^*(\mathbf{R}'\vec{x})\, g(\mathbf{R}'\vec{x})\, dx_1' \ldots dx_n'$$

$$(b, g) = \int f^*(\mathbf{R}'\vec{x})\, g(\mathbf{R}'\vec{x})\, dx_1 \ldots dx_n$$

From Eq. (3-5)

$$(f, g) = \int \left[R^{-1} f(\vec{x})\right]^* R^{-1} g(\vec{x})\, dx_1 \ldots dx_n$$

We have therefore that $(f, g) = (R^{-1} f, R_g^{-1})$ or $(f, g) = (Rf, Rg)$. This we take as the definition of a unitary operator. We might note in passing that it is also true that $Rfg = Rf, Rg$.

In this way we have defined for every real orthogonal coordinate transformation $\mathbf{R}'$ a corresponding operator R which is both linear and unitary.

2. Relation to Schrödinger's Equation

Let us apply these concepts to Schrödinger's equation. In quantum mechanics we are concerned with eigenstates of a Hamiltonian operator H which may be defined in a coordinate system $\vec{x}$. We denote the operator in this coordinate system as $H(\vec{x})$. In general, of course, the Hamiltonian operator is a function of derivatives with respect to the coordinates as well as the coordinates themselves. $H(\vec{x})$ merely expresses the fact that H is expressed in the coordinate system $\vec{x}$. It does not mean that the Hamiltonian operator is only a function of these coordinates.

If we allow $H(\vec{x})$ to operate on a function $\psi(\vec{x})$ we have $g(\vec{x}) = H(\vec{x})\,\psi(\vec{x})$. Using the relation (3-4) for a coordinate transformation, we have

$$\begin{aligned} g(\vec{x}) = H(\vec{x})\,\psi(\vec{x}) = Rg(\mathbf{R}'\vec{x}) &= R\left[H(\mathbf{R}'\vec{x})\,\psi(\mathbf{R}'\vec{x})\right] \\ &= RH(\mathbf{R}'\vec{x})\,R^{-1}\,\psi(\vec{x}) \end{aligned} \tag{3-7}$$

Since this is valid for all ψ we have the result that

$$H(\vec{x}) = R\,H(\mathbf{R}'\vec{x})\,R^{-1} \tag{3-8}$$

The effect of the operator $H(\vec{x})$ is the same as the effect of the operator $R\,H(\mathbf{R}'\vec{x})\,R^{-1}$. Under certain circumstances a change of coordinates in the Hamiltonian may leave that Hamiltonian invariant.

$$H(\mathbf{R}'\vec{x}) = H(\vec{x}) \tag{3-9}$$

In this case Eq. (3-8) becomes

$$H(\vec{x}) = R\,H(\vec{x})\,R^{-1} \tag{3-10}$$

or

$$R\,H(\vec{x}) = H(\vec{x})\,R \tag{3-11}$$

The operator R commutes with the Hamiltonian and from this we conclude that R is a constant of the motion. Eigenstates of our Hamiltonian can be found which are simultaneously eigenstates of the operator R. We might consider the collection of all coordinate transformations $\mathbf{R}'$ which leave the Hamiltonian invariant. We shall now show that these coordinate transformations form a group.

Theorem 13: The collection of all coordinate transformations $\mathbf{R}'$ which leave the Hamiltonian invariant ($H(\mathbf{R}'\vec{x}) = H(\vec{x})$) forms a group.

Proof: It is clear that the coordinate transformation which does not change the coordinates forms the identity element of the group. The product of two coordinate transformations both of which leave the Hamiltonian invariant also leaves the Hamiltonian invariant. This follows from $H(\mathbf{S}'\,\mathbf{R}'\vec{x}) = H(\mathbf{R}'\vec{x}) = H(\vec{x})$. The associative law holds. That the inverse of $\mathbf{R}'$ leaves the Hamiltonian unchanged is also obvious. By hypothesis we have $H(\mathbf{R}'\,\mathbf{R}'^{-1}\vec{x}) = H(\mathbf{R}'^{-1}\vec{x}) = H(\vec{x})$. In this way we have proved that the collection of coordinate transformations which leaves the Hamiltonian invariant forms a group.

From the preceding discussion we can now conclude that the operators R corresponding to the $\mathbf{R}'$ which leave the Hamiltonian invariant also form a group. This is called the group of the Schrödinger equation. Let us now consider this group. For these operators we have seen that HR = RH. Suppose we had a degenerate eigenstate of the Schrödinger equation

$$H\psi_n = E\psi_n \qquad (n = 1 \ldots \ell) \tag{3-12}$$

(ℓ is the degeneracy of the state) and operate on this state with the operator R. Let us operate on both sides of (3-12) from the left with R, an operator which leaves the Hamiltonian invariant. From Eq. (3-11) we have that

$$\begin{aligned} R\,H\psi_n &= H\,R\,\psi_n = E\,R\,\psi_n \\ H(R\psi_n) &= E(R\psi_n) \end{aligned} \tag{3-13}$$

From this we see that $R\psi_n$ is also an eigenstate of the Hamiltonian with energy E. Since this is the case it must be expressible as a linear combination of the degenerate eigenstates.

$$R\psi_n = \sum_{m=1}^{\ell} \Gamma(R)_{mn}\, \psi_m \tag{3-14}$$

If we now operate on (3-14) with an operator S which leaves the Hamiltonian invariant we obtain, due to the linearity of these operators,

$$\begin{aligned} SR\psi_n &= \sum_{m=1}^{\ell} \Gamma(R)_{mn}\, S\psi_m \\ &= \sum_{m=1}^{\ell} \sum_{q=1}^{\ell} \Gamma(R)_{mn}\, \Gamma(S)_{qm}\, \psi_q \end{aligned} \tag{3-15}$$

We also know from definition that

$$SR\psi_n = \sum_{q=1}^{\ell} \Gamma(SR)_{qn}\, \psi_q \tag{3-16}$$

From this we obtain the result that

$$\Gamma(SR) = \Gamma(S)\,\Gamma(R) \tag{3-17}$$

In other words, the matrices describing the transformations of the degenerate set of eigenstates under an operator R form a representation of the group of operators which leaves the Hamiltonian invariant. If we assume that the eigenstates $\psi_1 \cdots \psi_\ell$, with the energy E, form an orthonormal set, we obtain

$$\begin{aligned} (\psi_m, \psi_n) &= \delta_{mn} \\ &= (R\psi_m, R\psi_n) = \sum_{p,q} \Gamma(R)^*_{pm}\, \Gamma(R)_{qn}\, (\psi_p, \psi_q) \\ &= \sum_{p,q} \Gamma(R)^*_{pm}\, \Gamma(R)_{qn}\, \delta_{pq} \\ &= \sum_{p} \Gamma(R)^\dagger_{mp}\, \Gamma(R)_{pn} \end{aligned} \tag{3-18}$$

or

$$\Gamma(R)^\dagger\, \Gamma(R) = 1$$

Thus we see that an orthogonal normalized set of functions leads to a unitary representation of the group of Schrödinger's equation.

Let us also notice that we induce a similarity transformation on the representation $\Gamma(R)$ if we form any other linearly independent set of ℓ functions out of our

original degenerate set.

$$\phi_m = \sum_{n=1}^{\ell} S_{nm} \psi_n \tag{3-19}$$

Here $\mathbf{S}$ is a non singular matrix and $\mathbf{S}^{-1}$ is its inverse. Let us see what representations the ϕ's produce.

$$\begin{aligned} R\phi_m &= \sum_{n=1}^{\ell} S_{nm} R\psi_n \\ &= \sum_{n=1}^{\ell} S_{nm} \sum_{p=1}^{\ell} \Gamma(R)_{pm} \psi_p \\ &= \sum_{n,p,q=1}^{\ell} S_{nm} \Gamma(R)_{pm} S^{-1}_{qp} \phi_q \\ &= \sum_{q=1}^{\ell} \Gamma'(R)_{qm} \phi_q \end{aligned}$$

From this we see that a non singular linear transformation of the degenerate eigenstates induces a similarity transformation on the representation

$$\Gamma'(R) = \mathbf{S}^{-1} \Gamma(R) \mathbf{S} \tag{3-20}$$

By this similarity transformation we could completely reduce the representation $\Gamma(R)$. Thus, we see that there are two possibilities. Either the set of degenerate states corresponding to a single energy level produces an irreducible representation of the group or through a similarity transformation the representation could be completely reduced. In the event that the set of functions corresponding to a given energy level generate a reducible representation of the group, we say that there is an accidental degeneracy between those irreducible representations which appear in the reducible representation.

From these considerations we see that much can be learned about the properties of the solutions of Schrödinger's equation just by the consideration of the symmetry of the Hamiltonian. Knowing the group of the Schrödinger equation allows us at once to state that every eigenstate of the Hamiltonian can be chosen in such a way that it, along with the other eigenstates of the same energy, generate an irreducible representation of the group. This, of course, tells us the behavior of the eigenstates under the various symmetry operations involved. In general, this information proves quite useful, but in order to know the actual positions of the energy levels we must go still further and actually solve the equation. This is a formidable task which can only be carried out by approximate calculations either by perturbation or variational techniques. Whereas we have learned something of the general nature of the solutions

of Schrödinger's equation from group theoretical considerations we have not exhausted the usefulness of the application of group theory to quantum mechanics. Just in the sphere of the approximate calculations group theory plays an important role in the simplification of the calculations. Since we know our solutions to Schrödinger's equation generate irreducible representations, we would generally find it to our advantage to start any approximate calculation by making wave functions which at least have the proper symmetry behavior under the group of Schrödinger's equation. In the next section, we shall develop powerful tools which enable us to simplify many of the methods used to calculate solutions of the Schrödinger problem.

3. Bases for Irreducible Representations, Hypercomplex Numbers and Projection Operators

Any set of functions $f_1, f_2, \ldots f_\ell$ which, under the operation of some element of a group $\mathcal{G}$, go into linear combinations of one another is said to form a basis for the representation. Thus if

$$Rf_i = \sum_{i=1}^{\ell} \Gamma(R)_{ij} f_j \tag{3-21}$$

The functions f_i are said to form a basis for the representation $\Gamma(R)$. The particular function f_i is said to transform according to the i^{th} column of this representation. If $\Gamma(R)$ is an irreducible representation then the functions f_i are said to form a basis for an irreducible representation. The functions included in a basis are referred to individually as partners in the basis for the representation. In this terminology, we see that the solutions of Schrödinger's equation can be chosen to form bases for irreducible representations of the group of Schrödinger's equation. In case there is no accidental degeneracy, the representation for which the degenerate eigenfunctions form a basis will be irreducible. In the event of an accidental degeneracy, the representation for which the eigenstates of a given energy form a basis is a reducible representation. It can be completely reduced into two or more irreducible representations. If this is the case the functions corresponding to the same eigenvalue can be broken up in the same way as the matrices. We could label the degenerate eigenfunctions

$$f_{11}, f_{12}, \ldots f_{1j_1}; f_{21}, \ldots f_{2j_2}; \ldots; f_{\ell 1}, \ldots f_{\ell j_\ell} \tag{3-22}$$

Here the functions $f_{i1}, \ldots f_{ij_i}$ form a basis for one of the ℓ irreducible representations which is contained in the reducible representation. The functions between the semicolons in (3-22) transform amongst themselves in an irreducible manner. This is merely a reflection of the blocking off of the matrices in the representation when

it is put in its completely reduced form.

As we mentioned at the close of the preceding section, we shall in general only be able to solve Schrödinger's equation approximately and we shall find that simplifications arise when we can confine our attention to approximate eigenfunctions which transform irreducibly according to the group of Schrödinger's equation. In order to make functions which transform in the suitable manner, we shall make use of entities called hypercomplex numbers which we shall find act like projection operators. They take out of any function that part of it which transforms in a specified manner.

We found it convenient in our discussion of class multiplication to introduce a sum of elements taken from a given group. We might generalize this concept. Let us assume we had a group $\mathcal{G}$ of order g with elements $R_1 = E$, R_2, ... R_g and we formed an entity

$$\rho = \sum_{i=1}^{g} a_i R_i = a_1 R_1 + a_2 R_2 + \ldots a_g R_g \tag{3-23}$$

Here a_1, ... a_g are in general complex numbers. This quantity is called a hypercomplex number. It is clear that the sum of two hypercomplex numbers is again a hypercomplex number. Thus if

$$\eta = \sum_i b_i R_i$$

$$\rho + \eta = \sum_i (a_i + b_i) R_i \tag{3-24}$$

The product of two hypercomplex numbers is again a hypercomplex number. $\rho\eta$ is given by

$$\rho\eta = \sum_{i,j} a_i b_j R_i R_j \tag{3-25}$$

Since R_i and R_j are elements of a group the sum on the right-hand side of (3-25) is once again a sum over group elements. The coefficient of R_ℓ in $\rho\eta$ would just be the sum of $a_i b_j$ for all i and j such that $R_i R_j = R_\ell$. Under multiplication the hypercomplex number (1)E forms the identity since

$$(1)E\rho = \sum_i a_i E R_i = \rho$$

If $\Gamma(R)$ are the matrices of dimension n representing the group $\mathcal{G}$, then we can form particularly useful hypercomplex numbers by forming the numbers

$$\rho_{ij} = \sum_R \Gamma(R)^t_{ij} R \tag{3-26}$$

Here $\Gamma(R)^t$ is the representation adjugate to $\Gamma(R)$. That is $\Gamma(R)^t = \widetilde{\Gamma(R^{-1})}$. Let us multiply the hypercomplex number ρ_{ij} from the left by S, a member of the group $\mathcal{G}$.

$$S\rho_{ij} = \sum_R \Gamma(R)^t_{ij} SR \tag{3-27}$$

If we let $SR = R'$; $R = S^{-1}R'$ we obtain

$$\begin{aligned} S\rho_{ij} &= \sum_{R'} \Gamma(S^{-1}R')^t_{ij} R' \\ &= \sum_{R'} \sum_k \Gamma(S^{-1})^t_{ik} \Gamma(R')^t_{kj} R' \\ &= \sum_k \sum_{R'} \Gamma(S)_{ki} \Gamma(R')^t_{kj} R' \\ &= \sum_k \Gamma(S)_{ki} \rho_{kj} \end{aligned} \tag{3-28}$$

Thus we see that the hypercomplex numbers $\rho_{1j}, \rho_{2j}, \cdots \rho_{nj}$ (for all j) transform amongst themselves as partners in the representation $\Gamma(R)$. Thus we could put the hypercomplex numbers in a matrix array.

$$\begin{matrix} \rho_{11} \rho_{12} \cdots \rho_{1n} \\ \rho_{21} \rho_{22} \cdots \rho_{2n} \\ \cdot \\ \cdot \\ \cdot \\ \rho_{n1} \rho_{n2} \cdots \rho_{nn} \end{matrix} \tag{3-29}$$

The hypercomplex numbers in any column when multiplied by an element S of $\mathcal{G}$ transform as basis elements for the representation $\Gamma(S)$. The functions $\rho_{i1}, \rho_{i2} \cdots \rho_{in}$ (across any row) have the same transformation properties even though they are, in general, distinct. Thus

$$\begin{aligned} S\,\rho_{ij} &= \sum_k \Gamma(S)_{ki} \rho_{kj} \\ S\,\rho_{i\ell} &= \sum_k \Gamma(S)_{ki} \rho_{k\ell} \end{aligned} \tag{3-30}$$

We see from this that the hypercomplex numbers ρ_{ij} and $\rho_{i\ell}$ transform in the same manner.

In particular, we could form hypercomplex numbers from irreducible representations in the following way

$$\rho^{a}_{ij} = \sum_{R} \Gamma_{a}(R)^{t}_{ij} R \tag{3-31}$$

If $\Gamma_{a}(R)$ is unitary

$$\rho^{a}_{ij} = \sum_{R} \Gamma_{a}(R)^{*}_{ij} R \tag{3-32}$$

Here $\Gamma_{a}(R)$ is the a^{th} irreducible representation of the group $\mathcal{G}$. These particular hypercomplex numbers have some interesting properties.

Consider the product $\rho^{a}_{ij} \rho^{\beta}_{k\ell}$ where a and β denote irreducible representations of dimension n_{a} and n_{β} respectively. In this case

$$\rho^{a}_{ij} \rho^{\beta}_{k\ell} = \sum_{R} \sum_{R'} \Gamma_{a}(R)^{t}_{ij} \Gamma_{\beta}(R')^{t}_{k\ell} R R' \tag{3-33}$$

If we let $RR' = R''$ $(R' = R^{-1} R'')$

$$\begin{aligned} \rho^{a}_{ij} \rho^{\beta}_{k\ell} &= \sum_{R} \sum_{R''} \Gamma_{a}(R)^{t}_{ij} \Gamma_{\beta}(R^{-1}R'')^{t}_{k\ell} R'' \\ &= \sum_{R} \sum_{R''} \sum_{m=1}^{n_{\beta}} \Gamma_{a}(R)^{t}_{ij} \Gamma_{\beta}(R^{-1})^{t}_{km} \Gamma_{\beta}(R'')^{t}_{m\ell} R'' \\ &= \sum_{R} \sum_{m} \Gamma_{a}(R)^{t}_{ij} \Gamma_{\beta}(R)_{mk} \rho^{\beta}_{m\ell} \end{aligned}$$

Using the orthogonality relations (Eq. (2-113) of Chapter II)

$$\begin{aligned} \rho^{a}_{ij} \rho^{\beta}_{k\ell} &= \sum_{m=1}^{n_{\beta}} \frac{g}{n_{\beta}} \delta_{a\beta} \delta_{im} \delta_{kj} \delta^{\beta}_{m\ell} \\ &= \frac{g}{n_{\beta}} \delta_{a\beta} \delta_{kj} \rho^{\beta}_{i\ell} \end{aligned} \tag{3-34}$$

Thus we see that $\rho^{a}_{ij} \rho^{\beta}_{k\ell}$ vanishes unless $a = \beta$ and even in this event the product vanishes unless $j = k$. These hypercomplex numbers are particularly useful if we draw them from the group of Schrödinger's equation.

We recall that the group of unitary operators R which commute with the Hamiltonian was called the group of Schrödinger's equation if these operators correspond to real orthogonal coordinate transformations. These operators act on functions of the coordinates. We might imagine that for the group of Schrödinger's equation we have the irreducible representation $\Gamma_{a}(R)$. We could then form the hypercomplex numbers (3-31). These hypercomplex numbers are operators on the functions

of coordinates. Let us see what effect they have on an arbitrary function of the coordinates $\phi(x_1, \ldots, x_n)$.

$$\phi^{\alpha}_{ij} = \rho^{\alpha}_{ij}\,\phi = \sum_{R} \Gamma_{\alpha}(R)^{t}_{ij}\, R \tag{3-35}$$

What we are doing here is to take the function ϕ and form the g functions $R\phi$ from this function (as R runs over the group $\mathcal{G}$) and then form linear combinations of these g functions with coefficients taken from an irreducible representation. The g functions $R\phi$ may or may not be linearly independent. If we operate on ϕ^{α}_{ij} with any operator S of the group of Schrodinger's equation we obtain, by use of (3-28)

$$S\phi^{\alpha}_{ij} \sum_{k} \Gamma_{\alpha}(S)_{ki}\, \phi^{\alpha}_{kj} \tag{3-36}$$

Thus the function $\phi^{\alpha}_{ij} = \rho^{\alpha}_{ij}\,\phi$ transforms as a basis for the α irreducible representation. The partners in this basis are $\phi^{\alpha}_{1j}, \phi^{\alpha}_{2j}, \ldots, \phi_{n\alpha, j}$. Thus, from a function ϕ we can make n_{α}^{2} functions corresponding to the α irreducible representation. These functions are

$$\begin{matrix} \phi^{\alpha}_{11}\, \phi^{\alpha}_{12} \cdots \phi^{\alpha}_{1n_{\alpha}} \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \cdot \qquad\qquad \cdot \\ \phi^{\alpha}_{n_{\alpha}1}\, \phi^{\alpha}_{n_{\alpha}2} \cdots \phi^{\alpha}_{n_{\alpha}n_{\alpha}} \end{matrix} \tag{3-37}$$

The functions in any column form partners in the basis for the α irreducible representation. Each column forms a basis for the same representation, the α^{th}. These n_{α}^{2} functions may or may not be linearly independent.

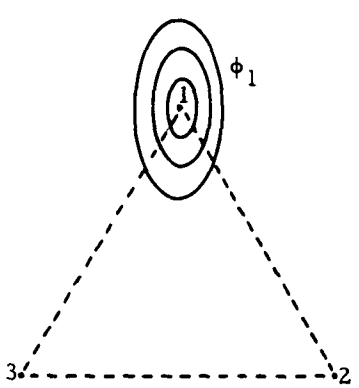


Fig. 3-3

The operators ρ^{α}_{ij} take an arbitrary function and project out of it that portion of it which transforms as a partner in the basis for the α irreducible representation. They can be thought of as projection operators. They are useful when it is desired to form from a given function one which transforms in a prescribed manner. This is often necessary in simplifications of approximate treatments of Schrödinger's equation. In order to clarify the behavior of these operators let us study a simple example taken from the group C_{3v}.

We might imagine a function in two dimensions ϕ_1 which is situated around the vertex of an equilateral triangle as illustrated in Fig. 3-3. The contours of constant

value are shown in the figure. The function has the property that under the operation σ_1 (reflection through a line passing through 1 and perpendicular to the line joining 2 and 3) it goes into itself. By applying all the operations of the group C_{3v} to this function we arrive at the following three functions:

$$\begin{aligned} C_3\phi_1 &= \sigma_3\phi_1 = \phi_2 \\ C_3^2\phi_1 &= \sigma_2\phi_1 = \phi_3 \\ E\phi_1 &= \sigma_1\phi = \phi_1 \end{aligned} \tag{3-38}$$

These three functions form a representation of the group C_{3v} and this representation is of dimension 3. Let us now consider the effect of applying the projection operators for irreducible representations on this function ϕ_1. We shall take our irreducible representations as given in Eq. (2-107) of Chapter II.

Let us consider first the projection operator associated with the identity representation. From (3-31)

$$\rho'_{11} = E + C_3 + C_3^2 + \sigma_1 + \sigma_2 + \sigma_3$$

Using (3-38) we have

$$\rho'_{11}\phi_1 = 2\phi_1 + 2\phi_2 + 2\phi_3 = 2(\phi_1 + \phi_2 + \phi_3)$$

By the application of the operator ρ'_{11} we have formed a function $\rho'_{11}\phi_1$ which transforms as a basis for the identity representation of the group C_{3v}. In this case it is just the sum of functions like ϕ_1 centered about the vertices 1, 2, and 3 of the equilateral triangle.

Now consider the second irreducible representation on (2-107) of Chapter II

$$\rho^2_{11} = E + C_3 + C_3^2 - \sigma_1 - \sigma_2 - \sigma_3$$

$$\begin{aligned} \rho^2_{11}\phi_1 &= \phi_1 + \phi_2 + \phi_3 - \phi_1 - \phi_3 - \phi_2 \\ &= 0 \end{aligned}$$

From this we see that if we try to project out of ϕ_1 a part that transforms as the representation $\Gamma_2(R)$ we cannot do this. In other words, ϕ_1 does not contain the second irreducible representation.

For the third irreducible representation we can form four projection operators

$$\rho^3_{11} = E - \frac{1}{2}C_3 - \frac{1}{2}C_3^2 - \sigma_1 + \frac{1}{2}\sigma_2 + \frac{1}{2}\sigma_3$$

$$\rho^3_{12} = \frac{\sqrt{3}}{2}C_3 - \frac{\sqrt{3}}{2}C_3^2 - \frac{\sqrt{3}}{2}\sigma_2 + \frac{\sqrt{3}}{2}\sigma_3$$

$$\rho^3_{21} = -\frac{\sqrt{3}}{2}C_3 + \frac{\sqrt{3}}{2}C_3^2 - \frac{\sqrt{3}}{2}\sigma_2 + \frac{\sqrt{3}}{2}\sigma_3$$

$$\rho^3_{22} = E - \frac{1}{2}C_3 - \frac{1}{2}C_3^2 + \sigma_1 - \frac{1}{2}\sigma_2 - \frac{1}{2}\sigma_3$$

Applying these to the function ϕ_1 we obtain

$$\rho^3_{11}\phi_1 = \phi_1 - \frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 - \phi_1 + \frac{1}{2}\phi_3 + \frac{1}{2}\phi_2 = 0$$

$$\rho^3_{12}\phi_1 = \frac{\sqrt{3}}{2}\phi_2 - \frac{\sqrt{3}}{2}\phi_3 - \frac{\sqrt{3}}{2}\phi_3 + \frac{\sqrt{3}}{2}\phi_2 = \sqrt{3}(\phi_2 - \phi_3)$$

$$\rho^3_{21}\ _1 = \frac{-\sqrt{3}}{2}\phi_2 + \frac{\sqrt{3}}{2}\phi_3 - \frac{\sqrt{3}}{2}\phi_3 + \frac{\sqrt{3}}{2}\phi_2 = 0$$

$$\rho^3_{22}\ _1 = \phi_1 - \frac{1}{2}\phi_2 - \frac{1}{2}\phi_3 + \phi_1 - \frac{1}{2}\phi_3 - \frac{1}{2}\phi_2 = 2\phi_1 - \phi_2 - \phi_3$$

What have we obtained through the use of these projection operators? We see that the irreducible representation $\Gamma_3(R)$ is contained only once in this function ϕ_1. The partners in the basis for the third representation are the functions $\rho^3_{12}\phi_1$ and $\rho^3_{22}\phi_1$ or $\sqrt{3}(\phi_2 - \phi_3)$ and $2\phi_1 - \phi_2 - \phi_3$. This is what we expect from relation (3-36).

Let us now see if this checks what we might expect by considering the number of times the irreducible representation generated by the functions ϕ_1, ϕ_2, and ϕ_3 contains the various irreducible representations of the group C_{3v}. Let us call the reducible representation generated by ϕ_1, ϕ_2, and ϕ_3, $\Gamma(R)$. The characters of this representation are easily seen to be

$$\chi(E) = 3 \qquad \chi(\sigma_1) = 1$$

$$\chi(C_3) = 0 \qquad \chi(\sigma_2) = 1$$

$$\chi(C_3^2) = 0 \qquad \chi(\sigma_3) = 1$$

Using the result of Theorem 9, we find that the number of times the various irreducible representations are contained in $\Gamma(R)$ is given by

$$c_a = \frac{1}{g}\sum_R \chi(R)\,\chi_a^*(R)$$

$$c_1 = \frac{1}{6}\left[3(1) + 0(1) + 0(1) + 1(1) + (1)(1) + 1(1)\right]$$

$$c_1 = 1$$

$$c_2 = \frac{1}{6}\left[3(1) + 0(1) + 0(1) + (1)(-1) + 1(-1) + 1(-1)\right]$$

$$c_2 = 0$$

$$c_3 = \frac{1}{6}\left[3(2) + 0(-1) + 0(-1) + 1(0) + 1(0) + 1(0)\right]$$

$$c_3 = 1$$

Thus the first irreducible representation is contained once in the reducible representation. The second is contained not at all and the third is contained once. This, of course, is just the result which we obtained through the use of our projection operators.

We mentioned in connection with projection operators that they extract that portion of a function which transforms according to a given irreducible representation. It is quite informing to look into this property further. Suppose we had a group $\mathcal{G}$ with r irreducible representations. Then we could form the g (g is the order of the group)

$$\rho^{\alpha}_{ij} = \sum \Gamma_{\alpha}(R)^{*}_{ij} R \qquad \begin{matrix} \alpha = 1, \ldots, r \\ i, j = 1, \ldots, n_{\alpha} \end{matrix}$$

Now let us consider an arbitrary function ϕ and take just the projection operators arising from the diagonal elements in the irreducible representation and apply them to ϕ.

$$\phi^{\alpha}_{ii} = \rho^{\alpha}_{ii}\,\phi \tag{3-39}$$

As i goes from 1 to n_{α} we select functions which transform according to the i^{th} column of the α irreducible representation. (In general, as we have seen, ϕ^{α}_{ii} is not a partner in the same basis as ϕ^{α}_{jj}). Let us now add up the functions ϕ^{α}_{ii} over α and i multiplying each by n_{α}/g.

$$\begin{aligned} \sum_{\alpha, i} \frac{n_{\alpha}}{g} \phi^{\alpha}_{ii} &= \sum_{R} \sum_{\alpha i} \frac{n_{\alpha}}{g} \Gamma_{\alpha}(R)^{*}_{ii} R\phi \\ &= \sum_{R} \sum_{\alpha} \frac{n_{\alpha}}{g} \chi_{\alpha}(R)^{*} R\phi \end{aligned} \tag{3-40}$$

Using the result of Eq. (2-150) of Chapter II, we obtain

$$\sum_{a,i} \frac{n_a}{g} \phi_{ii}^a = E\phi = \phi$$
$$\phi = \sum_a \sum_i \frac{n_a}{g} \phi_{ii} \tag{3-41}$$

What we have done by the use of these projection operators is to decompose an arbitrary function into a sum of functions which transform as the various irreducible representations of the group. This is very familiar to us. When we decompose an arbitrary function of x, y, and z into a sum of spherical harmonics of the angular spherical coordinates times functions of the distance from the origin, we are doing the same thing.

$$f(x, y, z) = \sum_{\ell m} f_{\ell m}(r)\, e^{im\phi}\, P_\ell^m(\cos\theta)$$

In this case $f_{\ell m}(r)\, e^{im\phi}\, P_\ell^m(\cos\theta)$ transforms in a specified way according to the entire rotation group in three dimensions. (The group consists of all rotations about the origin.)

We do not always have at our disposal the complete matrices of an irreducible representation of a group. In general, we have only the character table. This is sufficient information to construct projection operators which do not give as much information as the operators (3-31) but which do give some useful results. Consider the operator

$$\eta_a = \sum_R \chi_a^*(R)\, R$$
$$= \sum_i \rho_{ii}^a$$

In terms of these operators, Eq. (3-41) can be rewritten as

$$\phi = \sum_a \frac{n_a}{g} (\eta_a \phi)$$

Thus, the function $\eta_a\phi$ contains the sum of all parts of the function ϕ which transform as the a irreducible representation. Thus, these character projection operators enable us to determine immediately if an arbitrary function contains any portion which transforms as part of a basis for the a irreducible representation. Since character tables are, in general, readily available for the simple groups, these projection operators prove quite useful.

We can go even further into the theory of projection operators and derive results useful to quantum mechanics. First, let us form projection operators for the a irreducible representation

$$\rho^{a}_{ij} = \sum_{R} \Gamma_{a}(R)^{*}_{ij} R$$

Now imagine we had a set of functions which transform as partners in a basis for this representation; $f_1, \ldots, f_{n_a}$

$$Rf_i = \sum_{j=1}^{n_a} \Gamma_a(R)_{ji} f_j$$

We could now apply the operator ρ^{a}_{ij} to f_j

$$\rho^{a}_{ij} f_j = \sum_{R} \Gamma_a(R)^{*}_{ij} R f_j$$

$$= \sum_{R} \sum_{k} \Gamma_a(R)^{*}_{ij} \Gamma_a(R)_{kj} f_k$$

Using the orthogonality relations for the matrix elements of an irreducible representation, we obtain

$$\rho^{a}_{ij} f_j = \sum_{k} \frac{g}{n_a} \delta_{ik} f_k \qquad (3\text{-}42)$$

$$= \frac{g}{n_a} f_j$$

We see that ρ^{a}_{ij} when applied to f_j gives a multiple of f_i (another partner in the same irreducible representation). These operators appear as "step" operators which take us from one partner in an irreducible representation to another.

Now let us consider the integral (inner product) of the product of two functions ρf and ηg where ρ and η are hypercomplex numbers.

$$(\rho f, \eta g) = \int (\rho f)^{*} \eta g \, dx_1, \ldots dx_n \qquad \rho = \sum a_R R$$

$$(\rho f, \eta g) = \sum_{R, R'} a^{*}_{R} b_{R'} (Rf, R'g) \qquad \eta = \sum b_R R$$

From the unitary nature of the operators we have

$$(\rho f, \eta g) = \sum_{R, R'} a^{*}_{R} b_{R'} (f, R^{-1} R' g)$$

If we define $\eta^{\dagger} = \sum a^{*}_{R} R^{-1}$, we have

$$(\rho f, \eta g) = (f, \rho^{\dagger} \eta g) \qquad (3\text{-}43)$$

In particular, if

$$\rho = \rho_{ij}^{\alpha} = \sum_R \Gamma_\alpha(R)_{ij}^* R$$

$$\eta = \rho_{ij}^{\beta} = \sum_R \Gamma_\beta(R)_{k\ell}^* R$$

where Γ_α and Γ_β are unitary irreducible representations, we have

$$(\rho_{ij}^{\alpha} f, \rho_{k\ell}^{\beta} g) = (f, \rho_{ij}^{\alpha\dagger} \rho_{k\ell}^{\beta} g)$$

But

$$\rho_{ij}^{\alpha\dagger} = \sum_R \Gamma_\alpha(R)_{ij} R^{-1} = \sum_R \Gamma_\alpha(R^{-1})_{ij} R = \sum_R \Gamma_\alpha(R)_{ji}^* R = \rho_{ji}^{\alpha}$$

We therefore obtain

$$(\rho_{ij}^{\alpha} f, \rho_{k\ell}^{\beta} g) = (f, \rho_{ji}^{\alpha} \rho_{k\ell}^{\beta} g)$$

Using (3-34) of this chapter

$$(\rho_{ij}^{\alpha} f, \rho_{k\ell}^{\beta} g) = \frac{g}{n_\beta} \delta_{\alpha\beta} \delta_{kj} (f, \rho_{j\ell}^{\beta} g) \tag{3-44}$$

We can now prove a useful theorem.

> Theorem 14: Functions which are part of bases for different irreducible representations of a group $\mathcal{G}$ and functions transforming according to different columns of the same irreducible representations are orthogonal.

Proof: Let $f_1^{\alpha}, \ldots f_{n_\alpha}^{\alpha}$ form a basis for the α irreducible representation and $g_1^{\beta}, \ldots, g_{n_\beta}^{\beta}$ form a basis for the β irreducible representation. From the relation (3-42) this can be written as

$$(g_i^{\beta}, f_j^{\alpha}) = \frac{n_\alpha n_\beta}{g^2} (\rho_{ii}^{\beta} g_i, \rho_{jj}^{\alpha} f_j)$$

From Eq. (3-44) this becomes

$$(g_i^{\beta}, f_j^{\alpha}) = \frac{n_\alpha n_\beta}{g^2} \frac{g}{n_\beta} \delta_{\alpha\beta} \delta_{ij} (g_i^{\beta}, \rho_{jj}^{\alpha} f_j^{\alpha})$$

We have proven our theorem. g_i^{β} and f_j^{α} are orthogonal if $\alpha \neq \beta$. They are even orthogonal if $\alpha = \beta$ if $i \neq j$. We can also see that if $\alpha = \beta$, $i = j$

$$(g_i^{\alpha}, f_i^{\alpha}) = (g_j^{\alpha}, f_j^{\alpha}) \quad \text{for all i and j corresponding to a given } \alpha \tag{3-45}$$

This is true since

$$(g_i^\alpha,\ f_i^\alpha) = \frac{n_\alpha^{\,2}}{g^2}(\rho_{ij}^\alpha\, g_j^\alpha,\ \rho_{ij}^\alpha\, f_j^\alpha)$$
$$= \frac{n_\alpha}{g}(g_j^\alpha,\ \rho_{jj}^\alpha f_j^\alpha)$$
$$= (g_j^\alpha,\ f_j^\alpha)$$

We generally have the problem of finding matrix elements of our Hamiltonian H between functions. In this connection we have an additional theorem.

Theorem 15: For the group of the Schrödinger equation (using the notation of the last theorem)

$$(g_i^\beta,\ Hf_j^\alpha) = 0$$

unless $\alpha = \beta$, $i = j$; and in addition

$$(g_i^\alpha,\ Hf_i^\alpha) = (g_j^\alpha,\ Hf_j^\alpha)$$

for all i and j corresponding to a given α

Proof:

$$(g_i^\beta,\ Hf_j^\alpha) = \frac{n_\alpha n_\beta}{g^2}(\rho_{ii}^\beta g_i^\beta,\ H\rho_{jj}^\alpha f_j^\alpha)$$
$$= \frac{n_\alpha n_\beta}{g^2}(g_i^\beta,\ \rho_{ij}^\beta H\rho_{jj}^\alpha f_j^\alpha)$$

Since all the operators in the group commute with the Hamiltonian

$$\rho_{ii}^\beta H = H\rho_{ii}^\beta$$

therefore

$$(g_i^\beta,\ Hf_j^\alpha) = \frac{n_\alpha n_\beta}{g^2}(g_i^\beta,\ H\rho_{ii}^\beta\rho_{jj}^\alpha f_j^\alpha)$$
$$= \frac{n_\alpha}{g}\,\delta_{\alpha\beta}\,\delta_{ij}(g_i^\beta,\ H\rho_{jj}^\alpha f_j^\alpha)$$

In an analogous way, using the fact that $\rho_{ij}^\alpha H = H\rho_{ij}^\alpha$ and the method of Theorem 14, we can prove

$$(g_i^{\alpha},\ Hf_i^{\alpha}) = (g_j^{\alpha},\ Hf_j^{\alpha}) \tag{3-46}$$

We have proved this for the Hamiltonian operator H. It is clear that the same theorem is true for any operator V which is invariant under the same symmetry operations as the Hamiltonian.

From these discussions we can gain a greater insight into the degeneracy of the solutions of Schrödinger's equation. We recall that the solutions of Schrödinger's equation could be chosen so that the eigenfunctions all form bases for irreducible representations of the group of Schrödinger's equation. Functions transforming as partners in a basis for the same irreducible representation had the same energy. In the event two irreducible representations had the same energy, we said that we had an accidental degeneracy. Let us assume that we had solutions of Schrödinger's equation $H\psi = E\psi$. Let us denote the solutions by $\psi_1^{\alpha, n}$. By this we mean that $\psi_i^{\alpha, n}$ transforms according to the i^{th} column of the α irreducible representation. n denotes which energy level we are discussing. In general, there will be more than one set of functions which are solution of Schrödinger's equation which transform according to the α irreducible representation. n is the index which distinguishes these. (In the case of the hydrogen atom n would denote the principle quantum number.)

