Chapter 2
Group Theory

The formal mathematical treatment of the symmetry of physical systems discussed in Chap. 1 is called *group theory*. This chapter summarizes the fundamental properties of group theory that will be used to treat physical examples of symmetry in the succeeding chapters. This book is focused on the practical use of group theory and does not attempt to cover derivations of the fundamental postulates or advanced aspects of this topic. For a rigorous treatment of group theory the reader is referred to [1].

A group is defined as a collection of elements that obey certain criteria and are related to each other through a specific rule of interaction. The rule of interaction is referred to generically as the "multiplication" of two elements. However, the interaction may not be the normal multiplication of two numbers since the elements of a group may not be simple numbers. The number of elements in group h is called the *order of the group*. There are four requirements for a set of elements to form a group:

1. One element, designated E and called the identity element, commutes with all the other elements of the group and multiplication of an element by E leaves the element unchanged. That is, $EA=AE=A$.
2. The result of multiplying any two elements in a group (including the product of an element with itself) is an element of the group. That is, $AB=C$ where A, B, and C are all elements of the group.
3. Every element of the group must have a reciprocal element that is also an element of the group. That is, $AR=RA=E$ where A is an element of the group, R is its reciprocal, and E the identity element and R and E are both members of the group.
4. The associative law of multiplication is valid for the product of any three elements of the group. That is, $A(BC)=(AB)C$.

It is not necessary for the products of elements of a group to obey the commutative law. That is, the element resulting in the product AB may not be the same as the element resulting in the product BA. If the elements of a specific group happen to obey the commutative law the group is said to be *Abelian*.

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Group multiplication Table

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

The properties of a group discussed above can be exemplified in a group multiplication table. Consider a group consisting of six elements represented by the letters A, B, C, D, E, and F that obey the multiplication table shown above. The elements in the table are the product of the element designating its column and the element designating its row. Following this convention, the table shows that the identity element is a member of the group, the product of any two elements is an element of the group, and each group element has an element in the group that is its inverse. Each element appears only once in any given row or column. The associative law holds but the commutative law does not hold for all products so the group is not Abelian. The order of the group is 6.

The multiplication table is useful in identifying subgroups within the whole group. These are subsets of the total set of group elements that meet the requirements of being a group without requiring the other elements of the total group. By inspection, it can be seen that the elements D, E, and F form a subgroup of order 3. Also there are three subgroups of order 2: E,A; E,B; and E,C. Of course the element E by itself always forms a subgroup of order 1. Note that the orders of the subgroups are integral factors of the order of the total group.

Another useful concept in dealing with a group is organizing its elements in conjugate pairs through the use of a similarity transformation. To find the conjugate of an element A, the triple product of A with another element of the group and its reciprocal element is formed. For example,

$$B = X^{-1}AX.$$

This type of product is a similarity transformation, and the elements A and B are said to be conjugates of each other. Every element is conjugate with itself. Also, if A is conjugate with two elements B and C then B and C are conjugate with each other. A complete set of elements that are conjugate to each other form a *class* of the group.

From the multiplication table of the group of elements A, B, C, D, E, F shown above, it is easily seen that E by itself forms a class of order 1. The elements A, B, C form a class of order 3. This can be seen by taking all possible similarity transformations on element A, which gives

$$E^{-1}AE = A, \quad A^{-1}AA = A, \quad B^{-1}AB = C, \quad C^{-1}AC = B, \quad D^{-1}AD = B,$$
$$F^{-1}AF = C,$$

and then doing the same for elements B and C. Similarly, taking all possible similarity transformations on elements D and F show that they form a class of order 2. Note that it is always true that the order of a class is an integral factor of the order of the group.

The type of group of interest here is a *symmetry group*. The elements of this type of group are a complete set of relevant symmetry operations that obey the rules of a group. The specific symmetry groups of interest are those defining the crystal classes discussed in Chap. 1.

2.1 Basic Concepts of Group Theory

The basic concepts of group theory can be demonstrated by considering the spatial symmetry of an object with a specific geometrical shape. The way such an object is transformed by operations about a specific point in space is referred to as *point group* symmetry. The symmetry operations for point groups include rotations about axes, reflections through planes, inversion through a central point, and combinations of these.

By convention, different types of symmetry elements have specific designations [1–4]. To reiterate the designations listed in Chap.1, the identity operation, describing the situation where no transformation takes place, is designated as E. Rotation about an axis of symmetry is designated by C_n which indicates that the object is spatially identical after a rotation of $2\pi/n$ about this axis. For example, a rotation of 180° is represented by the twofold symmetry operation C_2 while a fourfold symmetry axis C_4 represents a rotation of 90°. Since n rotations of C_n take the object back to its original position, $C_n^n = E$. If a reflection plane is perpendicular to the highest order symmetry axis, it is designated by σ_h. If the reflection plane contains the highest order symmetry axis, it is designated by σ_v. Mirror planes diagonal to the rotation axes are designated as σ_d. Mirror operations take twice result in E. For an object possessing a center of symmetry, the inversion operation is designated by i and $i^2{=}E$. There are also combined operations. For example the inversion operation is a combined rotation and reflection, $i{=}C_2\sigma_h$. A combined rotation–reflection operation with the mirror plane perpendicular to the rotation axis is called an improper rotation and designated by S_n. Thus, $S_n{=}\sigma_h C_n$. The order of successive symmetry operations is important since not all of them commute.

As discussed above, it is convenient to organize the elements of a group into *classes* where all elements in the same class are related to each other by a unitary transformation of another operator of the group. For example, if $T^{-1}AT = A'$ where all of these are elements of the group, A and A' are members of the same class. As stated before, the order of a class must be an integral factor of the order of the group.

The action of the elements of a symmetry group on the physical properties of a system is described in terms of mathematical transformations. The physical properties may be expressed as vectors, matrices, or tensors of higher rank as discussed in

Chap. 3. These form vector spaces, and their transformations in this vector space are the image of the symmetry transformations in coordinate space. For example, the state vectors of a quantum mechanical system transform into each other in the same way as the symmetry transformations of the coordinates describing the system. When the mathematical description of the physical properties of a system transform in the same way as a symmetry group, they are said to be a *representation* of that group. The symmetry elements act as linear operators to produce transformations in a specific representation of the group. A group will have a number of different types of representations associated with different physical properties.

Every group has a one-dimensional *trivial representation* consisting of assigning the number one to all elements of the group. In general, a set of matrices of a specific dimension are assigned to the elements of the group to make a representation of the group. These matrices must obey the same multiplication table as the elements of the group. The matrix of a representation is square and the number of elements in a row or column is the *dimension* of the representation, which is equal to its degeneracy. It is possible to construct many different representations of this type for the same group.

It is always possible to find a similarity transformation that puts a matrix into a box diagonal form

$$A' = T'AT = \begin{pmatrix} [A_1] & & 0 \\ & [A_2] & \\ 0 & & [A_3] \end{pmatrix}. \tag{2.1}$$

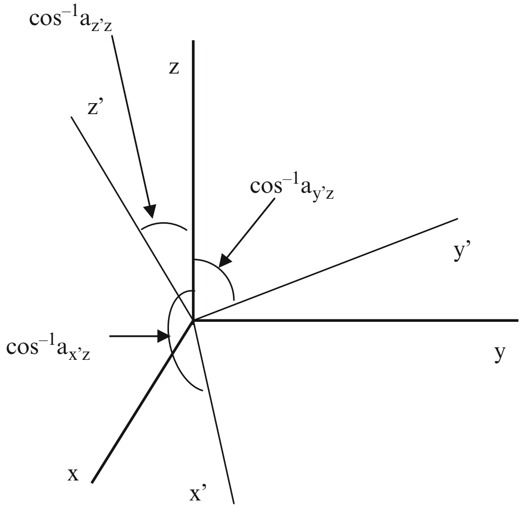
In this case A and A' are matrices representing *reducible representations* while the A_i are matrices represent *irreducible representations*. The sum of the squares of the dimensions of the irreducible representations of a group is equal to the order of the group:

$$\sum_{\mathrm{i}} d_i^2 = h. \tag{2.2}$$

The number of irreducible representations of a group is equal to the number of classes in the group.

The spatial position of an object is represented by vectors in Cartesian coordinates. A transformation of the object can be represented by a transformation of these coordinate vectors. The object moves from a vector position designated by the coordinates (x,y,z) to a new position designated by the coordinates (x', y', z') as shown in Fig. 2.1. Any vector $\mathbf{r}$ can be expressed in terms of its Cartesian coordinates using the unit vectors, $\hat{\mathbf{x}}, \hat{\mathbf{y}}$, and $\hat{\mathbf{z}}$. A transformation operation can then be applied to each component and the new components recombined to give the transformed vector $\mathbf{r}'$. If a rotation about the major symmetry axis (usually taken to be the z-axis) is designated by an angle θ, the transformation is given as

Fig. 2.1 Transformation of Cartesian coordinates



$$\begin{aligned} x' &= x\cos\theta + y\sin\theta \\ y' &= -x\sin\theta + y\cos\theta\,. \\ z' &= z \end{aligned} \tag{2.3}$$

In matrix form this coordinate transformation is written as

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \overset{\rightharpoonup}{\overset{\rightharpoonup}{\mathbf{A}}} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} a_{x'x} & a_{x'y} & a_{x'z} \\ a_{y'x} & a_{y'y} & a_{y'z} \\ a_{z'x} & a_{z'y} & a_{z'z} \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}. \tag{2.4}$$

The matrix elements $a_{i'j}$ are the direction cosines of the coordinate represented by i' with respect to the coordinate represented by j as shown in Fig. 2.1. For the example of a rotation about the z-axis given by (2.3) the transformation matrix is

$$\overset{\rightharpoonup}{\overset{\rightharpoonup}{\mathbf{A}}}(\mathbf{C}_{\theta(z)}) = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{2.5}$$

A symmetry operation consisting of a mirror reflection plane perpendicular to the z-axis would be represented by the matrix

$$\overset{\rightharpoonup}{\overset{\rightharpoonup}{\mathbf{A}}}(\sigma_h) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}, \tag{2.6}$$

so that the transformation is

$$\begin{aligned} x' &= x \\ y' &= y \\ z' &= -z. \end{aligned} \tag{2.7}$$

Every element of a symmetry group can be represented by a transformation matrix such as the examples given in (2.5) and (2.6).

In the mathematical manipulation of matrices, one useful property is the sum of the diagonal elements which is called the *trace* of the matrix. In the examples of the two transformation matrices given above,

$$\mathbf{Tr}\vec{\vec{\mathbf{A}}}(\mathrm{C}_{\theta(\mathrm{z})}) = \sum_i a_{ii} = 2\cos\theta + 1 \tag{2.8}$$

and

$$\mathbf{Tr}\vec{\vec{\mathbf{A}}}(\sigma_h) = \sum_{ii} a_{ii} = 1. \tag{2.9}$$

The trace of a transformation matrix representing a symmetry operation is called the *character* of the operation in that representation and is designated by χ.

Characters of matrix operators have special properties that make them useful working with group theory.

1. Since the trace of a matrix is invariant under a similarity transformation, all symmetry operations belonging to the same class of the group have the same character.
2. The character of a reducible representation is equal to the sum of the characters of the irreducible representations that it contains.
3. The number of times that a specific irreducible representation is contained in the reduction of a reducible representation can be determined by

$$n^{(i)} = \frac{1}{h}\sum_A \chi_A^{(i)} \chi_A. \tag{2.10}$$

   Here $\chi_A^{(\mathrm{i})}$ is the character of the operation A in the ith irreducible representation while χ_A is the character of the same operation in the reducible representation. The sum is over all of the symmetry operations of the group of order h.
4. For any irreducible representation, the sum of the squares of the characters of all the operations equals the order of the group

$$\sum_A \chi_i^2(A) = h. \tag{2.11}$$

5. The set of characters for two different irreducible representations are orthogonal

$$\sum_A \chi_i(A)\chi_j(A) = 0, \quad i \neq j. \tag{2.12}$$

6. The *direct product* of two representations is found by multiplying the characters of a specific operation in these two representations to give the character of that operation in the product representation. A direct product representation is usually a reducible representation of the group.

Another important property of transformation matrices is that irreducible representations are orthogonal and obey the relationship

$$\sum_A [\Gamma_i(A)_{mn}]\left[\Gamma_j(A)_{m'n'}\right]^* = \frac{h}{\sqrt{d_i d_j}}\delta_{ij}\delta_{mm'}\delta_{nn'}. \tag{2.13}$$

Here $\Gamma_i(A)_{mn}$ is the mn matrix element of the transformation matrix for operation A in the Γ_i irreducible representation.

Each representation of a symmetry group operates on a set of functions that transform into each other under that representation of the group. These are *called basis functions* for that representation. For physical systems they represent a specific physical property of the system. In the example of the coordinate transformation discussed above, the vector coordinates x, y, and z are the set of basis functions. Any property described by a vector will transform like this set of basis functions according to the representation of the group of symmetry elements for the system. The rotation axes R_x, R_y, and R_z can also act as a set of basis functions for irreducible representations of a group. These differ from the spatial coordinates because a symmetry operation may change the direction of rotation. A third common set of basis functions are the six components of a pseudovector arising from a vector product. These basis functions are discussed in the examples given below, and in Chap. 4 it is shown how spherical harmonic functions can also be used as basis functions.