Let us now apply a perturbation V which is invariant under the group of Schrödinger's equation. We could attempt to find the eigenfunctions and eigenvalues of the new Hamiltonian H + V by expanding the perturbed wave function in terms of $\psi_i^{\alpha, n}$, setting up the matrix of interaction. From our discussion in the last paragraph we notice that the matrix element $(\psi_i^{\alpha, n}(H + V)\psi_i^{\alpha', n'})$ will vanish unless $\alpha = \alpha'$, $i = i'$. Thus to find the eigenvalues all we need do is solve the secular problem between functions transforming as the same column in the same irreducible representation and then do this for all representations and columns in this representation. There is an additional simplification since

$$(\psi_i^{\alpha, n}(H + V)\ \psi_i^{\alpha, n'}) = (\psi_j^{\alpha, n}(H + V)\ \psi_j^{\alpha, n'})$$

From this we see that if we focus our attention on a particular irreducible representation the matrix of interaction is the same for all functions transforming according to one column as it is for functions transforming according to any other column. Thus the eigenvalues and eigenvectors of these two problems are the same. Thus, if

$$\phi_i^{\alpha, n} = \sum c_{\alpha, n}\, \psi_i^{\alpha, n}$$

is a solution to the perturbed problem, so is

$$\phi_j^{\alpha, n} = \sum c_{\alpha, n} \psi_j^{\alpha, n}$$

From the transformation properties of the ψ's we see that $\phi_i^{\alpha, n}$ and $\phi_j^{\alpha, n}$ are partners in the basis for the same irreducible representation and, of course, correspond to the same energy level. From this we see that any symmetric perturbation cannot split the degeneracies inherent in a given irreducible representation. All the perturbation can do is to shift the energies about. This is not the case for an accidental degeneracy. The matrix of interaction affecting one irreducible representation corresponding to a given energy level of the unperturbed problem can be quite different from that corresponding to another irreducible representation with the same unperturbed energy. This type of degeneracy can be split by a symmetric perturbation. This is the reason for calling it an accidental degeneracy. It depends not on the symmetry of the Hamiltonian but on its more detailed characteristics.

This is about as far as we can carry the general discussion of the group of Schrödinger's equation without looking in detail at the form of specific Hamiltonians and discussing in detail the groups of these Hamiltonians.

In many problems of atomic, molecular, and solid state physics, it is convenient to start with a spin free Hamiltonian representing the interaction of electrons with each other and with the nuclei. Let us deal with an n electron problem. Let us denote the position of the α nucleus with charge z_α by $\vec{R}_\alpha$ and the position of the i^{th} electron by $\vec{r}_i$. The Hamiltonian for this problem we shall take to be

$$\sum_{i=1}^{n} -\nabla_i^2 + \sum_{\alpha} -\nabla_\alpha^2 + \frac{1}{2} \sum_{i \neq j} \frac{2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i, \alpha} \frac{2Z_\alpha}{|\vec{r}_i - \vec{R}_\alpha|} + \frac{1}{2} \sum_{\alpha \neq \beta} \frac{2Z_\alpha Z_\beta}{|\vec{R}_\alpha - \vec{R}_\beta|} \qquad (3\text{-}47)$$

(This Hamiltonian is in atomic units.) The first term is the kinetic energy of the electrons, the second is the kinetic energy of the nuclei. The last three terms represent the Coulomb interactions between the electrons with each other and the nuclei and the Coulomb interactions of the nuclei amongst themselves. This Hamiltonian has certain invariant properties. We notice that it is invariant under interchanges of the coordinates of the electrons. It is also invariant under interchanges of the identical nuclei. Any rotation of the coordinates of all the particles or inversion through the origin will leave the Hamiltonian unchanged. Since spin coordinates for the electrons and nuclei do not appear in the Hamiltonian it is also invariant under interchanges of the spin coordinates of the electrons. We have not exhausted the invariant properties of this Hamiltonian. We shall not go further in enumerating the invariances of this Hamiltonian since in the problems of atomic, molecular, and solid state physics we often concern ourselves with approximate Hamiltonians in which we hold all the nuclei fixed and just solve for the electronic wave functions and energy levels which arise from this

Hamiltonian. In this case the Hamiltonian (outside of an additive constant) is given by

$$H = \sum - \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,a} \frac{2Z_a}{|\vec{r}_i - \vec{R}_a|} \qquad (3\text{-}48)$$

We shall now consider in detail the groups associated with this Hamiltonain. It is invariant under interchanges of the space coordinates of the electrons. These operations are permutations of n objects and there are n! such operations. Secondly, it is invariant under any rotation, reflection or inversion of the coordinates of all the electrons which would leave their positions relative to the identical nuclei involved unchanged. Thus, if there were identical nuclei located at the corners of an equilateral triangle, the Hamiltonian would be invariant under the group C_{3v}. Any operation of this group applied to the total electronic system would leave its energy unaltered. The Hamiltonian is invariant under permutations of the spin coordinates of the various electrons and also under any rotations of the spins of all the electrons since spin coordinates do not appear in this Hamiltonian.

It is clear that all the permutations of the space coordinates of the electrons form a group as do the reflections, rotations, and inversions which send identical nuclei into each other. It is also clear that if we call the permutations of space coordinates P^S and the reflections, rotations, and inversions R, that $P^S R = R P^S$. The order in which the permutation and rotation are carried out is immaterial and we could say the group of permutations of space coordinates commutes with the group of symmetry operations (rotations, etc.). If we call $\mathcal{S}$ the group of spatial permutations and $\mathcal{G}$ the group of symmetry operations, the Hamiltonian is invariant under a group $\mathcal{S} \times \mathcal{G}$. The elements of this group are just the products of pairs of elements taken from $\mathcal{S}$ and $\mathcal{G}$. This is called the direct product of these two groups. Now let us take the direct products of the matrices in the irreducible representations of $\mathcal{S}$ and $\mathcal{G}$.

$$\Gamma_{a\beta}(P^S R) = \Gamma_a(P^S) \times \Gamma_\beta(R)$$

It is easy to show that this new set of matrices $\Gamma_{a\beta}(P^S R)$, when defined for all products of P^S and R, will form a representation of the group $\mathcal{S} \times \mathcal{G}$. We can also show that this representation is irreducible. Let us use Theorem 10 to prove this. If $\mathcal{S}$ is of the order g' and $\mathcal{G}$ is of the order g, then $\mathcal{S} \times \mathcal{G}$ is of the order gg'. If we take the sum of the squares of the characters of the matrices $\Gamma_{a\beta}(P^S R)$, we obtain

$$\sum_{P^S, R} |\chi_{a\beta}(P^S R)|^2 = \sum_{P^S, R} |\chi_a(P^S)|^2 |\chi_\beta(R)|^2$$

$$= \sum_{P^S} |\chi_a(P^S)|^2 \sum_R |\chi_\beta(R)|^2$$

This yields

$$\sum_{P^S, R} |\chi_{\alpha\beta}(P^S R)|^2 = gg'$$

Thus, we have shown that the products of the irreducible representations of the commuting groups yields irreducible representations of the product group. It is not difficult to show that we exhaust the irreducible representations in the group $\mathcal{S} \times \mathcal{G}$ in this way.

Similarly, the group of spin permutations commutes with both $\mathcal{S}$ and $\mathcal{G}$. We shall call these spin permutations P^σ. We could now define a group consisting of the products of the three groups above and find the irreducible representations of this product group from the irreducible representations of the three groups. In general, we see that in specifying the irreducible representations of the entire group of Schrödinger's equation we can specify the irreducible representations of the groups whose products go into making up the group of Schrödinger's equation. This enables us to discuss one at a time the individual groups that go into the group of Schrödinger's equation. In the next chapter we discuss the permutation groups of spin and space coordinates. This is the most general invariant property of the Hamiltonian (3-48). The groups which send identical nuclei into each other depends on the precise location of the nuclei in a problem and we shall restrict our discussion of these groups to a later section.

Chapter IV

PERMUTATION GROUPS AND THE DIRAC VECTOR MODEL

In the last chapter we saw that the Hamiltonians which we were considering were invariant under permutations of spatial and spin coordinates. In order to study the consequences of this invariance on our eigenstates, we shall need a familiarity with the symmetric groups (all permutations of n objects). There is a wealth of literature on the properties of these groups and their irreducible representations. We shall not go into the properties of these groups in detail. A few of the more general properties of the symmetric group are all that we shall require for our purposes.

1. Permutation Groups

In Chapter I, we introduced the concept of a permutation. For the first n integers, a permutation was defined as the operation which rearranged these numbers. The operation was specified by the symbol P and defined by

$$P = \begin{pmatrix} 1 & 2 & \cdots & n \\ a_1 & a_2 & & a_n \end{pmatrix} \tag{4-1}$$

The meaning of this symbol was that 1 was replaced by a_1, 2 by a_2, ... n by a_n. $a_1 \ldots a_n$ were distinct integers taken from 1 ... n. The order in which we write the columns is immaterial. Thus

$$P = \begin{pmatrix} 1 & 2 & \cdots & n \\ a_1 & a_2 & \cdots & a_n \end{pmatrix} = \begin{pmatrix} 2 & 1 & 5 & \cdots & n \\ a_2 & a_1 & a_5 & \cdots & a_n \end{pmatrix}$$

The inverse of a permutation P is given by

$$P^{-1} = \begin{pmatrix} a_1 & a_2 & \cdots & a_n \\ 1 & 2 & \cdots & n \end{pmatrix} \tag{4-2}$$

The product of a permutation S and a permutation P

$$S = \begin{pmatrix} 1 & 2 & \cdots & n \\ b_1 & b_2 & \cdots & b_n \end{pmatrix} = \begin{pmatrix} a_1 & a_2 & \cdots & a_n \\ c_1 & c_2 & \cdots & c_n \end{pmatrix}$$

is given by

$$SP = \begin{pmatrix} a_1 & a_2 & \cdots & a_n \\ c_1 & c_2 & \cdots & c_n \end{pmatrix} \begin{pmatrix} 1 & 2 & \cdots & n \\ a_1 & a_2 & \cdots & a_n \end{pmatrix} = \begin{pmatrix} 1 & 2 & \cdots & n \\ c_1 & c_2 & \cdots & c_n \end{pmatrix}$$

It is easily verified that the operations effecting the n! rearrangements of the integers 1 through n form a group called the symmetric group of degree n which has n! elements.

Of particular interest are the cyclic permutations. Thus, if we have q objects, a cyclic permutation is

$$\begin{pmatrix} 1 & 2 & 3 & \dots & q \\ 2 & 3 & 4 & \dots & q\ 1 \end{pmatrix}$$

In other words, the first object is replaced by the second, the second by the third, etc., the q^{th} being replaced by the first. It is convenient to use a special symbol for the permutations of this kind. We denote this permutation by (1 2 3 ... q). It will be understood that by this symbol we mean

$$\begin{pmatrix} 1 & 2 & 3 & \dots & q \\ 2 & 3 & 4 & \dots & q\ 1 \end{pmatrix}$$

It will be also understood that (1 2 3 ... q) = (2 3 4 ... q 1), etc.

The concept of a cyclic permutation allows us to decompose our permutations in a meaningful way. We can decompose any permutation into cycles. Any permutation will then appear as a product of commuting cycles with no common integers. We could carry out this process as follows: Let us start with any object μ_1. μ_1 is replaced by μ_2, we can then find that μ_2 is replaced by μ_3. Eventually we must end up with some object being replaced by μ_1. In this way, at least part of the effect of the general permutation is given by the cycle $(\mu_1, \mu_2 \cdots \mu_r)$. Here $r \leqslant n$. If this does not exhaust the number of objects, we can choose an element not in the set $\mu_1 \cdots \mu_r$ and proceed in a similar way. This will give us another cycle which we might take to be $\lambda_1, \lambda_2 \cdots \lambda_s)$. Now $s + r \leqslant n$. We can carry out this process until we exhaust the n objects. We can then write the effect of our permutation as $(\mu_1, \mu_2 \cdots \mu_r)(\lambda_1 \cdots \lambda_s)(\dots) \cdots (\gamma_1 \cdots \gamma_q)$ where $r + s + \dots + q = n$. In other words, by this method of decomposition we have written the permutation as a product of disjoint cycles. The order of the cycles does not matter since the cycles act on different objects.

As an example let us decompose the permutation

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 4 & 3 & 2 & 5 & 7 & 6 & 1 \end{pmatrix}$$

into cycles. We see that 1 is replaced by 4, 4 by 5, 5 by 7, and 7 by 1. Thus, the first cycle is (1 4 5 7). This leaves 2, 3 and 6 left over. 2 is replaced by 3 and 3 by 2. This leaves 6 over which is replaced by itself. We have that

$$P = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ 4 & 3 & 2 & 5 & 7 & 6 & 1 \end{pmatrix} = (1\ 4\ 5\ 7)(2\ 3)(6)$$

In this way, we see that any permutation can be decomposed into cycles. It is clear that the decomposition of a permutation into cycles is unique since different products of cycles correspond to different permutations. (In this last statement, we assume that two products of disjoint cycles are the same if the only different is in the order of the factors.)

Let us assume that a permutation from the symmetric group of degree n is decomposed into cycles. Let us say there are λ_1 cycles of length 1, λ_2 cycles of length 2, etc. there being λ_n cycles of length n.

$$n = \lambda_1 + 2\lambda_2 + 3\lambda_3 + \ldots n\lambda_n$$

In the example given above there is one cycle of length one, one cycle of length two, and one cycle of length three. In this symmetric group of degree 7 there is more than one permutation which has one cycle each of lengths one, two, and three. The permutation (1 2 4 5)(6 7)(3) is one of this type. It is easily seen that for the symmetric group of degree n with λ_1 cycle of length 1, etc. up to λ_n cycles of length n, there are

$$\frac{n!}{1^{\lambda_1}\lambda_1!\ 2^{\lambda_2}\lambda_2!\ \ldots\ r^{\lambda_r}\lambda_r!} \tag{4-3}$$

permutations having what we shall call the same cycle structure (the same number r of cycles of each length). We can show that the permutations with the same cycle structure belong to the same class.

Let us suppose that we had two permutations with the same cycle structure. Both of these can be decomposed in the same way into cycles. Let us say that they both have r cycles of lengths $\lambda_1, \lambda_2 \ldots \lambda_r$

$$P = (a_1\ a_2\ \ldots\ a_{\lambda_1})(b_1\ b_2\ \ldots\ b_{\lambda_2})\ldots(d_1\ \ldots\ d_{\lambda_r})$$

$$P' = (a_1'a_2'\ldots\ a_{\lambda_1}')(b_1'b_2'\ldots\ b_{\lambda_2}')\ldots(d_1'\ldots\ d_{\lambda_r}')$$

Consider the permutations

$$T = \begin{pmatrix} a_1' \ldots a_{\lambda_1}'\ b_1' \ldots b_{\lambda_2}' \ldots d_1' \ldots d_{\lambda_r}' \\ a_1\ \ldots\ a_{\lambda_1}\ b_1\ \ldots\ b_{\lambda_2} \ldots d_1\ \ldots\ d_{\lambda_r} \end{pmatrix}$$

$$T^{-1} = \begin{pmatrix} a_1\ \ldots\ a_{\lambda_1}\ b_1\ \ldots\ b_{\lambda_2} \ldots d_1\ \ldots\ d_{\lambda_r} \\ a_1' \ldots a_{\lambda_1}'\ b_1' \ldots b_{\lambda_2}' \ldots d_1' \ldots d_{\lambda_r}' \end{pmatrix}$$

We can verify by direct multiplication that

$$T^{-1}\,P\,T = P'$$

In this way, we have shown that permutations with the same cycle structure belong to the same class. The number of permutations in a given class is given by the formula (4-3).

The number of different classes is the number of different cycle structures. Th is is seen to be the number of ways in which the number n can be decomposed into a sum of positive integers. For the symmetric group of degree 4, for example, there will be 5 classes

$$4 = 4$$
$$4 = 3 + 1$$
$$4 = 2 + 2$$
$$4 = 2 + 1 + 1$$
$$4 = 1 + 1 + 1 + 1$$

Since the number of irreducible representations is equal to the number of classes we have the result that the number of irreducible representations of the symmetric group of degree n is equal to the number of ways that the number n can be decomposed into a sum of positive integers.

In general, we shall omit in writing the cycle structure all cycles of length 1. It will be understood that the missing integers are left unchanged. For example

$$(1\ 4\ 5\ 7)(2\ 3)(6) = (1\ 4\ 5\ 7)(2\ 3)$$

Cycles of length 2 are called transpositions. All the cycles of length 2 taken together form a class of the symmetric group. Every cycle can be decomposed into a product of transpositions.

$$(a_1 a_2 \cdots a_q) = (a_1 a_2)(a_2 a_3) \cdots (a_{q-1} a_q)$$

In this way, any permutation in the symmetric group can be decomposed into a product of transpositions. This decomposition is not unique. It turns out to be the case, however, that all permutations are of one of two types. A permutation can be decomposed into an odd number of transpositions or it can be decomposed into an even number of transpositions. We shall now define what are called even and odd permutations and show that even permutations can be decomposed into an even number of transpositions, and odd permutations into an odd number of transpositions.

Consider the product of the differences of the independent variables $x_1, x_2, \cdots x_n$

$$\begin{aligned} &(x_1 - x_2)(x_1 - x_3) \cdots\cdots (x_1 - x_n) \\ &\quad \times (x_2 - x_3)(x_2 - x_4) \cdots (x_2 - x_n) \\ &\qquad \times (x_3 - x_4) \cdots\cdots \\ &\qquad\quad \cdots \\ &\qquad\qquad \times (x_{n-1} - x_n) \end{aligned} \tag{4-4}$$

If we permute the indices 1 through n, it is clear that there are two possibilities. We either get back the original form (4-4) or we get the negative of the form. Permutations which send the form into itself are called even permutations. Those which send (4-4) into its negative are called odd permutations. From this we conclude at once that a product of two even or two odd permutations is again an even permutation and that the product of an odd and an even permutation is an odd permutation. By applying a transposition to the form (4-4) we see that it goes into its negative. Transpositions are therefore odd permutations. It is clear then that any odd permutations must be decomposable only into products of odd numbers of transpositions and even permutations are decomposed into products of even numbers of transpositions. We can also conclude from the process of decomposing cycles into transpositions that all permutations in a given class must be either all odd or all even. Since a permutation and its inverse have the same cycle structure (therefore belong to the same class) the inverse of an odd permutation is an odd permutation and the inverse of an even permutation is an even permutation.

Since the product of two even permutations is again an even permutation we can conclude that the collection of all even permutations in a symmetric group is a subgroup of that symmetric group. This is called the alternating group. It is, of course, an invariant subgroup, since for any even permutation P, $T^{-1} P T$ is also an even permutation. We can see that the alternating group contains half as many elements as the corresponding symmetric group. Consider PP' where P is an odd permutation. If we let P run over all even permutations, PP' must run over all odd permutations. Every odd permutation must appear in the collection of permutations PP' since we can solve $P' = P^{-1}P''$ which must be an even permutation and hence a member of the alternating group.

This information is sufficient to gain some insight into the irreducible representations of the symmetric group. One representation can be found at once namely the symmetric representation $\Gamma_1(P) = 1$. If we represent all elements in the alternating group by + 1 and all the odd permutations by - 1, we also get an irreducible representation of the symmetric group. We denote this representation by $\Gamma_1'(P)$ and call it the antisymmetric representation. There are no other one-dimensional representations of the symmetric group. We can see this most easily by writing every permutation as a product of transpositions. Every transposition can be represented by either one or minus one. (All transpositions belong to the same class, hence for a one-dimensional representation they must have the same matrices representing them.) They must be represented ± 1 since the square of any transposition is the identity element. Since any permutation can be written as the product of an even or an odd number of permutations depending on whether the permutation is even or odd, it is clear that the two one-dimensional representations we have given above exhaust the possibilities.

All other representations of the symmetric group must have dimension greater

than one. Let us assume that we have an irreducible representation $\Gamma_a(P)$. By forming the direct product of this representation with $\Gamma_1'(P)$ we form a new representation of the same dimension

$$\Gamma_a'(P) = \Gamma_a(P) \times \Gamma_1'(P) \tag{4-5}$$

In this representation all the matrices representing the odd permutations are mutliplied by - 1 and all the matrices representing even permutations by + 1. For the symmetric group of degree n we have from Theorem 10

$$\sum_P |\chi_a(P)|^2 = n!$$

From this we conclude that

$$\sum_P |\chi_a'(P)|^2 = n!$$

Therefore, the representation (4-5) is also an irreducible representation. For every irreducible representation $\Gamma_a(P)$ of the symmetric group there is an irreducible representation $\Gamma_a'(P) = \Gamma_a(P) \times \Gamma_1'(P)$ which we shall call the associated representation.

This by no means exhausts the knowledge of the properties of the irreducible representation of the symmetric group. These groups have been studied in great detail and there is a wealth of knowledge concerning their properties and irreducible representations. For our purposes we shall not need for the present any further properties of the symmetric group. We are now in a position to apply our knowledge of the symmetric group to the eigenfunctions of Schrödinger's equation.

2. Permutations of Spin Coordinates

We recall that associated with every electron is a spin angular momentum. For an electron this angular momentum can have a z component of either $\frac{1}{2}\hbar$ or $-\frac{1}{2}\hbar$. By this we mean that if we form the usual angular momentum operators $s^2 = s_x^2 + s_y^2 + s_z^2$, and s_z we can, for a particle of spin $\frac{1}{2}$ (for example, an electron) find eigenstates of these operators which we shall denote by $\alpha(i)$ and $\beta(i)$, and which have the properties that

$$s^2\alpha(i) = h^2 \frac{1}{2}(\frac{3}{2})\, \alpha(i)$$

$$s^2\beta(i) = \hbar^2 \frac{1}{2}(\frac{3}{2})\, \beta(i)$$

$$s_z\alpha(i) = +\frac{1}{2}\hbar\, \alpha(i)$$

$$s_z\beta(i) = -\frac{1}{2}\hbar\, \beta(i)$$

By the argument i of the functions $\alpha(i)$ and $\beta(i)$ we mean that this corresponds to the spin of the i^{th} particle. It is sometimes convenient to define additional operators listed below

$$\sigma_x = \left(\frac{2}{\hbar}\right) s_x$$

$$\sigma_y = \left(\frac{2}{\hbar}\right) s_y$$

$$\sigma_z = \left(\frac{2}{\hbar}\right) s_z$$

$$\sigma^+ = \sigma_x + i\sigma_y$$

$$\sigma^- = \sigma_x - i\sigma_y$$

$$s^+ = s_x + is_y$$

$$s^- = s_x - is_y$$

The reader may recall that from the properties of angular momentum these operators have the properties

$$\sigma^+\alpha = 0$$

$$\sigma^+\beta = 2\alpha \qquad \sigma_z\alpha = \alpha$$

$$\sigma^-\alpha = 2\beta \qquad \sigma_z\beta = -\beta$$

$$\sigma^-\beta = 0$$

The functions $\alpha(i)$ and $\beta(i)$ form a complete set as far as the spin coordinates of an electron are concerned. Any function of all the coordinates (space plus spin) of an electron can be expanded in terms of these functions. Thus

$$\psi^+(x_i, y_i, z_i)\,\alpha(i) + \psi^-(x_i, y_i, z_i)\,\beta(i)$$

where ψ^+ and ψ^- are arbitrary functions, is the most general function we can have of all the coordinates of an electron.

For an n electron problem if we took all possible products of the spin eigenfunctions $\alpha(i)$ and $\beta(i)$ of the individual electrons we would have a complete set as far as the spin properties of the n electron problem were concerned. There are 2^n such product functions. Any function of all the coordinates of all the electrons could be written as a sum of these 2^n functions each multiplied by a function of the spatial coordinates of all of the electrons. Each of these 2^n spin product functions is an eigenstate of an operator

$$S_z = \sum_{i=1}^{n} s_{z_i}$$

with eigenvalues ranging from $\frac{1}{2}n\hbar$ to $-\frac{1}{2}n\hbar$. Since each of our one-electron spin eigenfunctions are eigenstates of the operators s_{z_i} the eigenvalue of the operator S_z when acting on a spin product function will just give as eigenvalue the sum of the eigenvalues of the particular one-electron spin functions which made up the product. Thus, if there were m particles with spin $+\frac{1}{2}$ and n - m particles with z component of spin $-\frac{1}{2}$ the eigenvalue of S_z for this spin product function would be $m - \frac{1}{2}n$. We shall denote by M_S the eigenvalues of the operator S_z and by m_{s_i} the eigenvalues of the operator for the z component of spin angular momentum of the i^{th} particle. We have therefore for a spin product function

$$M_S = \sum_i m_{s_i} = m - \frac{1}{2}n$$

We can see that for an n electron system the number of spin product functions with a z component of total spin M_S, is

$$\frac{n!}{(n-m)!\,m!} = \frac{n!}{(\frac{n}{2}+M_S)!\,(\frac{n}{2}-M_S)!}$$

Even though these 2^n spin product functions form a complete set as far as spin properties are concerned it is more convenient to form linear combinations of these spin product functions so that they are eigenstates of the total spin operator

$$S^2 = \sum_{i,j} (s_{x_i} s_{x_j} + s_{y_i} s_{y_j} + s_{z_i} s_{z_j})$$

In doing so we maintain the property that the functions are, in addition, eigenstates of the operator S_z. For this total angular momentum operator we have eigenvalues $S(S+1)\hbar$. A state with this value of spin can have as z component of its spin M_S = S, S - 1, ... -S.

Let us see how we can, in a systematic manner, build up states which are eigenstates of S^2 and S_z. (We shall refer to states which are eigenstates of S^2 as states of definite multiplicity.) To do this we start with one electron add another and couple their spins in the familiar way to form a state of spin S = 1 and another state with total spin S = 0. If we now add a third electron, we can, from the state S = 1 of the two-electron problem, form a state with $S = \frac{1}{2}$ and another with $S = \frac{3}{2}$. By combining the third electron with the S = 0 state of the two-electron problem we form a state with $S = \frac{1}{2}$ in addition to the state we have already formed with $S = \frac{1}{2}$. We have for the three-electron problem, by this procedure, two states with $S = \frac{1}{2}$ and one state with $S = \frac{3}{2}$. We can now continue this problem forming states for the four-electron problem. The number of states obtained for each multiplicity for the n electron problem

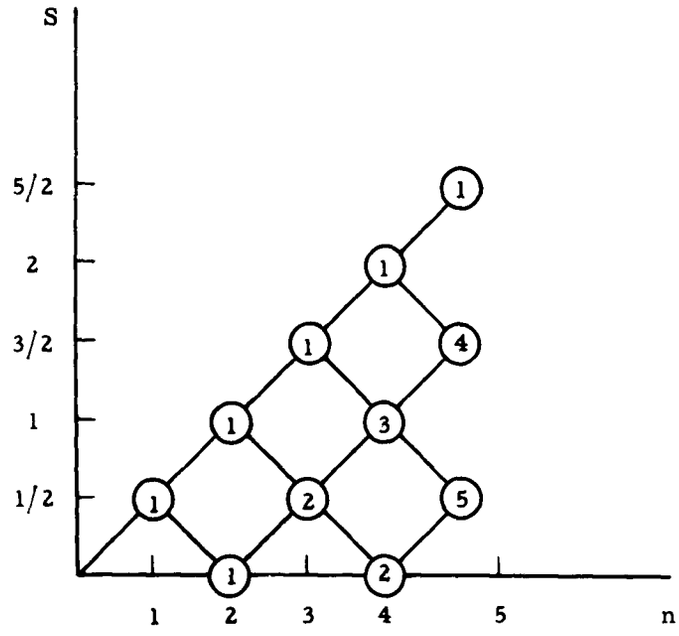


Fig. 4-1

is shown in the form of a branching diagram (Fig. 4-1). The numbers in the circles show the number of states of spin S of the n electron problem. By the number of states of spin S we mean the number of states with spin S and a given value of M_S. For each state of spin S of the n electron problem there will be 2S + 1 states with M_S taking on values from S to - S.

We can actually calculate the number of states of the n electron problem in spin space which are eigenstates of S^2 and S_z. We have found a formula for the number of states with a given value of M_S above. If we evaluate this formula for M_S = S + 1, we have the total number of states with their total spin greater or equal to S + 1 and M_S = S + 1. If we now take the difference between this number and the number of states with M_S = S, we shall find the number of states with total spin equal to S and a given value of M_S. This number is given by

$$\frac{n!}{(S + \frac{1}{2}n)!\,(\frac{1}{2}n - S)} - \frac{n!}{(S + 1 + \frac{1}{2}n)!\,(\frac{1}{2}n - S - 1)}$$

If we were to multiply this number by 2S + 1 and sum over S from 0 or $\frac{1}{2}$ (depending on whether n was odd or even) to $\frac{1}{2}$n, we would obtain the total number of states which is 2^n.

Let us check this for the five-electron problem. We see from Fig. 4-1 that there is one state with $S = \frac{5}{2}$. This means that there are five states with this value of S and M_S values ranging from $-\frac{5}{2}$ to $\frac{5}{2}$. For $S = \frac{3}{2}$ there are four independent states which can be formed for each value of M_S. There are four different values of M_S possible for $S = \frac{3}{2}$. This yields 16 more states. For $S = \frac{1}{2}$ there are five states and two M_S values. This yields 10 more states. We thus see that we check the number of states as $6 + 4(4) + 5(2) = 32 = 2^5$. We have therefore the same number of states in the scheme where S^2 and S_z are diagonal as we had in the simple product scheme for n = 5. This can be proved quite generally, but we shall not do it here the proof being quite straightforward.

We can actually exhibit a method of progressively forming states of definite multiplicity (S^2 a good quantum number) as we increase the number of electrons. Suppose we wanted to arrive at the states corresponding to a given value of S and n. The lines on the branching diagram indicate that these are constructed by adding one electron to the states corresponding to $S \pm 1/2$ and n - 1 electrons to form a state with spin S for the n electron problem.

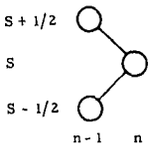


Fig. 4-2

The problem of compounding angular momentum is discussed in many texts. If we call $\phi(S, M_S)$ a state for which $S^2\phi(S, M_S) = S(S+1)\hbar^2\phi(S, M_S)$; $S_z\phi(S, M_S) = M_S\hbar\phi(S, M_S)$ and we add one electron to this system then we can form the states

$$\Psi(S + \tfrac{1}{2}, S + \tfrac{1}{2}) = \phi(S, S)\alpha$$

$$\Psi(S + \tfrac{1}{2}, S - \tfrac{1}{2}) = \frac{\sqrt{2S}\,\phi(S, S-1)\alpha + \phi(S, S)\beta}{\sqrt{2S+1}} \qquad (4\text{-}6)$$

$$\Psi(S - \tfrac{1}{2}, S - \tfrac{1}{2}) = \frac{\phi(S, S-1)\alpha - \sqrt{2S}\,\phi(S, S)\beta}{\sqrt{2S+1}}$$

With the repeated application of the formula (4-6) we can carry out the construction of states of given multiplicity and M_S by adding one electron at a time. If we label the q states corresponding to S + 1/2 and n - 1 electrons as $\psi_\ell(S + 1/2, M_S; n-1)\ \ell = 1 \ldots q$, and the p states corresponding to S - 1/2, M_S and n - 1 electrons as $\psi_\ell(S - 1/2, M_S; n-1)\ \ell = 1 \ldots p$, we can form p + q states with spin S and $M_S = S$. They are given in (4-7).

$$\psi_k(S, S, n) = \frac{\psi_k(S + \frac{1}{2}, S - \frac{1}{2}, n-1)\alpha - \sqrt{2S+1}\,\psi_k(S + \frac{1}{2}, S + \frac{1}{2}, n-1)\beta}{\sqrt{2S+2}} \qquad k = 1 \ldots p$$

$$\psi_k(S, S, n) = \psi_{k-p}(S - \tfrac{1}{2}, S - \tfrac{1}{2}, n-1)\alpha \qquad k = p+1 \ldots p+q \qquad (4\text{-}7)$$

In these formulas $\psi(S \pm \frac{1}{2}, M_S, n-1)$ depends on the coordinates of the first n - 1 electrons and α and β depend on the spin coordinate of the n^{th} electron. We have written here the states with $M_S = S$. In order to get the states with M_S ranging down to - S, all

we need do is to apply the step down operator

$$S^- = \frac{\hbar}{2} \sum_{i=1}^{n} \sigma_i^-$$

to these states and then normalize the resulting states. In this way, we can construct all states $\psi_\ell(S, M_S, n)$ for all S, M_S and n by building up our states from those of one electron. The states which we construct in this way can easily be seen, from the method of construction, to be normal and orthogonal.

This treatment represents at least one way of making states of definite multiplicity and M_S. It is a rather clumsy method and seems to have little to do with permutations of the spin coordinates. It will, however, turn out to be the case that the states $\psi_\ell(S, M_S, n)$ $\ell = 1 \ldots p + q$ form a basis for an irreducible representation of the group of spin coordinate permutations. Let us see how this comes about.

Since our Hamiltonian does not involve spin it is certainly invariant under permutations of the spin coordinates. We have, in the preceding paragraphs, constructed states which form a complete set as far as spin properties are concerned for an n electron system. Let us see what effect the spin permutation operators have on these states. We shall denote the spin permutation operators by P^σ. There are n! such operators. For example, if we denote by P^σ_{ij}, the operator corresponding to the interchange of the spin coordinate of the i^{th} and the j^{th} electron, we have

$$P^\sigma_{ij}\, \alpha(i)\, \beta(j) = \alpha(j)\, \beta(i)$$

Let us see what effect one of these spin permutation operators has on any n electron spin state which has M_S as a good quantum number. We shall denote this state by ψ and understand that it is any linear combination of spin product functions with the same value of M_S and which corresponds to n electrons.

$$S_z \psi = M_S \hbar \psi; \; S_z = \sum_{i=1}^{n} s_{z_i}$$

It is clear that S_z is an operator symmetric in all the spin coordinates and therefore S_z commutes with any operator representing permutations of the spin coordinates. $(S_z P^\sigma = P^\sigma S_z)$ This means, of course, that the state $P^\sigma \psi$ is also a state with the same value of M_S. In a similar way, since $S^2 = (s_1 + s_2 \ldots + s_n)^2$, then $P^\sigma S^2 = S^2 P^\sigma$. If ψ were a state of definite multiplicity, then $P^\sigma \psi$ is also a state of definite multiplicity with the same value of S as ψ. Thus we see that $P^\sigma \psi_\ell(S, M_S, n)$ must be some linear combination of the states corresponding to the same S, M_S, and of course n. We have, therefore, the result that

$$P^{\sigma}\psi_{\ell}(S, M_S, n) = \sum_{j=1}^{p+q} \Gamma(P^{\sigma})_{j\ell}\,\psi_j(S, M_S, n)$$

It is easily seen that if $''P^{\sigma} = {}'P^{\sigma}P^{\sigma}$ then

$$\Gamma(''P^{\sigma}) = \Gamma({}'P^{\sigma})\,\Gamma(P^{\sigma})$$

In this way we see that the matrices representing the effects on the set of functions corresponding to a given S, M_S, and n form a representation of the group of spin permutations of degree n. The dimension of this representation is given by the number of states of a definite multiplicity and M_S for the n electron problem. This is the number indicated in the circles in the branching diagram (Fig. 4-2) and we have also derived a formula for this number. We can show more about these representations. We can show that for a given n the representations corresponding to a given S is the same for all M_S (if the method of construction which we outlined is used). We shall also be able to show that the representations corresponding to the same n but different S are inequivalent and irreducible.

If we confine ourselves to a given S then for a particular M_S, we have

$$P^{\sigma}\psi_{\ell}(S, M_S, n) = \sum_{j=1}^{p+q} \Gamma(P^{\sigma})_{j\ell}\psi_j(S, M_S, n)$$

Let us apply

$$S^{\pm} = \left(\frac{\hbar}{2}\right) \sum_{i=1}^{n} \sigma_i^{\pm}$$

to both sides of this relation. We know that $S^{\pm}\psi_{\ell}(S, M_S, n) = c_{S, M_S}\psi_{\ell}(S, M_S \pm 1, n)$. It is also clear, since $S^{\pm}$ is an operator invariant under permutations of the spin coordinates that

$$P^{\sigma}S^{\pm}\psi_{\ell}(S, M_S, n) = \sum_{j} \Gamma(P^{\sigma})_{j\ell}\,S^{\pm}\psi_j(S, M_S, n)$$

or

$$P^{\sigma}\psi_{\ell}(S, M_S \pm 1, n) = \sum_{j} \Gamma(P^{\sigma})_{j\ell}\,\psi_j(S, M_S \pm 1, n)$$

In this way we see that, by repeated use of the step up and step down operators, we can show that $\psi_{\ell}(S, M_S, n)$; $\ell = 1 \ldots$ form bases for the same representation as we vary M_S.

In order to show that the spin eigenfunctions corresponding to a given S, M_S, and n form bases for irreducible representations of the group and that the representations corresponding to different values of S and the same n are inequivalent, we shall

need an interesting identity called the Dirac identity. This states that

$$P_{12}^{\sigma} = \frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\} \tag{4-8}$$

This is easily shown, since we can write

$$\vec{\sigma}_1 \cdot \vec{\sigma}_2 = \frac{1}{2}\left[\sigma_1^{+}\sigma_2^{-} + \sigma_2^{+}\sigma_1^{-}\right] + \sigma_{1z}\sigma_{2z}$$

Any spin function of the n coordinates can be written

$$\begin{aligned}\phi(s_1, s_2 \cdots s_n) = \quad & \alpha(1)\,\alpha(2)\,\phi_1(s_3 \cdots s_n) \\ + \quad & \alpha(1)\,\beta(2)\,\phi_2(s_3 \cdots s_n) \\ + \quad & \beta(1)\,\alpha(2)\,\phi_3(s_3 \cdots s_n) \\ + \quad & \beta(1)\,\alpha(2)\,\phi_4(s_3 \cdots s_n)\end{aligned}$$

In this the s's represent the spin coordinates of the electrons. We can easily see that

$$\begin{aligned}\frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\}\alpha(1)\,\alpha(2) &= \alpha(1)\,\alpha(2) \\ \frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\}\alpha(1)\,\beta(2) &= \beta(1)\,\alpha(2) \\ \frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\}\beta(1)\,\alpha(2) &= \alpha(1)\,\beta(2) \\ \frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\}\beta(1)\,\beta(2) &= \beta(1)\,\beta(2)\end{aligned}$$

From this we conclude that P_{12}^{σ} has the same effect on $\alpha(1)\,\alpha(2)$, $\alpha(1)\,\beta(2)$, $\beta(1)\,\alpha(2)$ and $\beta(1)\,\beta(2)$ as $\frac{1}{2}\left\{1 + \vec{\sigma}_1 \cdot \vec{\sigma}_2\right\}$ does. For any function of spins we have that

$$P_{12}^{\sigma}\,\phi(s_1, s_2, \cdots s_n) = \frac{1}{2}\left\{1 + \sigma_1 \cdot \sigma_2\right\}\phi(s_1, s_2, \cdots s_n)$$

In a similar way for any coordinates i and j

$$P_{ij}^{\sigma} = \frac{1}{2}\left\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\right\}$$

Let us now form the sum of all permutations which represent transpositions. Since all these transpositions have the same cycle structure we are summing all the operations in a given class.

$$\begin{aligned}
\sum_{\substack{\text{pairs}\\ i\neq j}} P_{ij}^{\sigma} &= \sum_{\substack{\text{pairs}\\ i\neq j}} \frac{1}{2}\left\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\right\} \\
&= \sum_{i\neq j} \frac{1}{4}\left\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\right\} \\
&= \frac{1}{4}\left[n(n-1) + \left(\sum_i \vec{\sigma}_i\right)^2 - \sum_{i=1}^{n} \vec{\sigma}_i^{\,2}\right] \qquad (4\text{-}9) \\
&= \frac{1}{4}\left[n(n-1) + \left(\frac{4}{\hbar^2}\right) S^2 - 3n\right] \\
&= \frac{n^2}{4} - n + \frac{S^2}{\hbar^2}
\end{aligned}$$

Now let us imagine that we applied $\sum P_{ij}^{\sigma}$ to a function $\psi_{\ell}(s_1, \ldots, s_n)$ which was a partner in a basis for an irreducible representation of the permutation group of spin coordinates.

$$\frac{1}{2} \sum_{\substack{\text{pairs}\\ i\neq j}} P_{ij}^{\sigma}\, \psi_{\ell}(s_1, s_2, \ldots, s_n) = \frac{1}{2} \sum_{\substack{\text{pairs}\\ i\neq j}} \sum_{k\ell} \Gamma_a(P_{ij}^{\sigma})_{k\ell}\, \psi_k(s_1, s_2, \ldots, s_n)$$

The sum of $\Gamma_a(P_{ij}^{\sigma})$ is just the sum of all matrices representing elements in a given class. We have seen from Equations (2-140) and (2-141) of Chapter II that

$$\sum_{\substack{\text{pairs}\\ i\neq j}} \Gamma_a(P_{ij}^{\sigma}) = \frac{h\,\chi_a(P_{ij}^{\sigma})}{\chi_a(E)}\, 1$$

where h is the number of elements in the class of transposition (i.e., $n - 1)/2$) and $\chi_a(E)$ is the dimension of the irreducible representation. We have obtained, therefore, that

$$\sum_{\substack{\text{pairs}\\ i\neq j}} P_{ij}^{\sigma} \psi_{\ell}(s_1, \ldots, s_n) = \frac{n(n-1)}{\chi_a(E)}\, \chi_a(P_{ij}^{\sigma})\, \psi_{\ell}(s_1, \ldots, s_n)$$

On the one hand we see that for partners in a basis for an irreducible representation of the permutation group of spin coordinates the operator

$$\sum_{\substack{\text{pairs}\\ i\neq j}} P_{ij}^{\sigma}$$

is diagonal. This means that basis functions for an irreducible representation (from (4-9)) are eigenfunctions of S^2 and therefore states of definite multiplicity. On the

other hand, if we have an irreducible representation which has as its basis a set of functions which are eigenfunctions of S^2 then for bases with different multiplicities we have different characters for the class of transpositions. Thus, if the multiplicities of two irreducible representations are different then the representations are inequivalent since they differ in the character of at least one class (the class of transpositions).

We shall now go on and prove that for the n electron case states of definite multiplicity and M_S form irreducible representations of the permutation group of spin coordinates. We shall prove this by induction. We shall assume that for the n - 1 electron problem the states $\psi_\ell(S, M_S, n-1)$ $\ell = 1 \ldots$ form bases for irreducible representations of the permutation group of degree n - 1 and then prove that if we add another electron (the n^{th}) we shall have states $\psi_\ell(S, M_S, n)$ $\ell = 1 \ldots$ which form bases for an irreducible representation of the symmetric group of degree n.

We saw that the functions of definite multiplicity and M_S could be constructed from the definite multiplicity states of the n - 1 electron problem by Eq. (4-7). By hypothesis we assume that $\psi_\ell(S + \frac{1}{2}, M_S, n-1)$; $\ell = 1 \ldots q$ forms the basis for an irreducible representation $\Gamma'(P^\sigma)$, and $\psi_\ell(S - \frac{1}{2}, M_S, n-1)$; $\ell = 1 \ldots p$ forms a basis for an irreducible representation $\Gamma''(P^\sigma)$ of the permutation group of degree n - 1. From the last paragraphs we see that since Γ' and Γ'' have as their bases states of different multiplicities they are inequivalent irreducible representations. The group of all permutations of the first n - 1 spin coordinates forms a subgroup of the group of all permutations of n things. Consider the functions (4-7) of the n electron problem. If we apply any operation P^σ which belongs to the permutation group of the first n - 1 coordinates to one of the states $\psi_k(S, S, n)$ we leave the n^{th} coordinate unaffected and obtain

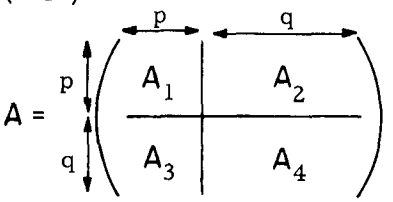
$$P^\sigma \psi_k(S, S, n) = \sum_{\ell=1}^{p} \Gamma'(P^\sigma)_{\ell k} \psi_\ell(S, S, n); \quad k = 1 \ldots p$$

$$P^\sigma \psi_k(S, S, n) = \sum_{\ell=p+1}^{p+q} \Gamma'(P^\sigma)_{\ell k} \psi_\ell(S, S, n); \quad k = p+1 \ldots p+q$$

Thus the functions $\psi_k(S, S, n)$ $k = 1 \ldots p + q$ form a representation which, for members of the permutation group which leaves the n^{th} coordinate invariant, has the form

$$\Gamma(P^\sigma) = \begin{array}{c} \\ p \\ q \end{array} \overset{\begin{array}{cc} p & q \end{array}}{\begin{pmatrix} \Gamma'(P^\sigma) & 0 \\ 0 & \Gamma''(P^\sigma) \end{pmatrix}} \tag{4-10}$$

Let us find a matrix A which commutes with every $\Gamma(P^\sigma)$ for P^σ a member of the group of permutations of the first n - 1 coordinates. We can block off this matrix A in a similar manner to (4-10)



From $\Gamma(P^\sigma)\ A = A\Gamma(P^\sigma)$ we obtain

$$A_1\Gamma'(P^\sigma) = \Gamma'(P^\sigma)A_1$$

$$A_4\Gamma''(P^\sigma) = \Gamma''(P^\sigma)A_4$$

$$\Gamma'(P^\sigma)A_2 = A_2\Gamma''(P^\sigma)$$

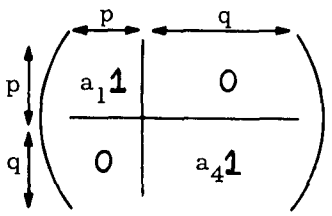
$$\Gamma''(P^\sigma)A_3 = A_3\Gamma'(P^\sigma)$$

Since Γ' and Γ'' are inequivalent irreducible representations of the group of permutations of the first n - 1 coordinates, we have from Theorems 5 and 7 that

$$A_1 = a_1 \qquad A_2 = 0$$

$$A_4 = a_4 \qquad A_3 = 0$$

Thus the only matrix which can possibly commute with all the matrices $\Gamma(P^\sigma)$, where we now let P^σ run over all permutations in the symmetric group of degree n, is a matrix of the form



Let us now consider a permutation P^σ_{in} operating on a state $\psi_k(S, S, n) = \psi_{k-p}(S - \frac{1}{2}, S - \frac{1}{2}, n - 1)\ \alpha(n)$ $k = p + 1 \ldots p + q$. In the state $\psi_{k-p}(S - \frac{1}{2}, S - \frac{1}{2}, n - 1)$ some spin, say the i^{th}, in one of the spin product functions which go into this state, must appear with β spin (unless $S = n/2$). Therefore, we can write $P^\sigma_{in}\psi_k(S, S, n) = g(s_1, s_2, \ldots s_n) + g'(s_1 \ldots s_{n-1})\ \beta(n)$. Such a function cannot be expanded as a sum of the

functions of the form $\psi_k(S, S, n)$ $k = p + 1 \ldots p + q$ since all these functions involve the factor $a(n)$. Thus in

$$P^{\sigma}_{in}\, \psi_k(S, S, n) = \sum_{\ell=1}^{p+q} \Gamma(P^{\sigma}_{in})_{\ell k}\, \psi_{\ell}(S, S, n) \qquad k = p+1 \ldots p + q$$

at least one element $\Gamma(P^{\sigma}_{in})_{\ell' k'}$ for $k' = p + 1 \ldots p + q$, $\ell' = 1 \ldots p$ must be non zero. In order to have $\mathbf{A}$ commute with this matrix we must have

$$a_1\, \Gamma(P^{\sigma}_{in})_{\ell' k'} = a_4\, \Gamma(P^{\sigma}_{in})_{\ell' k'}$$

or

$$a_1 = a_4$$

In this way we see that the only matrix which commutes with all the matrices $\Gamma(P^{\sigma})$ representing elements of the symmetric group of degree n is a constant times the unit matrix. In this way we conclude from Theorem 6, that the representation $\Gamma(P^{\sigma})$ is an irreducible representation of the symmetric group of degree n. In the proof of this theorem we have tacitly assumed that, for the states $\psi_k(S, S, n)$ of the n electron problem states of spins $S + \frac{1}{2}$ and $S - \frac{1}{2}$ of the n - 1 electron problem contributed. For the top state and, for n even, for the bottom states on the branching diagram corresponding to a given n this is not true. From Eq. (4-7), we see at once that for these cases the states $\psi_k(S, S, n)$ automatically form irreducible representations of the symmetric group of degree n since they all come from one irreducible representation of the group of degree n - 1.

In the above discussion, we have shown that for an n electron problem that the collection of spin functions which have a definite multiplicity and M_S form a basis for an irreducible representation of the symmetric group of degree n. We have also seen that for different multiplicities we have inequivalent irreducible representations. Let us see what we can learn of these irreducible representations. For the two-electron problem with $M_S = 0$ we can form two states, a singlet

$$\frac{\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)}{\sqrt{2}}$$

and a triplet

$$\frac{\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)}{\sqrt{2}}.$$

In this case the permutation group is a group of order two with elements E and P^{σ}_{12}

It is clear that the singlet forms the antisymmetric representation of this group and the triplet forms a basis for the symmetric representation. Let us now consider the state of maximum multiplicity of the n electron problem. (The multiplicity of this state will be n/2. The state $\psi(\frac{n}{2}, \frac{n}{2}, n)$ can be written as

$$\psi(\tfrac{n}{2}, \tfrac{n}{2}, n) = \alpha(1)\,\alpha(2)\,\alpha(3) \ldots \alpha(n)$$

Thus, the states of highest multiplicity form bases for the symmetric representation of the symmetric group. From the branching diagram we see that this is the only representation which has dimension one except for n = 2. We see in this way that for n > 2 it is impossible to find basis functions in an n electron spin space for the other one-dimensional representation of the symmetric group (antisymmetric representation). This is true of other representations of the symmetric group. For n > 2 there are representations of the symmetric group which cannot find basis functions in spin space. This is because we have in that space only a limited number (2^n) independent functions at our disposal and in general this number of independent functions is insufficient to form bases for all the irreducible representations of the symmetric group of degree n.

We can illustrate this point further to give a greater insight into the complete parallel between states of definite multiplicity and the irreducible representations of the symmetric group by considering the projection operators which we set up in Section 3 of this Chapter. We have seen that for an n electron problem the states of a given spin and M_S form a basis for an irreducible representation of the group of permutations of spin coordinates. On the other hand, it is clear that any collection of our spin product functions that form a basis for an irreducible representation of the symmetric group of degree n is an eigenstate of S^2. It is clear that these states are eigenfunctions of S^2 since they are eigenstates of operator

$$\sum_{\substack{\text{pairs} \\ i \neq j}} P_{ij}^{\sigma}$$

giving $\frac{n(n-1)}{2\chi(E)}\chi(P_{ij}^{\sigma})$ as an eigenvalue. Since

$$\sum_{\substack{\text{pairs} \\ i \neq j}} P_{ij}^{\sigma} = \frac{n^2}{4} - n + \frac{S^2}{\hbar^2}$$

they are also eigenfunctions of S^2. In addition the collection of states then forms a basis for an irreducible representation of the symmetric group can be chosen to be eigenstates of S_z with the same value of M_S by confining our attention to spin product functions with some definite value of M_S. By our method of construction in Eq. (4-7)

we have shown one method of making eigenstates of S^2 and M_S and therefore bases for the irreducible representations of the symmetric group. The states we obtained in this way were not unique. After we had formed the states for the n electron system which were eigenstates of S^2 and S_z we could take any linear combination of those for a given n, S, and M_S and as long as these states were linearly independent they would serve equally well as a basis for an irreducible representation of the symmetric group. In the next paragraph we shall outline another method of obtaining states which are eigenstates of S^2 and S_z for the n electron system which will in general give different states than the method of Eq. (4-7) but which, of course, is equally satisfactory.

From this we see that if we set up linear combinations of spin product functions for the n electron problem with a given M_S that form bases for irreducible representations of the permutation group acting on spin coordinates, we shall have found states of a definite multiplicity and M_S. We have at our disposal a method of projecting out bases for irreducible representations of a group by the use of the projection operators we introduced earlier. In this way we see that the projection operators for the symmetric group will form from an arbitrary spin function states of a definite multiplicity. If we apply the projection operator to a state which is an eigenfunction of S_z, since the projection operator is just a linear combination of operators of the group of spin coordinate permutations, we shall also obtain a function which is an eigenfunction of S_z. Thus the operators,

$$\sum_{P^\sigma} \Gamma_a(P^\sigma)_{ij} P^\sigma$$

where $\Gamma_a(P^\sigma)$ is an irreducible representation of the symmetric group, are projection operators for states of definite multiplicity. For some irreducible representations of the symmetric group, these projection operators will yield nothing when applied to all of the 2^n spin product functions. These correspond to just those irreducible representations which cannot find a basis in the space of spin product functions.

Let us illustrate these remarks from the case of the symmetric group of degree three. As we have seen from the first chapter this group is isomorphic with the group C_{3v}, and therefore we have all the irreducible representations from (2-107) of Chapter II. The projection operators are

$$\zeta^1_{11} = P_1 + P_2 + P_3 + P_4 + P_5 + P_6$$

$$\zeta^2_{11} = P_1 + P_2 + P_3 - P_4 - P_5 - P_6$$

$$\zeta^3_{11} = P_1 - \tfrac{1}{2}P_2 - \tfrac{1}{2}P_3 - P_4 + \tfrac{1}{2}P_5 + \tfrac{1}{2}P_6$$

$$\zeta^3_{12} = \frac{\sqrt{3}}{2} P_2 - \frac{\sqrt{3}}{2} P_3 - \frac{\sqrt{3}}{2} P_5 + \frac{\sqrt{3}}{2} P_6$$

$$\zeta^3_{21} = -\frac{\sqrt{3}}{2} P_2 + \frac{\sqrt{3}}{2} P_3 - \frac{\sqrt{3}}{2} P_5 + \frac{\sqrt{3}}{2} P_6$$

$$\zeta^3_{22} = P_1 - \frac{1}{2} P_2 - \frac{1}{2} P_3 + P_4 - \frac{1}{2} P_5 - \frac{1}{2} P_6$$

Let us use the definitions of the permutations $P_1 \ldots P_6$ from Chapter I and apply these projection operators to the state $\alpha(1)\,\alpha(2)\,\beta(3)$ with $M_S = \frac{1}{2}$

$$\zeta^1_{11}\,\alpha(1)\,\alpha(2)\,\beta(3) = 2\left[\alpha(1)\,\alpha(2)\,\beta(3) + \alpha(1)\,\beta(2)\,\alpha(3) + \beta(1)\,\alpha(2)\,\alpha(3)\right]$$

$$\zeta^2_{11}\,\alpha(1)\,\alpha(2)\,\beta(3) = \alpha(1)\,\alpha(2)\,\beta(3) + \beta(1)\,\alpha(2)\,\alpha(3) + \alpha(1)\,\beta(2)\,\alpha(3)$$

$$- \alpha(1)\,\beta(2)\,\alpha(3) - \beta(1)\,\alpha(2)\,\alpha(3) - \alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^2_{11}\,\alpha(1)\,\alpha(2)\,\beta(3) = 0$$

$$\zeta^3_{11}\,\alpha(1)\,\alpha(2)\,\beta(3) = \alpha(1)\,\alpha(2)\,\beta(3) - \frac{1}{2}\beta(1)\,\alpha(2)\,\alpha(3) - \frac{1}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$- \alpha(1)\,\beta(2)\,\alpha(3) + \frac{1}{2}\beta(1)\,\alpha(2)\,\alpha(3) + \frac{1}{2}\alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^3_{11}\,\alpha(1)\,\alpha(2)\,\beta(3) = \frac{3}{2}\alpha(1)\,\alpha(2)\,\beta(3) - \frac{3}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$\zeta^3_{21}\,\alpha(1)\,\alpha(2)\,\beta(3) = -\frac{\sqrt{3}}{2}\beta(1)\,\alpha(2)\,\alpha(3) + \frac{\sqrt{3}}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$- \frac{\sqrt{3}}{2}\beta(1)\,\alpha(2)\,\alpha(3) + \frac{\sqrt{3}}{2}\alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^3_{21}\,\alpha(1)\,\alpha(2)\,\beta(3) = \frac{\sqrt{3}}{2}\left[\alpha(1)\,\alpha(2)\,\beta(3) + \alpha(1)\,\beta(2)\,\alpha(3) - 2\beta(1)\,\alpha(2)\,\alpha(3)\right]$$

$$\zeta^3_{12}\,\alpha(1)\,\alpha(2)\,\beta(3) = \frac{\sqrt{3}}{2}\beta(1)\,\alpha(2)\,\alpha(3) - \frac{\sqrt{3}}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$- \frac{\sqrt{3}}{2}\beta(1)\,\alpha(2)\,\alpha(3) + \frac{\sqrt{3}}{2}\alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^3_{12}\,\alpha(1)\,\alpha(2)\,\beta(3) = \frac{\sqrt{3}}{2}\alpha(1)\,\alpha(2)\,\beta(3) - \frac{\sqrt{3}}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$= \frac{1}{\sqrt{3}}\,\zeta^3_{11}\,\alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^3_{22}\,\alpha(1)\,\alpha(2)\,\beta(3) = \alpha(1)\,\alpha(2)\,\beta(3) - \frac{1}{2}\beta(1)\,\alpha(2)\,\alpha(3) - \frac{1}{2}\alpha(1)\,\beta(2)\,\alpha(3)$$

$$+ \alpha(1)\,\beta(2)\,\alpha(3) - \frac{1}{2}\beta(1)\,\alpha(2)\,\alpha(3) - \frac{1}{2}\alpha(1)\,\alpha(2)\,\beta(3)$$

$$\zeta^3_{22}\,\alpha(1)\,\alpha(2)\,\beta(3) = \frac{1}{2}\alpha(1)\,\alpha(2)\,\beta(3) + \frac{1}{2}\alpha(1)\,\beta(2)\,\alpha(3) - \beta(1)\,\alpha(2)\,\alpha(3)$$

$$= \frac{1}{\sqrt{3}}\,\zeta^3_{21}\,\alpha(1)\,\alpha(2)\,\beta(3)$$

From this we see that the antisymmetric representation $\Gamma_2(P^\sigma)$ cannot find a basis. The two-dimensional representation finds a basis as does the symmetric representation. We see from the branching diagram that the two-dimensional representation has as its basis states with $S = \frac{1}{2}$. The symmetric representation has as its basis the function $\zeta^1_{11}\ \alpha(1)\ \alpha(2)\ \beta(3)$. From the properties of the projection operators we know all the states we have constructed in this way are orthogonal. They are not, however, normalized but it is simple to accomplish this. The two states with $S = \frac{1}{2}$, $M_S = \frac{1}{2}$ are not unique and any independent linear combination of them is a state with the same eigenvalues. Forming two new independent states out of the two doublet states just induces a similarity transformation on the irreducible representation. As we mentioned above, this is true for any set of states of the n electron problem in spin space with a given S and M_S. It is always possible to perform a similarity transformation on the representation by taking linear combinations of the states.

This completes the discussion of the spin eigenfunctions. We have seen that our Hamiltonian is invariant under permutations of the spin coordinates and that we could set up a complete set of functions in the space of all spin which were eigenstates of S^2 and S_z and that such states, for a given S and M_S, form bases for irreducible representations of the group of permutations of the spin coordinates. In the next section, we discuss the invariance of the Hamiltonian under permutations of the spatial coordinates of the n electrons, and then see how the representations of spatial permutations and spin permutations are connected in such a way that we obey the Pauli exclusion principle.

3. Permutations of Spatial Coordinates and the Pauli Exclusion Principle

The Hamiltonian we are considering

$$H = \text{const.} + \sum_{i=1}^{n} -\nabla_i^2 + \frac{1}{2}\sum_{i\neq j}\frac{2}{|\vec{r}_i - \vec{r}_j|} + \sum_{i,a}\frac{2Z_a}{|\vec{r}_i - \vec{R}_a|} \tag{4-11}$$

is invariant under any permutation of the spatial coordinates of the n electrons. Let us call these operations P^S. There are, of course, n! operations in this group and it is isomorphic with the group of spin permutations, P^σ. We could, in principle, find eigenfunctions of the Hamiltonian (4-11). We know from our general considerations that the eigenfunctions of this Hamiltonian corresponding to a given energy will form a basis for an irreducible representation of the group of permutations of spatial coordinates. We can, therefore, for our Hamiltonian (4-11), find eigenfunctions corresponding to an eigenvalue E which are functions of the spatial coordinates and form bases for an irreducible representation of the permutation group of spatial coordinates. We can, clearly, multiply any of these eigenstates with any function of spin coordinates and still have an eigenstate of our problem with the same energy. In principle we could find all

our energy levels by just finding the spatial eigenstates of our Hamiltonian (4-11). This would be the entire story if it were not for the Pauli exclusion principle. This states that for any permutation of both space and spin coordinates the wave function must behave in an antisymmetric manner. Any permutation of both space and spin can be written as the product of the space permutation P^S and the corresponding spin permutation P^σ. (P^S and P^σ are thought of as corresponding to the same abstract permutation P. The first acts on spin and the second on spatial coordinates.) It is clear that since the two types of permutations act in different spaces, $P^S P^\sigma = P^\sigma P^S$. The Pauli exclusion principle then states that the only allowed states are ones for which

$$P^S P^\sigma \Psi(\vec{r}_1 \dots \vec{r}_n, s_1 \dots s_n) = \pm \Psi(\vec{r}_1 \dots \vec{r}_n, s_1 \dots s_n) \tag{4-12}$$

$\pm$ depending on whether the permutation is even or odd.

Let us see how this exclusion principle influences the wave functions and energy levels of the n electron problem. It is clear that we must combine spin functions with spatial functions so that the total wave function can obey this antisymmetry principle.

Since the Hamiltonian we are considering does not involve spin we must combine only spatial eigenstates of our Hamiltonian corresponding to one energy level so that we may have an eigenstate of the Hamiltonain with spin coordinates included in it. We know that the spatial eigenstates corresponding to one energy level are partners in a basis for an irreducible representation of the group of permutations of spatial coordinates. Let $\psi_1(\vec{r}_1 \dots \vec{r}_n) \dots \psi_q(\vec{r}_1 \dots \vec{r}_n)$ have the property that

$$H\psi_\ell = E\psi_\ell$$

and

$$P^S \psi_k = \sum_{\ell=1}^{q} \Gamma(P)_{\ell k} \psi_\ell$$

where $\Gamma(P)$ are matrices in an irreducible representation of the symmetric group. There may, in the case of accidental degeneracy or some additional degeneracy induced by another subgroup of the group of Schrödinger's equation, be more bases for irreducible representations of the group of spatial permutations corresponding to this energy. This will not influence the validity of the argument that follows.

The most general state we could make whose coordinates are both the space and the spin coordinates of the n electrons and whose space parts are taken from the ψ_ℓ's is

$$\Psi(\vec{r}_1 \dots \vec{r}_n \;\; s_1 \dots s_n) = \sum_{\ell=1}^{q} \psi_\ell(\vec{r}_1 \dots \vec{r}_n)\, g_\ell(s_1 \dots s_n) \tag{4-13}$$

The g_ℓ's are any functions of the spin coordinates alone. Put another way the g_ℓ's are linear combinations of the 2^n independent spin product functions. Let us see what the Pauli principle tells us about the g_ℓ's.

$$P^S P^\sigma \Psi(\vec{r}_1 \cdots \vec{r}_n, s_1 \cdots s_n) = \pm \Psi(\vec{r}_1 \cdots \vec{r}_n, s_1 \cdots s_n)$$

$$\sum_{\ell=1}^{q} P^S P^\sigma \psi_\ell(\vec{r}_1 \cdots \vec{r}_n)\, g_\ell(s_1 \cdots s_n) = \pm \sum_{\ell=1}^{q} \psi_\ell\, g_\ell \tag{4-14}$$

Since we know the effect of P^S on ψ_k we can write

$$\sum_{\ell=1}^{q} \sum_{k=1}^{q} \Gamma(P)_{k\ell}\, \psi_k\, P^\sigma g_\ell = \pm \sum_{\ell=1}^{q} \psi_\ell\, g_\ell$$

We can always choose our ψ_k's to be an orthogonal and normal set in which case $\Gamma(P)$ is unitary. Let us multiply both sides of the last equation by ψ_m^* and integrate over all the spatial coordinates. Using the orthogonality of the ψ_k's we obtain

$$\sum_{\ell=1}^{q} \Gamma(P)_{m\ell}\, P^\sigma\, g_\ell = \pm\, g_m \tag{4-15}$$

If we now in (4-13) multiply by $\Gamma(P^{-1})_{km}$ and sum over m we obtain

$$P^\sigma\, g_k = \pm \sum_m \Gamma(P^{-1})_{km}\, g_m \tag{4-16}$$

$$P^\sigma\, g_k = \pm \sum_m \Gamma(P)^*_{mk}\, g_m \tag{4-17}$$

Thus the g_k's transform as the associated representation of $\Gamma(P)^*$ that is $\Gamma'(P)^*$.

We now know that the spin functions g_k must transform under the permutation group of spin coordinates according to an irreducible representation of the symmetric group. This means, as we have seen, that they must be eigenstates of S^2 and can be chosen to be eigenstates of S_z. Except for the case of an accidental degeneracy we can associate with each energy level a value of S and the corresponding $2S + 1$ values of M_S.

It would seem that, in the case we neglect magnetic interactions, we get the same energy levels whether we include spin or not. Thus we might think that by finding all the spatial eigenstates of the Hamiltonian (4-11) we would find all the energy levels which arise. All we would need do to find the wave functions is to obey the exclusion principle by combining states of the one energy level with the spin states which form a basis for a particular representation of the permutation group of spin coordinates. The irreducible representation which we use is the one which is that associated with the complex conjugate of the irreducible representation which is generated by the

spatial eigenstates. This is indeed the case. We do get all the energy levels in this way. The only trouble is that by solving the Schrödinger equation for spatial wave functions we get too many energy levels. Let us see how this comes about by an example.

There would surely be a spatial eigenstate of the Hamiltonian (4-11) which forms a basis for the symmetric representation $\Gamma_1(P)$ of the permutation group of spatial coordinates

$$H\psi_o = E_o\psi_o$$

$$P^s\psi_o(\vec{r}_1 \ldots \vec{r}_n) = \psi_o(\vec{r}_1 \ldots \vec{r}_n)$$

We have seen that in order to obey the exclusion principle we must find a spin state $g_o(s_1 \ldots s_n)$ such that g_o transforms as the complex conjugate of the representation which is associated with $\Gamma_1(P)$. In this case this means the antisymmetric representation $\Gamma_1'(P)$. Therefore

$$P^\sigma g_o(s_1 \ldots s_n) = \pm g_o(s_1 \ldots s_n)$$

depending on whether P is even or odd. We have already seen that for $n > 2$ you cannot, in the complete set of 2^n spin functions, find a function which has the property that it forms a basis for the antisymmetric representation of the symmetric group. Thus we see that for $n > 2$ the spatial function that behaves in a completely symmetric manner under the group of permutations of the spatial coordinates can never find in spin space a function such that the product obeys the exclusion principle. We must, therefore, throw away the energy level E_o. As we mentioned there are other representations of the symmetric group which cannot find a basis in spin space. Any time that $\Gamma'(P)^*$ is one of these missing representations then the set of spatial functions which transform like $\Gamma(P)$ and the associated energy level must be dropped from consideration, since we cannot obey the exclusion principle and these states are therefore not physically meaningful. We could look at the process as follows. We could find all the energy levels of our problem by finding all the spatial eigenstates of the Hamiltonian (4-11). After we had accomplished this all we would need to do is throw away those energy levels which have eigenfunctions which cannot be made antisymmetric by the addition of the n spin coordinates. We can easily check which eigenstates we must throw out by seeing whether $\Gamma'(P)^*$ can find a basis in the collection of 2^n spin product functions. Once we have thrown those energy levels away we can make the remaining states antisymmetric by adding spin coordinates and then associate with each state a definite multiplicity and M_S. This is how it comes about that through the exclusion principle the energy levels depend on the spin quantum number S even though our Hamiltonian

depends only on spatial coordinates.

In the next section, we shall see how the concepts of this section can be put to use in an approximate method of finding the eigenstates of our Hamiltonian. This method is called the Dirac Vector Model. In addition, we shall be able to show how this vector model ties in with the determinantal method of treating the n electron problem.

4. Dirac Vector Model and the Determinantal Method

A. Simple Vector Model

In the last section, we showed that only certain eigenvalues of the n electron Hamiltonian (4-11) were physically meaningful. The eigenvalues which were meaningful were those which were compatible with the Pauli Exclusion principle. Thus, if the degenerate eigenstates corresponding to some eigenvalue E of the Hamiltonian (4-11) form a basis for an irreducible representation $\Gamma(P)$ of the group of permutations of spatial coordinates this state may or may not be admissable. The only energy levels which were admissable were those for which basis functions for the representation of the permutation group of spin coordinates $\Gamma'(P)$* could be found amongst the collection of 2^n spin product functions. As we observed, this was not always possible. This also influences any approximate calculation of the eigenstates of the Hamiltonian (4-11). We can calculate approximate eigenstates of the Hamiltonian and be assured that they are physically meaningful by making sure that the spatial wave functions have the desired symmetry properties. If we do this we know that we can always make a totally antisymmetric state of the same energy by the addition of spin coordinate functions. We shall discuss one such approximate method in this section.

We might hope that by taking a product of one-electron wave functions we could find an approximate solution to our many electron problem. Thus, if ϕ_1, ϕ_2 ... ϕ_n are n linearly independent spatial functions of the coordinates of one electron, we might form an approximate wave function

$$\begin{aligned} \Phi_o &= \phi_1(\vec{r}_1)\,\phi_2(\vec{r}_2)\cdots\phi_n(\vec{r}_n) \\ &= \phi_1(1)\;\;\phi_2(2)\;\;\cdots\phi_n(n) \end{aligned} \tag{4-18}$$

If we took the expectation value of the Hamiltonian (4-11) with respect to this wave function $(\Phi_o, H\Phi_o)$ we would get some approximate value for the energy. It is clear from the unitary nature of the permutation operators and from the fact that they commute with the Hamiltonian, that $P^s\Phi_o$ has the same expectation value of the Hamiltonian as Φ_o. Thus we have n! states $P^s\Phi_o$ which are degenerate. In order to find the best

energy we can obtain from these states, we should take a linear combination of them with arbitrary coefficients multiplying each, and minimize the energy with respect to variations of the linear coefficients. There would be n! unknown coefficients and we would be led to a secular determinant of order n! in the usual way. Our knowledge of the symmetry of the Hamiltonian comes to our aid. We can factor our secular determinant at once by making states which form bases for irreducible representations of the group of spatial permutations. Let us do this.

Before starting it will be to our advantage to introduce some new operators. If P^S corresponds to the permutation

$$P = \begin{pmatrix} 1 & 2 & \cdots & n \\ p_1 & p_2 & \cdots & p_n \end{pmatrix} \tag{4-19}$$

then

$$P^S \Phi_o = \phi_1(p_1)\, \phi_2(p_2) \cdots \phi_n(p_n) \tag{4-20}$$

We could introduce operators P^f which, instead of permuting the coordinates, permute the functions ϕ_ℓ. Thus, if P corresponds to (4-19) $P^f \Phi_o = \phi_{p_1}(1)\, \phi_{p_2}(2) \cdots \phi_{p_n}(n)$. These operators have meaning only for the n! functions $P^S \Phi_o$ is concerned, it is clear that

$$\begin{aligned} P^S P^f \Phi_o &= \phi_{p_1}(p_1)\, \phi_{p_2}(p_2) \cdots \phi_{p_n}(p_n) \\ &= \Phi_o \end{aligned} \tag{4-21}$$

or

$$P^S \Phi_o = (P^{-1})^f \Phi_o \tag{4-22}$$

We might also notice that

$$\begin{aligned} P'^S(P^S \Phi_o) &= (P^{-1})^f (P'^{-1})^f \Phi_o \\ &= (P^{-1})^f (P'^{-1})^f P^f (P^{-1})^f \Phi_o \\ &= (P^{-1})^f (P'^{-1})^f P^f (P^S \Phi_o) \end{aligned} \tag{4-23}$$

Thus for operation on $P^S \Phi_o$ the operator corresponding to P'^S is $(P^{-1})^f (P'^{-1})^f P^f$. We see that care must be exercised in the use of these operators. For example, we know that

$$\begin{aligned} (P'^S \Phi_o,\ P^S H \Phi_o) &= (P^{-1S} P'^S \Phi_o,\ H \Phi_o) \\ &= (P'^S \Phi_o,\ H P^S \Phi_o) \end{aligned} \tag{4-24}$$

This is an expression of the unitary nature of P^S. For the P^f's we have a different situation.

$$\begin{aligned}(P'^f\Phi_o,\ P^f H\Phi_o) &= ((P'^{-1})^S\Phi_o,\ P^{-1S}H\Phi_o)\\ &= (P^S(P'^{-1})^S\Phi_o,\ H\Phi_o)\\ &= (P'^f(P^{-1})^f\Phi_o,\ H\Phi_o)\end{aligned} \tag{4-25}$$

With this digression on the operators P^f, we can continue.

We wished to form out of the n! functions $P^S\Phi_o$ suitable linear combinations which formed bases for the irreducible representations of the symmetric group of degree n. We might first ask which representations of the symmetric group can find bases amongst these n! functions. Let us assume that the ϕ_ℓ's are an orthonormal set. That is

$$(\phi_n,\ \phi_m) = \delta_{n,m} \tag{4-26}$$

Let us find the inner product of $P^f\Phi_o$ and $P'^f\Phi_o$.

$$(P^f\Phi_o,\ P'^f\Phi_o) = \prod_{\ell=1}^{n}(\phi_{p_\ell},\phi_{p'_\ell})$$

From the orthogonality properties of the ϕ's we see that this product would vanish unless $p_\ell = p'_\ell$ for all ℓ. In other words

$$\begin{aligned}(P^f\Phi_o,\ P'^f\Phi_o) &= 0 \text{ unless } P = P'\\ (P^f\Phi_o,\ P^f\Phi_o) &= 1\end{aligned} \tag{4-27}$$

Thus the n! functions $P^S\Phi_o$ (or $P^f\Phi_o$) form an orthonormal set. It is clear that under any permutations, P'^S, any of these n! functions is sent into one of the other functions. For example if $P'P = P''$

$$P'^S(P^S\Phi_o) = P''^S\Phi_o$$

Thus, the functions $P^S\Phi_o$ form a basis for what we described, in Section 6 of Chapter II, as the regular representation. We may recall that this representation had the property that it contained every irreducible representation as often as its order.

Knowing this, let us construct the functions which form bases for the irreducible representations of the group of permutations of spatial coordinates through the use of the projection operators which we introduced earlier. Thus, if we want a set

of functions which form bases for the α irreducible representation of the symmetric group, we first form the hypercomplex numbers

$$\zeta^{\alpha}_{ij} = \sum_{P} \Gamma_{\alpha}(P)^{*}_{ij} P^{S} \quad i, j = 1 \ldots n_{\alpha} \tag{2-28}$$

n_{α} is the dimension of the representation. If we now apply these operators to the function Φ_{o}, we obtain approximate wave functions

$$\Phi^{\alpha}_{ij} = \sqrt{\frac{n_{\alpha}}{n!}}\, \zeta^{\alpha}_{ij} \Phi_{o} \tag{2-29}$$

We have inserted the factor $\sqrt{\frac{n_{\alpha}}{n!}}$ in order to normalize this function. Thus

$$(\Phi^{\alpha}_{ij}, \Phi^{\alpha}_{ij}) = \frac{n_{\alpha}}{n!} (\zeta^{\alpha}_{ij} \Phi_{o}, \zeta^{\alpha}_{ij} \Phi_{o})$$

From relation (3-44) of the last chapter we obtain

$$\begin{aligned}(\Phi^{\alpha}_{ij}, \Phi^{\alpha}_{ij}) &= \frac{n_{\alpha}}{n!} \frac{n!}{n_{\alpha}} (\Phi_{o}, \zeta^{\alpha}_{jj} \Phi_{o}) \\ &= \sum_{P} \Gamma(P)^{*}_{jj} (\Phi_{o}, P^{S} \Phi_{o}) \\ &= \Gamma(E)^{*}_{jj} (\Phi_{o}, \Phi_{o}) \\ &= 1\end{aligned}$$

We may recall that the functions $\Phi^{\alpha}_{1j} \ldots \Phi^{\alpha}_{n_{\alpha}j}$ form a basis for the α irreducible representation. This is true for all j. From this we know at once that the functions $\Phi^{\alpha}_{1j} \ldots \Phi^{\alpha}_{n_{\alpha}j}$ for a particular value of j form an orthonormal set. We have n_{α} such sets of functions ($j = 1 \ldots n_{\alpha}$) each set forming a basis for the α irreducible representation. If these n_{α} sets of functions are linearly independent then we have the bases for the irreducible representation α contained n_{α} times in the regular representation. This is not difficult to show. Thus

$$\begin{aligned}(\Phi^{\alpha}_{ij}, \Phi^{\alpha}_{ij'}) &= \frac{n_{\alpha}}{n!} (\zeta^{\alpha}_{ij} \Phi_{o}, \zeta^{\alpha}_{ij'} \Phi_{o}) \\ &= \frac{n_{\alpha}}{n!} \frac{n!}{n_{\alpha}} (\Phi_{o}, \zeta^{\alpha}_{jj'} \Phi_{o}) \\ &= \sum_{P} \Gamma(P)^{*}_{jj'} (\Phi_{o}, P^{S} \Phi_{o}) \\ &= \Gamma(E)^{*}_{jj'} (\Phi_{o}, \Phi_{o}) \\ &= \delta_{jj'}\end{aligned}$$

In this way we see that the functions Φ^{α}_{ij} for all i and j form an orthonormal set. The functions Φ^{α}_{ij} i = 1 ... n_{α} (for a given j) are partners in a basis for the α irreducible representation. There are n_{α} such sets of partners. We see from Theorem 15 that there will be no matrix elements of the Hamiltonian between functions corresponding to different α or different i values in (4-29). There will be matrix elements of the Hamiltonian between Φ^{α}_{ij} and $\Phi^{\alpha}_{ij'}$. The Hamiltonian matrix (from Theorem 15) between Φ^{α}_{ij} and $\Phi^{\alpha}_{ij'}$, since both of these functions transform according to the same column of the same irreducible representation for all j and j', is the same as the Hamiltonian matrix between $\Phi^{\alpha}_{i'j}$ and $\Phi^{\alpha}_{i'j'}$. Thus, in order to find the n_{α} energy levels arising from the approximate wave functions $P^S\Phi_o$ which correspond to the α irreducible representation all we need do is to find the roots of the secular equation arising from the states Φ^{α}_{ij}(j = 1, 2, ... n_{α}). Let us do this.