2.2 Character Tables

A *character table* for a symmetry group lists the characters for each class of operations in the group for each of the irreducible representations of the group. The character tables for each of the 32 crystallographic point groups discussed in Chap. 1 are given in Tables 2.1–2.32. These are very useful in the application of group theory to determine the properties of crystals [4–6].

Table 2.1 Character table for point group C_1

C_1	E
A	1

Table 2.2 Character table for point group C_s

C_s	E	σ_h	Basis components		
A'	1	1	$x,y,$	R_z	x^2,y^2z^2,xy
A''	1	−1	$z,$	R_x,R_y	yz,xz

Table 2.3 Character table for point group C_i

C_i	E	i	Basis components		
A_g	1	1		R_x,R_y,R_z	x^2,y^2,z^2,xy,xz,yz
A_u	1	−1	x,y,z		

Table 2.4 Character table for point group for C_2

C_2	E	C_2	Basis components		
A	1	1	z	R_z	$x^2,y^2,z^2,\ xy$
B	1	−1	x,y	R_x,R_y	yz,xz

Table 2.5 Character table for point group C_{2h}

C_{2h}	E	C_2	i	σ_h	Basis components		
A_g	1	1	1	1		R_z	$x^2,y^2,z^2,\ xy$
B_g	1	−1	1	−1		R_x,R_y	yz,xz
A_u	1	1	−1	−1	z		
B_u	1	−1	−1	1	x,y		

Table 2.6 Character table for point group C_{2v}

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$	Basis components		
A_1	1	1	1	1	z		x^2,y^2,z^2
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xy
B_2	1	−1	−1	1	y	R_x	yz

Table 2.7 Character table for point group D_2

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	Basis components		
A	1	1	1	1			x^2,y^2,z^2
B_1	1	1	−1	−1	z	R_z	xy
B_2	1	−1	1	−1	y	R_y	xz
B_3	1	−1	−1	1	x	R_x	yz

Table 2.8 Character table for point group D_{2h}

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Basis components		
A_g	1	1	1	1	1	1	1	1			x^2,y^2,z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1		R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1		R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1		R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1			
B_{1u}	1	1	−1	−1	−1	−1	1	1	z		
B_{2u}	1	−1	1	−1	−1	1	−1	1	y		
B_{3u}	1	−1	−1	1	−1	1	1	−1	x		

Table 2.9 Character table for point group C_4

C_4	E	C_4	C_2	C_4^3	Basis components		
A	1	1	1	1	z	R_z	x^2+y^2,z^2
B	1	−1	1	−1			x^2-y^2,xy
E*	2	0	−2	0	(x,y)	(R_x,R_y)	(yz,xz)

Table 2.10 Character table for point group C_{4h}

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4	Basis components		
A_g	1	1	1	1	1	1	1	1		R_z	x^2+y^2,z^2
B_g	1	−1	1	−1	1	−1	1	−1			x^2-y^2,xy
E_g*	2	0	−2	0	2	0	−2	0		(R_x,R_y)	(yz,xz)
A_u	1	1	1	1	−1	−1	−1	−1	z		
B_u	1	−1	1	−1	−1	1	−1	1			
E_u*	2	0	−2	0	2	0	−2	0	(x,y)		

Table 2.11 Character table for point group C_{4v}

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	Basis components		
A_1	1	1	1	1	1	z		x^2+y^2,z^2
A_2	1	1	1	−1	−1		R_z	
B_1	1	−1	1	1	−1			x^2-y^2
B_2	1	−1	1	−1	1			xy
E	2	0	−2	0	0	(x,y)	(R_x,R_y)	(yz,xz)

Table 2.12 Character table for point group S_4

S_4	E	S_4	C_2	S_4^3	Basis components		
A	1	1	1	1		R_z	x^2+y^2,z^2
B	1	−1	1	−1	z		x^2-y^2,xy
E*	2	0	−2	0	(x,y)	(R_x,R_y)	(yz,xz)

Table 2.13 Character table for point group D_4

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	Basis components		
A_1	1	1	1	1	1			x^2+y^2,z^2
A_2	1	1	1	−1	−1	z	R_z	
B_1	1	−1	1	1	−1			x^2-y^2
B_2	1	−1	1	−1	1			xy
E	2	0	−2	0	0	(x,y)	(R_x,R_y)	(yz,xz)

Table 2.14 Character table for point group D_{4h}

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	Basis components		
A_{1g}	1	1	1	1	1	1	1	1	1	1			x^2+y^2,z^2
A_{2g}	1	1	1	−1	−1	1	1	1	−1	−1		R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1			x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1			xy
E_g	2	0	−2	0	0	2	0	−2	0	0		(R_x,R_y)	(yz,xz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1			
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z		
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1			
B_{2u}	1	1	1	−1	1	−1	1	−1	1	−1			
E_u	2	0	−2	0	0	−2	0	2	0	0	(x,y)		

Table 2.15 Character table for point group D_{2d}

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$	R	$2RS_4$	RC_2	$2RC_2'$	$2R\sigma_d$	Basis components		
A_1	1	1	1	1	1	1	1	1	1	1			x^2+y^2,z^2
A_2	1	1	1	−1	−1	1	1	1	−1	−1		R_z	
B_1	1	−1	1	1	−1	1	−1	1	1	−1			x^2-y^2
B_2	1	−1	1	−1	1	1	−1	1	−1	1	z		xy
E	2	0	−2	0	0	2	0	−2	0	0	(x,y)	(R_x,R_y)	(yz,xz)
$D_{1/2}$	2	$\sqrt{2}$	0	0	0	−2	$-\sqrt{2}$	0	0	0			
${}_2S$	2	$-\sqrt{2}$	0	0	0	−2	$\sqrt{2}$	0	0	0			

Table 2.16 Character table for point group C_3

C_3	E	C_3	C_3^2	Basis components		
A	1	1	1	z	R_z	x^2+y^2,z^2
E*	2	−1	−1	(x,y)	(R_x,R_y)	$(x_2-y_2,xy)(yz,xz)$

Table 2.17 Character table for point group C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components		
A_1	1	1	1	z		x^2+y^2,z^2
A_2	1	1	−1		R_z	
E	2	−1	0	(x,y)	(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$

Table 2.18 Character table for point group C_{3h}

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5	Basis components		
A'	1	1	1	1	1	1		R_z	x^2+y^2,z^2
E'*	2	−1	−1	2	−1	−1	(x,y)		(x^2-y^2,xy)
A''	1	1	1	−1	−1	−1	z		
E''*	2	−1	−1	−2	1	1		(R_x,R_y)	(yz,xz)

Table 2.19 Character table for point group D_3

D_3	E	$2C_3$	$3C_2$	Basis components		
A_1	1	1	1			x^2+y^2,z^2
A_2	1	1	−1	z	R_z	
E	2	−1	0	(x,y)	(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$