The n_{α} states (j = 1 ... n_{α}) are orthonormal. To find the energy levels we must solve the secular determinant

$$| H^{\alpha} - E^{\alpha} 1 | = 0 \tag{4-30}$$

The α means that we are finding those energy levels corresponding to the α irreducible representation. The matrix H^{α} is given by

$$H^{\alpha}_{jj'} = \frac{n_{\alpha}}{n!} \frac{n!}{n_{\alpha}} (\zeta^{\alpha}_{ij} \Phi_o, H \zeta^{\alpha}_{ij'} \Phi_o) \tag{4-31}$$

By using Eq. (3-44) of the last chapter, we can rewrite this as

$$\begin{aligned} H^{\alpha}_{jj'} &= \frac{n_{\alpha}}{n!} \frac{n!}{n_{\alpha}} (\Phi_o, H \zeta^{\alpha}_{jj'} \Phi_o) \\ &= \sum_P \Gamma(P)^*_{jj'} (\Phi_o, H P^S \Phi_o) \end{aligned} \tag{4-32}$$

If we define

$$V(P) = (\Phi_o, H P^S \Phi_o) \tag{4-33}$$

we obtain

$$\begin{aligned} H^{\alpha}_{jj'} &= \sum_P \Gamma(P)^*_{jj'} V(P) \\ H^{\alpha} &= \sum_P \Gamma(P)^* V(P) \end{aligned} \tag{4-34}$$

The matrix elements V(P) could be written out explicitly, but we shall delay this for the moment.

Thus we see that if we take the roots of (4-30) we shall have the approximate energy levels corresponding to the α irreducible representation. Once again we must employ the exclusion principle. This just throws away certain irreducible representations. Any representation $\Gamma_\alpha(P)$ must be discarded if $\Gamma'_\alpha(P)^*$ cannot find a basis in the space of the 2^n spin product functions. If we have one of these admissable representations, then this representation, we recall, is specified by the number of electrons and the spin S. The proper antisymmetric unperturbed wave functions will be given

$$\sum_{i=1}^{n_\alpha} \Phi^\alpha_{ij}\, \psi_i(S, M_S, n) \qquad j = 1 \ldots n_\alpha \tag{4-35}$$

where

$$P^\sigma \psi_i = \sum_{j=1}^{n_\alpha} \Gamma'_\alpha(P)^*_{ji}\, \psi_j$$

There are n_α such antisymmetric wave functions corresponding to a given multiplicity. After diagonalization of the Hamiltonian matrix connecting the states Φ^α_{ij} $j = 1 \ldots n_\alpha$ there will be n_α linear combinations of the n_α states in (4-35) which are the best approximate wave functions for the spin which we can obtain from the type of functions which we have considered.

We can reformulate the problem somewhat differently. Let us consider the effective Hamiltonian

$$H_{eff.} = \sum_P V(P)\, P^f \tag{4-36}$$

We call this an effective Hamiltonian because it involves the function permutation operators P^f and only has meaning for the functions $P^S \Phi_o$. It is not difficult to see that we get the same Hamiltonian matrix using the functions $P^S \Phi_o$ and the effective Hamiltonian that we do if we use the functions $P^S \Phi_o$ and the real Hamiltonian (4-11).

$$\begin{aligned} V(P^{-1}P') &= (P^S \Phi_o,\, H P'^S \Phi_o) = (P^S \Phi_o, \sum_{P''} V(P'')\, P''^f P'^S \Phi_o) \\ &= \sum_{P''} V(P'')(P^S \Phi_o,\, P''^f (P'^{-1})^f \Phi_o \\ &= \sum_P V(P'')(P^S \Phi_o,\, P'^S (P''^{-1})^S \Phi_o \end{aligned} \tag{4-37}$$

Because of the orthogonality of the $P^S \Phi_o$'s this yields

$$\begin{aligned} (P^S \Phi_o,\, H_{eff}\, P'^S \Phi_o) &= V(P^{-1}P') \\ &= (P^S \Phi_o,\, H P'^S \Phi_o) \end{aligned}$$

Thus when finding the Hamiltonian matrix between the functions $P^S \Phi_0$ or for that matter $\zeta^a_{ij} \Phi_0$ we could equally well use the effective Hamiltonian (4-36) as our Hamiltonian (4-11). We can also easily see that an effective Hamiltonian

$$\sum_P V(P) P^S$$

will give the same energy levels as (4-36). If we take as our basic set of functions $P^f \Phi_0$ instead of $P^S \Phi_0$ we get the same matrix of interaction for this Hamiltonian as we do for the Hamiltonian (4-36). (These two sets are, of course, related by a unitary transformation, the one set just being the other set with the functions relabeled. $((P^{-1})^f \Phi_0 = P^S \Phi_0$)

$$\begin{aligned}(P^f \Phi_0, \sum_{P''} V(P'') P''^S P'^f \Phi_0) &= ((P^{-1})^S \Phi_0, \sum_{P''} V(P'') P''^S (P'^{-1})^S \Phi_0 \\ &= V(P^{-1} P')\end{aligned} \tag{4-38}$$

As far as the states $P^f \Phi_0$ or $P^S \Phi_0$ are concerned we can use either the Hamiltonians

$$\sum_P V(P) P^f \text{ or } \sum_P V(P) P^S$$

and get the same energy levels by a variation procedure as we do from the original Hamiltonian (4-11).

There is yet another effective Hamiltonian which we can construct which has useful properties. We can show that the Hamiltonian

$$\sum_P \Gamma_1'(P) V(P) P^\sigma \tag{4-39}$$

when matrix elements are taken in the space of spin product functions, also gives the same energy levels as the effective Hamiltonians we have just discussed. (Let us recall that $\Gamma_1'(P)$ is the antisymmetric representation of the symmetric group.) We first notice that there are no matrix elements connecting spin product functions with different M_S since the effective Hamiltonian does not change M_S. For states of a given M_S there can be formed eigenstates of S^2 as we have done in an earlier section. States with a given value of spin and M_S, we have seen, will transform as a basis for an irreducible representation of the symmetric group. We have denoted these states by $\psi_i(S, M_S, n)$ and it will be assumed that these states form a basis for the irreducible representation $\Gamma_a'(P)^*$. (We note in passing that there is a one-to-one correspondence between S and a.) We see that

$$(\psi_i(S, M_S, n) \sum_P \Gamma_1'(P)\, V(P)\, P^\sigma\, \psi_j(S', M_S, n))$$

$$= \sum_P \Gamma_1'(P)\, V(P) \sum_k (\psi_i(S, M_S, n)\ \Gamma_a'(P)^*_{kj}\, \psi_k(S', M_S, n))$$

$$= \delta_{SS} \sum_P \Gamma_a(P)^*_{ij}\, V(P).$$

We notice that for the functions $\psi_j(S, M_S, n)$ $j = 1 \ldots n_a$ corresponding to a given M_S, we get the same Hamiltonian matrix as we did for the original Hamiltonian and the functions Φ^a_{ij} $j = 1 \ldots n_a$. The energy levels we obtain will be the same. Since our original spin product functions are just linear combinations of the functions $\psi_j(S, M_S, n)$ we get the same energy levels by using the Hamiltonian (4-39) and the spin product functions.

We now make use of the form of the Hamiltonian (4-11) to find an explicit expression for the matrix element V(P).

$$V(P) = (\Phi_o, H P^S \Phi_o) = (P^f \Phi_o, H \Phi_o)$$

$$= \int \phi_{p_1}^*(1)\, \phi_{p_2}^*(2) \ldots \phi_{p_n}^*(n) \left[- \sum_{i=1}^{n} \nabla_i^2 + \sum_{i,a} \frac{2Z_a}{|r_i - R_a|} + \sum_{i>j} \frac{2}{|r_i - r_j|} \right] \phi_1(1) \ldots \phi_n(n)$$

$$d\tau_1 \ldots d\tau_n. \qquad (4\text{-}40)$$

We can see at once from the orthogonality of the ϕ's and from the fact that all the operators in the Hamiltonian involve no more than the coordinates of two electrons, that in order for V(P) to be non vanishing P must be either a transposition or the identity element. Explicitly we have

$$V(E) = \sum_i \int \phi_i^*(r) \left[- \nabla^2 + \sum_a \frac{2Z_a}{|\vec{r} - \vec{R}_a|} \right] \phi_i(r)\, d\tau$$

$$+ \sum_{i>j} \frac{\phi_i^*(r_1)\, \phi_i(r_1)\ 2\phi_j^*(r_2)\, \phi_j(r_2)}{|r_1 - r_2|}\, d\tau_1\, d\tau_2$$

$$= \sum_i Q_i + \sum_{i>j} J_{ij} \qquad (4\text{-}41)$$

$$Q_i = \int \phi_i^*(r) \left[- \nabla^2 + \sum_a \frac{2Z_a}{|r - R_a|} \right] \phi_i(r)\, d\tau$$

$$J_{ij} = \int \frac{\phi_i^*(r_1)\, \phi_i(r_1)\ \ 2\phi_j^*(r_2)\, \phi_j(r_2)}{|r_1 - r_2|}$$

For the transpositions we have

$$V(P_{ij}) = \int \frac{\phi_i^*(r_1)\,\phi_j(r_1)\,2\phi_i(r_2)\,\phi_j^*(r_2)}{|r_1 - r_2|}\,d\tau_1\,d\tau_2 \qquad (4\text{-}42)$$

$$= K_{ij}$$

J_{ij} and K_{ij} are the familiar Coulomb and exchange integrals. In this case the Hamiltonian matrix connecting states transforming as the α irreducible representation of the group of spatial permutations becomes

$$H^{\alpha} = \sum_i Q_i + \sum_{i>j} J_{ij} + \sum_{i>j} \Gamma_{\alpha}(P_{ij}) K_{ij} \qquad (4\text{-}43)$$

with similar simple expressions for the effective Hamiltonians. The spin Hamiltonian (4-39) can be written through the use of the Dirac identity as

$$\sum_i Q_i + \sum_{i>j} J_{ij} - \sum_{i>j} \frac{1}{2}\left\{1 + \vec{\sigma}_i \cdot \vec{\sigma}_j\right\} K_{ij} = \sum_i Q_i + \sum_{i>j} (J_{ij} - \tfrac{1}{2}K_{ij}) - \frac{1}{2}\sum_{i>j} K_{ij}\,\vec{\sigma}_i \cdot \vec{\sigma}_j \qquad (4\text{-}44)$$

The form of (4-44) is what gives rise to the expression "vector model". The Hamiltonian (4-44) looks like the dot product interaction between angular momentum. With the expression (4-43) or (4-44) we see that the energy differences arising from the states $P^S \Phi_o$ depend only on the exchange integrals K_{ij}. The Q_i's and the J_{ij}'s just give an additive term to the energy.

We shall not go into any detailed application of vector model at this point since there are many cases discussed in the literature and other texts. We shall go on in the next paragraphs to discuss how the vector model is altered if some of the orbitals in the function Φ_o are identical.

B. Doubly Filled Orbitals

It is not always a good approximation to assume that an n electron wave function consists of the sum of products of n distinct one-electron wave functions. As is well known from the concept of a closed shell in atomic structure it is sometimes best to have two electrons assigned to a single spatial wave function. (We cannot have any more than two electrons assigned to a single spatial wave function since it is not possible to construct a totally antisymmetric wave function including spin from such a wave function.) Let us see how doubly filled orbitals influence the procedure of the Dirac vector model.

Let us assume that we have a wave function

$$\Phi_o = \phi_1(1)\,\phi_2(2) \ldots \phi_n(n)$$

where in addition orbitals ϕ_1 and ϕ_2 are identical

$$\phi_1 = \phi_2 \tag{4-45}$$

With this wave function we could again use the projection operators ζ^a_{ij} to construct states which have proper transformation properties under the permutation group. There are simplifications, however, which result from the fact that the orbital ϕ_1 is doubly filled. Let us see how this comes about.

We can, of course, choose as an irreducible representation of the symmetric group $\Gamma_a(P)$ one in which $\Gamma_a(P_{12})$ is diagonal. (Any unitary matrix can be diagonalized by a unitary transformation.) From the fact that $\Gamma_a(P_{12})\ \Gamma_a(P_{12}) = \Gamma(E)$ we conclude that the diagonal elements are ± 1. Let us arrange these diagonal elements so that +1's occur first and then the -1's occur along the diagonal.

$$\Gamma_a(P_{12}) = \begin{array}{c} \\ p \\ q \end{array} \begin{array}{c} \begin{array}{cc} p & q \end{array} \\ \left(\begin{array}{c|c} +1 & 0 \\ \hline 0 & -1 \end{array}\right) \end{array} \tag{4-46}$$

The dimension of the "+1 block" is p and the dimension of the "-1 block" is q. Here $p + q = n_a$ is the dimension of the a irreducible representation. With such a form for the a irreducible representation let us see what the effect of the projection operator ζ^a_{ij} is on Φ_o. We notice first that since $\phi_1 = \phi_2$, $P^S_{12}\Phi_o = \Phi_o$. Therefore

$$\Phi_o = \left(\frac{E + P^S_{12}}{2}\right)\Phi_o \tag{4-47}$$

Using this fact we obtain

$$\begin{aligned}
\Phi^a_{ij} &= \sqrt{\frac{n_a}{2n!}}\,\zeta^a_{ij}\Phi_o = \sqrt{\frac{n_a}{2n!}}\sum_P \Gamma\ (P)^*_{ij}\,P^S\left[\frac{E + P^S_{12}}{2}\right]\Phi_o \\
&= \sqrt{\frac{n_a}{2n!}}\,\frac{1}{2}\sum_P \left[\Gamma_a(P)^*_{ij}\,P^S + \Gamma_a(P\,P_{12})_{ij}\,P^S\right]\Phi_o \\
&= \sqrt{\frac{n_a}{2n!}}\,\frac{1}{2}\sum_P \left[\Gamma_a(P)^*_{ij} + \sum_k \Gamma_a(P)^*_{ik}\,\Gamma_a(P_{12})^*_{kj}\right]P^S\Phi_o
\end{aligned}$$

From the form of $\Gamma_a(P_{12})$ we conclude

$$\begin{aligned}
\Phi^a_{ij} &= \sqrt{\frac{n_a}{n!}}\,\zeta^a_{ij}\,\Phi_o \qquad & j &= 1 \ldots p \\
\Phi^a_{ij} &= 0 & j &= p+1 \ldots n_a
\end{aligned} \tag{4-48}$$

(The factor $\sqrt{\frac{n_a}{2n!}}$ will turn out to be a normalizing factor.) We notice that in this case we do not get n_a sets of functions which form bases for the a irreducible representation. Instead, we get only p bases. Since the only states which interact are those which have the same a and i, we shall only have a matrix of interaction, for the a irreducible representation, of order p instead of n_a, the order we would obtain if we had n distinct orbitals.

We might at this point check the orthonormality of the wave functions (4-48) we have constructed. This can be easily accomplished.

$$
\begin{aligned}
&(\Phi^a_{ij}, \Phi^a_{ik}) \qquad j,k = 1 \ldots p \\
&\quad = \frac{n!}{n_a}\frac{n_a}{2n!}(\Phi_o, \zeta^a_{jk}\Phi_o) \\
&\quad = \frac{1}{2}\sum_P \Gamma_a(P)^*_{jk}(\Phi_o, P^s\Phi_o) = \frac{1}{2}\sum_P \Gamma_a(P)^*_{jk}(\Phi_o, (P^{-1})^f\Phi_o)
\end{aligned}
\tag{4-49}
$$

We have made use of Eq. (4-44) of the last chapter in deriving this. From the orthogonality of the ϕ's we see that only two terms will contribute to the sum in (4-49). P must be either E or P_{12}. In this case we get

$$
(\Phi^a_{ij}, \Phi_{ik}) = \frac{1}{2}\Gamma_a(E)(\Phi_o, \Phi_o) + \frac{1}{2}\Gamma_a(P_{12})^*_{jk}(\Phi_o, \Phi_o) \qquad j,k = 1 \ldots p
$$

Since $\Gamma_a(P_{12})^*_{jk} = \delta_{jk}$, $j,k = 1 \ldots p$ we finally obtain the desired result

$$
(\Phi^a_{ij}, \Phi^a_{ik}) = \delta_{jk}
$$

We have now seen the limitations on the functions Φ^a_{ij} because of the doubly filled orbital. Let us now see what the spin part of the wave function must be like in order to be compatible with the doubly filled orbital in the space part.

We have already seen that the spin part of the wave function must transform like $\Gamma_a'(P)^*$. In this case for P_{12} we have

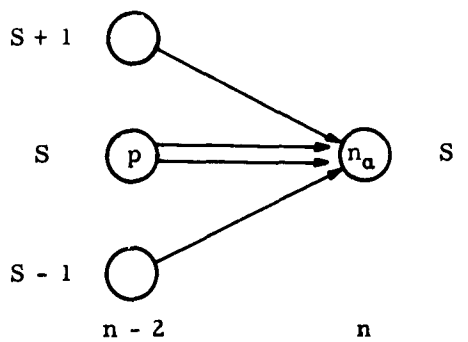
$$
\Gamma_a'(P_{12})^* = \begin{array}{c} \\ p \\ q \end{array}
\begin{array}{c}
\begin{array}{cc} p & q \end{array} \\
\left(\begin{array}{cc} -1 & 0 \\ 0 & +1 \end{array}\right)
\end{array}
$$

Thus we see that the functions $\psi_j(S, M_S, n)$ which form a basis for this representation will be divided into two groups. The first p transform antisymmetrically under P_{12} the remaining q symetrically. Let us see how such states might have been constructed from the branching diagram.

We constructed the states of the branching diagram originally by adding one electron at a time. We could equally well have proceeded by adding two electrons at a time starting with either n = 0 or 1 and proceeded in this way to construct our states. The states for the two electrons which we add we can take to be

$$\begin{aligned} &\alpha(1)\,\alpha(2) \\ &\beta(1)\,\beta(2) \\ &\frac{\alpha(1)\,\beta(2) + \beta(1)\,\alpha(2)}{\sqrt{2}} \\ &\frac{\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)}{\sqrt{2}} \end{aligned} \qquad (4\text{-}50)$$

The first three are the states with S = 1 and $M_S = +1, -1, 0$. The fourth is the two-electron state with $S = M_S = 0$. If we had the states $\psi_j(S, M_S, n - 2)$ for the n - 2 electron problem we could construct the states for the n electron problem in the following manner.



We could combine a spin 1 with a spin S + 1 to give a spin S (upper arrow). We could combine a spin 1 with a spin S to give a spin S (one of the middle arrows). We could combine a spin S - 1 with a spin 1 to give a spin S (lower arrow). Let us say that these three methods give rise to the last q of the n_a states $\psi_j(S, M_S, n)$. These three methods would involve the first three of the two-electron functions in (4-50). The first p of the n_a states we would obtain by combining a spin 0 of the two-electron problem with the spin S of the n - 2 electron problem. This would yield a spin S (other middle arrow). We can now write the spin eigenfunctions in the form

$$\psi_j(S, M_S, n) = \psi_j(S, M_S, n-2)\left[\frac{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)}{\sqrt{2}}\right] \qquad j = 1 \ldots p$$

$$\psi_j(S, M_S, n) = e_j(s_3 \ldots s_n)\,\alpha(1)\,\alpha(2)$$
$$+ f_j(s_3 \ldots s_n)\,\beta(1)\,\beta(2) \qquad (4\text{-}51)$$
$$+ g_j(s_3 \ldots s_n)\left[\frac{\alpha(1)\,\beta(2) + \alpha(2)\,\beta(1)}{\sqrt{2}}\right] \qquad j = p+1 \ldots n_a$$

(We have assumed here that $\psi_j(S, M_S, n-2)$ depends on the spin coordinates $s_3 \ldots s_n$.) We have not written the explicit form of e, f, and g in terms of the $\psi_j(S, M_S, n-2)$'s since we shall not need these forms for our purposes.

It is clear that the first p functions in (4-51) $\psi_j(S, M_S, n)$ are those corresponding to $\Gamma_a'(P_{12})^*_{ii} = -1$, $i = 1 \ldots p$. The second $n_a - p$ functions correspond to $\Gamma_a'(P_{12})^*_{ii} = +1$, $i = p+1 \ldots n_a$. From the method of construction the functions $\psi_j(S, M_S, n)$, $j = 1 \ldots p$ form a basis for an irreducible representation of the group of permutations of the last n - 2 coordinates. Let us call this representation $\Gamma_a'(P)$ where P is a permutation which leaves 1 and 2 unaffected. For one of these permutations we have

$$\Gamma_a(P) = \begin{array}{c} \\ p \\ q \end{array} \begin{array}{c} \begin{array}{cc} p & q \end{array} \\ \left(\begin{array}{c|c} \Gamma_a'(P) & 0 \\ \hline 0 & \Gamma_a''(P) \end{array}\right) \end{array} \qquad (4\text{-}52)$$

Let us consider permutations not in this group, namely $P_{1\ell}$ and $P_{2\ell}$. Here ℓ lies between 3 and n. These have matrices which we can block off as in (4-52)

$$\Gamma_a(P_{1\ell}) = \left(\begin{array}{c|c} \Gamma_a'(P_{1\ell}) & A \\ \hline B & \Gamma_a''(P_{1\ell}) \end{array}\right) \qquad (4\text{-}53)$$

From the fact that $\Gamma_a(P_{12})\ \Gamma_a(P_{1\ell})\ \Gamma_a(P_{12}) = \Gamma_a(P_{2\ell})$ we conclude

$$\Gamma_a(P_{2\ell}) = \left(\begin{array}{c|c} \Gamma_a'(P_{1\ell}) & -A \\ \hline -B & \Gamma_a''(P_{1\ell}) \end{array}\right) \tag{4-54}$$

We shall actually be able to find $\Gamma_a'(P_{1\ell})$ because of the restrictive nature of the spin product functions. We first notice that

$$\Gamma_a(P_{1\ell}) + \Gamma_a(P_{2\ell}) = \left(\begin{array}{c|c} 2\Gamma_a'(P_{1\ell}) & 0 \\ \hline 0 & 2\Gamma_a''(P_{1\ell}) \end{array}\right) \tag{4-55}$$

We also notice that

$$\begin{aligned} &(P^{\sigma}_{1\ell} + P^{\sigma}_{2\ell})\, \psi_j(S, M_S, n) \qquad j = 1 \ldots p \\ &\quad = (P^{\sigma}_{1\ell} + P^{\sigma}_{2\ell})\, \psi_j(S, M_S, n-2) \left[\frac{\alpha(1)\,\beta(2) - \alpha(2)\,\beta(1)}{\sqrt{2}}\right] \end{aligned} \tag{4-56}$$

Since ψ_j contains in its decomposition into spin product functions, functions containing either $\alpha(\ell)$ or $\beta(\ell)$

$$\begin{aligned} \psi_j(S, M_S, n-2) = {} & \chi_j^{+}(s_3 \cdots s_{\ell-1}, s_{\ell+1} \cdots s_n)\, \alpha(\ell) \\ & + \chi_j^{-}(s_3 \cdots s_{\ell-1}, s_{\ell+1} \cdots s_n)\, \beta(\ell) \end{aligned} \tag{4-57}$$

Combining (4-57) and (4-56) we see that

$$(P^{\sigma}_{1\ell} + P^{\sigma}_{2\ell})\, \psi_j(S, M_S, n) = \psi_j(S, M_S, n)$$

or
$$\Gamma_{a'}'(P_{1\ell})^* + \Gamma_{a'}'(P_{2\ell})^* = 1 \tag{4-58}$$

or
$$\Gamma_{a'}(P_{1\ell}) + \Gamma_{a'}(P_{2\ell}) = -\tfrac{1}{2}1$$

Or, finally

$$\Gamma_a(P_{1\ell}) = \begin{array}{c|c} p \\ p \left\{ \begin{array}{c|c} -\frac{1}{2}1 & A \\ \hline B & \Gamma_{a''}(P_{1\ell}) \end{array} \right. \end{array} \tag{4-59}$$

We are now in a position to define the secular problem for the states arising from the wave functions Φ^a_{ij} $j = 1 \ldots p$.

$$\begin{aligned} H^a_{jk} &= (\Phi^a_{ij}, H\Phi^a_{ik}) \\ &= \frac{n_a}{2n!}(\zeta^a_{ij}\Phi_o, H\zeta^a_{ik}\Phi_o) \\ &= \frac{1}{2}(\Phi_o, H\zeta^a_{jk}\Phi_o) \\ &= \frac{1}{2}\sum_P \Gamma_a(P)^*_{jk}(\Phi_o, HP^S\Phi_o) \\ &= \frac{1}{2}\sum_P \Gamma_a(P)^*_{jk} V(P) \end{aligned} \tag{4-60}$$

where

$$\begin{aligned} V(P) &= (\Phi_o, HP^S\Phi_o) \\ &= (P^f\Phi_o, H\Phi_o) \end{aligned}$$

As we did for the case of the n distinct orbitals we can simplify this expression by using the orthogonality of the orbitals. We shall assume that the set of orbitals $\phi_3 \ldots \phi_n$ are distinct and orthonormal and in addition orthogonal to $\phi_1 \ldots \phi_2$. It is clear from the fact that our Hamiltonian only involves two-electron operators that if $P^f\Phi_o$ has more than two functions "out of position", considering ϕ_1 and ϕ_2 as identical $V(P) = (\Phi_o, HP^S\Phi_o) = (P^f\Phi_o, H\Phi_o)$ will vanish. The only way that we can have this situation is to have for the P's giving non-vanishing matrix elements $P = E$, P_{ij}, $P_{ij}P_{12}$. We may also notice that $K_{1\ell} = K_{2\ell}$, $J_{1\ell} = J_{2\ell}$, $K_{11} = J_{11} = K_{12} = J_{12} = K_{22} = J_{22}$. Therefore, we have that

$$\begin{aligned} V(E) &= 2Q_1 + J_{11} + 2\sum_{\ell \neq 1} J_{1\ell} + \sum_{\substack{k \neq m \\ \ell, m \neq 1}} J_{\ell m} \\ V(P_{\ell m}) &= K_{\ell m} \qquad \ell, m \neq 1, 2 \end{aligned} \tag{4-61}$$

$$V(P_{12}) = V(E)$$

$$V(P_{\ell m} P_{12}) = V(P_{\ell m}) \qquad \ell, m \neq 1\ 2 \qquad \text{((4-61) con'd)}$$

$$V(P_{1j}) = V(P_{1j} P_{12}) = V(P_{2j}) = V(P_{2j} P_{12}) = K_{1j} \qquad j \neq 1, 2$$

From these expressions for the matrix elements of the Hamiltonian matrix (4-60) we see that we only need the matrix elements $\Gamma_a(P)_{jk}$ where $j, k = 1 \ldots p$ from the matrices $\Gamma_a(P)$. Using the forms of the matrices representing E, P_{ij}, and $P_{ij} P_{12}$ we obtain (since P_{ij} for $i, j \neq 1, 2$) is a permutation of the last n - 2 coordinates) from (4-46), (4-55) and (4-59)

$$\begin{aligned} H^a_{jk} &= \frac{1}{2}\left[V(E) + V(P_{12})\right]\delta_{jk} \\ &+ (-\tfrac{1}{2})(\tfrac{1}{2})\left[2 \sum_{\ell \neq 1\ 2} K_{1\ell} + \sum_{\ell \neq 1\ 2} K_{2\ell}\right]\delta_{jk} \\ &+ \frac{1}{2} \sum_{\substack{\ell \neq m \\ \ell\ m \neq 1\ 2}} \Gamma_a(P_{\ell m})_{ij}\left[K_{\ell m} + K_{\ell m}\right] \end{aligned} \qquad (4\text{-}62)$$

$$\begin{aligned} H^a &= \left[2Q_1 + J_{11} + 2 \sum_{\ell \neq 1, 2} J_{1\ell} + \sum_{\substack{\ell \neq m \\ \ell, m \neq 1, 2}} J_{\ell m}\right] 1 \\ &+ \sum_{\substack{\ell, m \\ \ell, m \neq 1\ 2}} \Gamma_{a'}(P_{\ell m})\, K_{\ell m} \end{aligned}$$

We notice that we need only the matrices $\Gamma_{a'}(P_{\ell m})$ representing transpositions amongst the last n - 2 coordinates. In other words we have just the matrices forming an irreducible representation of the group of permutations of the last n - 2 coordinates. This makes sense since the two electrons in the filled orbits form a singlet and the only spins which are admissable are those which arise from the remaining n - 2 electrons. As far as the secular equation connecting states of the same symmetry is concerned, the splitting of levels is due only to exchange integrals between the unpaired orbits. The energy expression for the case of more than one paired orbital is also easily obtained. We shall not discuss the derivation in detail since they follow in a straightforward manner from the case of one paired orbit.

If $\phi_3 = \phi_4$ we could choose the matrix $\Gamma_{a'}(P_{34})$ to be diagonal with the diagonal elements + 1 or - 1 with the + 1 diagonal elements appearing first. We could then easily show that the normalized wave functions obtained from projection operators would be

$$\Phi_{ij} = \sqrt{\frac{n_a}{4n!}}\, \zeta_{ij}\, \Phi_o \tag{4-63}$$

(The factor 4 arising from the fact that $\Phi_o = P^S_{12}\Phi_o = P^S_{34}\Phi_o = P^S_{12}P^S_{34}\Phi_o$.) The wave functions Φ^a_{ij} would now vanish for all j corresponding to the negative eigenvalues of $\Gamma_{a'}(P_{34})$ in addition to its vanishing for all those j corresponding to a negative eigenvalue to P_{12}. Once again we could correlate the positive eigenvalues of $\Gamma_{a'}(P_{34})$ with spin states where the third and fourth electrons are in a singlet state and in calculating the Hamiltonian matrix we would find that we only needed to know the matrices representing the permutations of the n - 4 electron problem. We could carry on this procedure if there were more filled orbitals. Let us assume that the first 2p orbitals are paired. That is

$$\begin{aligned} \phi_1 &= \phi_2 \\ \phi_3 &= \phi_4 \\ &\vdots \\ \phi_{2p-1} &= \phi_{2p} \end{aligned} \tag{4-64}$$

The remaining n - 2p orbitals are unpaired. All distinct orbitals we shall take as forming an orthonormal set. In this case the wave functions would be

$$\Phi^a_{ij} = \sqrt{\frac{n_a}{2^p n!}}\, \zeta^a_{ij}\, \Phi_o \tag{4-65}$$

If we choose the representation $\Gamma_a(P)$ which has first $\Gamma_a(P_{12})$ diagonal with a block of + 1's and a block of - 1's and then divide the + 1 block making a representation where $\Gamma_{a'}(P_{34})$ is diagonal with blocks + 1 and - 1, etc., then for our Hamiltonian matrix of this symmetry we obtain

$$\begin{aligned} H^a &= \Big\{ \sum_{\mu=1}^{p} 2Q_\mu + \sum_{\mu,\nu} \left[4J_{\mu\nu} - 2K_{\mu\nu}\right] + \sum_{\mu} J_{\mu\mu} \\ &\quad + \sum_{\mu,j} \left[2J_{\mu j} - K_{\mu j}\right] + \sum_{i}\sum_{j} J_{ij} \Big\} 1 \\ &\quad + \sum_{i>j} \Gamma_a(P_{ij})\, K_{ij} \\ &= \text{const} + \sum_{i>j} \Gamma_a(P_{ij})\, K_{ij} \end{aligned} \tag{4-66}$$

Here the summation over the Greek indices runs over paired orbitals (1 ... p). The summation over the Roman indices runs over the n - 2p unpaired orbitals. The matrices

$\Gamma_a(P_{ij})$ are an irreducible representation of the n - 2p electron problem and correspond to one of the multiplicities of that problem. The spin functions which form a basis for the spin permutation representation associated with $\Gamma_a(P_{ij})$ are the spin functions

$$\frac{\left[\alpha(1)\,\beta(2) - \beta(1)\,\alpha(2)\right]}{\sqrt{2}} \frac{\left[\alpha(3)\,\beta(4) - \beta(3)\,\alpha(4)\right]}{\sqrt{2}} \times \cdots \frac{\left[\alpha(2p-1)\,\beta(2p) - \beta(2p-1)\,\alpha(2p)\right]}{\sqrt{2}} \times \psi_j(S, M_S, n-2p) \tag{4-67}$$

where ψ_j forms a basis for an irreducible representation of the permutation group of the last n - 2p coordinates. It is clear from this that the functions in (4-67) also form an irreducible representation of permutations of the last n - 2p coordinates.

Before leaving the problem of paired orbitals we can derive expressions for the average energies of all states of a given multiplicity for the n electron problem arising from the wave functions $P^S\Phi_o$ where Φ_o has paired orbitals and n - 2p unpaired orbitals. In order to do this all we need do is to take the character of all the matrices in (4-66) since this gives us the trace of the Hamiltonian matrix H^a. This traces when divided by the order of the matrix gives the average energy of the states of a symmetry. We know from the property that a trace of matrix is invariant under a unitary transformation that we shall not change this average energy if we diagonalize the Hamiltonian matrix (H^a). This of course is nothing more than the average energy of all states of a given multiplicity since there is a one to one correspondence between a and multiplicity. We know, however, that the characters of all the matrices $\Gamma_a(P_{ij})$ are the same ($\chi_a(P_{ij})$). From Eq. (4-9) and the subsequent discussion in that section it is easy to see that the average energy of states of spin S when there are p paired orbitals and n - 2p unpaired orbitals is given by

$$\sum_{\mu=1}^{p} 2Q_\mu + \sum_{\mu,\nu}\left[4J_{\mu\nu} - 2K_{\mu\nu}\right] + \sum_{\mu} J_{\mu\mu} + \sum_{\mu,\nu}\left[2J_{\mu j} - K_{\mu j}\right] + \sum_{i>j} J_{ij} - \left(\frac{2}{n'(n'-1)}\right)\left[\frac{n'^2}{4} - n' + S(S+1)\right]\sum_{i>j} K_{ij} \qquad n' = (n-2p) \tag{4-68}$$

This completes the discussion of the paired orbitals. We can go even further in the discussion of the vector model by discussing the interaction between the states $P^S\Phi_o$ and $P^S\Phi_o'$ where Φ_o' is composed of a product of one-electron functions in a different way than Φ_o. This is called configuration interaction and we shall discuss this next.

C. Configuration Interaction

So far we have assumed that as far as the spatial part of the many-electron wave function is concerned we could restrict ourselves to the states arising from the functions $P^S \Phi_0$ where Φ_0 is a product of one-electron wave functions. It is clear that in order to form a complete set as far as spatial wave functions are concerned we must include more than the functions $P^S \Phi_0$. Thus we might imagine that for the coordinates of one electron the functions $\phi_1 \cdots \phi_\infty$ form a complete set. For the many-electron space we could form a complete set by taking all possible products of this complete set of one-electron functions. We would take a product of one of the ϕ's of coordinate one times one of the ϕ's of coordinate 2, etc., down to the coordinates of the last electron. This gives us a way of forming many electron functions in terms of which we could expand any arbitrary function. Thus for any arbitrary function of the spatial coordinates of n electrons, $f(\vec{r}_1 \cdots \vec{r}_n)$ we have

$$f(\vec{r}_1 \cdots \vec{r}_n) = \sum_{q_1 \cdots q_n = 1}^{\infty} A_{q_1, q_2 \cdots q_n} \phi_{q_1}(r_1) \cdots \phi_{q_n}(r_n) \qquad (4\text{-}69)$$

Here $A_{q_1 \cdots q_n}$ are constant coefficients. So far in our discussion of the vector model we have restricted the spatial parts of our wave function in such a way that the only functions appearing in the summation (4-69) are those which can be obtained from one another by permutations of the spatial coordinates. The wave functions which arise from these restricted functions we say arise from a single configuration. A configuration is specified if we specify which one-electron orbitals are occupied and how many times each is occupied. (In order to be consistent with the exclusion principle an occupied orbital must be occupied either once or twice.) The spatial wave functions of a single configuration are therefore taken from the functions $P^S \Phi_0$ where Φ_0 is a product of some selection of our complete set of one-electron functions. Since these do not form a complete set we shall have to relax this restriction and include more configurations in our problem to form a good approximation to the many-electron wave function. The problem of finding the wave function as a combination of the functions taken from more than one configuration is the problem of configuration interaction.

We can form the states $P^S \Phi_0$, $P^S \Phi_1 \cdots P^S \Phi_\mu, P^S \Phi_\nu$. Here the single index μ specifies which one-electron functions are occupied and how many times each is occupied. It thus specifies a configuration. We now wish to express our many-electron wave function, as far as spatial coordinates are concerned, as a linear combination of the functions $P^S \Phi_0 \cdots P^S \Phi_\mu \cdots$. We need only consider linear combinations of functions transforming according to the same column of the same irreducible representation. This we can accomplish by means of the projection operators. We can form the states

$$\Phi_{ij}^{a,\nu} = c_{a,\nu}\,\zeta_{ij}^{a}\,\Phi_{\nu} \tag{4-70}$$

Here $\Phi_{ij}^{a,\nu}$ is the j^{th} function transforming according to the i^{th} column of the a irreducible representation arising from the ν^{th} configuration. $c_{a,\nu}$ is a normalization constant. We wish to form linear combinations of these functions for fixed a and i to form the best possible approximation to the wave function transforming according to the i^{th} column of the a irreducible representation. This we do, as usual, by minimizing the expectation value of the energy by variation of the linear coefficients in the expansion of the wave function. In this way we become involved in the solution of secular equations. We must find, in this procedure, the matrix elements of the Hamiltonian with respect to the functions $\Phi_{ij}^{a,\mu}$ and $\Phi_{ij'}^{a,\mu'}$ for fixed a and i.

This can easily be done if we assume that our one-electron orbitals are orthogonal. We shall recall that for a given configuration some of the functions $\Phi_{ij}^{a,\nu}$ vanished if there were doubly filled orbitals. Let us say that the configuration ν has p_ν paired orbitals, the remaining $n - 2p_\nu$ being unpaired. Of all the configurations considered, let us assume that ν has the maximum number of paired orbitals and we shall assume that in Φ_ν these paired orbitals appear in the product first. We shall also assume that in all the other configurations considered the paired orbitals appear first. In this case, we chose as the representation $\Gamma_a(P)$ for the symmetric group of degree n a representation where $\Gamma_a(P_{12})$ is diagonal with +1's appearing first along the diagonal. We can further specify the representation by demanding that $\Gamma_a(P_{34})$ be diagonal in such a way that the + 1 diagonal elements corresponding to the + 1 diagonal elements of $\Gamma_a(P_{12})$ come first. In a similar way we can proceed until we have diagonalized $\Gamma_a(P_{12})$, $\Gamma_a(P_{34})$ ... $\Gamma_a(P_{2p_\nu - 1,\, 2p_\nu})$. We then block off columns of matrices $\Gamma_a(P)$ such that the column blocked off corresponds to all + 1's in the upper left-hand corner of all the matrices $\Gamma_a(P_{12})$ ... $\Gamma_a(P_{2p_\nu - 1,\, 2p_\nu})$. Let us say that the first n_a^ν columns of the matrices $\Gamma_a(P)$ have + 1 along the first n_a^ν diagonal elements of all of the matrices $\Gamma_a(P_{12})$ ... $\Gamma_a(P_{2p_\nu - 1,\, 2p_\nu})$. In this case we recall that for a given configuration Φ_μ we would obtain (Eq. (4-65)

$$\begin{aligned} \Phi_{ij}^{a,\mu} &= \sqrt{\frac{n_a}{2^{p_\mu} n!}}\,\zeta_{ij}^{a}\,\Phi_{\mu} \quad \text{for } j < n_a \\ \Phi_{ij}^{a,\mu} &= 0 \quad \text{for } j > n_a \end{aligned} \tag{4-71}$$

For the matrix elements between the μ and the μ' configuration we would have only

$$H_{jk}^{a;\,\mu,\,\mu'} = (\Phi_{ij}^{a,\mu},\, H\Phi_{ik}^{a,\mu'}) \qquad j = 1 \ldots n_a^\mu,\; k = 1 \ldots n_a^{\mu'} \tag{4-72}$$

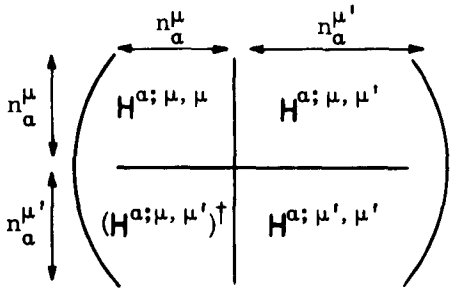
or

$$H^{a;\mu,\mu'} = \frac{1}{\sqrt{2^{p_\mu} 2^{p_{\mu'}}}} (\Phi_\mu, H \zeta^a_{jk} \Phi_{\mu'}) = \frac{1}{\sqrt{2^{p_\mu} 2^{p_{\mu'}}}} \sum_P \Gamma_a(P)^*_{jk} (\Phi_\mu, H P^S \Phi_{\mu'}) \tag{4-72}$$

For the matrix elements from one configuration we have

$$H^{a,\mu,\mu} = \frac{1}{2^{p_\mu}} \sum_P \Gamma_a(P)^*_{jk} (\Phi_\mu, H P^S \Phi_\mu) \qquad \mu = 1 \ldots n^\mu_a \tag{4-73}$$

Here and in (4-72) $\Gamma_a(P)$ are matrices forming an irreducible representation of the symmetric group of degree n taken to be in the specified form for the matrices $\Gamma_a(P_{12})$ $\ldots \Gamma_a(P_{2p_\nu - 1, 2p_\nu})$ which we mentioned above. As far as the configurations μ and μ' are concerned the Hamiltonian matrix would be



(4-74)

To find the energies all we need do is subtract $1E$ from this matrix and solve for the roots of the resulting secular determinant.

We could go still further and use the orthogonality of the one-electron functions to write explicit forms for the matrix elements $(\Phi_\mu, H P^S \Phi_{\mu'})$. We can see, for example, because of the orthogonality of the one-electron orbitals, that Φ_μ and $\Phi_{\mu'}$ can only differ at most by two orbitals or else there would be no matrix element connecting these two configurations. We shall not pursue this any further since this runs along the same lines as our considerations for a single configuration.

There is one further extension which we could make in the discussion of the vector model. We have assumed that the one-electron functions which we have used are orthogonal. If this were not the case many complications would arise. These can, however, be formally handled in the framework of the vector model. The first thing that would change would be the normalization of the functions $\Phi^{a,\nu}_{ij} = c_{\nu,a} \zeta^a_{ij} \Phi_\nu$. For non orthogonal one-electron functions in order to normalize $\Phi^{a,\nu}_{ij}$ we would demand

$$
\begin{aligned}
1 &= (\Phi_{ij}^{a,\nu}, \Phi_{ij}^{a,\nu}) \\
&= c_{\nu,a}^2 \frac{n!}{n_a} (\Phi_\nu, \zeta_{jj}^a \Phi_\nu) \\
&= c_{\nu,a}^2 \frac{n!}{n_a} \sum_P \Gamma_a(P)_{jj}^* (\Phi_\nu, P^S \Phi_\nu) \qquad (4\text{-}75) \\
c_{\nu,a} &= \sqrt{\frac{n_a}{n!}} \Big(\sum_P \Gamma_a(P)_{jj}^* S_\nu(P) \Big)^{-1/2} \\
S_\nu(P) &= (\Phi_\nu, P^S \Phi_\nu)
\end{aligned}
$$

$S_\nu(P)$ can, of course, be expressed as a product of the one-electron integrals of the products of pairs of one-electron functions. The only quantity necessary to evaluate $c_{\nu,a}$ is

$$\sum_P \Gamma_a(P)_{jj}^* S_\nu(P)$$

This may not, in general, be an easy expression to evaluate. Formally, at least, we can normalize the function in this manner. To complete the discussion of the vector model for non orthogonal functions we need only find the Hamiltonian matrix with respect to the functions $\Phi_{ij}^{a,\nu}$ and $\Phi_{ij'}^{a,\nu'}$. In this case the functions would not be orthogonal and as is familiar we can set up the secular determinant by taking the matrix elements of H - E with respect to $\Phi_{ij}^{a,\nu}$ and $\Phi_{ij}^{a,\nu'}$. We must be careful to remember that in this case in the form of the Hamiltonian matrix higher permutations than transpositions can occur in

$$\sum_P \Gamma_a(P)_{jj'}^* c_{a,\nu} c_{a,\nu'} (\Phi_\nu, (H - E) \Phi_{\nu'})$$

There is no basic reason why the vector model cannot be used for the non orthogonal functions even though the labor becomes more formidable.

This completes our discussion of the Dirac vector model. In the next section, we show how this method is related to the familiar determinantal method.

D. Relation to the Determinantal Method

We have seen how, through the use of the Dirac vector model, we can find approximate eigenvalues and eigenvectors for the n electron problem. In essence, we treated spatial coordinates and spin coordinates separately and then formed totally antisymmetric states at a late stage in the formalism. There is another approach to the n electron problem which forms approximate antisymmetric functions right at the start. This approach is the determinantal method and we shall give a brief description

of this procedure and then show the relation of it to the vector model.

In the determinantal method, we again start with a complete set of one-electron spatial orbitals $\phi_1 \cdots \phi_\ell \cdots$. As far as spin functions are concerned α and β form a complete set for one electron. We could, therefore, form a complete set of space-spin orbitals for one electron by taking all the functions $\phi_1 \cdots \phi_\ell \cdots$ and multiplying them by α and then by β. Thus the functions $\phi_\ell(\vec{r}_1)\,\alpha(1)$; $\phi_\ell(\vec{r}_1)\,\beta(1)$, $\ell = 1 \ldots \infty$ form a complete set in the spin and spatial coordinates of the electron 1. A complete set of functions in the space of n electrons (including spin coordinates) could be formed by taking the products of any choice of the functions $\phi_\ell(\vec{r}_n)\begin{matrix}\alpha(n)\\ \beta(n)\end{matrix}$ for the n electrons and multiplying them together. We know that we must obey the exclusion principle, so that, we must make linear combinations of these product functions to form functions that are totally antisymmetric. This is most conveniently done by forming determinantal wave functions.

Determinantal wave functions are formed in the following manner. Let us say that

$$\chi_i(\vec{r}_1, s_1) = \phi_{\ell_i}(\vec{r}_1)\begin{Bmatrix}\alpha(1)\\ \beta(1)\end{Bmatrix} \qquad i = 1 \ldots n$$

are n one-electron space spin functions which we wish to use in forming an antisymmetric wave function. We could form the determinant

$$\frac{1}{\sqrt{n!}}\begin{vmatrix} \chi_1(1) \cdots \chi_1(n) \\ \chi_2(1) \cdots \chi_2(n) \\ \vdots \\ \chi_n(1) \cdots \chi_n(n) \end{vmatrix} \tag{4-76}$$

$$= \frac{1}{\sqrt{n!}} \sum_P (-1)^P P^s P^\sigma \chi_1(\vec{r}_1, s_1)\, \chi_2(\vec{r}_2, s_2) \cdots \chi_n(\vec{r}_n, s_n)$$

(The factor $\frac{1}{\sqrt{n!}}$ is a normalizing factor if the ϕ's are orthogonal and normalized.) We could, of course, form a great many determinants in this way each of which would behave, as we see from the definition, antisymmetrically under simultaneous permutations of both space and spin coordinates. These determinants would form a complete set as far as totally antisymmetric functions of the space and spin coordinates of the n electrons are concerned. We could then, in principle, take matrix elements of our Hamiltonian (4-11) between these approximate wave functions and get wave functions which form approximations to the wave functions for the n electron problem.

We know, however, that our work will be simplified if we take combinations

of these determinantal wave functions which are eigenstates of S^2 and S_z, the total spin operators. If we do this, we know that there are no matrix elements of the Hamiltonian between states of different S or M_S since S^2 and S_z commute with the Hamiltonain. Thus to start an approximate calculation it is best to start with those linear combinations of determinants which are eigenstates of both S^2 and S_z. This is usually accomplished by taking all determinantal states which involve the same spatial one-electron orbitals but with different spin orbitals assigned to each spatial orbital and forming proper linear combinations of these states to diagonalize the operators involved. Thus if $\phi_1 \ldots \phi_n$ were the n spatial orbitals involved and they were all distinct we could form 2^n determinantal wave functions by taking the product of any spatial orbital ϕ_i $i = 1 \ldots n$ and either α or β spin. (In the event that two of the spatial orbitals $\phi_1 \ldots \phi_n$ were the same we would have to put this spatial function into our determinant once with α spin and once with β spin to obey the exclusion principle. We would therefore get only 2^{n-1} determinantal states.) We could then make linear combinations of these states and diagonalize S^2 and S_z. This can most easily be done through the use of the vector model and in doing so we shall se how to pass from the determinantal method to the vector model and back again.

We wish to form those linear combinations of determinants which are eigenstates of S^2 and S_z and which involve the spatial orbitals $\phi_1 \ldots \phi_n$. (We assume these to be distinct. The case of paired orbitals will follow in a straightforward manner and we shall leave this to the reader.) We had formed the states, in the spin coordinates of the n electrons, $\psi_i(S, M_S, n)$ $i = 1 \ldots n_\alpha$ which were eigenstates of S^2 and S_z and as we noted earlier these states formed a basis for an irreducible representation of the symmetric group of degree n. If we now take the product

$$\Phi_o \psi_i(S, M_S, n) = \phi_1(1)\, \phi_2(2) \ldots \phi_n(n)\, \psi_i(S, M_S, n) \qquad i = 1 \ldots n_\alpha \tag{4-77}$$

we have a function which is an eigenstate of S^2 and S_z. It is not, however, antisymmetric. Let us do this by antisymmetrizing it.

$$\frac{1}{\sqrt{n!}} \sum_P (-1)^P P^S P^\sigma \Phi_o \psi_i(S, M_S, n) \qquad i = 1 \ldots n_\alpha \tag{4-78}$$

This is also an eigenstate of S^2 and S_z since S^2 and S_z commute with $P^S P^\sigma$. It can also be written as a linear combination of the determinantal states we have written above. This is because the ψ_i's are linear combinations of spin product functions. Thus $\Phi_o \psi_i(S, M_S, n)$ is a linear combination of $\Phi_o = \phi_1(1) \ldots \phi_n(n)$ and products of α's and β's of the spin coordinates 1 through n. These when antisymmetrized will lead to a sum of determinants in (4-78) which is an eigenstate of S^2 and S_z. In each determinant will be n one-electron space spin orbitals (products of the ϕ's with either an α or

a β). Thus, in this way, we have formed linear combinations of determinants which are eigenstates of S^2 and S_z. As far as wave functions involving the n spatial orbitals $\phi_1 \cdots \phi_n$ are concerned we would have to calculate the eigenvalues of a matrix of interaction of order n_a corresponding to all states of a given multiplicity and M_S in (4-78). We shall be able to show that this matrix is exactly the one that we get from the Dirac vector model by only considering the spatial orbitals $\phi_1 \cdots \phi_n$.

Let us first note that we can rewrite the wave function (4-78) in terms of the functions Φ^a_{ij} (4-29). We know that $\psi_i(S, M_S, n)$ forms a partner in a basis for an irreducible representation of the symmetric group of degree n. Let us call this representation $\Gamma_a'(P)^* = \Gamma_1'(P) \times \Gamma_a(P)^*$ where we have chosen the representation in this form for simplicity. We can now make use of this fact in (4-78)

$$\begin{aligned} &\frac{1}{\sqrt{n!}} \sum_P \Gamma_1'(P)\, P^S P^\sigma \Phi_o \psi_j(S, M_S, n) \\ &\quad = \frac{1}{\sqrt{n!}} \sum_P \Gamma_1'(P) P^S \Phi_o \sum_i \Gamma_a'(P)^*_{ij} \psi_i(S, M_S, n) \\ &\quad = \sum_i \frac{1}{\sqrt{n!}} \left[\sum_P \Gamma_a(P)^*_{ij} P^S \Phi_o \right] \psi_i(S, M_S, n) \end{aligned} \tag{4-79}$$

Using (4-29) we obtain

$$\begin{aligned} &\sum_i \frac{1}{\sqrt{n!}} \sum_P (-1)^P P^S P^\sigma \Phi_o \psi_j(S, M_S, n) \\ &\qquad = \frac{1}{\sqrt{n_a}} \sum_i \Phi^a_{ij} \psi_i(S, M_S, n) \qquad j = 1 \ldots n_a \end{aligned} \tag{4-80}$$

This is exactly the antisymmetric wave function which we obtain from the vector model (Eq. (4-35)). Let us now see that the Hamiltonian matrix we obtain from the functions (4-78) is exactly the same as the one we obtain in the vector model. We must find the matrix elements of the Hamiltonian (4-11) between the j and j' function in (4-78). Using (4-80) we obtain

$$H_{jj'} = \frac{1}{n_a} \left(\sum_i \Phi^a_{ij} \psi_i,\ H \sum_{i'} \Phi^a_{i'j'} \psi_{i'} \right) \tag{4-81}$$

using the orthonormality of the functions ψ_i we obtain, because the Hamiltonian does not depend on spin coordinates, from the integration over these spin coordinates

$$H_{jj'} = \frac{1}{n_a} \sum_i (\Phi^a_{ij}, H \Phi^a_{ij'}) \tag{4-82}$$

From Theorem 15 $(\Phi^a_{ij}, H\Phi^a_{ij'}) = (\Phi^a_{kj}, H\Phi^a_{kj'})$. We therefore have finally that

$$H_{jj'} = (\Phi^{a}_{ij}, H\Phi^{a}_{ij'}) \tag{4-83}$$

Comparison with (4-31) shows us that this is exactly the Hamiltonian matrix which we obtain from the vector model. Thus, the determinantal method and the vector model are exactly equivalent in the results they arrive at as far as the energy and the approximate wave function are concerned. In addition the considerations of this section have led us to a method of making antisymmetric states of definite multiplicity and M_S from the functions $\psi_i(S, M_S, n)$. These, we shall recall, could be obtained through the use of the projection operators made of the spin permutation operators. The equivalence between the vector model and the determinantal method for the cases of closed shells and configuration interaction also follows through in a trivial manner.

Chapter V

SPACE GROUPS

In the preceding chapter we considered some of the invariant properties of the Hamiltonian (3-47) of Chapter III. We considered, in particular, the invariance of the Hamiltonian under permutations of the spin and spatial coordinates. In addition we mentioned that the Hamiltonian (3-47) of Chapter III was invariant under other operations. In this chapter, we go on to discuss some of the possible additional invariances of the Hamiltonian using as an example the invariance of certain Hamiltonians under space groups.

We notice first that the Hamiltonian (3-47) of Chapter III is invariant under any spatial operation which preserves distances. Such coordinate transformations are called orthogonal coordinate transformations. Thus, if the three cartesian coordinates of all the particles involved simultaneously undergo the same orthogonal transformation our Hamiltonian will be left invariant. In the next section, we discuss such length preserving transformations.

1. Orthogonal Transformations

Let us denote the three cartesian coordinates as x_1, x_2, and x_3. The most general linear combination which these coordinates could undergo would be a transformation of the form

$$\begin{aligned} x_1' &= R_{11}x_1 + R_{12}x_2 + R_{13}x_3 + t_1 \\ x_2' &= R_{21}x_1 + R_{22}x_2 + R_{23}x_3 + t_2 \\ x_3' &= R_{31}x_1 + R_{32}x_2 + R_{33}x_3 + t_3 \end{aligned} \tag{5-1}$$

In vector and matrix notation, we have

$$\vec{x}' = \mathbf{R}\vec{x} + \vec{t} \tag{5-2}$$

(Here $\vec{x}'$ is regarded as a column vector $\begin{pmatrix} x_1 \\ x_2 \\ x_3 \end{pmatrix}$.) In order to be a length preserving transformation, if we had two points $\vec{x}$ and $\vec{y}$ and let them undergo this transformation, we should demand that

$$|x_1 - y_1|^2 + |x_2 - y_2|^2 + |x_3 - y_3|^2 = |x_1' - y_1'|^2 + |x_2' - y_2'|^2 + |x_3' - y_3'|^2 \tag{5-3}$$

where we have restricted ourselves to letting the coordinates take on only real values. The restriction of having a length preserving transformation puts a restriction on $\mathbf{R}$.

Thus, if $\vec{\xi} = \vec{x} - \vec{y}$; $\vec{\xi}' = \vec{x}' - \vec{y}'$

$$\begin{aligned} (\vec{x}' - \vec{y}') &= R(\vec{x} - \vec{y}) \\ \vec{\xi}' &= R\vec{\xi} \\ \xi_1'^2 + \xi_2'^2 + \xi_3'^2 &= \tilde{\vec{\xi}}'\vec{\xi}' = \tilde{\xi}\tilde{R}R\xi \\ &= \tilde{\xi}\xi \end{aligned} \tag{5-4}$$

As is familiar from elementary courses on matrices this demands that R be a real orthogonal transformation (see footnote on p. 53)

$$\begin{aligned} \tilde{R}R &= 1 \\ \tilde{R} &= R^{-1} \end{aligned} \tag{5-5}$$

Thus we see that the most general transformation which preserves lengths is one of the form (5-2) where R has the property (5-5). The part $\vec{t}$ of the transformation can be considered as a translation of the coordinates and we shall now proceed to interpret R.

We first notice that since $\tilde{R}R = 1$ and since det $\tilde{R}$ = det R

$$\begin{aligned} (\det R)^2 &= 1 \\ \det R &= \pm 1 \end{aligned} \tag{5-6}$$

Thus the determinant of the transformation can be either $\pm$ 1. We also know from the fact that any unitary matrix can be diagonalized by a unitary transformation that we can find a unitary matrix U such that

$$U^\dagger RU = D \tag{5-7}$$

where D is a diagonal matrix the diagonal elements of which are solutions of the secular determinant being set equal to zero.

$$\det \left[R - \lambda 1\right] = 0 \tag{5-8}$$

since R is a real matrix it is a familiar theorem from algebra that the roots of this equation must be either real or complex and the complex roots must appear in pairs one member of the pair being the complex conjugate of the other member of the pair. Thus we see that in order to have det $R = \pm 1$ and a solution to (5-8) we can always put

$\mathbf{D}$ in the form

$$\mathbf{D} = \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & e^{i\phi} & 0 \\ 0 & 0 & e^{-i\phi} \end{pmatrix} \tag{5-9}$$

If we now let $\mathbf{D}$ undergo the unitary transformation

$$\mathbf{V} = \begin{pmatrix} 1 & 0 & 0 \\ & 1/\sqrt{2} & i/\sqrt{2} \\ 0 & 1/\sqrt{2} & -i/\sqrt{2} \end{pmatrix} \tag{5-10}$$

we shall, as simple matrix multiplication shows, put $\mathbf{D}$ in the form

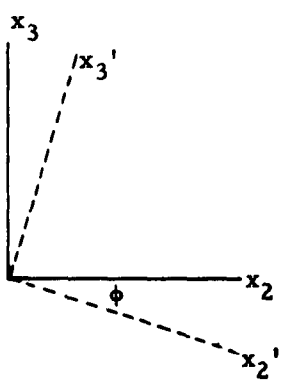
$$\mathbf{R}' = \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & \cos\phi & -\sin\phi \\ 0 & \sin\phi & \cos\phi \end{pmatrix} \tag{5-11}$$

Thus we see that any real orthogonal coordinate transformation in three dimensions can by the use of the transformation $\mathbf{UV}$ be put in the form (5-11)

$$\mathbf{R}' = \mathbf{V}^{\dagger}\mathbf{U}^{\dagger}\,\mathbf{R}\mathbf{U}\mathbf{V} \tag{5-12}$$

It is also not difficult to show that $\mathbf{UV}$ is a real matrix. Therefore, the transformation of coordinates $\mathbf{UV}$ is again a real orthogonal coordinate transformation. We see therefore that any real orthogonal coordinate transformation $\mathbf{R}$ can be put in the form (5-12) by a real orthogonal coordinate transformation. $\mathbf{R}'$ is easy to interpret. If we take the + sign in (5-11), in the coordinate system described by the transformation $\mathbf{UV}$, $\mathbf{R}'$ represents a rotation clockwise through an angle ϕ about the x_1 axis. Thus

$$\begin{aligned} x_1' &= x_1 \\ x_2' &= \cos\phi\, x_2 - \sin\phi\, x_3 \\ x_3' &= \sin\phi\, x_2 + \cos\phi\, x_3 \end{aligned} \tag{5-13}$$



If we take the - sign in (5-11) we have $\mathbf{R}'$ interpreted as a rotation through ϕ in the x_2 -- x_3 plane followed by a reflection through that plane.

In this manner, we see that in three dimensions we can interpret every real orthogonal coordinate transformation as either a rotation about an axis or a rotation about an axis followed by a reflection through the plane perpendicular to that axis. The pure rotations have det $\mathbf{R} = +1$ and are called proper

rotations. The rotations followed by reflections have det $\mathsf{R} = -1$ and in this case are called improper rotations.

It is clear that the collection of all real orthogonal coordinate transformations form a group. Some other facts are immediately obvious. The collection of all proper rotations forms a subgroup of this total group of all real orthogonal coordinate transformations. This group is called the pure rotation group in three dimensions. It is also clear that the product of two proper rotations is a proper rotation as is the product of two improper rotations. The product of a proper and an improper rotations is an improper rotation. From this we see that in any finite subgroup of the group of real orthogonal coordinate transformations there is either no improper rotations or as many proper as improper rotations. It is also not difficult to show that the complete group of orthogonal coordinate transformations can be considered as the direct product of the pure rotation group and a group consisting of the inversion

$$i = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{5-14}$$

and the identity. (This latter group clearly commutes with the full rotation group.)

We can also show that the collection of all coordinate transformations of the type (5-2) where R is a real orthogonal matrix and $\vec{t}$ is arbitrary forms a group. We shall show this a little later on and also show that the collection of pure translations

$$\vec{x}' = \vec{x} + \vec{t} \tag{5-15}$$

forms an invariant subgroup of this group of transformations (5-2). The Hamiltonian (3-47) of Chapter III is invariant under this group if we let the coordinates of all the particles undergo the same transformation. Since we know that the eigenfunctions of the Hamiltonian must form bases for irreducible representations of the group of the Hamiltonian, we should study the irreducible representations of the full group of pure rotations in three dimensions. This is a lengthy topic in itself and we shall not pursue it in this set of notes. It is discussed in great detail in other texts.

The Hamiltonian (3-48) in Chapter III in which the nuclei are held fixed is in general invariant under some subgroup of the full group of real orthogonal coordinate transformations and in the case of crystals is also invariant under certain translations. In the case of molecules (outside of linear molecules) the Hamiltonian is invariant under only a finite subgroup of the full group of real orthogonal coordinate transformations. For example, we have discussed the group C_{3v} which leaves the ammonia molecule invariant. This is a finite subgroup which has proper rotations E, C_3, and C_3^2 and improper rotations σ_1, σ_2, and σ_3. From this we are able to say that the eigenfunctions of the ammonia molecule must transform irreducibly under the group C_{3v} of spatial

electronic coordinate transformations. As far as these proper and improper rotations are concerned the eigenfunctions must transform as either one of the one-dimensional representations or as the two-dimensional representation.

We shall not go into a discussion of the groups which leave various molecules invariant since these are in general rather simple groups the character tables and irreducible representations of which can be found in many texts. We shall, instead go on to discuss crystals which are in general invariant under translations as well as rotations. We shall, from this, gain a familiarity with certain groups of importance in molecular physics as a by-product. Before doing this it will be to our advantage to introduce some convenient notation.

We shall be dealing with coordinate transformations of the form (5-2). Let us denote the operator corresponding to this coordinate transformation as

$$\left\{R|\vec{t}\right\} \tag{5-16}$$

This operator corresponds to the coordinate transformation $\vec{x}' = R\vec{x} + \vec{t}$. This convenient notation is due to F. Seitz. In order to become familiar with this notation, let us see how we multiply two operators. This corresponds to two successive coordinate transformations. Let us first apply the transformation

$$\vec{x}' = R\vec{x} + \vec{t}$$

and then the coordinate transformation

$$\vec{x}'' = S\vec{x}' + \vec{t}' \tag{5-17}$$

By direct substitution we see at once that

$$\begin{aligned} \vec{x}'' &= S(R\vec{x} + \vec{t}) + \vec{t}' \\ \vec{x}'' &= SR\vec{x} + S\vec{t} + \vec{t}' \end{aligned} \tag{5-18}$$

$S\vec{t} + \vec{t}'$ is, of course, again a translation. We have, therefore, as our basic rule for the product of two operators of the type (5-16)

$$\left\{S|\vec{t}'\right\}\left\{R|\vec{t}\right\} = \left\{SR|\vec{t}' + S\vec{t}\right\} \tag{5-19}$$

Let us now find the inverse of the operator $\left\{R|\vec{t}\right\}$. We can see from our rule for matrix multiplication that the inverse is given by

$$\left\{R|\vec{t}\right\}^{-1} = \left\{R^{-1}|-R^{-1}\vec{t}\right\} \tag{5-20}$$

The existence of R^{-1} follows at once from the fact that R is a real orthogonal matrix. From its definition the operator $\left\{R|\vec{t}\right\}$ can be interpreted in the following way. We first apply the proper or improper rotation R and then translate through a vector distance $\vec{t}$. A pure translation will be $\left\{E|\vec{t}\right\}$ where E corresponds to the identity real orthogonal matrix. A pure rotation (proper or improper) would be $\left\{R|0\right\}$. The operator which corresponds to leaving the coordinate system completely unchanged is the operator $\left\{E|0\right\}$. In the future we shall modify our notation somewhat to correspond to the notation prevalent in this field and denote the unitary operators corresponding to real orthogonal coordinate transformations by a small Greek letter α, β, etc. (the identity will be denoted by ϵ). The translations will be denoted by the letters a, b, c, d, etc.

We shall now show, using our convenient notation, that the collection of all coordinate transformations of the type $\vec{x}' = R\vec{x} + \vec{t}$ forms a group where R is a real orthogonal matrix. Thus, if we have the operators $\left\{\alpha|\vec{t}\right\}$ and $\left\{\beta|\vec{t}'\right\}$ the product also corresponds to a coordinate transformation of the type (5-2). The existence of an inverse we have already demonstrated and the associative law follows at once from the definition of these operators. The identity is the operator $\left\{\epsilon|0\right\}$. The fact that the collection of operators $\left\{\epsilon|t\right\}$ (pure translations) forms an invariant subgroup can also be shown easily. These operators form a group since

$$\left\{\epsilon|\vec{t}\right\}\left\{\epsilon|\vec{t}'\right\} = \left\{\epsilon|\vec{t}+\vec{t}'\right\} \tag{5-21}$$

That the operators form an invariant subgroup of the operators $\left\{\alpha|\vec{t}\right\}$ can be shown from the fact that

$$\begin{aligned}\left\{\alpha^{-1}|-\alpha^{-1}\vec{t}\right\}\left\{\epsilon|\vec{t}'\right\}\left\{\alpha|\vec{t}\right\} &= \left\{\alpha^{-1}|-\alpha^{-1}\vec{t}+\alpha^{-1}t'\right\}\left\{\alpha|t\right\} \\ &= \left\{\epsilon|\alpha^{-1}t'\right\}\end{aligned} \tag{5-22}$$

The last operator in (5-22) being again a pure translation. Thus, we see that the collection of all possible pure translations forms an invariant subgroup of the collection of all real orthogonal coordinate transformations followed by translations.

The Hamiltonian (3-47) of Chapter III is invariant under all operators of the type $\left\{\alpha|\vec{t}\right\}$ where α corresponds to a real orthogonal coordinate transformation and $\vec{t}$ is a translation. The Hamiltonian (3-48) of Chapter III with the nuclei held fixed is generally invariant under some subgroup of the group of all operators $\left\{\alpha|\vec{t}\right\}$. If we consider operations only on the electronic spatial coordinates when considering the

Hamiltonian (3-48) of Chapter III, the Hamiltonian will be sent into itself by operators $\{a|\vec{t}\}$ which send identical nuclei into one another. Thus, it would only be for an infinite solid that we would be allowed to make any translation at all which would send the nuclei into one another. It is these infinite solids which we shall now discuss.

The fundamental fact about a periodic solid is that it can be subdivided into finite unit cells. The entire solid can then be thought of as being made up of these unit cells. The properties of all the cells that go into making up the crystal are identical and they can be brought into one another by translations called primitive translations. It is convenient to make these unit cells as small as possible without altering the fact that the entire solid can be generated by just translating through primitive translations one of these unit cells. We can guarantee these assertions by demanding that the solid be invariant under translations

$$\vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3 \tag{5-23}$$

where n_1, n_2, and n_3 are integers and $\vec{t}_1$, $\vec{t}_2$, and $\vec{t}_3$ are three basic translations such that all primitive translations $\vec{R}_n$ can be written in the form (5-23). $\vec{t}_1$, $\vec{t}_2$, and $\vec{t}_3$ can be written in terms of their components along the x_1, x_2, and x_3 axes.

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \\ t_{13} \end{pmatrix}; \quad \vec{t}_2 = \begin{pmatrix} t_{21} \\ t_{22} \\ t_{23} \end{pmatrix}; \quad \vec{t}_3 = \begin{pmatrix} t_{31} \\ t_{32} \\ t_{33} \end{pmatrix}. \tag{5-24}$$

These three vectors are linearly independent. In terms of our notation, the solid is invariant under $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a primitive translation. In addition, the solid may be invariant under additional operators $\{a|\vec{a}\}$ where a corresponds to a real orthogonal coordinate transformation and $\vec{a}$ is a translation (not necessarily a primitive translation). We can see that the collection of a's must form a group. In addition, it is clear that the collection of all primitive translations must form an invariant subgroup of the entire group which leaves the solid invariant. Thus, we see that if $\vec{R}_n$ is a primitive translation then, since

$$\{a|\vec{a}\}\{\epsilon|\vec{R}_n\}\{a^{-1}|-a^{-1}\vec{a}\} = \{\epsilon|a\vec{R}_n\} \tag{5-25}$$

$a\vec{R}_n$ is also a primitive translation. The collection of all points generated by the vectors $\vec{R}_n$ is called the lattice. We shall be concerned with the study of groups which leave a periodic solid invariant and which have as an invariant subgroup a group of primitive translations. Such groups are called space groups. One interesting property

of space groups is that there are only a finite number of them. We shall start by becoming familiar with the space groups in one and two dimensions for which we can do a careful job of enumerating all the possible space groups. This will illustrate all the fundamental points concerning three-dimensional space groups and we shall not do a complete job of enumerating all the possible three-dimensional space groups.

2. One-Dimensional Space Groups

In one dimension, the basic primitive translation we shall take to be t which corresponds to the coordinate transformation

$$x' = x + t \tag{5-26}$$

The lattice then consists of the points $x_n = nt$ where n is a positive or negative integer. We wish to find all possible groups of operators of the form $\{\alpha|a\}$ which contain $\{\epsilon|nt\}$ as an invariant subgroup where α is a real orthogonal coordinate transformation. If α corresponds to a real orthogonal matrix of dimension one, it must correspond to either the matrix $\epsilon = (1)$ or the matrix $i = (-1)$. The matrix (-1) corresponds to the coordinate transformation

$$x' = ix = -x \tag{5-27}$$

The first possibility is that our one-dimensional chain is only invariant under pure translation operators and no other operator of the form $\{\alpha|a\}$ is permitted. A figure which has this property is illustrated in Fig. 5-1. The arrows can be considered to be attached to the lattice points and the arrows themselves indicate the symmetry.

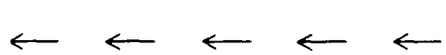


Fig. 5-1

The second possibility is that the linear chain may, in addition, be invariant under an operator of the form $\{i|a\}$. If this is the case it is invariant under all operators $\{i|a + nt\} = \{\epsilon|nt\}\{i|a\}$. It is possible that a may not be a primitive translation. We shall now show that if this is the case then a coordinate system can be chosen such that a = 0. The transformation corresponding to $\{i|a\}$ is

$$x' = ix + a = -x + a \tag{5-28}$$

Let us now go to a new coordinate system defined by

$$\begin{aligned} x &= y + q \\ x' &= y' + q \end{aligned} \tag{5-29}$$

In this case the relation between y and y' becomes

$$\begin{aligned} y' + q &= i(y + q) + a \\ y' &= -y - q - q + a \\ y' &= -y - 2q + a \end{aligned} \tag{5-30}$$

Thus, if we choose our coordinate system y such that $q = a/2$ we find that in this coordinate system $\{i|a\}$ goes over into $\{i|0\}$. In this way, we see that the only other group consists of the operators $\{i|nt\}$ in addition to the operator $\{\epsilon|nt\}$. This symmetry is illustrated in Fig. 5-2

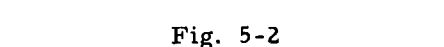


Fig. 5-2

This exhausts the one-dimensional space groups. We see that there are only two space groups in one dimension and that for both of them the only translational parts of the operators involved which appear are the primitive translations. We saw that one useful trick that we could employ was to perform a coordinate transformation so as to make the translation a equal to zero. This is a device which we shall employ to great advantage in our study of two-dimensional space groups. These two-dimensional space groups are much more interesting and we shall proceed with them in the next section.

3. Two-Dimensional Space Groups

In two dimensions we have a plane figure invariant under a space group which has as an invariant subgroup a group of primitive translations of the form

$$\vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2$$

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} t_{21} \\ t_{22} \end{pmatrix} \tag{5-31}$$

In addition to the primitive translations $\{\epsilon|\vec{R}_n\}$, it may be that our space group contains other operators of the form $\{\alpha|a\}$. The part, α, of this operator must correspond to a real orthogonal coordinate transformation in two dimensions. Let us first see what restrictions we must put on the real orthogonal two-dimensional matrices corresponding to the operators α. First, we shall see what form real orthogonal two-dimensional matrices R can have.

A real orthogonal two-dimensional matrix R can be diagonalized by a unitary transformation U. The diagonal elements of the diagonalized matrix are the roots of the equation

$$\det(R - \lambda 1) = 0 \tag{5-32}$$

If they are complex, the two roots must be complex conjugates of one another. In this case

$$U^{\dagger}RU = \begin{pmatrix} e^{i\phi} & 0 \\ 0 & e^{-i\phi} \end{pmatrix} \tag{5-33}$$

By applying the transformation

$$V = \begin{pmatrix} 1/\sqrt{2} & i/\sqrt{2} \\ 1/\sqrt{2} & -i/\sqrt{2} \end{pmatrix} \tag{5-34}$$

we can find the transformation UV such that

$$V^{\dagger}U^{\dagger}RUV = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix} \tag{5-35}$$

It is not difficult to show that UV is real and orthogonal and at the same time show that its determinant may be made + 1. Thus, one possibility is that R corresponds to a clockwise coordinate rotation through an angle ϕ. In this case det R = + 1 and R can be written in the form (5-35). This is a two-dimensional proper rotation. The only other possibility not covered by (5-35) is that the roots of (5-32) are real. The only possibility in the case of real roots not covered by (5-35) is the case that if R is diagonalized it has the form

$$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \tag{5-36}$$

In this case, det R = -1. These we shall refer to as two-dimensional improper rotations. Any improper rotation can by a real orthogonal coordinate transformation with determinant + 1 be put in the form (5-36). In this way we see that every real orthogonal coordinate transformation can be put in either the form (5-35) or (5-36) by a real orthogonal coordinate transformation with determinant + 1. Thus, by a suitable proper rotation every improper rotation can be put in the form (5-36). We see that this corresponds to the transformation

$$\begin{aligned} x_1' &= -x_1 \\ x_2' &= x_2 \end{aligned} \tag{5-37}$$

This is just a reflection through the x_2 axis. If we perform a rotation of our coordinate

system through ϕ, the matrix representing a rotation through an angle ϕ just goes into itself. Thus

$$\begin{pmatrix} \cos\phi' & \sin\phi' \\ -\sin\phi' & \cos\phi' \end{pmatrix}\begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} \cos\phi' & -\sin\phi' \\ \sin\phi' & \cos\phi' \end{pmatrix} = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix} \tag{5-38}$$

This is just a reflection of the fact that all rotations in a plane commute.

In analogy to the first section of this chapter, we can see that in two dimensions the proper rotations form a group and that in any finite subgroup of the full group of real orthogonal coordinate transformations in two dimensions there must be either no improper rotations or as many proper as improper rotations. In this way we have learned something of the two-dimensional real orthogonal matrices. They correspond either to a rotation or a reflection through some line. This is not much of a restriction on the group of α's which can appear in $\{\alpha|a\}$. We shall now show that there are only a finite number of groups of α's which are possible in the group of all operators $\{\alpha|a\}$ which have as an invariant subgroup a group of primitive translations.