Table 2.20 Character table for point group D_{3d}

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3\sigma_d$	Basis components		
A_{1g}	1	1	1	1	1	1			x^2+y^2,z^2
A_{2g}	1	1	−1	1	1	−1		R_z	
E_g	2	−1	0	2	−1	0		(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$
A_{1u}	1	1	1	−1	−1	−1			
A_{2u}	1	1	−1	−1	−1	1	z		
E_u	2	−1	0	−2	1	0	(x,y)		

Table 2.21 Character table for point group S_6

S_6	E	C_3	C_3^2	i	S_6^5	S_6	Basis components		
A_g	1	1	1	1	1	1		R_z	x^2+y^2,z^2
E_g^*	2	−1	−1	2	−1	−1		(R_x,R_y)	$(x^2-y^2,xy)(yz,xz)$
A_u	1	1	1	−1	−1	−1	z		
E_u^*	2	−1	−1	−2	1	1	(x,y)		

Table 2.22 Character table for point group C_6

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5	Basis components		
A	1	1	1	1	1	1	z	R_z	x^2+y^2,z^2
B	1	−1	1	−1	1	−1			
E_1^*	2	1	1	−2	1	1	(x,y)	(R_x,R_y)	(xz,yz)
E_2^*	2	−1	1	2	1	−1			(x^2-y^2,xy)

Table 2.23 Character table for point group C_{6h}

C_{6h}	E	C_6	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3	Basis components		
A_g	1	1	1	1	1	1	1	1	1	1	1	1		R_z	x^2+y^2,z^2
B_g	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1			
E_{1g}^*	2	1	−1	−2	−1	1	2	1	−1	−2	−1	1		(R_x,R_y)	(xz,yz)
E_{2g}^*	2	−1	−1	2	−1	−1	2	−1	−1	2	−1	−1			(x^2-y^2,xy)
A_u	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	z		
B_u	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1			
E_{1u}^*	2	1	−1	−2	−1	1	−2	−1	1	2	1	−1	(x,y)		
E_{2u}^*	2	−1	−1	2	−1	−1	−2	1	1	−2	1	1			

Table 2.24 Character table for point group C_{6v}

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$	Basis components		
A_1	1	1	1	1	1	1	z		x^2+y^2,z^2
A_2	1	1	1	1	−1	−1		R_z	
B_1	1	−1	1	−1	1	−1			
B_2	1	−1	1	−1	−1	1			
E_1	2	1	−1	−2	0	0	(x,y)	(R_x,R_y)	(xz,yz)
E_2	2	−1	−1	2	0	0			(x^2-y^2,xy)

Table 2.25 Character table for point group D_6

D_6	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	Basis components		
A_1	1	1	1	1	1	1			x^2+y^2,z^2
A_2	1	1	1	1	−1	−1	z	R_z	
B_1	1	−1	1	−1	1	−1			
B_2	1	−1	1	−1	−1	1			
E_1	2	1	−1	−2	0	0	(x,y)	(R_x,R_y)	(xz,yz)
E_2	2	−1	−1	2	0	0			(x^2-y^2,xy)

Table 2.26 Character table for point group D_{6h}

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Basis components		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1			x^2+y^2,z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1		R_z	
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1			
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1			
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0		(R_x,R_y)	(xz,yz)
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0			(x^2-y^2,xy)
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1			
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z		
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1			
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1			
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	(x,y)		
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0			

Table 2.27 Character table for point group D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$	Basis components		
A_1'	1	1	1	1	1	1			x^2+y^2,z^2
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x,y)		(x^2-y^2,xy)
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x,R_y)	(xz,yz)

Table 2.28 Character table for point group T

T	E	$3C_2$	$4C_3$	$4C_3^2$	Basis Components		
A	1	1	1	1			z^2
E*	2	2	−1	−1			x^2+y^2, x^2-y^2
T	3	−1	0	0	(x,y,z)	(R_x,R_y,R_z)	(xz,yz, xy)

Table 2.29 Character table for point group T_h

T_h	E	$3C_2$	$4C_3$	$4C_3^2$	i	$3\sigma_h$	$4iC_3$	$4iC_3^2$	Basis Components	
A_g	1	1	1	1	1	1	1	1		$x^2+y^2+z^2$
E_g^*	2	2	−1	−1	2	2	−1	−1		$(2z^2-x^2-y^2, x^2-y^2)$
T_g	3	−1	0	0	3	−1	0	0	(R_x, R_y, R_z)	xz, yz, xy
A_u	1	1	1	1	−1	−1	−1	−1		
E_u^*	2	2	−1	−1	−2	−2	1	1		
T_u	3	−1	0	0	−3	1	0	0	(x, y, z)	

Table 2.30 Character table for point group T_d

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Basis components		
A_1	1	1	1	1	1			$x^2+y^2+z^2$
A_2	1	1	1	−1	−1			
E	2	−1	2	0	0			$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1	1	(x, y, z)		(xz, yz, xy)

Table 2.31 Character table for point group O

O	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	Basis components		
A_1	1	1	1	1	1			$x^2+y^2+z^2$
A_2	1	1	−1	−1	1			
E	2	−1	0	0	2			$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(x, y, z)	(R_x, R_y, R_z)	
T_2	3	0	1	−1	−1			(xz, yz, xy)

Table 2.32 Character table for point group O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Basis components
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1	
E_g	2	−1	0	0	2	2	0	−1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1	(xz, yz, xy)
$D_{1/2g}$	2	1	0	$\sqrt{2}$	0	2	$\sqrt{2}$	1	0	0	
${}_2S_g$	2	1	0	$-\sqrt{2}$	0	2	$-\sqrt{2}$	1	0	0	
$D_{3/2g}$	4	−1	0	0	0	4	0	−1	0	0	
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1	
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1	
E_u	2	−1	0	0	2	−2	0	1	−2	0	
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1	
$D_{1/2u}$	2	1	0	$\sqrt{2}$	0	−2	$-\sqrt{2}$	−1	0	0	
${}_2S_u$	2	1	0	$-\sqrt{2}$	0	−2	$\sqrt{2}$	−1	0	0	
$D_{3/2u}$	4	−1	0	0	0	−4	0	1	0	0	

Table 2.32 Character table for point group O_h (continued)

O_h	R	$8RC_3$	$6RC_2$	$6RC_4$	$3RC_4^2$	Ri	$6RS_4$	$8RS_6$	$3R\sigma_h$	$6R\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
$D_{1/2g}$	−2	−1	0	$-\sqrt{2}$	0	−2	$-\sqrt{2}$	−1	0	0
$_2S_g$	−2	−1	0	$\sqrt{2}$	0	−2	$\sqrt{2}$	−1	0	0
$D_{3/2g}$	−4	1	0	0	0	−4	0	1	0	0
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1
$D_{1/2u}$	−2	−1	0	$-\sqrt{2}$	0	2	$\sqrt{2}$	1	0	0
$_2S_u$	−2	−1	0	$\sqrt{2}$	0	2	$-\sqrt{2}$	1	0	0
$D_{3/2u}$	−4	1	0	0	0	4	0	−1	0	0