We find that there are restrictions on the possible proper rotations that leave a translation group invariant. Proper rotations in two dimensions are of the form

$$\alpha \rightarrow \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix} \tag{5-39}$$

Without changing the form of these proper rotations we can choose a rotated coordinate system so that the smaller, $\vec{t}_1$, of the primitive translations $\vec{t}_1$ and $\vec{t}_2$ has the form

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \tag{5-40}$$

A rotation α must (as we have seen) send this into another primitive translation $\alpha\vec{t}_1$

$$\alpha\vec{t}_1 = \begin{pmatrix} \cos\phi & -\sin\phi \\ \sin\phi & \cos\phi \end{pmatrix}\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} = \begin{pmatrix} t_{11}\cos\phi \\ t_{11}\sin\phi \end{pmatrix} \tag{5-41}$$

If $\vec{t}_1$ and $\alpha\vec{t}_1$ are primitive translations then $\vec{t}_1 - \alpha\vec{t}_1$ must also be a primitive translation

$$\alpha\vec{t}_1 - \vec{t}_1 = \begin{pmatrix} t_{11}(\cos\phi - 1) \\ t_{11}\sin\phi \end{pmatrix} \tag{5-42}$$

The square of the length of this vector is $4t_{11}^2 \sin^2(\phi/2)$. Since t_{11} is the shortest primitive translation we have

$$4t_{11}^2 \sin^2(\phi/2) \geqslant t_{11}^2 \tag{5-43}$$

This means

$$\pi/3 \leqslant \phi \leqslant 5\pi/3 \text{ or } \phi = 0$$

$\phi = 0$ is permitted since in this case $a\vec{t}_1 - \vec{t}_1 = 0$. $\vec{t}_1$ must also be shorter than

$$a\vec{t}_1 + \vec{t}_1 = \begin{pmatrix} t_{11}(\cos\phi + 1) \\ t_{11}\sin\phi \end{pmatrix} \tag{5-44}$$

This means that

$$4t_{11}^2 \cos^2(\phi/2) \geqslant t_{11}^2 \quad -2\pi/3 \leqslant \phi \leqslant 2\pi/3 \text{ or } \phi = \pi, -\pi \tag{5-45}$$

In addition if a is an allowed rotation a^{-1} is also an allowed rotation and $a^{-1}\vec{t}_1$ is a primitive translation

$$a^{-1}\vec{t}_1 = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} = \begin{pmatrix} t_{11}\cos\phi \\ -t_{11}\sin\phi \end{pmatrix} \tag{5-46}$$

Therefore $a^{-1}\vec{t}_1 + a\vec{t}_1$ must be a primitive translation with length greater than $\vec{t}_1$

$$a^{-1}\vec{t}_1 + a\vec{t}_1 = \begin{pmatrix} 2t_{11}\cos\phi \\ 0 \end{pmatrix} \tag{5-47}$$

This yields

$$4t_{11}^2 \cos^2\phi \geqslant t_{11}^2 \quad -\pi/3 \leqslant \phi \leqslant \pi/3;\ 2\pi/3 \leqslant \phi \leqslant 4\pi/3 \text{ or } \phi = \pi/2,\ 3\pi/2 \tag{5-48}$$

The restrictions (5-43), (5-45) and (5-48) leave as the only possibilities proper rotations through angles

$$\phi = 0,\ \pi/3,\ 2\pi/3,\ 4\pi/3,\ 5\pi/3,\ \pi/2,\ \pi,\ 3\pi/2$$

We shall denote the operators corresponding to these by ε, C_6, $C_3 = C_6^2$, C_3^2, C_6^5, C_4, $C_4^2 = C_2$, C_4^3 respectively. All of these rotations cannot occur at once in a group of rotations. The possible groups of proper rotations which we can construct from these rotations are

Group	Elements
E	ε
C_2	$\varepsilon,\ C_2$
C_4	$\varepsilon,\ C_4,\ C_2 = C_4^{\,2},\ C_4^{\,3}$
C_3	$\varepsilon,\ C_3,\ C_3^{\,2}$
C_6	$\varepsilon,\ C_6,\ C_3 = C_6^{\,2},\ C_2C_6^{\,3},\ C_3^{\,2} = C_6^{\,4},\ C_6^{\,5}$

(5-49)

We notice that all of these groups are cyclic.

We have now obtained five groups of proper rotations. We know that a subgroup of the entire group of all real orthogonal two-dimensional matrices must either contain no improper rotations (we have enumerated the five possible groups of this type) or as many proper as improper rotations. The remaining groups of real orthogonal two-dimensional matrices which leave a two-dimensional lattice invariant can be obtained by multiplying all of the elements in each of the groups in (5-49) by a reflection σ which we can choose in the form

$$\begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}$$

which, in addition to the groups already enumerated, gives five new groups which are

Group	Elements
σ	$\varepsilon,\ \sigma$
C_{2v}	$\varepsilon,\ C_2,\ \sigma,\ \sigma C_2$
C_{4v}	$\varepsilon,\ C_4,\ C_2,\ C_4^{\,3},\ \sigma,\ \sigma C_4,\ \sigma C_2,\ \sigma C_4^{\,3}$
C_{3v}	$\varepsilon,\ C_3,\ C_3^{\,2},\ \sigma,\ \sigma C_3,\ \sigma C_3^{\,2}$
C_{6v}	$\varepsilon,\ C_6,\ C_3,\ C_2,\ C_3^{\,2},\ C_6^{\,5},\ \sigma,\ \sigma C_6,\ \sigma C_3,\ \sigma C_2,\ \sigma C_3^{\,2},\ \sigma C_6^{\,5}$

(5-50)

These groups can be visualized by the figures which they leave invariant. These are illustrated in Fig. 5-3.

We have now seen that there are only ten possible groups of real orthogonal coordinate transformations in two dimensions which would leave a two-dimensional lattice invariant. Thus, in space groups of two dimensions with operators of the form $\{a|\vec{a}\}$ in order to have a group of primitive translations as an invariant subgroup the collection of a's in these operators for a given space group must form one of the ten

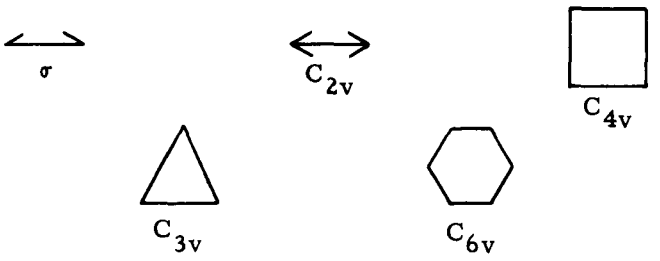


Fig. 5-3

possible groups given in (5-49) and (5-50). The group of a's corresponding to a given space group is called the point group and in two dimensions there are only ten possible point groups.

We shall now go back and show that not all possible groups of primitive translations (5-31) are left invariant by a space group having a given point group. We shall find that restrictions are put on the two primitive translations $\vec{t}_1$ and $\vec{t}_2$ depending on which point group the entire space group corresponds to. The fundamental fact we shall use is that if $\vec{R}_n$ is a primitive translation $a\vec{R}_n$ must also be a primitive translation. Here a corresponds to an allowed real orthogonal coordinate transformation in two dimensions. We shall proceed through the ten point groups in two dimensions showing for each what restrictions are put on the basic primitive translations $\vec{t}_1$ and $\vec{t}_2$.

ε: Clearly the point group consisting of only the identity puts no restrictions on the translation group. We can therefore take as our translation group a group which we call Γ_1 (see Fig. 5-4).

Γ_1:

$$\left\{\varepsilon|\vec{R}_n\right\} \vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} \vec{t}_2 = \begin{pmatrix} t_{21} \\ t_{22} \end{pmatrix} \vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 \qquad (5\text{-}51)$$

Here $\vec{t}_1$ and $\vec{t}_2$ need only be linearly independent.

C_2: C_2 corresponds to a matrix

$$\begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

and sends every primitive translation into its negative. From the definition of primitive translations, the negative of a primitive translation is also a primitive translation. No restriction is put on the translation group by C_2 and therefore Γ_1 is the general type of translation group left invariant by the space groups which have C_2 as a point group.

σ: In this case, let us choose our coordinate system so that the operator σ corresponds to the matrix

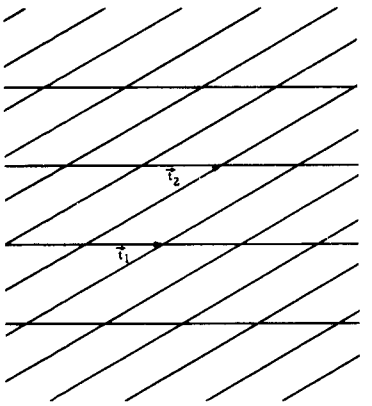


Fig. 5-4

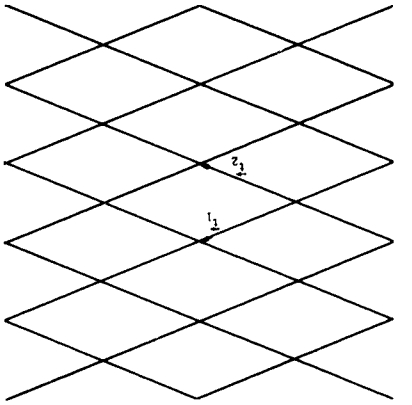


Fig. 5-5

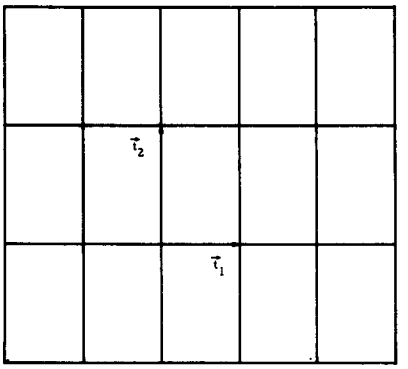


Fig. 5-6

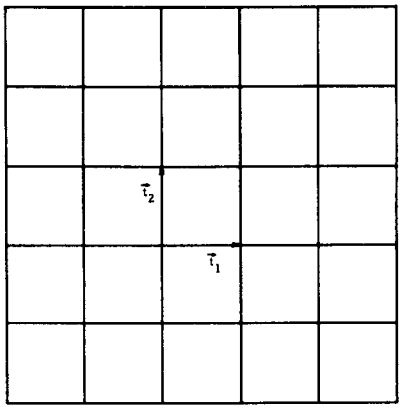


Fig. 5-7

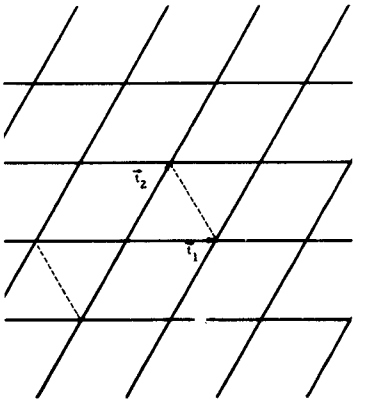


Fig. 5-8

$$\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

Let us assume that the shortest primitive translation in this coordinate system is

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix}$$

There are two possible cases either t_{12} is zero or it is not. If it is not then

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ -t_{12} \end{pmatrix} = \vec{t}_2$$

is also a primitive translation of the same length and we obtain in this way a group of translations Γ_2 (Fig. (5-5)

Γ_2:

$$\left\{\epsilon|\vec{R}_n\right\} \quad \vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} t_{11} \\ -t_{12} \end{pmatrix} \quad \vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 \tag{5-52}$$

In the event t_{12} is zero, we have

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}$$

Let us denote the other basic primitive translation by

$$\vec{t}_2 = \begin{pmatrix} t_{21} \\ t_{22} \end{pmatrix}$$

If $\vec{t}_2$ is a primitive translation $\vec{t}_2 + \sigma\vec{t}_2$ must also be a primitive translation and expressible in the form $n_1\vec{t}_1 + n_2\vec{t}_2$.

$$\vec{t}_2 + \sigma\vec{t}_2 = \begin{pmatrix} t_{21} \\ t_{22} \end{pmatrix} + \begin{pmatrix} t_{21} \\ -t_{22} \end{pmatrix} = \begin{pmatrix} 2t_{21} \\ 0 \end{pmatrix} = n_1\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + n_2\begin{pmatrix} t_{21} \\ t_{22} \end{pmatrix}$$

We see at once that $n_2 = 0$. If $n_1 = 0$, our two basic primitive translations are

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}; \quad \vec{t}_2 = \begin{pmatrix} 0 \\ t_{22} \end{pmatrix}$$

Let us denote this group by Γ_3. (See Fig. 5-6)

Γ_3:

$$\left\{\epsilon|\vec{R}_n\right\} \quad \vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} 0 \\ t_{22} \end{pmatrix} \quad \vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 \tag{5-53}$$

If $n_1 = 1$ we have as our basic primitive translations

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} \frac{1}{2}t_{11} \\ t_{21} \end{pmatrix}$$

but in this case

$$\sigma\vec{t}_2 = \begin{pmatrix} \frac{1}{2}t_{11} \\ -t_{21} \end{pmatrix}$$

and $\vec{t}_2$ would serve equally well as basic primitive translations since $\vec{t}_2 - \sigma\vec{t}_2 = \vec{t}_1$. This is just the same as Γ_2 therefore we have nothing new. For $n_1 \geqslant 2$ we get nothing new since by subtracting $\vec{t}_1$ from $\vec{t}_2$ we can always get a shorter vector than $\vec{t}_2$ contrary to the hypothesis.

C_{2v}: Supplementing the group σ with C_2 to form the group C_{2v} adds no new restrictions so that Γ_2 and Γ_3 are also left invariant by C_{2v}.

C_4: We can always rotate our coordinate system for this group of coordinate transformations in such a way that

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}$$

without changing the form of the coordinate transformations in C_4 since they are all proper rotations. In this case

$$C_4\vec{t}_1 = \begin{pmatrix} 0 & -1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ t_{11} \end{pmatrix}$$

Γ_4:

$$\left\{\epsilon|\vec{R}_n\right\} \quad \vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} 0 \\ t_{11} \end{pmatrix} \quad \vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 \tag{5-54}$$

(See Fig. 5-7)

C_{4v}: Adding the additional operator σ and its products will clearly add nothing new to C_4 since the lattice is already invariant under the four reflections in the group C_{4v} provided one of them is chosen to be a reflection through one of the coordinate axes. Therefore Γ_4 is left invariant by the group C_{4v}.

C_3: We can again choose our coordinate system such that

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}.$$

In this case $-C_3{}^2\vec{t}_1$ is an independent vector of equal length

$$\vec{t}_2 = -C_3{}^2\vec{t}_1 = -\begin{pmatrix} -1/2 & +\sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix}\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix}$$

The vectors $\vec{t}_1$ and $\vec{t}_2$ are then inclined at an angle of 60° and we arrive at the group Γ_5 (see Fig. 5-8).

Γ_5:

$$\{\varepsilon|\vec{R}_n\} \quad \vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix} \quad \vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 \tag{5-55}$$

C_{3v}, C_6, C_{6v}: We see at once from the symmetry of the lattice that it is invariant under the operations of C_{6v} provided the x_1 or x_2 axis is a line of reflection symmetry. This can most easily be seen by putting in the dotted primitive translations in Fig. 5-8. We see from this that the entire lattice can be generated by a set of hexagons and hence the entire lattice has hexagonal symmetry (C_{6v}). Thus, C_{6v} causes no new restrictions to be put on Γ_5. Hence Γ_5 is invariant under C_3, C_{3v}, C_6, C_{6v}. In this way, we can construct a table of the point groups and the most general type of lattice they keep invariant.

Point Group	Lattice	Point Group	Lattice
ε	Γ_1	C_{4v}	Γ_4
C_2	Γ_1	C_3	Γ_5
σ	Γ_2, Γ_3	C_{3v}	Γ_5
C_{2v}	Γ_2, Γ_3	C_6	Γ_5
C_4	Γ_4	C_{6v}	Γ_5

We can now proceed with the actual enumeration of the space groups in two dimensions. These groups will consist of operators of the form $\{a|\vec{a}\}$ where a is the rotational part of the operator (proper or improper) and $\vec{a}$ is the translational part of the operator. Let us first note that there is a restriction placed on the vectors $\vec{a}$ which appear with any rotational operator a. Suppose that $\{a|\vec{a}\}$ and $\{a|\vec{b}\}$ were two operators of the space group having the same rotational part. Since we have a group of the inverse of $\{a|\vec{b}\}$ namely $\{a^{-1}|-a^{-1}\vec{b}\}$ is also a member of the group. Therefore we have that $\{a|\vec{a}\}\{a^{-1}|-a^{-1}\vec{b}\}$ is a member of the group. This yields

$$\{a|\vec{a}\}\{a^{-1}|-a^{-1}\vec{b}\} = \{\varepsilon|\vec{a}-\vec{b}\} \tag{5-57}$$

From this we conclude that $\vec{a} - \vec{b}$ is a primitive translation. Thus, the translational parts of operators which have the same rotational part are expressible in the form $\vec{a} + \vec{R}_n$. We can thus associate $\vec{a}$ with the rotational part α. We might choose to associate with α the shortest translation which appears with α as a translational part. We can see, therefore, that there are two possibilities. We can either associate with α a zero translation or some non-primitive translation.

From this discussion, we are able to see one way in which we can form space groups from the point groups and the lattices that they leave invariant. We could associate with every rotational operator the zero translation and then take all possible products of these operators with the pure translations. In our notation, we take all possible products of $\{\alpha|0\}$ for all α in the point group and the pure translations $\{\varepsilon|\vec{R}_n\}$.

We noticed in the case of one-dimensional space groups that it was possible, by a change of coordinates, to go to a coordinate system where we could associate with a given rotational operator a zero translation. Let us see how this works out in general. We recall that an operator $\{\alpha|\vec{t}\}$ corresponds to the coordinate transformation

$$\vec{x}' = R\vec{x} + \vec{t} \tag{5-58}$$

where R is the matrix corresponding to α. Suppose we now go to a new coordinate system $\vec{y}$ and see what the operator $\{\alpha|\vec{t}\}$ becomes in this new coordinate system. Let the new coordinate system be defined in terms of the old by the equation

$$\begin{aligned} \vec{x} &= S\vec{y} + \vec{q} \\ \vec{x}' &= S\vec{y}' + \vec{q} \end{aligned} \tag{5-59}$$

Here S is a real orthogonal matrix. By substitution we find that

$$\begin{aligned} S\vec{y}' + \vec{q} &= R\left[S\vec{y} + \vec{q}\right] + \vec{t} \\ \vec{y}' &= S^{-1}RS\vec{y} + S^{-1}\left[\vec{t} - \vec{q} + R\vec{q}\right] \end{aligned} \tag{5-60}$$

Thus, in the new coordinate system the translational part of the operator $\{\alpha|\vec{t}\}$ is $S^{-1}\left[\vec{t} - \vec{q} + R\vec{q}\right]$. We can always associate with α a zero translation if we can find a $\vec{q}$ such that

$$\vec{t} - \vec{q} + R\vec{q} = \vec{R}_n \tag{5-61}$$

We can, under certain circumstances, determine $\vec{q}$ in such a way that this relation is satisfied. In order to find a $\vec{q}$ satisfying (5-61), we must solve a set of simultaneous

linear inhomogeneous equations for the components of $\vec{q}$. These equations will, in general, have a solution provided that $\det(R - 1) \neq 0$. Let us see, in two dimensions, under what conditions this relation is satisfied.

We consider first the proper rotations in two dimensions. In this case, R can be expressed in the form (5-35) and we can evaluate $\det(R - 1)$

$$\det(R - 1) = \begin{vmatrix} \cos\phi - 1 & -\sin\phi \\ \sin\phi & \cos\phi - 1 \end{vmatrix} = 4\sin^2(\phi/2) \qquad (5\text{-}62)$$

The only condition under which this vanishes is for the identity rotation $\phi = 0$ or 2π. We see at once that it is possible in two dimensions to change our coordinate system by a pure translation $\vec{q}$ so that we can associate with any rotation the zero translation. We notice that all the point groups in two dimensions (5-49) and (5-50) either have a cyclic subgroup of two-dimensional proper rotations or consist entirely of a cyclic group of proper rotations. If we choose our coordinate system so that we can associate with the smallest non zero proper rotation a zero translation, then it is clear that all powers of this proper rotation will have associated with them a zero translation. Hence it is possible in two dimensions to always choose a coordinate system such that the proper rotations have zero translations associated with them.

We can now go down the list of point groups in (5-56) and find which space groups can be associated with each point group. We shall do this in the order of point groups listed in (5-56) and shall give for each space group the elements whose products can generate the space group.

ϵ: This is a group of pure translations with no restrictions on the primitive translations. The group is given by $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is from the translation group Γ_1, the most general translation group. In Fig. 5-9, we have illustrated this group. We have attached to each lattice site in Γ_1 a figure with no special symmetry.

C_2: Γ_1 is again the lattice which is left invariant by the point group C_2. We might suppose that we could associate a non primitive translation with the operation C_2. We have seen from the discussion in the previous paragraphs that this is not the case since by a coordinate translation we can always eliminate a non primitive translation associated with the operation C_2. We saw that for all point groups consisting of nothing but proper rotation operators we could associate zero translations with the rotation operators. In Fig. 5-10 we have illustrated the space group generated by $\{C_2|0\}$ and $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is taken from Γ_1.

σ: Let us consider first the case where we associate with the point group σ the lattice Γ_2. It may be that we can associate with the operation σ a non primitive translation $\vec{v}$. If this is the case, the operator $\{\sigma|\vec{v}\}$ is a member of the group as is

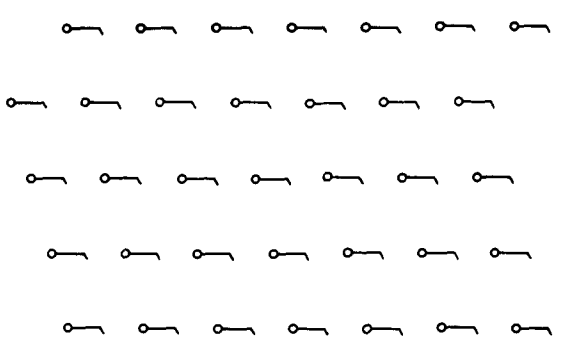


Fig. 5-9

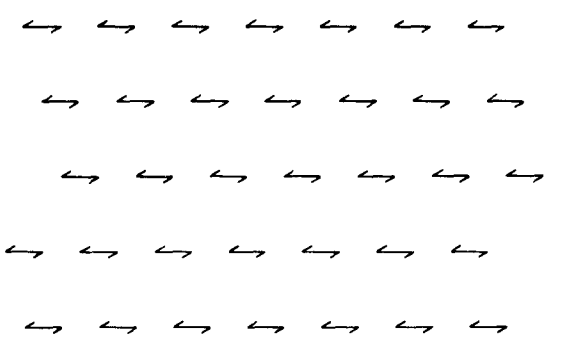


Fig. 5-10

its square

$$\left\{\sigma|\vec{v}\right\}\left\{\sigma|\vec{v}\right\} = \left\{\varepsilon|\sigma\vec{v}+\vec{v}\right\} \qquad \vec{v} = \begin{pmatrix} v_{11} \\ v_{12} \end{pmatrix} \tag{5-63}$$

This means that $\sigma\vec{v} + \vec{v}$ must be a primitive translation. Looking back at the definition of Γ_2 we see that

$$\sigma\vec{v} + \vec{v} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} v_{11} \\ v_{12} \end{pmatrix} + \begin{pmatrix} v_{11} \\ v_{12} \end{pmatrix} = \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} + n\begin{pmatrix} t_{11} \\ -t_{12} \end{pmatrix} \tag{5-64}$$

From this we see, at once, that m = n and that $v_{11} = m\, t_{11}$. Thus, the most general form of our non primitive translation is

$$\vec{v} = \begin{pmatrix} m\, t_{11} \\ v_{12} \end{pmatrix}$$

Since we can subtract primitive translations from this non primitive translation and since

$$\begin{pmatrix} 2t_{11} \\ 0 \end{pmatrix} = \vec{t}_1 + \vec{t}_2$$

the only case we need consider is the case m = 1 or

$$\vec{v} = \begin{pmatrix} t_{11} \\ v_{12} \end{pmatrix}$$

Let us now see if we can eliminate this non primitive translation by a translation of our coordinate system. In order to do this, we must find a vector $\vec{q}$ (see Eq. (5-61) such that

$$\vec{v} + \sigma\vec{q} - \vec{q} = \vec{R}_n \tag{5-65}$$

In particular, take

$$\vec{R}_n = \vec{t}_1 = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix}$$

Then (5-65) becomes

$$\begin{pmatrix} t_{11} \\ v_{12} \end{pmatrix} + \begin{pmatrix} q_{11} \\ q_{12} \end{pmatrix} - \begin{pmatrix} q_{11} \\ -q_{12} \end{pmatrix} = \begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix}$$

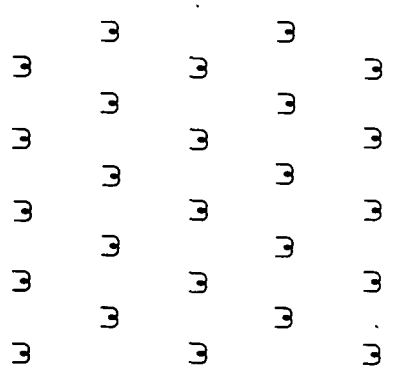


Fig. 5-11

Thus, a coordinate translation with q_{11} arbitrary and $2q_{12} = t_{12} - v_{12}$ will allow us to associate with σ a zero translation. Thus, we get a point group generated by $\{\sigma|0\}$ and $\{\varepsilon|\vec{R}_n\}$ where $\vec{R}_n$ comes from Γ_2. This group is illustrated in Fig. 5-11.

The next possibility is to associate with the point group σ the translation group Γ_3 (5-53). In this case, if we associate with σ a translation $\vec{v}$, the equation (5-65), as a condition on $\vec{v}$, becomes

$$\begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + n\begin{pmatrix} 0 \\ t_{22} \end{pmatrix} \tag{5-66}$$

$$n = 0$$

$$v_{11} = \frac{m}{2} t_{11}$$

Once again, we can subtract primitive translations from $\vec{v}$ and need only consider the cases m = 0, 1. Thus, the most general non primitive translation which we can associate with σ is of the form

$$\vec{v} = \begin{pmatrix} \frac{m}{2} t_{11} \\ v_{12} \end{pmatrix} \qquad m = 0, 1$$

We must now see if we can eliminate this non primitive translation associated with σ.

If we perform a coordinate translation through $\vec{q}$, $\vec{v}$ goes into Eq. (5-66) $\vec{v} - \vec{q} + \sigma\vec{q}$. If we can make this into a primitive translation, then we can associate with σ the zero translation

$$\vec{v} - \vec{q} + \sigma\vec{q} = \begin{pmatrix} \frac{m}{2} t_{11} \\ v_{12} \end{pmatrix} - \begin{pmatrix} q_{11} \\ q_{12} \end{pmatrix} + \begin{pmatrix} q_{11} \\ -q_{12} \end{pmatrix} \tag{5-67}$$

We can, therefore, by setting $v_{12} = 2q_{12}$ make the second component of the non primitive translation vanish. The first component will only be a primitive translation in the case $m = 0$. Thus, we get two new space groups associated with the point group σ and the translation group Γ_3. The first ($m = 0$) is generated by $\{\sigma|0\}$ and $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ belongs to Γ_3. This is illustrated in Fig. 5-12. The second is generated by $\{\sigma|\vec{v}\}$ where

$$\vec{v} = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}$$

and $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ belongs to Γ_3. This group is illustrated in Fig. 5-13.

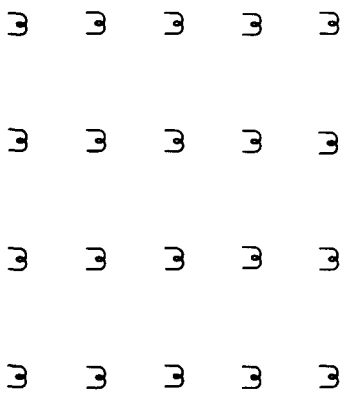


Fig. 5-12

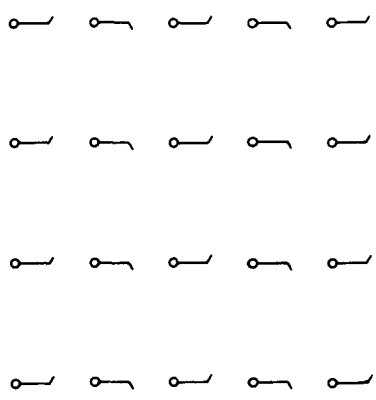


Fig. 5-13

C_{2v}: The operations of the point group are

$$C_2 \to \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \sigma \to \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

$$\sigma' \to \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \epsilon \to \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \tag{5-68}$$

We can, at once, shift our coordinate system so that C_2 has associated with it a zero

translation. If we associate with σ the non primitive translation $\vec{v}$, then since $\{\sigma|\vec{v}\}\{C_2|0\} = \{\sigma'|\vec{v}\}$ we can also associate with σ' the non primitive translation $\vec{v}$. One condition on $\vec{v}$ is that

$$\{\sigma|\vec{v}\}\{\sigma|\vec{v}\} = \{\varepsilon|\sigma\vec{v} + \vec{v}\} \qquad \sigma\vec{v} + \vec{v} = \text{primitive translation} \tag{5-69}$$

Since the group contains the operator $\{C_2|0\}$, which is the inversion in two dimensions, $\{\sigma|-\vec{v}\}$ is also an allowed operation. Thus, another condition on $\vec{v}$ is given by

$$\{\sigma|-\vec{v}\}\{\sigma|\vec{v}\} = \{\varepsilon|\sigma\vec{v} - \vec{v}\} \qquad \sigma\vec{v} - \vec{v} = \text{primitive translation} \tag{5-70}$$

Let us first consider the point group C_{2v} associated with the lattice Γ_2. In this case conditions (5-69) and (5-70) become

$$\sigma\vec{v} + \vec{v} = \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} + n\begin{pmatrix} t_{11} \\ -t_{12} \end{pmatrix}$$

$$\sigma\vec{v} - \vec{v} = \begin{pmatrix} 0 \\ 2v_{12} \end{pmatrix} = p\begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix} + q\begin{pmatrix} t_{11} \\ -t_{12} \end{pmatrix}$$

We see that $m = n$, $p = q$, and $v_{11} = mt_{11}$; $v_{12} = pt_{12}$. The most general non primitive translation we need consider is

$$\vec{v} = \begin{pmatrix} mt_{11} \\ pt_{12} \end{pmatrix}$$

We can try to translate our coordinate system to make this non primitive translation associated with σ a primitive one. In doing so, we must be careful to remember that we have already translated our coordinate system so as to associate with C_2 a zero translation. It may be possible to find a translation of our coordinate system which does not distrub the fact that C_2 has associated with it the zero translation. In order to associate with σ, a primitive translation by shifting the origin of coordinates through $\vec{q}$ we must satisfy the condition (5-61)

$$\vec{v} - \vec{q} + \sigma\vec{q} = \text{primitive translation}$$

$$\begin{pmatrix} m\,t_{11} \\ p\,t_{12} \end{pmatrix} - \begin{pmatrix} q_{11} \\ q_{12} \end{pmatrix} + \begin{pmatrix} q_{11} \\ -q_{12} \end{pmatrix} = \begin{pmatrix} m\,t_{11} \\ p\,t_{12} \end{pmatrix} + \begin{pmatrix} 0 \\ -2q_{12} \end{pmatrix} = \text{primitive translation} \tag{5-71}$$

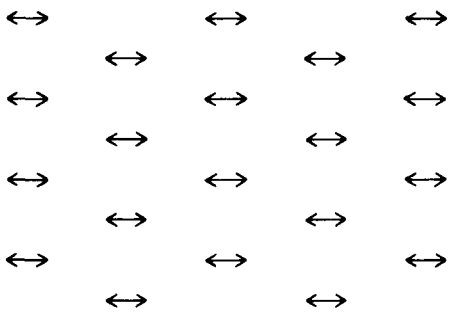


Fig. 5-14

If we let the primitive translation in (5-71) be

$$m\begin{pmatrix} t_{11} \\ t_{12} \end{pmatrix}$$

then we can solve this relation with $q_{12} = \left[(p-m)/2\right] t_{12}$. We notice that we still are free to choose q_{11} so that C_2 still has primitive translations associated with it. The new translations associated with C_2 is (from Eq. (5-60))

$$C_2\vec{q} - \vec{q} = -2\vec{q} = \begin{pmatrix} 2q_{11} \\ (m-p)\,t_{12} \end{pmatrix}$$

If we let $2q_{11} = (m-p)\,t_{11}$ we still have a primitive translation associated with C_2. The group we obtain in this way is the group generated by $\left\{C_2|0\right\}$; $\left\{\sigma|0\right\}$ and $\left\{\varepsilon|\vec{R}_n\right\}$ where $\vec{R}_n$ is taken from Γ_2. There are no non primitive translations in this group and the group is illustrated in Fig. 5-14.

The next possibility is to associate with the point group C_{2v} the translation group Γ_3. We again choose a coordinate system such that C_2 has a zero translation associated with it. We assume that σ has the non primitive translation $\vec{v}$ associated with it. The conditions on $\vec{v}$ are (Eqs. (5-69) and (5-70)) given below for the translation group Γ_3.

$$\begin{aligned} \sigma\vec{v} + \vec{v} &= \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + n\begin{pmatrix} 0 \\ t_{22} \end{pmatrix} \\ \sigma\vec{v} - \vec{v} &= \begin{pmatrix} 0 \\ 2v_{12} \end{pmatrix} = p\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + q\begin{pmatrix} 0 \\ t_{22} \end{pmatrix} \end{aligned} \qquad (5\text{-}72)$$

We see from these relations that $p = n = 0$ and $\vec{v}$ must have the form

$$\vec{v} = \begin{pmatrix} \frac{m}{2} t_{11} \\ \frac{q}{2} t_{22} \end{pmatrix}.$$

By subtracting primitive translations from v we can see that the only cases we need consider are the cases $m = q = 0$; $m = 1$, $q = 0$ and $m = 1$, $q = 1$.

In the case of the point group C_{2v} associated with the translation group Γ_2 we were able to make all non primitive translations associated with σ primitive trans-

lations by shifting our origin of coordinates without affecting the fact that C_2 has associated with it primitive translations. In the case of the translation group Γ_3, it turns out to be impossible to do this. We arrive, therefore, at three new space groups. The first (m = q = 0) is generated by $\{C_2|0\}$; $\{\sigma|0\}$; $\{\varepsilon|\vec{R}_n\}$ with $\vec{R}_n$ belonging to Γ_3. This is illustrated in Fig. 5-14. The second is generated by $\{C_2|0\}$; $\{\sigma|\frac{m}{2}\}$; $\{\varepsilon|\vec{R}_n\}$ with $\vec{R}_n$ belonging to Γ_3 and $\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}$. This is illustrated in Fig. 5-15. The third is generated by $\{C_2|0\}$; $\{\sigma|\frac{\vec{t}_1+\vec{t}_2}{2}\}$; $\{\varepsilon|\vec{R}_n\}$ with $\vec{R}_n$ belonging to Γ_3 and $\vec{t}_2 = \begin{pmatrix} 0 \\ t_{22} \end{pmatrix}$. This is illustrated in Fig. 5-16.

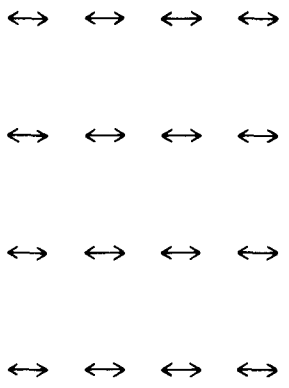


Fig. 5-14

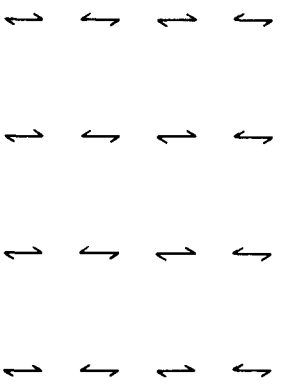


Fig. 5-15

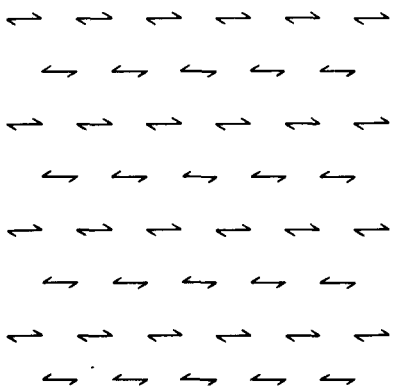


Fig. 5-16

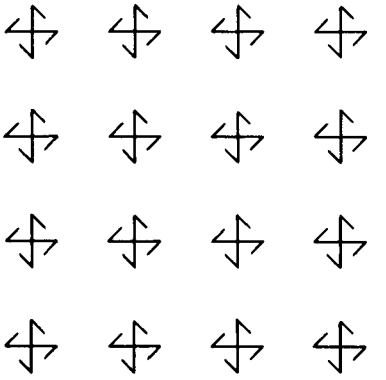


Fig. 5-17

C_4: This is a group with which we must associate the lattice Γ_4. As we have seen, because this is a cyclic group consisting of proper rotations, we can always choose the coordinate system in such a way that there are no non primitive translations in the space group. We have a new space group illustrated in Fig. 5-17 and generated by $\{C_4|0\}$; $\{\varepsilon|\vec{R}\}$ with $\vec{R}_n$ belonging to Γ_4.

C_{4v}: For this group the operators in addition to σ and σ' are the rotations of the group C_4 and the reflections

$$\sigma_d \rightarrow \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_d' \rightarrow \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix}$$

If we choose our coordinate system such that the operator C_4 has associated with it a zero translation, then σ, σ', σ_d' and σ_d all have associated with them a translation $\vec{v}$ which may be non primitive. Two conditions on $\vec{v}$ are, in analogy to our work on the group σ and C_{2v}

$$\begin{aligned} \sigma\vec{v} + \vec{v} &= \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + n\begin{pmatrix} 0 \\ t_{11} \end{pmatrix} \\ \sigma'\vec{v} + \vec{v} &= \begin{pmatrix} 0 \\ 2v_{11} \end{pmatrix} = p\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + q\begin{pmatrix} 0 \\ t_{11} \end{pmatrix} \end{aligned} \tag{5-73}$$

From these two conditions, we see that $\vec{v}$ must have the form

$$\begin{pmatrix} \frac{m}{2} t_{11} \\ \frac{q}{2} t_{11} \end{pmatrix}.$$

In addition, the condition (5-74) must be satisfied.

$$\sigma_d\vec{v} + \vec{v} = \begin{pmatrix} \frac{m+q}{2} t_{11} \\ \frac{m+q}{2} t_{11} \end{pmatrix} = \text{primitive translation} \tag{5-74}$$

In order for this to be true, m and q must either both be even or both odd. If they are both even, $\vec{v}$ is a primitive translation. In this case we have a space group generated by $\{C_4|0\}$, $\{\sigma|0\}$, and $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a primitive translation of Γ_4. This group is illustrated in Fig. 5-18. In the event m and q are both odd, then we can, by subtacting off primitive translations from $\vec{v}$, put $\vec{v}$ in the form

$$\vec{v} = \begin{pmatrix} t_{11}/2 \\ t_{11}/2 \end{pmatrix}$$

Fig. 5-18

In this case, there is no way of shifting the origin of coordinates which will eliminate the non primitive $\vec{v}$ and preserve the fact that C_4 has nothing but primitive translations associated with it. This space group is generated by $\left\{C_4|0\right\}$, $\left\{\sigma|\frac{\vec{t}_1+\vec{t}_2}{2}\right\}$, and $\left\{\epsilon|\vec{R}_n\right\}$ where $\vec{R}_n$ belongs to Γ_4 and $\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}$, $\vec{t}_2 = \begin{pmatrix} 0 \\ t_{11} \end{pmatrix}$. This group is illustrated in Fig. 5-19.