There are different notations used to designate irreducible representations in group theory. Γ is used for a generic representation. The character tables shown here use the Mulliken notation which distinguishes between different types of irreducible representations. One-dimensional representations are designated by either A or B. The former is used when the character of the major rotation operation is 1 and the latter is used if the character of this operation is −1. Two-dimensional irreducible representations are designated by E and three-dimensional representations are designated by T. Subscripts 1 and 2 are used if the representation has symmetric ($\chi(C_2)=1$) or antisymmetric ($\chi(C_2)=-1$) twofold rotations perpendicular to the principal rotation axis or vertical symmetry plane. Primes and double primes are used to indicate symmetric or antisymmetric operations with respect to a horizontal plane of symmetry σ_h. If the group has a center of inversion symmetry, the subscripts g (*gerade*) and u (*ungerade*) are used to designate representations that are symmetric and antisymmetric with respect to this operation, respectively.

For each character table, the point group is designated by its Schoenflies notation in the top left-hand corner. The next part of the top row lists the symmetry elements of the group collected into classes. The final part of this row lists some of the possible basis functions for the irreducible representations. The first column of the character table below the first row lists the irreducible representations of the group in the order of increasing dimensions. The main body of the table lists the characters of the sy mmetry elements in each irreducible representation. The last column shows the components of a vector, rotation, or vector product basis function that transforms according to that specific irreducible representation and therefore acts as a basis for that representation.

In several of the character tables, the two-dimensional E representation is shown with an asterisk, E*. This is because the characters for this representation are imaginary or complex. Technically they should be decomposed into two different representations whose characters are complex conjugates of each other. Doing this allows for the rule of group theory to be fulfilled that the number of irreducible representations of a group is equal to the number of classes of elements in the group. However in applying group theory to physical problems, the characters need to be real so the sum of the characters of these two complex representations is used for the characters of the real representation. In each case the complex character for a rotation axis of order n is

$$\varepsilon_n^m = \exp(2\pi i/n) = \cos\frac{2\pi m}{n} + i\sin\frac{2\pi m}{n}. \tag{2.14}$$

Using this expression, $\varepsilon_n^0 = \varepsilon_n^n = 1$, $\varepsilon_n^{n/2} = -1$, and $\varepsilon_n^{n/4} = i$. Thus the double-valued representation E in the point group C_3 is actually two complex representations with sets of characters for the classes E, C_3, and C_3^2 of 1, $(-1/2 + i\sqrt{3}/2)$, $(-1/2 - i\sqrt{3}/2)$ and 1, $(-1/2 - i\sqrt{3}/2), (-1/2 + i\sqrt{3}/2)$. Adding these gives the set of characters for the classes of the E^* irreducible representation 2,−1,−1. Only the characters of the real representations are listed in the character tables.

If a system is characterized by a function that has half-integer values instead of integer values, it is necessary to work with *double groups* [3, 7–9]. In this case the order of the group increases and the number of irreducible representations increases accordingly. This situation occurs most commonly in dealing with spin or half-integer angular momentum in atomic physics. The spin of an electron is represented by a function that has two orientations with respect to an axis of quantization. The *Pauli spin operators* describing this situation are 2 × 2 matrices

$$\sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}, \quad \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}, \quad \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}. \tag{2.15}$$

These are related to the angular momentum operator $\mathbf{J}$ by

$$\sigma = 2\mathbf{J}.$$

Following the treatment of $\mathbf{J}$ in quantum mechanics, the angular momentum raising and lowering operators for spin can be expressed in terms of the Pauli spin operators [3].

The Pauli spin operators obey a multiplication table that has the properties of a group. A rotation about an axis n in the two dimensional spin representation is given by the operator

$$R(\varphi, \vec{n}) = e^{-i(1/2)\varphi\sigma\cdot\mathbf{n}} = \cos\frac{1}{2}\varphi - i\sigma\cdot\mathbf{n}\sin\frac{1}{2}\varphi. \tag{2.16}$$

The operator $R(\varphi,\mathbf{n})$ is also a 2 × 2 matrix.

An important result of (2.16) is that a rotation of 2π is not the identity operator for the group:

$$R(\varphi + 2\pi, \mathbf{n}) = \cos(\pi + \varphi/2) - \mathrm{i}\sigma \cdot \mathbf{n} \sin(\pi + \varphi/2)$$
$$= -\cos(\varphi/2) + \mathrm{i}\sigma \cdot \mathbf{n} \sin(\varphi/2) = -R(\varphi, \mathbf{n}).$$

Instead an operator representing a rotation of 4π must be introduced as the identity E while a rotation of 2π is a new operator R. Then R multiplied by all of the other operators of the group gives the additional group operators. This leads to additional irreducible representations.

In group theory, spin is represented by a two-dimensional irreducible representation $\Gamma_{1/2}$. For some spatial operations the characters for C_n and RC_n are different and these are referred to as *double valued*. The complete spatial and spin state of a system is represented by the product of $\Gamma_{1/2}$ with the irreducible representations describing the spatial state of the system. In some cases this direct product results in other new irreducible representations of the group. The character tables for the D_{2d} and O_h groups show examples of the extra elements and irreducible representations associated with double groups. These double-valued representations are discussed in greater detail in Chap. 4 and examples given of how to determine the characters of the half-integer representations. These concepts are especially important for treating magnetic properties and the effects of time reversal in quantum mechanical systems.

The irreducible representations for space groups are discussed in Chap. 8.

2.3 Group Theory Examples

2.3.1 C_{3v} Point Group

The best way to demonstrate the use of group theory is to work out some specific examples. Consider an object with the shape of an equilateral triangle as shown in Fig. 2.2. By inspection, this object has six symmetry elements: the identity E; rotation by 120° around the z-axis C_3; rotation by 240° around the z-axis C_3^2; mirror reflection through the plane containing the y and z axes σ_1; and mirror reflections through the planes containing the z-axis and either axis 2 or axis 3, designated σ_2 and σ_3, respectively. Therefore the order of the group is 6. These elements can be displayed in a multiplication table as shown in Table 2.33. This shows that the product of any two elements is an element of the group. It also shows that every element of the group has a reciprocal element that is an element of the group. It also shows that the associative law of multiplication holds for these elements. Thus all of the criteria for being a group have been met.