C_3: With this point group, we must associate the lattice Γ_5. The real orthogonal coordinate transformation corresponding to C_3 is

$$C_3 \rightarrow \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \tag{5-74}$$

Since the group is generated by powers of this proper rotation we can adjust the origin of our coordinate system so that with all the operators in the group we can associate a zero translation. We thus have a new space group generated by $\left\{C_3|0\right\}$ and $\left\{\epsilon|\vec{R}_n\right\}$. Here $\vec{R}_n$ is a primitive translation from Γ_5. This group is illustrated in Fig. 5-20.

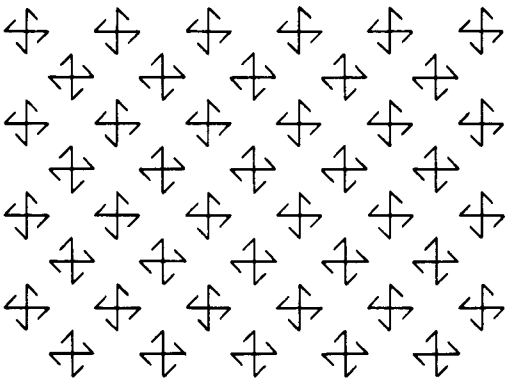


Fig. 5-19

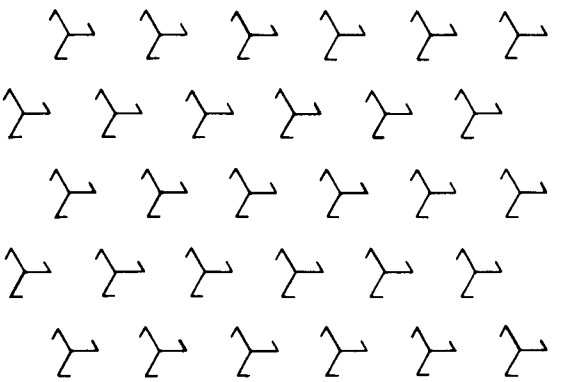


Fig. 5-20

C_{3v}: This point group leaves the lattice Γ_5 invariant. In the case of this point group, a new situation arises. If we choose our coordinate system so that one of the reflections, σ, to have the form

$$\sigma \rightarrow \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{5-75}$$

there are two possible ways we can orient the lattice Γ_5 (see Fig. 5-8). The one has primitive translations

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}, \quad \vec{t}_2 = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix}$$

and the other has primitive translations

$$\vec{t}_1 = \begin{pmatrix} \sqrt{3}/2\ t_{11} \\ 1/2\ t_{11} \end{pmatrix}, \quad \vec{t}_2 = \begin{pmatrix} \sqrt{3}/2\ t_{11} \\ -1/2\ t_{11} \end{pmatrix}$$

In the first case, one of the basic primitive translations lies along the x_1 axis and the other at 60° with respect to the x_1 axis. In the second case, the two primitive translations lie at 30° above and below the x_1 axis. The situation does not arise for any other of our point groups in two dimensions. We must examine these two possibilities.

Let us consider the first of these two possibilities. First, consider the case where

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \qquad \vec{t}_2 = \begin{pmatrix} 1/2\ t_{11} \\ \sqrt{3}/2\ t_{11} \end{pmatrix}.$$

We may by translation choose our coordinate system so that C_3 has associated with it a zero translation. If we associate with σ a translation $\vec{v}$ then we can associate with the reflections $\sigma' = \sigma C_3$ and $\sigma'' = \sigma C_3^{\,2}$ the same translation. In analogy to our previous work, we can see that we have as a condition on $\vec{v}$

$$\sigma\vec{v} + \vec{v} = \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = n\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + q\begin{pmatrix} 1/2\ t_{11} \\ \sqrt{3}/2\ t_{11} \end{pmatrix} \tag{5-76}$$

From this we see that $q = 0$ and that $v_{11} = (n/2)t_{11}$. We can by subtracting $\vec{t}_2$ from $\vec{v}$ over and over again reduce $\vec{v}$ to a form where $v_{11} = 0$. We also have the condition on $\vec{v}$ that

$$\sigma'\vec{v} + \vec{v} = p\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + m\begin{pmatrix} 1/2\ t_{11} \\ \sqrt{3}/2\ t_{11} \end{pmatrix} \tag{5-77}$$

In component form

$$\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix}\begin{pmatrix} 0 \\ v_{12} \end{pmatrix} + \begin{pmatrix} 0 \\ v_{12} \end{pmatrix} = \begin{pmatrix} -\sqrt{3}/2\ v_{12} \\ 3/2\ v_{12} \end{pmatrix} = p\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} + m\begin{pmatrix} 1/2\ t_{11} \\ \sqrt{3}/2\ t_{11} \end{pmatrix} \tag{5-78}$$

where

$$\sigma' = \sigma C_3 \rightarrow \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}\begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix}$$

From (5-78) we see that $v_{12} = (m/\sqrt{3})t_{11}$. Thus from (5-76) and (5-77) we conclude that

$$\begin{pmatrix} 0 \\ \frac{m}{\sqrt{3}} t_{11} \end{pmatrix}$$

We must now see if we can shift our origin in such a way that we can associate with σ a primitive translation, and still associate with C_3 primitive translations. In order to find a translation of origin through a distance $\vec{q}$ which associates with σ a primitive translation we must make $\vec{v} - \vec{q} + \sigma\vec{q}$ equal to a primitive translation. (See Eq. (5-60) In component form

$$\vec{v} - \vec{q} + \sigma\vec{q} = \begin{pmatrix} 0 \\ \frac{m}{\sqrt{3}} t_{11} \end{pmatrix} - \begin{pmatrix} q_{11} \\ q_{12} \end{pmatrix} + \begin{pmatrix} q_{11} \\ -q_{12} \end{pmatrix} \tag{5-79}$$

Thus, if we choose $q_{12} = \frac{m}{2\sqrt{3}} t_{11}$ we associate with σ primitive translations. Let us see what translation this shift of coordinates associates with C_3. Originally we had a zero translation associated with C_3. In the new coordinate system, the corresponding translation associated with C_3 will be

$$\begin{aligned} -\vec{q} + C_3\vec{q} &= -\begin{pmatrix} q_{11} \\ \frac{m}{2\sqrt{3}} t_{11} \end{pmatrix} + \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix}\begin{pmatrix} q_{11} \\ \frac{m}{2\sqrt{3}} t_{11} \end{pmatrix} \\ &= \begin{pmatrix} -3/2\, q_{11} & -\frac{m}{4} t_{11} \\ \sqrt{3}/2\, q_{11} & -\frac{\sqrt{3}}{4} m\, t_{11} \end{pmatrix} \end{aligned} \tag{5-80}$$

If we choose $q_{11} = +(m/2)t_{11}$ then we have

$$-\vec{q} + C_3\vec{q} = -m\begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \tag{5-81}$$

Since this is a primitive translation we have still associated with C_3 primitive translations. Thus, we see we have a space group whose point group is C_{3v} which is generated by $\{C_3|0\}$, $\{\sigma|0\}$, $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a primitive translation of Γ_5 and

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix} \quad \vec{t}_2 = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix}$$

This space group is illustrated in Fig. 5-21).

We now proceed with the other case where

$$\vec{t}_1 = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix}, \qquad \vec{t}_2 = \begin{pmatrix} 1/2\, t_{11} \\ -\sqrt{3}/2\, t_{11} \end{pmatrix}.$$

In this case (5-76) becomes

$$\sigma\vec{v} + \vec{v} = \begin{pmatrix} 2v_{11} \\ 0 \end{pmatrix} = m\begin{pmatrix} \sqrt{3}/2\, t_{11} \\ 1/2\, t_{11} \end{pmatrix} + n\begin{pmatrix} \sqrt{3}/2\, t_{11} \\ -1/2\, t_{11} \end{pmatrix} \tag{5-82}$$

From this we conclude that $m = n$ and that $v_{11} = (m\sqrt{3}/2)\, t_{11}$. Eq. (5-78) becomes

$$\begin{pmatrix} -\sqrt{3}/2\, v_{12} \\ 3/2\, v_{12} \end{pmatrix} = p\begin{pmatrix} \sqrt{3}/2\, t_{11} \\ 1/2\, t_{11} \end{pmatrix} + q\begin{pmatrix} \sqrt{3}/2\, t_{11} \\ -1/2\, t_{11} \end{pmatrix} \tag{5-83}$$

From which we conclude that

$$\begin{aligned} -v_{12} &= (p + q)\, t_{11} \\ 3v_{12} &= (p - q)\, t_{11} \end{aligned} \tag{5-84}$$

or

$$v_{12} = p\, t_{11}$$

Thus, we see that $\vec{v}$ must have the form

$$\begin{pmatrix} \sqrt{3}/2\, m\, t_{11} \\ p\, t_{11} \end{pmatrix}$$

We shall not go through the details again, but it is possible again to show that by trans-

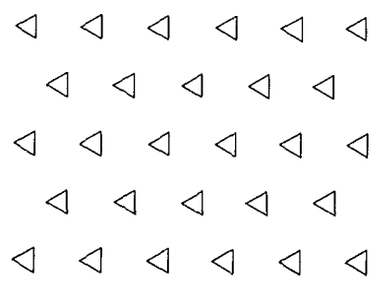


Fig. 5-21

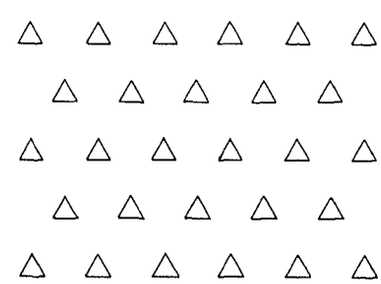


Fig. 5-22

lation through a vector $\vec{q}$ we can adjust our coordinate system so that both σ and C_3 have associated with them zero translations. We have, therefore, a new space group generated by $\{C_3|0\}$, $\{\sigma|0\}$, and $\{\varepsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a primitive translation from Γ_5 and

$$\vec{t}_1 = \begin{pmatrix} \sqrt{3}/2\, t_{11} \\ 1/2\, t_{11} \end{pmatrix} \qquad \vec{t}_2 = \begin{pmatrix} \sqrt{3}/2\, t_{11} \\ -1/2\, t_{11} \end{pmatrix}$$

This group is illustrated in Fig. 5-22.

C_6: This point group leaves the lattice Γ_5 invariant and consist of a cyclic group of proper rotations. We can associate with all the point group operators a zero translation. This space group is generated by $\{C_6|0\}$ and $\{\varepsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a primitive translation from Γ_5. The group is illustrated in Fig. 5-23.

C_{6v}: In this case the lattice Γ_5 is left invariant. In distinction to the case of the point group C_{3v}, there is only one way we can orient the lattice with respect to the reflection lines. One of the reflection lines must coincide with one of the basic primitive translations. We can adjust the origin of our coordinate system such that C_6 has associated with it primitive translations. In a completely analogous way to C_{3v}, we can simultaneously adjust the origin so that σ has a zero translation associated with it. Thus we get one new space group. This group is generated by $\{C_6|0\}$, $\{\sigma|0\}$, and $\{\varepsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a translation of Γ_5 and

$$\vec{t}_1 = \begin{pmatrix} t_{11} \\ 0 \end{pmatrix}, \qquad \vec{t}_2 = \begin{pmatrix} 1/2\, t_{11} \\ \sqrt{3}/2\, t_{11} \end{pmatrix}$$

This group is illustrated in Fig. 5-24.

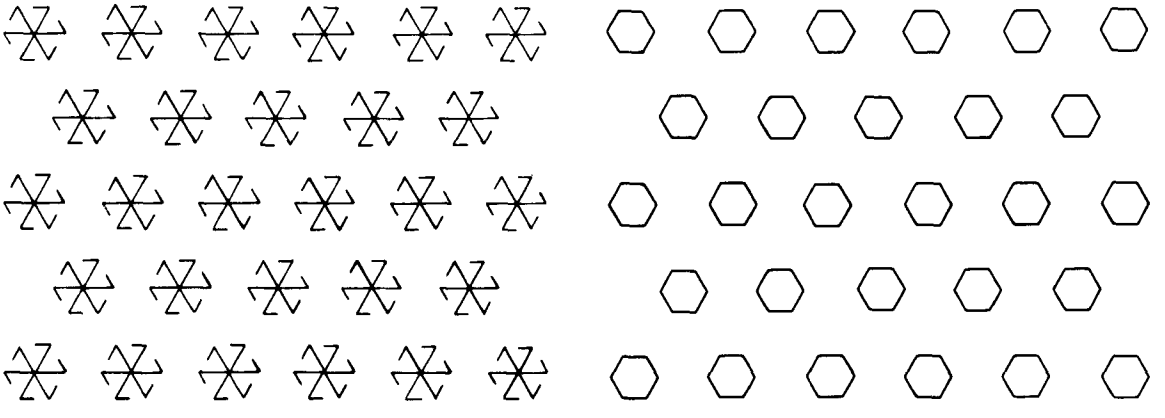


Fig. 5-23

Fig. 5-24

This completes our enumeration of the two-dimensional space groups. We see that they are 17 in number. Of these all but four (Figs. 5-19, 5-16, 5-15, 5-12) have primitive translations associated with all the operators in the point group. The remaining four space groups have reflections in them which always have a translational part which is non primitive.

4. Three-Dimensional Space Groups

We shall not, in detail, derive the number of space groups in three dimensions by the process of enumeration. The same processes which we carried out in two dimensions can be carried out in much the same way in three dimensions.

We would first find that we were limited in the number of point groups which we could have. That is, for groups of operators of the from $\{\alpha|\vec{a}\}$ which have as an invariant subgroup a group of primitive translations $\{\varepsilon|\vec{R}_n\}$, the rotational parts of the operators, α, must form a group. This is called the point group. There are only a limited number of point groups which leave a subgroup of primitive translations invariant. There are only 32 possible point groups or as they are sometimes called crystal classes.

In analogy to our work on the two-dimensional space groups, we could then in turn find for each of these point groups what restrictions were put on the lattices (invariant subgroup of primitive translations) which were left invariant by the space group corresponding to a given point group. In two dimensions, we found that there were five lattices. In three dimensions, we would find that there are 14 lattices. These are called the 14 Bravais lattices and vary from one with no restrictions on the three basic primitive translations to highly restricted ones like the simple cubic lattice consisting of three basic primitive translations of equal length which are mutually perpendicular.

We could then go on and start the process of enumeration of the space groups in three dimensions. We sould proceed by associating with each operator α a translational part $\vec{a}$ knowing that in the space group α will always appear associated with $\vec{a}$ or $\vec{a}$ plus a primitive translation. We would again find that there were restrictions put on $\vec{a}$. We would also find that there were two general types of space groups in three dimensions. One type has associated with every rotational operator in the group the zero translation. The other type does not have this property. In all, we would find a total of 230 space groups in three dimensions.

To sum up our enumeration of space groups we find the following. There are two space groups in one dimension, 17 space groups in two dimensions, and 230 space groups in three dimensions. There are two point groups in one dimension, ten in two dimensions and 32 in three dimensions. There is one lattice in one dimension, five lattices in two dimensions and 14 lattices in three dimensions of various degrees

of restriction. With the familiarity with space groups we have gained we shall proceed with the problem of their irreducible representations.

5. Irreducible Representations of Space Groups

In this section, we shall discuss the irreducible representations of space groups and shall evolve a mode of describing and classifying them. This method of classification makes use of the fact that every space group contains a group of primitive translations as an invariant subgroup. We therefore start with a description of the irreducible representations of a group of pure translations. This forms the simplest of all space groups.

A. Irreducible Representations of a Group of Primitive Translations

We shall restrict our attention in the general discussion here to three-dimensional groups of primitive translations, but the generalization to more or fewer dimensions will be immediately obvious.

Let us consider a group $\mathcal{T}$ of primitive translations $\{\varepsilon|\vec{R}_n\}$. Here $\vec{R}_n$ is of the form

$$\vec{R}_n = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3 \tag{5-85}$$

where $\vec{t}_1$, $\vec{t}_2$, and $\vec{t}_3$ are three linearly independent basic primitive translations. In order to confine ourselves to finite groups, we shall make this group finite in the following way. We shall assume that

$$\{\varepsilon|\vec{t}_1\}^N = \{\varepsilon|\vec{t}_2\}^N = \{\varepsilon|\vec{t}_3\}^N = \{\varepsilon|0\} \tag{5-86}$$

This means that the group $\mathcal{T}$ is the direct product of three groups (see Chapter III, Section 3): the group generated by $\{\varepsilon|\vec{t}_1\}$ and its powers, the group $\{\varepsilon|\vec{t}_2\}$ and its powers, and the group $\{\varepsilon|\vec{t}_3\}$ and its powers. It is possible to define the group $\mathcal{T}$ as a direct product of these three groups because the primitive translations all commute hence these three groups commute with each other. We know therefore that the irreducible representations of the group $\mathcal{T}$ will be the direct product of the representations of the groups generated by $\{\varepsilon|\vec{t}_1\}$, $\{\varepsilon|\vec{t}_2\}$ and $\{\varepsilon|\vec{t}_3\}$. All we need do is study the representations of one of these groups.

The representations of the group of $\{\varepsilon|\vec{t}_1\}$ and its powers is easy to find. This is an Abelian group and hence has nothing but one-dimensional representations. *

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*This is most easily seen from the fact that in an Abelian group every element is in a class by itself and thus there are as many irreducible representations as elements. In order for the sum of the squares of the dimensions of the irreducible representations to be equal to the order of the group, every representation must be one dimensional.

Since $\left\{\epsilon|\vec{t}_1\right\}^N = \left\{\epsilon|0\right\}$ and since $\left\{\epsilon|0\right\}$ must be rperesented by 1 we have that $\left\{\epsilon|\vec{t}_1\right\}$ must be represented by

$$e^{i(\frac{2\pi}{t_1}\frac{p_1}{N})t_1}$$

We have in this way N irreducible representations, one for each value of the integer p_1 from 0 to N - 1. Multiplying the irreducible representations of the three one-dimensional translation groups we find that $\left\{\epsilon|\vec{R}_n\right\}$ will be represented by

$$e^{i\vec{k}\cdot\vec{R}_n} \tag{5-86}$$

where $R_n = n_1\vec{t}_1 + n_2\vec{t}_2 + n_3\vec{t}_3$ and $k = k_1\vec{b}_1 + k_2\vec{b}_2 + k_3\vec{b}_3$. In (5-86), we have defined the three vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ by the relations

$$\vec{t}_i \cdot \vec{b}_j = 2\pi\,\delta_{ij} \qquad i, j = 1, 2, 3 \tag{5-87}$$

k_1, k_2, and k_3 are given by

$$k_i = \frac{p_i}{N} \qquad \begin{matrix} p_i = 0, 1 \ldots N - 1 \\ i = 1, 2, 3 \end{matrix} \tag{5-88}$$

In this way, we see that the vector $\vec{k}$ defines the irreducible representation of the group of pure translations. There is one irreducible representation for each value of k_1, k_2, and k_3; a total of N^3 in all. As we let the number N become very large, we see that the allowed $\vec{k}$ vectors, in the three-dimensional space spanned by $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ will become very dense. In the limit as N goes to infinity there is an irreducible representation corresponding to every $\vec{k}$ vector for which $0 \leqslant k_1 < 1$; $0 \leqslant k_2 < 1$; $0 \leqslant k_3 < 1$. These relations define a parallelopiped and we see that there is one irreducible representation of the group of pure translations for each point within the parallelopiped as well as one for each point on the surface except for the excluded surfaces $k_1 = 1$, $k_2 = 1$, or $k_3 = 1$. We shall call the space defined by the vectors $\vec{b}_1$, $\vec{b}_2$, and $\vec{b}_3$ as $\vec{k}$-space.

It is clear that any point $\vec{k}$ outside of the fundamental parallelopiped, which we have defined in the last paragraph, can be expressed in the form

$$\vec{k} = \vec{k}' + \vec{K}_q \tag{5-89}$$

where $\vec{K}_q = q_1\vec{b}_1 + q_2\vec{b}_2 + q_3\vec{b}_3$. In (5-89), q_1, q_2, and q_3 are integers, and $\vec{k}'$ is inside of the fundamental parallelopiped or on one of the surfaces $k_1 = 0$, $k_2 = 0$, or $k_3 = 0$. It is clear that these points outside of the fundamental parallelopiped give

rise to irreducible representations of the group of primitive translations, but the representation corresponding to the point $\vec{k}$ in (5-89) is exactly the same as that corresponding to the point $\vec{k}'$ in the same equation.

We shall call the vectors $\vec{K}_q$ the lattice vectors of $\vec{k}$-space and it is clear that as the q's in (5-89) run over all integers we do indeed define a lattice in this $\vec{k}$-space. We also see that all the irreducible representations of the group of pure translations correspond to $\vec{k}$ vectors within or on a surface $k_1 = 0$, $k_2 = 0$ or $k_3 = 0$, the fundamental parallelopiped, and that any point outside of the fundamental parallelopiped gives rise to a representation identical with some point on the inside or on the surfaces $k_i = 0$ $(i = 1, 2, 3)$.

We shall not go into the details here but it is also easy to show that other fundamental volumes beside our fundamental parallelopiped could be defined which have the property that points on the surface and all points in the interior correspond to all the irreducible representations of the group of pure translations. One of these is of particular interest and we shall use it as the volume which defines our irreducible representations of the group of pure translations in all of our later work. This is called a Brillouin zone and is defined in the following way. Imagine that we erected all of the planes which are the perpendicular bisectors of the primitive translations of $\vec{k}$-space. These planes, bisecting lines which extend from the origin outward, will enclose a volume about the origin. It is not difficult to show that the volume enclosed in this way along with non equivalent points on the surfaces (points corresponding to different irreducible representations, i.e., not differing by a lattice vector of $\vec{k}$-space) will house all the irreducible representations of the group of pure translations.

Let us illustrate these remarks on the irreducible representations of groups of translations by an example taken from the two-dimensional translation groups which we defined earlier in this chapter in Section 3. Consider the group Γ_5 defined in that section. This was a group whose two basic primitive translations were of equal length and inclined with respect to each other at an angle of 60°. If we call t the length of these two translations then they are given by

$$\vec{t}_1 = \begin{pmatrix} t \\ 0 \end{pmatrix} \qquad \vec{t}_2 = \begin{pmatrix} 1/2\, t \\ \sqrt{3}/2\, t \end{pmatrix} \tag{5-90}$$

The two basic lattice vectors of $\vec{k}$-space are given by Eq. (5-87)

$$\vec{b}_1 = \frac{4\pi}{3}\frac{1}{t}\begin{pmatrix} +\sqrt{3}/2 \\ -1/2 \end{pmatrix} \qquad \vec{b}_2 = \frac{4\pi}{\sqrt{3}}\frac{1}{t}\begin{pmatrix} 1 \\ 0 \end{pmatrix} \tag{5-91}$$

The fundamental parallelopiped is illustrated in Fig. 5-25. The dots represent the

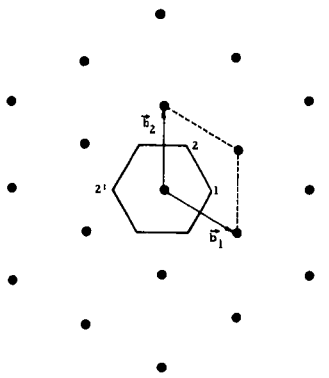


Fig. 5-25

lattice points in $\vec{k}$-space, and the hexagon at the center is the Brillouin zone constructed by erecting the perpendicular bisectors of the vectors from the origin to the lattice points. For the Brillouin zone, every point in the interior represents a different representation of the group Γ_5. All the points on the hexagon from 1 through 2 (but not including) 2' represent further distinct representations of this group of pure translations. The remaining points on the surface of this Brillouin zone correspond to representations which are the same as those we have already included. Thus, the point 2' corresponds to the same representation of the group of translations as the point 2 since the $\vec{k}$ vectors of these two points differ by the lattice vector of the reciprocal space $\vec{b}_1 + \vec{b}_2$. All the points on the edge of the hexagon opposite the edge 1 - 2 differ from the corresponding points on the edge 1 - 2 by the vector $\vec{b}_1 + \vec{b}_2$ and therefore yield no new representations of the group Γ_5.

In this way, we see how we may, in general, visualize the irreducible representations of a group of pure translations by the construction of a $\vec{k}$-space and the first Brillouin zone. The work to follow on the irreducible representation of space groups will make use of the insight we have gained into the irreducible representations of groups of pure translations and we shall have further discussion of Brillouin zones in that work.

B. The Nature of the Irreducible Representations of Space Groups

We are now in a position to study the irreducible representations of space groups. We shall assume that we are given an irreducible representation of a space group and then study its properties.

We denote the space group by $\mathcal{G}$ and a typical element of this group by $\{a|\vec{a}\}$. This group has a group of pure translations as an invariant subgroup. We shall call this subgroup $\mathcal{T}$ and an element of the subgroup is $\{\varepsilon|\vec{R}_n\}$. Let us assume that we have an irreducible representation of the group $\mathcal{G}$ which has dimension n. The matrices in this irreducible representation will be denoted by $D(\{a|\vec{a}\})$. We can without loss of generality assume that $D(\{a|\vec{a}\})$ forms a unitary representation of the group $\mathcal{G}$. Let us now put this representation in a special form and study its properties.

The matrices representing the pure translations, namely $D(\{\varepsilon|\vec{R}_n\})$ certainly form a representation of the group of pure translations. We can assume that the representation $D(\{a|\vec{a}\})$ has been put in such a form as to completely reduce the matrices representing the pure translations. Since we have seen that the group

of pure translations has nothing but one-dimensional representations, this means that all the matrices representing pure translations will be diagonal matrices. Let us assume that our representation $D(\{a|\vec{a}\})$ has this property. We know that the representations of the subgroup of pure translations which appear along the diagonal can be specified by their $\vec{k}$-vector. We can again, without loss of generality assume that all diagonal elements of the matrices representing pure translations which translate according to $\vec{k}_1$ are grouped together as are those elements which translate according to $\vec{k}_2$, $\vec{k}_3$, ... $\vec{k}_q$. Here we have assumed that q distinct representations of the group of pure translations appear along the diagonal of the matrices $D(\{\varepsilon|\vec{R}_n\})$. Thus, the matrices representing pure translations are of the following form

$$D(\{\varepsilon|\vec{R}_n\}) = \begin{pmatrix} e^{i\vec{k}_1\cdot\vec{R}_n} & & & & & \\ & e^{i\vec{k}_1\cdot\vec{R}_n} & & & & \\ & & \ddots & & & \\ & & & e^{i\vec{k}_j\cdot\vec{R}_n} & & \\ & & & & e^{i\vec{k}_j\cdot\vec{R}_n} & \\ & & & & & \ddots \\ & & & & & & e^{i\vec{k}_q\cdot\vec{R}_n} \end{pmatrix} \tag{5-92}$$

We know that if $\vec{R}_n$ is a primitive translation so is $(a^{-1})\vec{R}_n$, since

$$\{a|\vec{a}\}^{-1}\{\varepsilon|\vec{R}_n\}\{a|\vec{a}\} = \{\varepsilon|a^{-1}\vec{R}_n\} \tag{5-93}$$

The matrix representing $a^{-1}\vec{R}_n$ will be

$$D(\{\varepsilon|a^{-1}\vec{R}_n\}) = \begin{pmatrix} e^{ia\vec{k}_1\cdot\vec{R}_n} & & & & \\ & e^{ia\vec{k}_1\cdot\vec{R}_n} & & & \\ & & \ddots & & \\ & & & \ddots & \\ & & & & e^{ia\vec{k}_q\cdot\vec{R}_n} \end{pmatrix} \tag{5-94}$$

where we have made use of the fact that $\vec{k}\cdot(a^{-1}\vec{R}_n) = a\vec{k}\cdot\vec{R}_n$. From the very nature of unitary representations of a group, we know that

$$D(\{\varepsilon|a^{-1}\vec{R}_n\}) = D(\{a|\vec{a}\})^{\dagger}\, D(\{\varepsilon|\vec{R}_n\})\, D(\{a|\vec{a}\}) \tag{5-95}$$

It is easily seen that if one diagonal matrix is sent into another diagonal matrix by a unitary transformation then the diagonal matrix elements of the second matrix must be the same as those of the original matrix except possibly for the order. From this, we see that the matrices (5-92) and (5-95) must have the same diagonal elements except possibly for order since they are sent into one another by the unitary transformation (5-95). Therefore, if $e^{i\vec{k}_1 \cdot \vec{R}_n}$ occurs along the diagonal of (5-92) so must $e^{i\alpha\vec{k}_1 \cdot \vec{R}_n}$ for all α in the point group and for all $\vec{R}_n$. Not only must $e^{i\alpha\vec{k}_1 \cdot \vec{R}_n}$ appear along the diagonal of (5-92) but it must also appear as often as $e^{i\alpha\vec{k}_1 \cdot \vec{R}_n}$. It might be that in addition to $e^{i\vec{k}_1 \cdot \vec{R}_n}$ and $e^{i\alpha\vec{k}_1 \cdot \vec{R}_n}$ for all α there occurs some other diagonal elements of the form $e^{i\vec{k}' \cdot \vec{R}_n}$ not included in this set. If this is the case, we could break the diagonal matrix (5-92) up into two parts in the manner we have illustrated in (5-96). In this illustration, the two non vanishing blocks are diagonal

$$\left(\begin{array}{c|c} e^{i\alpha\vec{k}_1 \cdot \vec{R}_n} \text{ for all } \alpha & 0 \\ \hline 0 & \begin{array}{l}\text{other diagonal elements of the} \\ \text{form } e^{i\vec{k}' \cdot \vec{R}_n}\end{array} \end{array}\right) \tag{5-96}$$

matrices. We know that for some value of $\vec{R}_n$ any diagonal element in the upper block will differ from any given value of $\vec{R}_n$ in the lower block. If we block off all the matrices in the irreducible representation in a similar manner, we can show from the relation (5-97) or (5-96)

$$D\left(\left\{\alpha|\vec{a}\right\}\right) D\left(\left\{\varepsilon|\alpha^{-1}\vec{R}_n\right\}\right) = D\left(\left\{\varepsilon|\vec{R}_n\right\}\right) D\left(\left\{\alpha|\vec{a}\right\}\right) \tag{5-97}$$

that the representation $D\left(\left\{\alpha|\vec{a}\right\}\right)$ will be of the form (5-98)

$$D\left(\left\{\alpha|\vec{a}\right\}\right) = \left(\begin{array}{c|c} D'\left(\left\{\alpha|\vec{a}\right\}\right) & 0 \\ \hline 0 & D''\left(\left\{\alpha|\vec{a}\right\}\right) \end{array}\right) \tag{5-98}$$

This means, of course, that we have reduced the representation contrary to our assumption that we were dealing with an irreducible representation.

This leaves us in the position that every diagonal element of (5-92) is of the form $e^{i\alpha\vec{k}_1 \cdot \vec{R}_n}$ where α is a member of the point group. From the discussion of the last paragraph, we can now rewrite the diagonal matrix (5-92) in a different form illustrating the fact that all the diagonal elements of the matrix arise from $\vec{k}$-vectors of the form $\alpha\vec{k}_1$. We have illustrated this in (5-99). In this illustration

$$D(\{\varepsilon|\vec{R}_n\}) = \begin{pmatrix} e^{i\vec{k}_1\cdot\vec{R}_n}\mathbf{1} & & & 0 \\ & e^{ia_2\vec{k}_1\cdot\vec{R}_n}\mathbf{1} & & \\ & & \ddots & \\ 0 & & & e^{ia_q\vec{k}_1\cdot\vec{R}_n}\mathbf{1} \end{pmatrix} \tag{5-99}$$

the n × n matrix $D(\{\varepsilon|\vec{R}_n\})$ is divided up into diagonal blocks with zeros elsewhere. The diagonal blocks are matrices of order d = n/q and each one is itself a diagonal matrix. $\mathbf{1}$ is the unit matrix of dimension n/q. $a_1 = \varepsilon$, $a_2, a_3 \ldots a_q$ are the selected elements of the point group which send $\vec{k}_1$ into $\vec{k}_1$, $\vec{k}_2$, ... $\vec{k}_q$ respectively. Thus

$$a_i\vec{k}_1 = \vec{k}_i \qquad (i = 1 \ldots q) \tag{5-100}$$

Here the $\vec{k}_i$ correspond to different representations of $\mathcal{T}$. Let us now block off all the matrices $D(\{a|\vec{a}\})$ in a similar way. Thus, we have

$$D(\{a|\vec{a}\}) = \begin{pmatrix} D_{11}(\{a|\vec{a}\}) & D_{12}(\{a|\vec{a}\}) & \ldots & D_{1q}(\{a|\vec{a}\}) \\ D_{21}(\{a|\vec{a}\}) & \ldots\ldots\ldots\ldots & & D_{2q}(\{a|\vec{a}\}) \\ \vdots & & & \vdots \\ D_{q1}(\{a|\vec{a}\}) & \ldots\ldots\ldots\ldots & & D_{qq}(\{a|a\}) \end{pmatrix} \tag{5-101}$$

Here $D_{ij}(\{a|\vec{a}\})$ (i, j = 1 ... q) is a d × d (d = n/q) matrix. We can now learn something of the matrices $D_{ij}(\{a|\vec{a}\})$. One thing which we already know is the form of the matrices $D(\{\varepsilon|\vec{R}_n\})$. In the notation of (5-101), these matrices would be given by

$$D_{ij}(\{\varepsilon|\vec{R}_n\}) = e^{ia_i\vec{k}_1\cdot\vec{R}_n}\,\mathbf{1}\delta_{ij} \tag{5-102}$$

Let us now go on to a study of the matrices representing other than pure translations. First, let us consider any element $\{\beta|\vec{b}\}$ of $\mathcal{G}$ which has the property that $e^{i\beta\vec{k}_1\cdot\vec{R}_n} = e^{i\vec{k}_1\cdot\vec{R}_n}$ for all $\vec{R}_n$. In terms of $\vec{k}_1$ this means that

$$\beta\vec{k}_1 = \vec{k}_1 + \vec{K}_q \tag{5-103}$$

where $\vec{K}_q$ is a lattice vector of $\vec{k}$-space. We note those elements of $\mathcal{G}$ which have this property form a group. Thus, if for $\left\{\beta'|\vec{b}'\right\}$; $e^{i\beta'\vec{k}_1 \cdot \vec{R}_n} = e^{i\vec{k}_1 \cdot \vec{R}_n}$ then

$$\begin{aligned} e^{i\beta'\beta\vec{k}_1 \cdot \vec{R}_n} &= e^{i\beta\vec{k}_1 \cdot \beta'^{-1}\vec{R}_n} \\ &= e^{i\vec{k}_1 \cdot \beta'^{-1}\vec{R}_n} \\ &= e^{i\beta'\vec{k}_1 \cdot \vec{R}_n} \\ &= e^{i\vec{k}_1 \cdot \vec{R}_n} \end{aligned} \tag{5-104}$$

and therefore $\left\{\beta'|\vec{b}'\right\}\left\{\beta|\vec{b}\right\}$ is a member of the group. We shall call this group the group of $\vec{k}_1$ and shall denote it by $\mathcal{K}$. It is clear for one thing that this group contains the entire group $\mathcal{T}$. For an element $\left\{\beta|\vec{b}\right\}$ of $\mathcal{K}$ we have

$$D(\left\{\epsilon|\vec{R}_n\right\})\ D(\left\{\beta|\vec{b}\right\}) = D(\left\{\beta|\vec{b}\right\})\ D(\left\{\epsilon|\beta^{-1}\vec{R}_n\right\}) \text{ for all } \vec{R}_n \tag{5-105}$$

For the first column of blocks in the product on both sides of (5-105), we have, using (5-102), that

$$\begin{aligned} e^{i\alpha_j\vec{k}_1 \cdot \vec{R}_n}\ D_{j1}(\left\{\beta|\vec{b}\right\}) &= D_{j1}(\left\{\beta|\vec{b}\right\})\, e^{i\vec{k}_1 \cdot \beta^{-1}\vec{R}_n} \\ &= D_{j1}(\left\{\beta|\vec{b}\right\})\, e^{i\vec{k}_1 \cdot \vec{R}_n} \end{aligned} \tag{5-106}$$

From this we see that $D_{j1}(\left\{\beta|\vec{b}\right\})$ is zero unless $j = 1$. (It can also be seen from the unitary nature of the representation that $D_{1j}(\left\{\beta|\vec{b}\right\}) = 0;\ j \neq 1.$) Therefore for all $\left\{\beta|\vec{b}\right\}$ belonging to $\mathcal{K}$, the group of $\vec{k}_1$, that

$$D(\left\{\beta|\vec{b}\right\}) = \left(\begin{array}{c|c} D_{11}(\left\{\beta|\vec{b}\right\}) & 0 \\ \hline 0 & \text{////} \end{array}\right) \tag{5-107}$$

From this, we see that the matrices $D_{11}(\left\{\beta|\vec{b}\right\})$, for all $\left\{\beta|\vec{b}\right\}$ belonging to the group $\vec{k}_1$, form a representation of $\mathcal{K}$.