The multiplication rules shown in Table 2.33 can be used to apply similarity transformations to these elements which allow them to be grouped into classes:

$EC_3E = C_3,$	$EC_3^2E = C_3^2,$
$C_3^2C_3C_3 = C_3,$	$C_3^2C_3^2C_3 = C_3^2,$
$C_3C_3C_3^2 = C_3,$	$C_3C_3^2C_3^2 = C_3^2,$
$\sigma_1C_3\sigma_1 = C_3^2,$	$\sigma_1C_3^2\sigma_1 = C_3,$
$\sigma_2C_3\sigma_2 = C_3^2,$	$\sigma_2C_3^2\sigma_2 = C_3,$
$\sigma_3C_3\sigma_3 = C_3^2,$	$\sigma_3C_3^2\sigma_3 = C_3.$

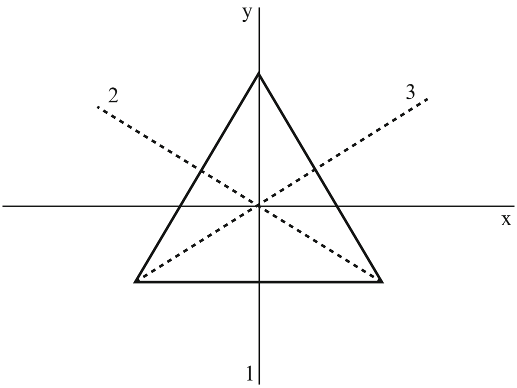


Fig. 2.2 Equilateral triangle. The z-axis direction is out of the page

Table 2.33 Multiplication table for equilateral triangle symmetry elements

	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

This shows that the elements C_3 and C_3^2 form one class having two symmetry elements. Proceeding in the same way for the three mirror planes show that the elements σ_1, σ_2, and σ_3 form another class. Also, the element E forms a class by itself.

Since there are three classes in this group there must be three irreducible representations for the group and the sum of the squares of their dimensions must equal the order of the group, 6. This is only possible if there are two one-dimensional irreducible representations and one two-dimensional irreducible representation. There are two ways to develop the character table for these representations. The first is to express the character table in terms of unknown characters and then use the orthogonality of irreducible representations to calculate the characters. In this case the three classes and three irreducible representations can be written as

	E	$2C_3$	3σ
A_1	1	1	1
A_2	1	a	b
E	2	c	d

which reflect the fact that the character of the identity operation is always the dimension of the representation and there is always one totally symmetric irreducible representation in which the character of each class is 1. Using (2.11) provides the following equations:

$$\frac{1}{6}\sum_r \gamma\left(A_1^2\right)\gamma\left(A_2^2\right) = (1+2a+3b)/6 = 0 \therefore 2a+3b = -1 \text{ so } a=1,\, b=-1,$$

$$\frac{1}{6}\sum_r \gamma(A_1)\gamma(E) = (2+2c+3d)/6 = 0 \therefore 2c+3d = -2,$$

$$\frac{1}{6}\sum_r \gamma(A_2)\gamma(E) = (2+2c-3d)/6 = 0 \therefore 2c-3d = -2.$$

Combining the last two expressions gives $c{=}-1$ and $d{=}0$, so the character table is

	E	$2C_3$	3σ
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

The second way to derive the character table for this group is to consider how the Cartesian coordinates transform under the elements of the group. In this case

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = E\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \quad \therefore E = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = C_3\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -\frac{1}{2}x + \frac{\sqrt{3}}{2}y \\ -\frac{\sqrt{3}}{2}x - \frac{1}{2}y \\ z \end{pmatrix} \quad \therefore\ C_3 = \begin{pmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \sigma_1\begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix} \quad \therefore\ \sigma_1 = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

This is a reducible representation Γ that has characters given in the following table: The final line in this table shows the reduction of the representation Γ in terms of the irreducible representations using the expression from (2.10)

	E	$2C_3$	3σ
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0
Γ	3	0	$1 = A_1{+}E$

$$n^{(i)} = \frac{1}{h}\sum_A \chi_A^{(i)}\chi_A.$$

For A_1 this gives $n^{(A1)} = (1/6)(3+0+3) = 1$. For A_2 it gives $n^{(A2)}$=(1/6)(3+0–3)=0. For E it gives $n^{(E)}$=(1/6)(6+0+0)=1.

The three transformation matrices found above have a box diagonal form

$$E = \left(\begin{array}{cc|c} 1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right),\ C_3 = \left(\begin{array}{cc|c} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \hline 0 & 0 & 1 \end{array}\right),\ \sigma_1 = \left(\begin{array}{cc|c} -1 & 0 & 0 \\ 0 & 1 & 0 \\ \hline 0 & 0 & 1 \end{array}\right).$$

The boxes in the upper left-hand corner are the matrices for the irreducible representation E while the boxes in the lower right-hand corner are the matrices for the irreducible representation A_1. Note that the traces of these box diagonal matrices give the characters for the E and A_1 representations and the characters for the A_2 irreducible representation can then be found from the orthogonality condition.

The transformation matrices for the three classes of symmetry elements operating on the vector components x,y,z as shown above shows that the z component acts as a basis for the A_1 irreducible representation while the components x and y transform into combinations of each other according to the irreducible representation E. Thus the set (x,y) form the basis for E.

The rotation axis R_z remains unchanged under operations of the E and C_3 classes but it changes sign under an operation of the σ class. Thus it transforms according to the A_2 irreducible representation. The other two rotation axes R_x and R_y transform into combinations of each other and therefore form a basis for the E irreducible representation.

Finally consider how the product of vector components transforms in this group. The conventional way to write the components of an axial vector formed by the product of two vectors is given in (2.17). The way the individual components transform under the symmetry operations of this group was described above, and this information can be used to determine how the product of these components transform. Then transformation matrices can be constructed for each symmetry element, and their traces are calculated to determine the characters of this reducible representation as done previously.

The six-dimensional column matrix for a vector product is

$$\begin{pmatrix} x^2 \\ y^2 \\ z^2 \\ 2yz \\ 2xz \\ 2xy \end{pmatrix}. \tag{2.17}$$

Using this as a basis vector, the transformation vectors for an element of each class are written as

$$E = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \end{pmatrix} \quad \therefore \gamma_E = 6,$$

$$\sigma_1 = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \quad \therefore \gamma_{\sigma_1} = 2,$$

$$C_3 = \begin{pmatrix} \frac{1}{4} & \frac{3}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{4} \\ \frac{3}{4} & \frac{1}{4} & 0 & 0 & 0 & \frac{\sqrt{3}}{4} \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ 0 & 0 & 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{\sqrt{3}}{2} & 0 & 0 & 0 & -\frac{1}{2} \end{pmatrix} \quad \therefore \gamma_{C_3} = 0$$

This irreducible representation can be reduced in terms of $2E$ and $2A_1$ irreducible representations. By observing the transformation properties, it can be seen that z^2 forms a basis function for one of the A_1 irreducible representations while $(x^2{+}y^2)$ forms a basis function for the other one. One of the E representations has the set (xz,yz) for a basis function and the other has the basis function set $(x^2{-}y^2,xy)$.