Now let us consider the matrix representing $\{a_j|\vec{a}_j\}$ where $\{a_j|\vec{a}_j\}$ is a specific operator of the space group for which $a_j\vec{k}_1 = \vec{k}_j$. From the fact that

$$D(\{\epsilon|\vec{R}_n\})\ D(\{a_j|\vec{a}_j\}) = D(\{a_j|\vec{a}_j\})\ D(\{\epsilon|a_j^{-1}\vec{R}_n\}) \tag{5-108}$$

we conclude, by comparing the i, 1^{th} blocks on both sides, that

$$e^{ia_i\vec{k}_1\cdot\vec{R}_n}\ D_{i1}(\{a_j|\vec{a}_j\}) = D_{i1}(\{a_j|\vec{a}_j\})\ e^{ia_j\vec{k}_1\cdot\vec{R}_n} \text{ for all } \vec{R}_n \tag{5-109}$$

This means that the only non vanishing block in the first column of $D(\{a_j|\vec{a}_j\})$ is the j^{th} block. This j, 1^{th} block must then, of course, be a unitary matrix because of the unitary nature of the matrices in the representation of the space group. If we allow all the matrices in $D(\{a|\vec{a}\})$ to undergo the unitary transformation

$$\psi = \begin{pmatrix} 1 & & & \\ & D_{12}(\{a_2|\vec{a}_2\}) & & \\ & & \ddots & \\ & & & D_{1j}(\{a_j|\vec{a}_j\}) \\ & & & \ddots \end{pmatrix} \tag{5-110}$$

then all the matrices representing $D(\{a_j|\vec{a}_j\})$ can be taken in such a form that $D_{j1}(\{a_j|\vec{a}_j\}) = 1$. This means that the only non vanishing block in the first column of $D(\{a_j|\vec{a}_j\})$ is the j^{th} which is the d × d unit matrix. We now have specified the first row and column of the matrices representing $\{\beta|\vec{b}\}$ where $\{\beta|\vec{b}\}$ is a member of $\mathcal{K}$ and the first column of the matrices representing $\{a_j|\vec{a}_j\}$ where $a_j\vec{k}_1 = \vec{k}_j$. This, it will turn out, is enough to specify the form of the entire representation $D(\{a|\vec{a}\})$.

First, we note that $\mathcal{K}$ and the elements $\{a_j|\vec{a}_j\}$ decompose $\mathcal{G}$ into its left cosets with respect to $\mathcal{K}$. Thus

$$\mathcal{G} = \mathcal{K} + \{a_2|\vec{a}_2\}\mathcal{K} + \ldots \{a_q|\vec{a}_q\}\mathcal{K} \tag{5-111}$$

This is most easily seen from the fact that for any element $\{a|\vec{a}\}$ we can find an element of the set $\{a_j|\vec{a}_j\}$ (j = 1 ... q) such that

$$e^{ia\vec{k}_1\cdot\vec{R}_n} = e^{ia_1\vec{k}_1\cdot\vec{R}_n} \tag{5-112}$$

where we have denoted the element in question by $\{a_\ell|\vec{a}_\ell\}$. This means that

$$a\vec{k}_1 = a_\ell\vec{k}_1 + \vec{K}_q$$

$$a_\ell^{-1}a\vec{k}_1 = \vec{k}_1 + a_\ell^{-1}\vec{K}_q \quad \text{(for a suitable } \vec{K}_q\text{)}$$

or

$$e^{ia_\ell^{-1}a\vec{k}_1 \cdot \vec{R}_n} = e^{i\vec{k}_1 \cdot \vec{R}_n} \quad \text{(for all } \vec{R}_n\text{)} \tag{5-113}$$

Thus $a_\ell^{-1}a$ must be the rotational part of some operator in $\mathcal{K}$. Therefore, we have that for any element $\{a|\vec{a}\}$ of $\mathcal{G}$

$$\begin{aligned} \{a_\ell|\vec{a}_\ell\}^{-1}\{a|\vec{a}\} &= \{\beta|\vec{b}\} \\ \{a|\vec{a}\} &= \{a_\ell|\vec{a}_\ell\}\{\beta|\vec{b}\} \end{aligned} \tag{5-114}$$

for some $\{a_\ell|\vec{a}_\ell\}$ and an element $\{\beta|\vec{b}\}$ of $\mathcal{K}$. This means of course that $\{a|\vec{a}\}$ is in the ℓ^{th} coset. We may also note in passing that for all elements in the j^{th} coset the rotational parts send $\vec{k}_1$ into $\vec{k}_j$ plus a lattice vector of the reciprocal lattice. We shall now show that we can specify all the elements in $D(\{a|\vec{a}\})$ where $\{a|\vec{a}\}$ is any element of $\mathcal{G}$ in terms of $D_{11}(\{\beta|\vec{b}\})$ where $\{\beta|\vec{b}\}$ belongs to the group $\mathcal{K}$. Consider the ℓ^{th} column of $D(\{a|\vec{a}\})$. We know that for some a_m

$$e^{ia\vec{k}_\ell \cdot \vec{R}_n} = e^{ia_m\vec{k}_1 \cdot \vec{R}_n} \text{ (for all } \vec{R}_n\text{)} \tag{5-115}$$

By multiplying (5-95) from the left with $D(\{a|\vec{a}\})$ and comparing the ℓ^{th} column of both sides of the resulting equation, we have for the j,ℓ^{th} block

$$D_{j\ell}(\{a|\vec{a}\})\, e^{ia\vec{k}_\ell \cdot \vec{R}_n} = e^{i\vec{k}_j \cdot \vec{R}_n} D_{j\ell}(\{a|\vec{a}\}) \tag{5-116}$$

This means that, using (5-115), we have $D_{j\ell}(\{a|\vec{a}\}) = 0$ unless $j = m$. Thus the only non vanishing block in the ℓ^{th} column of $D(\{a|\vec{a}\})$ is the m^{th} where m is fixed by (5-115). We shall now be able to find an explicit expression for $D_{\ell m}(\{a|\vec{a}\})$.

We know that $\{a|\vec{a}\}\{a_\ell|\vec{a}_\ell\} = \{a_m|\vec{a}_m\}\{\beta|\vec{b}\}$ for some element $\{\beta|\vec{b}\}$ of $\mathcal{K}$, since

$$e^{iaa_\ell\vec{k}_1 \cdot \vec{R}_n} = e^{ia_m\vec{k}_1 \cdot \vec{R}_n}$$

the left-hand side of the last equation, is a member of the m^{th} coset. For the matrices we have

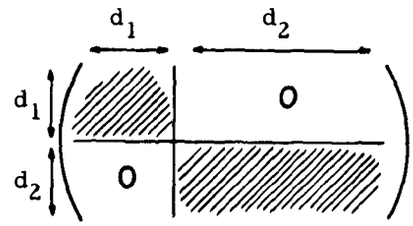
$$D(\{\alpha|\vec{a}\}) = D(\{\alpha_m|\vec{a}_m\})\, D(\{\beta|\vec{b}\})\, D(\{\alpha_\ell|\vec{a}_\ell\})^\dagger \tag{5-117}$$

For the m,ℓ^{th} block of $D(\{\alpha|\vec{a}\})$ we have

$$\begin{aligned} D_{m\ell}(\{\alpha|\vec{a}\}) &= \sum_{i,j} D_{mi}(\{\alpha_m|\vec{a}_m\})\, D_{ij}(\{\beta|\vec{b}\}) \left[D_{\ell j}(\{\alpha_\ell|\vec{a}_\ell\})\right]^\dagger \\ &= \sum_{i,j} 1\delta_{1i}\, D_{ij}(\{\beta|b\})\, 1\delta_{1j} \\ &= D_{11}(\{\beta|\vec{b}\}) \end{aligned} \tag{5-118}$$

Here we have made use of the nature of the first column of the matrices representing $\{\alpha_m|\vec{a}_m\}$ and $\{\alpha_\ell|\vec{a}_\ell\}$. In this way, we have expressed all the blocks in $D(\{\alpha|\vec{a}\})$ in terms of $D_{11}(\{\beta|\vec{b}\})$.

We can now show one more important fact. We mentioned that $D_{11}(\{\beta|\vec{b}\})$ forms a representation of the group $\mathcal{K}$. It actually must form an irreducible representation of this group. If we assume the contrary, then $D_{11}(\{\beta|\vec{b}\})$ can be put in the form



$$d_1 + d_2 = d \tag{5-119}$$

If this is the case, every block of $D(\{\alpha|\vec{a}\})$ for all the elements of $\mathcal{G}$ can be put in the same form. A moment's consideration will show that by rearranging rows and columns in $D(\{\alpha|\vec{a}\})$ this representation of $\mathcal{G}$ can be reduced into two representations one of dimension qd_1 and the other of dimension qd_2 contrary to the assumption that $D(\{\alpha|\vec{a}\})$ was irreducible.

This completes the discussion of the properties of the irreducible representation of the space group, but in the next paragraph we shall recapitulate the salient features without the details of the mathematical proofs.

We have been able to show that every irreducible representation $D(\{\alpha|\vec{a}\})$ of a space group $\mathcal{G}$ can be put in the form where the invariant subgroup of pure translations $\mathcal{T}$ is represented by matrices which are diagonal. If the representation is of dimension n, then the elements of the diagonal matrices can be arranged in such a way that the first d (where d is a divisor of n; $n/d = q$) diagonal elements are of the form $e^{i\vec{k}\cdot\vec{R}_n}$ in the matrix $D(\{\varepsilon|\vec{R}_n\})$ for all $\{\varepsilon|\vec{R}_n\}$. The remainder of the diagonal

elements can be arranged in (n/d) - 1 groups of d diagonal elements such that within any group the elements are of the form

$$e^{i\alpha_j \vec{k} \cdot \vec{R}_n} \quad (j = 2 \ldots , \ q = n/d)$$

Here α_j is a selected member of the point group which we associate with the space group element $\{\alpha_j | \vec{a}_j\}$. This blocking off of the translation matrices in turn leads to a blocking off of the matrices $D(\{\alpha|\vec{a}\})$ in the irreducible representation of $\mathcal{G}$. These matrices can be blocked off into d × d blocks which we label $D_{ij}(\{\alpha|\vec{a}\})$ (i, j = 1 ... q). Those elements $\{\beta|\vec{b}\}$ which have the property that

$$e^{i\beta\vec{k} \cdot \vec{R}_n} = e^{i\vec{k} \cdot \vec{R}_n} \quad \text{(for all } \vec{R}_n)$$

form a group $\mathcal{K}$ (which includes the entire group of pure translations). The matrices $D_{11}(\{\beta|\vec{b}\})$ form an irreducible representation of $\mathcal{K}$. The elements $\{\alpha_i|\vec{a}_i\}$ and the subgroup $\mathcal{K}$ can be used to divide the group $\mathcal{G}$ into its left cosets with respect to $\mathcal{K}$. For any element $\{\alpha|\vec{a}\}$ of the group $\mathcal{G}$ and for any α_ℓ we can find an α_m such that

$$e^{i\alpha\alpha_\ell \vec{k} \cdot \vec{R}_n} = e^{i\alpha_m \vec{k} \cdot \vec{R}_n}$$

We can then specify the matrix representing the element $\{\alpha|\vec{a}\}$ by saying that the only non vanishing block in the ℓ^{th} column of blocks is the m^{th} and the matrix which appears in this position is $D_{11}(\{\beta|\vec{b}\})$ where $\{\beta|\vec{b}\}$ belongs to $\mathcal{K}$ and where

$$\{\alpha|\vec{a}\}\{\alpha_\ell|\vec{a}_\ell\} = \{\alpha_m|\vec{a}_m\}\{\beta|\vec{b}\} \tag{5-120}$$

In particular for $\{\alpha_j|\vec{a}_j\}$ the only non vanishing block in the first column of blocks is the j^{th} which we have chosen for convenience to be the unit matrix. An equivalent way of specifying which block in the ℓ^{th} column is non vanishing is as follows. We notice that for an element $\{\alpha|\vec{a}\}$ of the group $\mathcal{G}$ we can multiply all the cosets from the left by this element and this merely effects a permutation of the cosets. The ℓ^{th} coset goes into the one for which we can find an $\{\alpha_m|\vec{a}_m\}$ and a $\{\beta|\vec{b}\}$ such that $\{\alpha|\vec{a}\}\{\alpha_\ell|\vec{a}_\ell\} = \{\alpha_m|\vec{a}_m\}\{\beta|\vec{b}\}$; namely the m^{th}. Thus the non vanishing blocks in the matrix representing an element $\{\alpha|\vec{a}\}$ show the way the cosets go into one another under the elements $\{\alpha|\vec{a}\}$. Let us call the form of the representation we have specified in the last paragraph the standard form.

We can also prove the converse of the theorem contained in the last paragraph. This would state that any representation of $\mathcal{G}$ which is in the standard form would be an irreducible representation of the group $\mathcal{G}$. This proof is quite straightforward and makes use of Theorem 6. The representation is most easily constructed in terms

of basis functions for the representation and the description of the basis functions for an irreducible representation of a space group in standard form is as follows: Imagine that we had d orthogonal functions $u_1^1 \ \ldots \ u_d^1$ which under translation through $\vec{R}_n$ are multiplied by $e^{i\vec{k}\cdot\vec{R}_n}$. If these functions form an irreducible representation of $\mathcal{K}$ (the group of elements $\{\beta|\vec{b}\}$ for which $e^{i\beta\vec{k}\cdot\vec{R}_n} = e^{i\vec{k}\cdot\vec{R}_n}$ (for all $\vec{R}_n$)) then the n = qd functions

$$u_j^i = \{a_i|\vec{a}_i\}\, u_j^1 \qquad \begin{matrix} i = 1 \ldots q \\ j = 1 \ldots d \end{matrix} \qquad (5\text{-}121)$$
$$\{a_1|\vec{a}_1\} = \{\varepsilon|0\}$$

form an irreducible representation of $\mathcal{G}$. Here $\{a_i|\vec{a}_i\}$ are the elements of $\mathcal{G}$ for which $\mathcal{G} = \mathcal{K} + \{a_2|a_2\}\mathcal{K} + \ldots + \{a_q|\vec{a}_q\}\mathcal{K}$. It is easy to show that the n functions we have specified in (5-121) form a basis for the standard form of the irreducible representation of space groups.

From the results of the last paragraph we can now see how to construct all of the irreducible representations of a given space group. We first select a $\vec{k}$-vector in or on the boundary of the Brillouin zone. For certain operators $\{\beta|\vec{b}\}$ of the group $\mathcal{G}$, $e^{i\beta\vec{k}\cdot\vec{R}_n} = e^{i\vec{k}\cdot\vec{R}_n}$. This means that $\beta\vec{k} = \vec{k} + \vec{K}_j$ where $\vec{K}_j$ is some lattice vector of $\vec{k}$-space. We construct all irreducible representations of this group of elements which have the property that the diagonal elements of the matrices representing pure translations are of the form $e^{i\vec{k}\cdot\vec{R}_n}$. This by our previous discussions will lead to all irreducible representations of $\mathcal{G}$ which are associated with the vector $\vec{k}$. As we let the $\vec{k}$-vector wander over the entire first Brillouin zone we get all irreducible representations of the group $\mathcal{G}$. Actually in order to get the distinct representations of the space group we need only let $\vec{k}$ range over that set of points in the Brillouin zone such that no two points $\vec{k}$ and $\vec{k}'$ of the set have the property that $\vec{k}' = a\vec{k} + \vec{K}_j$ where a is any member of the point group and $\vec{K}_j$ is any lattice vector of $\vec{k}$-space.

C. Additional Simplifications

We see from the discussion of the last paragraphs that the finding of the irreducible representations of a space group $\mathcal{G}$ which are associated with a $\vec{k}$-vector, $\vec{k}$, reduces to the finding of those irreducible representations of the group of the $\vec{k}$-vector (the group $\mathcal{K}$) which have the property that the matrices representing the group of pure translations $\mathcal{T}$ (which is a subgroup of $\mathcal{K}$) are of the form $e^{i\vec{k}\cdot\vec{R}_n}$ where $\{\varepsilon|\vec{R}_n\}$ is any translation in $\mathcal{T}$. We recall that $\mathcal{K}$ was defined as that group of operators $\{\beta|\vec{b}\}$ whose rotational parts β satisfy the condition $e^{i\beta\vec{k}\cdot\vec{R}_n} = e^{i\vec{k}\cdot\vec{R}_n}$ (or equivalent to $\beta\vec{k} = \vec{k} + \vec{K}_j$ where $\vec{K}_j$ is a lattice vector of k-space; $\mathcal{K}$ must be, of course, one of the possible space groups). It is possible to make simplifications in

finding the appropriate irreducible representations of $\mathcal{K}$. We shall pursue this here. First, for convenience we shall introduce some further notation.

In a space group whose elements are $\{\alpha|\vec{a}\}$ we know that the rotational parts, α, form a group which is called the point group. Let us denote this group by $\mathcal{G}_o$. It is clear that the rotational parts of the operators $\{\beta|\vec{b}\}$ in $\mathcal{K}$ must also form a group which is a subgroup of $\mathcal{G}_o$. We shall call this group $\mathcal{G}_o(\vec{k})$ indicating that it is the point group associated with $\mathcal{K}$ (the group of the k-vector).

We recall that as we allowed $\vec{k}$ to wander over the interior and surface of the Brillouin zone we could obtain all the irreducible representations of $\mathcal{G}$ by finding the appropriate irreducible representations of the group of the $\vec{k}$-vector ($\mathcal{K}$) for the $\vec{k}$-vector in question. Let us first consider points on the interior of the Brillouin zone. It is a property of the interior points of a Brillouin zone that the only value of $\vec{K}_j$ for which $\beta\vec{k} = \vec{k} + \vec{K}_j$ is $\vec{K}_j = 0$. In other words, $\vec{k}$ and $\beta\vec{k}$ cannot differ by any other lattice vector of the k-space than the zero vector. Thus, for any point in the interior of the Brillouin zone $\beta\vec{k} = \vec{k}$ is the condition for the operators in $\mathcal{K}$. $\mathcal{G}_o(\vec{k})$ is, of course, one of the 32 permissable point groups. The irreducible representations of the 32 point groups are well known. Let us denote by $\Gamma(\beta)$ one irreducible representation of the group $\mathcal{G}_o(\vec{k})$. Let us then notice that if we let $D_{11}(\{\beta|\vec{b}\})$, where $\{\beta|\vec{b}\}$ belongs to $\mathcal{K}$, be given by

$$D_{11}(\{\beta|\vec{b}\}) = e^{i\vec{k}\cdot\vec{b}}\,\Gamma(\beta) \tag{5-122}$$

then we obtain an irreducible representation of $\mathcal{K}$. First, we must show that $D_{11}(\beta|\vec{b})$ forms a representation of $\mathcal{K}$. If $\{\beta|\vec{b}\}$ and $\{\beta'|\vec{b}'\}$ are two operators in $\mathcal{K}$ their product is $\{\beta\beta'|\beta\vec{b}' + \vec{b}\}$. Multiplying the matrices representing these operators we obtain

$$\begin{aligned} D_{11}(\{\beta|\vec{b}\})\; D_{11}(\{\beta'|\vec{b}'\}) &= e^{i\vec{k}\cdot\vec{b}}\, e^{i\vec{k}\cdot\vec{b}'}\,\Gamma(\beta)\,\Gamma(\beta') \\ &= e^{i\vec{k}\cdot(\vec{b}+\vec{b}')}\,\Gamma(\beta\beta') \end{aligned} \tag{5-123}$$

The matrix representing the product is given by

$$\begin{aligned} D_{11}(\{\beta\beta'|\beta\vec{b}' + \vec{b}\}) &= e^{i\vec{k}\cdot(\beta\vec{b}'+\vec{b})}\;\Gamma(\beta\beta') \\ &= e^{i\beta^{-1}\vec{k}\cdot\vec{b}'}\, e^{i\vec{k}\cdot\vec{b}}\,\Gamma(\beta\beta') \\ &= e^{i\vec{k}\cdot(\vec{b}'+\vec{b})}\;\Gamma(\beta\beta') \end{aligned} \tag{5-124}$$

in the last line we have made use of the fact that if β is in the group of the $\vec{k}$-vector so is its inverse. Therefore, (5-122) forms a representation of the group of the $\vec{k}$-vector. Since the only matrix which commutes with all the matrices $\Gamma(\beta)$ is a constant times the unit matrix ($\Gamma(\beta)$ is irreducible), the only matrix which commutes with all the matrices $D_{11}(\{\beta|\vec{b}\})$ is a constant times the unit matrix and therefore $D_{11}(\{\beta|\vec{b}\})$ forms an irreducible representation of the group $\mathcal{K}$. Thus by knowing all the representations of the 32 point groups we can find all irreducible representations of the space groups associated with $\vec{k}$-vectors in the interior of the Brillouin zone.

Let us now consider a point on the surface of the Brillouin zone. For these points it may be that $\beta\vec{k} = \vec{k} + \vec{K}_j$ where $\vec{K}_j$ in some non zero lattice vector of $\vec{k}$-space. In this case, the results of the last paragraph do not hold in general. They do hold, however, for a special type of space group. We may recall that some space groups had the property that every operator in them contained, in its translational part, nothing but pure translations. This is another way of saying that every rotational operator in the group has associated with it the zero translation. This would mean that all the $\vec{a}$'s and $\vec{b}$'s of the previous paragraphs were primitive translations. Let us again define $D_{11}(\{\beta|\vec{b}\})$ to be $e^{i\vec{k}\cdot\vec{b}}\,\Gamma(\beta)$ where $\{\beta|\vec{b}\}$ is now an operator for which $\beta\vec{k} = \vec{k} + \vec{K}_j$ (for some $\vec{K}_j$). In this case, we again have an irreducible representation of $\mathcal{K}$. Equation (5-123) remains the same, but the proof in (5-124) proceeds differently. In this case we have

$$\begin{aligned} D_{11}(\{\beta\beta'|\beta\vec{b}' + \vec{b}\}) &= e^{i\vec{k}\cdot(\beta\vec{b}' + \vec{b})}\,\Gamma(\beta\beta') \\ &= e^{i\beta^{-1}\vec{k}\cdot\beta'}\, e^{i\vec{k}\cdot\vec{b}}\,\Gamma(\beta\beta') \\ &= e^{i(\vec{k}+\vec{K}_i)\cdot\vec{b}'}\, e^{i\vec{k}\cdot\vec{b}}\,\Gamma(\beta\beta') \\ &= e^{i\vec{k}\cdot(\vec{b}+\vec{b}')}\,\Gamma(\beta\beta') \end{aligned} \qquad (5\text{-}125)$$

In this way, we have made use of the fact that since β^{-1} is in the group of the $\vec{k}$-vector, $\beta^{-1}\vec{k} = \vec{k} + \vec{K}_i$ and also, the fact that $\vec{b}'$ is a primitive translation and therefore $e^{i\vec{b}'\cdot\vec{K}_i} = 1$. Thus, for this class of space groups we can find all irreducible representations of $\mathcal{G}$ for points on the surface of the Brillouin zone through the use of (5-122).

For points in $\vec{k}$-space on the boundary of the Brillouin zone whose group $\mathcal{K}$ contains operators with non primitive translations the situation is somewhat more complex. There are simplifications which can be made in this case as well. For most of the simple space groups of this type it is possible to find the irreducible representations associated with points on the surface of the Brillouin zone by making use of

special properties of these groups and we shall not go into the details here. Instead we illustrate our remarks by finding the irreducible representations of some simple space groups.

D. Examples of Irreducible Representations of Space Groups

Let us start by finding the irreducible representations of the two space groups in one dimension. The translation group is the same for both of these space groups and in one dimension $\vec{R}_n = n\vec{t}_1$. From Eq. (5-87) we can define the basic lattice vector of $\vec{k}$-space. In this case $\vec{b}_1 = (2\pi/|t_1|)\vec{u}$ where $\vec{u}$ is a unit vector in the direction of $\vec{t}_1$. In Fig. 5-26 we have illustrated by heavy dots the lattice points of $\vec{k}$-space. They are a series of equally spaced points which are a distance $(2\pi/|\vec{t}|)$ apart. By bisecting the two lattice vectors from the origin to the nearest neighbor lattice points in $\vec{k}$-space we obtain the Brillouin zone. The boundaries of this zone are illustrated by the two vertical lines on either side of the origin.

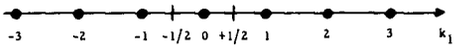


Fig. 5-26

The irreducible representations of the group of pure translations are given by $e^{i\vec{k}\cdot\vec{R}_n} = e^{i2\pi nk_1}$ where $\vec{k} = k_1\vec{b}_1$. Thus all irreducible representations of the group of pure translations are obtained by $\vec{k}$-values within the Brillouin zone

$$-\frac{\pi}{|t_1|} < \vec{k} < \frac{\pi}{|t_1|} \quad -\frac{1}{2} < k_1 < \frac{1}{2}$$

We note in passing that the two end points of the Brillouin zone correspond to the same irreducible representation of the group of pure translations since they differ by a lattice vector of $\vec{k}$-space $(\vec{b}_1)$.

One of the one-dimensional space groups consists of nothing but the pure translation group. For this space group we have already obtained the irreducible representations. They are all one-dimensional and are given by $D(\{\epsilon|\vec{R}_n\}) = e^{i2\pi nk_1}$ as $\vec{k}$ takes on all values in the Brillouin zone.

The other one-dimensional space group has elements $\{\epsilon|\vec{R}_n\}$ and $\{i|\vec{R}_n\}$ for all $\vec{R}_n$. Let us first consider the irreducible representation corresponding to $\vec{k} = 0$. It is clear that $i\vec{k} = -\vec{k} = \vec{k} = 0$. For this point the group of the $\vec{k}$-vector, $\mathcal{K}$, consists of the entire space group $\mathcal{G}$. $\mathcal{G}_0(\vec{k})$ is merely the group ϵ, i. Since this is an interior point of the Brillouin zone we can use the method of Eq. (5-122) to find the irreducible representations. In this case $e^{i\vec{k}\cdot\vec{R}_n} = 1$, and the irreducible representations of $\mathcal{G}_0(\vec{k})$ are the symmetric and antisymmetric representation. For this point, the matrices representing the elements of the space group $\mathcal{G}$ are given by

$$k = 0: \quad D(\{\epsilon|\vec{R}_n\}) = D_{11}(\{\epsilon|\vec{R}_n\}) = +1; \quad D(\{i|\vec{R}_n\}) = D_{11}(\{i|\vec{R}_n\}) = \pm 1 \text{ (for all } \vec{R}_n) \tag{5-126}$$

We thus have two irreducible representations of the space group for this point corresponding to the two choices of signs in (5-126).

Consider now any other interior point in the Brillouin zone. From the remark at the end of part B of this section all we need consider are the points in the right-hand side of the Brillouin zone. For these points the group of the $\vec{k}$-vector consists only of the group of pure translations, $\mathcal{T}$, since for these points $e^{-i\vec{k}\cdot\vec{R}_n} \neq e^{i\vec{k}\cdot\vec{R}_n}$. Using the notations of Eq. (5-122) we have $D_{11}(\{\varepsilon|\vec{R}_n\}) = e^{i2\pi k_1 n}$. Resolving $\mathcal{G}$ into its left cosets with respect to $\mathcal{K}$ we obtain $\mathcal{G} = \mathcal{T} + \{i|0\}\mathcal{T}$. The pure translations are represented by the diagonal matrices

$$D(\{\varepsilon|\vec{R}_n\}) = \begin{pmatrix} e^{i2\pi k_1 n} & 0 \\ 0 & e^{-i2\pi k_1 n} \end{pmatrix} \tag{5-127}$$

For the matrix representing the element $\{i|0\}$ we must see how the cosets go into one another under the operator $\{i|0\}$. It is clear that the first coset goes into the second and the second goes into the first. From this we learn that the only non vanishing block in the first column is the second and that the only non vanishing block in the second column is the first. We must now find which of the matrices $D_{11}(\{\beta|\vec{b}\})$ for $\{\beta|\vec{b}\}$ in $\mathcal{K}$ go into these non vanishing blocks. (In this case $\mathcal{K}$ is $\mathcal{T}$ and D_{11} has dimension 1.) We know that the non vanishing block in the first column is the unit matrix since $\{i|0\}$ is the element which takes the group $\mathcal{T}$ into the left coset $\{i|0\}\mathcal{T}$. In the second column, in order to find which matrix $D_{11}(\{\beta|\vec{b}\})$ for $\{\beta|\vec{b}\}$ in $\mathcal{K}$ goes into the first position we must solve the relation (5-120) which in this case becomes

$$\{i|0\}\{i|0\} = \{\varepsilon|0\}\{\beta|\vec{b}\} \tag{5-128}$$

Clearly $\{\beta|\vec{b}\} = \{\varepsilon|0\}$ and therefore for the matrix representing $\{i|0\}$ we have

$$D(\{i|0\}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \tag{5-129}$$

By multiplication of (5-127) and (5-129) we obtain the matrices representing $\{i|\vec{R}_n\}$.

$$D(\{i|\vec{R}_n\}) = \begin{pmatrix} 0 & e^{i2\pi k_1 n} \\ e^{-i2\pi k_1 n} & 0 \end{pmatrix} \tag{5-130}$$

The only remaining $\vec{k}$-value which we must discuss in order to complete our enumeration of the irreducible representations of this space group is the point $k_1 = +1/2$. For this point $e^{i\vec{k}\cdot\vec{R}_n} = e^{-i\vec{k}\cdot\vec{R}_n}$, the group of the $\vec{k}$-vector is the entire group $\mathcal{G}$. Once again $\mathcal{G}_o(\vec{k})$ is the group consisting of ϵ and i. This is the case of a point on the boundary of a Brillouin zone for a space group without non primitive translations. Thus, we can again use Eq. (5-122) to determine the irreducible representations. We therefore obtain in this case for the matrices representing the elements of the group

$$D(\{\epsilon|\vec{R}_n\}) = D_{11}(\{\epsilon|\vec{R}_n\}) = e^{i\pi n}(1) \qquad D(\{i|\vec{R}_n\}) = D_{11}(\{i|\vec{R}_n\}) = e^{i\pi n}(\pm 1) \tag{5-131}$$

The two signs in (5-130) specify the two possible representations of the space group at this point corresponding to the symmetric and antisymmetric representations of the group $\mathcal{G}_o(\vec{k})$. Thus, for the one-dimensional space group $\mathcal{T} + \{i|0\}$ we see that for $\vec{k} = 0$ we have two one-dimensional representations. For $\vec{k} \neq 0$ and not on the boundary of the Brillouin zone we have two-dimensional representations and for the boundary point we have again two one-dimensional representations.

As our final example we shall find the irreducible representations of the space group generated by $\{C_3|0\}$, $\{\sigma_1|0\}$ $\{\epsilon|\vec{R}_n\}$ where $\vec{R}_n$ is a translation of Γ_5 and

$$\vec{t}_1 = \begin{pmatrix} t \\ 0 \end{pmatrix}; \quad \vec{t}_2 = \begin{pmatrix} 1/2\ t \\ 3/2\ t \end{pmatrix}.$$

This group is illustrated in Fig. 5-21. We have already illustrated the Brillouin zone in Fig. 5-25 but we repeat it in Fig. 5-27 in order to illustrate some special points in the Brillouin zone. We recall that the point group of this space group consists of the operators E; the identity; C_3 and C_3^2: rotation through 120^o and 240^o clockwise; σ_1 reflection through the x axis; σ_2 reflection through an axis inclined at 60^o with respect to the positive x axis; and σ_3 a reflection through an axis inclined at -60^o with respect to the positive x axis. By the discussion at the end of part B of this section all we need consider to obtain all irreducible representations of the space groups are the points of k-space which are in or on the triangle Γ Z X. We notice that the space group under consideration is one of the type without non primitive translations. We can, therefore, use the method of Eq. (5-122) to find all the irreducible representations of the group of the $\vec{k}$-vector for boundary as well as interior points. We shall now discuss all possible points in the region Γ ZX and describe their irreducible representations.

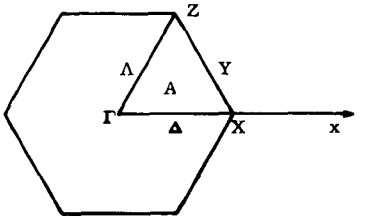


Fig. 5-27

Γ: For this point the group of the $\vec{k}$-vector is the entire group since $e^{i\beta\vec{k}\cdot\vec{R}_n} = 1$ for all $\vec{R}_n$ and all β since $\vec{k} = 0$. Thus, the matrices representing the elements of the group are

$$D(\{\beta|\vec{R}_n\}) = D_{11}(\{\beta|\vec{R}_n\}) = \Gamma_i(\beta) \tag{5-132}$$

where $\Gamma_i(\beta)$ is an irreducible representation of the group C_{3v} which in this case is the group $\mathcal{G}_o(\vec{k})$. In (5-133), we have listed the characters of the irreducible representations of the group C_{3v} and these correspond directly to the characters of the operators in the space group through the use of (5-132)

	E	C_3, C_3^2	$\sigma_1, \sigma_2, \sigma_3$
Γ_1	1	1	1
Γ_2	1	1	-1
Γ_3	2	-2	0

(5-133)

A: A is a general point inside of the Brillouin zone. The group of $\vec{k}$-vector consist of the group of pure translations $\mathcal{T}$. This group, of course, has nothing but the one-dimensional irreducible representation $e^{i\vec{k}\cdot\vec{R}_n}$. Dividing $\mathcal{G}$ into its cosets we obtain

$$\mathcal{G} = \mathcal{T} + \{C_3|0\}\mathcal{T} + \{C_3^2|0\}\mathcal{T} + \{\sigma_1|0\}\mathcal{T} + \{\sigma_2|0\}\mathcal{T} + \{\sigma_3|0\}\mathcal{T} \tag{5-134}$$

For simplicity let us denote E by a_1; C_3 by a_2, etc. If we do this, then it is quite easy to find the matrix representing an operator $\{a_i|0\}$. Consider the j^{th} column of the matrix representing $\{a_i|0\}$. The only non vanishing element in this column will be the k^{th} element for which $a_k = a_i a_j$. The matrix representing an element $\{\beta|\vec{R}_n\}$ of the group of the wave vector which will appear here is just given by the solution of the equation

$$\{a_i|0\}\{a_j|0\} = \{a_k|0\}\{\beta|\vec{R}_n\} \tag{5-135}$$

Clearly $\beta = \varepsilon$ and $\vec{R}_n = 0$. Therefore in the j^{th} column of the matrix representing $\{a_i|0\}$ the only non vanishing element will be the k^{th} for which $a_i a_j = a_k$. In this position will occur a 1. Thus, the matrix representing the element $\{a_i|0\}$ will just be a matrix with a single 1 in any row or column. (This is, of course nothing more than the regular representation of the group C_{3v}.) The matrix representing $\{\sigma_1|0\}$

$$D(\{\sigma_1|0\}) = \begin{pmatrix} 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix} \tag{5-136}$$

The matrix representing $\{\varepsilon|\vec{R}_n\}$ would be

$$D(\{\varepsilon|\vec{R}_n\}) = \begin{pmatrix} e^{ia_1\vec{k}\cdot\vec{R}_n} & & & & & \\ & e^{ia_2\vec{k}\cdot\vec{R}_n} & & & 0 & \\ & & e^{ia_3\vec{k}\cdot\vec{R}_n} & & & \\ & & & e^{ia_4\vec{k}\cdot\vec{R}_n} & & \\ & 0 & & & e^{ia_5\vec{k}\cdot\vec{R}_n} & \\ & & & & & e^{ia_6\vec{k}\cdot\vec{R}_n} \end{pmatrix} \tag{5-137}$$

all the remaining matrices in the representation can be obtained by multiplication of (5-137) by one of the matrices representing $\{a_i|0\}$.

Δ: The only operators in $\mathcal{K}$ are $\{\varepsilon|\vec{R}_n\}$ and $\{\sigma_1|\vec{R}_n\}$ for all $\vec{R}_n$. Thus the group $\mathcal{G}_o(\vec{k})$ is the group consisting of ε, σ_1 which has an antisymmetric and a symmetric representation which we may label Δ_1 and Δ_2. The matrices $D_{11}(\{\beta|\vec{b}\}$ for $\{\beta|\vec{b}\}$ in $\mathcal{K}$ have been given by (5-122). Here $\Gamma(\beta)$ must be either Δ_1 or Δ_2, i.e., $\Gamma(\varepsilon) = 1$, $\Gamma(\sigma_1) = \pm 1$. The characters of the operators in $\mathcal{G}_o(\vec{k})$ are given in (5-138)

	ε	σ_1
Δ_1	1	1
Δ_2	1	-1

(5-138)

Decomposing $\mathcal{G}$ into its cosets we obtain

$$\mathcal{G} = \mathcal{K} + \{C_3|0\}\mathcal{K} + \{C_3^2|0\}\mathcal{K} \tag{5-139}$$

Let us illustrate a matrix in this irreducible representation by finding the matrix representing $\{\sigma_1|0\}$. Using the notation introduced earlier $C_3 = a_2$; $C_3^2 = a_3$ the

only non vanishing block in the first column will be the first since $\{\sigma_1|0\}$ is in the group of the wave vector. The matrix element which will appear here will be ± 1 depending on whether we choose Δ_1 or Δ_2. In the second column, we have $\{\sigma_1|0\}\{C_3|0\} = \{C_3^2|0\}\{\sigma_1|0\}$ and therefore the non vanishing element in this column is the third and the matrix appearing here is $D_{11}(\{\sigma_1|0\})$ which is again ± 1. For the third column we have $\{\sigma_1|0\}\{C_3^2|0\} = \{C_3|0\}\{\sigma_1|0\}$. Thus here the non vanishing element is the second for which we have again ± 1. Thus the matrix representing $\{\sigma_1|0\}$ is

$$D(\{\sigma_1|0\}) = \begin{pmatrix} \pm 1 & 0 & 0 \\ 0 & 0 & \pm 1 \\ 0 & \pm 1 & 0 \end{pmatrix} \tag{5-140}$$

The signs depend on whether we choose Δ_1 or Δ_2 as the representation of $\mathcal{G}_o(\vec{k})$.

Λ: The argument is identical with the point Δ if we replace σ_1 by σ_2.

Y: For this point σ_3 sends $\vec{k}$ into a point on the opposite side of the hexagon. These two points differ by a lattice vector of $\vec{k}$-space namely $\vec{b}_1 + \vec{b}_2$. In this case the group $\mathcal{G}_o(\vec{k})$ is ϵ, σ_3 and the argument runs along the same lines as that for Δ and Λ.

X: For this $\vec{k}$ value all the operators of the point group either send X into X or one of the other points marked by an X. Since all these points differ by lattice vectors of $\vec{k}$-space, the group $\mathcal{K}$ is the same as $\mathcal{G}$ and $\mathcal{G}_o(\vec{k})$ is $\mathcal{G}_o$ or C_{3v}. We can find the irreducible representations by (5-122)

$$D(\{\beta|\vec{R}_n\}) = D_{11}(\{\beta|\vec{R}_n\}) = e^{i\vec{k}\cdot\vec{R}_n}\Gamma_i(\beta) \tag{5-141}$$

Here $\Gamma_i(\beta)$ is the i^{th} irreducible representation of C_{3v} and $\vec{k}$ is the $\vec{k}$-value of the point X. The irreducible representations of C_{3v} are already listed in (5-133).

Z: The argument for this point is the same as that for the point X.

To sum up the situation is as follows. For a general point, A, in the Brillouin zone we have a six-dimensional representation of the space group. For the points Γ, X, and Z we have two one-dimensional representations of the space group and one two-dimensional representation. For the points Y, Λ, Δ, we have two three-dimensional representations of the space group corresponding to each of the points.