If all of the information on basis functions is included in the character table for this group given above, it is identical with Table 2.17. This shows that the symmetry group for an equilateral triangle is point group C_{3v}.

For some applications it is important to take the direct product of representations and reduce the results in terms of the irreducible representations of the group. As an example for this group, the direct product of the E representation with itself is found by multiplying the character of the E representation for each symmetry class with itself. This gives the characters 4, 1, and 0 for the E, C_3, and σ classes of symmetry operations, respectively. These are the characters of a reducible representation and (2.10) can be used to show that this reduces to one E, one A_1, and one A_2 irreducible representations.

2.3.2 O_h Point Group

One of the most important symmetries in solid state physics is a regular octahedron with a center of inversion symmetry. This describes seven atoms arrayed along the x, y, and z axes of a cube as shown in Fig. 2.3 with the positions of the ions given in Table 2.34. Each side of the cube has a length $2a$. The angle φ is measured around the z-axis in the xy plane counterclockwise from the x-axis. The angle θ is measured around the y-axis in the xz plane counterclockwise from the z-axis.

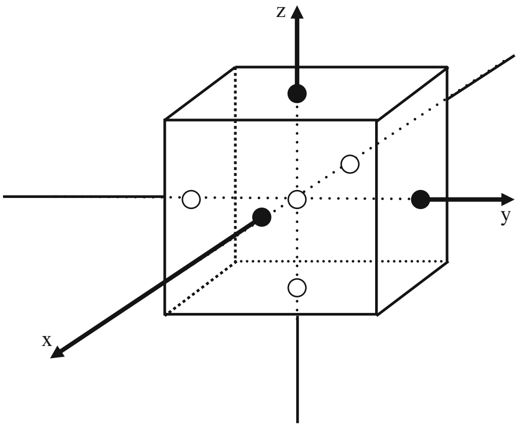


Fig. 2.3 Cubic O_h symmetry

Table 2.34 Ion positions in Fig. 2.3

x	y	z	r	θ	φ
0	0	0	0	0	0
a	0	0	a	$\pi/2$	0
0	a	0	a	$\pi/2$	$\pi/2$
$-a$	0	0	a	$\pi/2$	π
0	$-a$	0	a	$\pi/2$	$3\pi/2$
0	0	a	a	0	0
0	0	$-$a	a	π	0

The cubic O_h point group describes this symmetry. This group has 48 symmetry elements divided into 10 classes. The character table for the group is given in Table 2.32. The symmetry elements are as follows. First is the identity operation E and the inversion operation i which each forms a class by itself. Next there is a class of six C_4 elements describing ±90° rotations about the x, y, or z axes. Then there are three twofold axes of rotation C_2 about the x, y, or z axes. Also there are six twofold rotation axes C_2' that run from the center of an edge through the center of the cube to the center of the opposite edge. There are eight axes of ±120° rotation about the body diagonals of the cube. There are three mirror planes of symmetry going through the centers of the edges of the cube in the xy, xz, and yz planes. Note that these are equivalent to combined C_2i operations. Similarly, there are six diagonal planes of symmetry equivalent to combined $C_2'i$ operations. The reflection operations can also be combined with C_3 rotations and C_4 rotations to give eight S_6 and six S_4 operations, respectively.

Since there are 10 classes, there must be 10 irreducible representations for the O_h point group. The only way for the sum of the squares of the dimensions of 10 irreducible representations to equal the order of the group, 48, is $4(3)^2+2(2)^2+4(1)^2=48$. This shows that the group has four three-dimensional irreducible representations, two two-dimensional irreducible representations, and four one-dimensional representations. These are divided into two groups of five each, one that is even parity under inversion designated by subscript g and one that is odd parity under inversion designated by subscript u. These can by used to operate on even and odd parity basis functions, respectively. The character for a symmetry operation not involving inversion is the same for both even and odd parity. However, the character for a symmetry operation involving inversion in an odd parity representation is −1 times the character for the same element in the even parity version of the same representation.

For use with half-integer functions such as spin, the additional operation R of a 2π rotation must be introduced since E is a 4π rotation in this case. This results in three new g and three new u irreducible representations as shown in Table 4.32.

For situations involving high levels of symmetry such as O_h, it is sometimes useful to work with *subgroups* of the total group. A subgroup of is a subset of elements of the larger group that by themselves obey all of the mathematical requirements to be a group. For example, D_{3d} forms a subgroup of O_h consisting of the identity element, two threefold rotation operations, three C_2' operations, and the inversion operation multiplied by each of these elements. The character table for D_{3d} is given in Table 2.30. The irreducible representations of the group can be

O_h	D_{3d}
A_{1g}	A_{1g}
A_{2g}	A_{2g}
E_g	E_g
T_{1g}	$A_{2g}+E_g$
T_{2g}	$A_{1g}+E_g$

decomposed in terms of combinations of the irreducible representations of the subgroup. Comparing the characters of the common elements in O_h and D_{3d} shows the correlation between the irreducible representations of the group and its subgroup. For the even parity representations this is:

The results of this method of inspection can be checked against the predictions of (2.10). For example, for the T_{2g} irreducible representation of O_h the A_{1g} irreducible representation of D_{3d} will appear the following number of times:

$$n^{(T_{2g})} = \frac{1}{12}(1 \times 1 \times 3 + 2 \times 1 \times 0 + 3 \times 1 \times 1 + 1 \times 1 \times 3 + 2 \times 1 \times 0 + 3 \times 1 \times 1)$$
$$= 1,$$

while the A_{2g} irreducible representation will appear the following number of times:

$$n^{(T_{2g})} = \frac{1}{12}(1 \times 1 \times 3 + 2 \times 1 \times 0 + 3 \times (-1) \times 1 + 1 \times 1 \times 3 + 2 \times 1 \times 0 + 3 \times (-1) \times 1)$$
$$= 0.$$

This is consistent with the correlation table shown above.

From Table 2.32 it can be seen that the vector components (x,y,z) transform as the T_{1u} irreducible representations. As discussed in Sect. 2.4 and in Chap. 4, this is important in using group theory to determine allowed electromagnetic transitions. Also the irreducible representations for O_h involving half-integer quantities are shown in the table. Section 4.4 describes an example of using these representations for atoms with half-integer values of angular momentum.

2.4 Group Theory in Quantum Mechanics

In quantum mechanics a physical system is described by a Hamiltonian operator H. The allowed states of a system are described by a set of orthonormal eigenfunctions ψ_n and the energy of these states is a set of eigenvalues E_n. The sets of eigenfunctions and eigenvalues for the system are found by solving the *Schrödinger equation*

$$H|\psi_n\rangle = E_n|\psi_n\rangle$$

or

$$E_n = \langle\psi_n|H|\psi_n\rangle. \tag{2.18}$$

Since the Hamiltonian describes the physical system, it should be invariant under the same symmetry operations that leave the physical system invariant [2,5]. This is described as a similarity transformation on H by a symmetry operator A

$$H = A^{-1}HA. \tag{2.19}$$

This is the same as saying that a symmetry operator commutes with the Hamiltonian operator [2, 5]. The symmetry operators that leave H invariant form a group. Obviously an operator that does not change H at all is an element of the group and this is the identity operator. For two elements A and B

$$AHA^{-1} = H \quad \text{and} \quad BHB^{-1} = H \quad \text{so}(AB)H(AB)^{-1} = (AB)H(B^{-1}A^{-1}) = H,$$

which shows that the product of two elements is an element that leaves H invariant. Also, the associative law holds. Finally, if (2.19) is multiplied from the left with A and from the right with A^{-1} gives

$$AHA^{-1} = H,$$

which shows that the inverse of the element also leaves H invariant. Thus all the elements that leave H invariant conform to the properties of a group. This is called the group of the Schrödinger equation or the group of the Hamiltonian and is the same as the symmetry group of the system described by H.

If one of the operators of the group of the Hamiltonian A is applied to the initial Schrödinger equation given above,

$$AH|\psi_n\rangle = E_nA|\psi_n\rangle$$

or

$$H|A\psi_n\rangle = E_n|A\psi_n\rangle$$

since A and H commute. This shows that $| A\psi_n\rangle$ is also an eigenfunction belonging to the same eigenvalue E_n. In other words, the eigenfunctions transformed by an operator of the group of H belong to the same eigenvalue as the initial eigenfunctions. From (2.18),

$$E_n = \langle\psi_n|H|\psi_n\rangle = \langle\psi_n|A^{-1}HA|\psi_n\rangle = \langle A^{\dagger}\psi_n|H|A\psi_n\rangle = \langle\varphi_n|H|\varphi_n\rangle \tag{2.20}$$

where

$$|\varphi_n\rangle = A|\varphi_n\rangle = |A\varphi_n\rangle. \tag{2.21}$$

This derivation uses the fact that for symmetry operators in quantum mechanics their inverse is equal to their adjoint $\mathrm{A}^{-1} = \mathrm{A}\dagger$.

If E_n has only one eigenfunction then $\varphi_n = \psi_n$ except for a possible phase factor and E_n is said to be *nondegenerate*. If an eigenvalue has associated with it an orthonormal set of eigenfunctions, it is said to be degenerate, and any normalized linear combination of these eigenfunctions will also have the eigenvalue E_n. This is expressed as

$$E_n = \langle \Psi_I | H | \Psi_I \rangle$$

where

$$|\Psi_I\rangle = \sum_i^n a_i |\psi_i\rangle$$

and $|\Psi_I\rangle$ is normalized and $a_1^2 + a_2^2 + \cdots + a_n^2 = 1$. Thus

$$\langle \Psi_I | \Psi_I \rangle = \sum_{i=1}^n |a_i|^2 \langle \psi_i | \psi_i \rangle = 1.$$

There are n possible linear orthogonal combinations.

A symmetry operation of the system acting on a set of degenerate eigenfunctions takes them into a different linear orthogonal combination of the degenerate eigenfunctions:

$$A \begin{pmatrix} |\psi_1\rangle \\ |\psi_2\rangle \\ \vdots \\ |\psi_n\rangle \end{pmatrix} = \begin{pmatrix} a_{11}|\psi_1\rangle + a_{12}|\psi_2\rangle + \cdots + a_{1n}|\psi_n\rangle \\ a_{21}|\psi_1\rangle + a_{22}|\psi_2\rangle + \cdots + a_{2n}|\psi_n\rangle \\ \vdots \\ a_{n1}|\psi_1\rangle + a_{n2}|\psi_2\rangle + \cdots + a_{nn}|\psi_n\rangle \end{pmatrix}. \tag{2.22}$$

The discussion above shows that for quantum mechanical systems, if all symmetry operations for the system leave a specific eigenfunction unchanged (except for a phase factor), that function transforms like a nondegenerate solution of the Schrödinger equation. If some of the symmetry operations act on an eigenfunction to create new linearly independent eigenfunctions, all of these functions transform like members of a degenerate set of solutions to the Schrödinger equation.

From the discussion above, it can be seen that the eigenfunctions belonging to the same eigenvalue of a quantum mechanical system form a basis for one of the irreducible representations of group describing the system. The dimension of the irreducible representation is the same as the degeneracy of the eigenvalue. Thus

$$HA|\psi_i\rangle = E_i A|\psi_i\rangle$$

shows that both $|\psi_i\rangle$ and $A|\psi_i\rangle$ are eigenfunctions of E_i. If E_i is nondegenerate and the eigenfunctions are normalized, $A|\psi_i\rangle = \pm 1|\psi_i\rangle$. Applying all of the symmetry operations of the group generates a one-dimensional irreducible representation of the group with matrix elements (and characters) ± 1. That irreducible representation thus can be used to represent the energy state of the system associated with the eigenvalue for that specific eigenfunction. Considering the same procedure for a degenerate state of the system generates an irreducible representation of the system whose dimension is equal to the degeneracy of the state it represents.

Consider the example of a system with C_{3v} symmetry described in Sect. 2.3.1. A quantum mechanical system with this symmetry will have a nondegenerate eigenfunction that is the basis for the A_1 irreducible representation so it remains unchanged under all symmetry operations. It will have another nondegenerate eigenfunction that remains invariant under operations of the E and C_3 class but changes sign under σ class operations and therefore is the basis for the A_2 irreducible representation. Two other degenerate eigenfunctions will form the basis for the two-dimensional E irreducible representation. If this is designated Γ_3,

$$A(\psi_1\psi_2) = (\psi_1\psi_2)\begin{pmatrix} \Gamma_3(A)_{11}\Gamma_3(A)_{12} \\ \Gamma_3(A)_{21}\Gamma_3(A)_{22} \end{pmatrix},$$

where A is a symmetry operator in C_{3v}. This leads to

$$\begin{aligned} A\psi_1 &= \Gamma_3(A)_{11}\psi_1 + \Gamma_3(A)_{21}\psi_2, \\ A\psi_2 &= \Gamma_3(A)_{12}\psi_1 + \Gamma_3(A)_{22}\psi_2. \end{aligned}$$

This shows that ψ_1 transforms like the first column of the transformation matrix of the symmetry operator while ψ_2 transforms like the second column.

When spin–orbit interaction is important, the total wavefunction describing the system is the product of spatial and spin functions:

$$\Psi_i = \psi_i \sigma_i,$$

where σ_i represents the spin angular momentum of the system. In this case double-valued representations must by used. An example of this is given in Chap. 4.

Any physical process interacting with the system can be expressed as a quantum mechanical operator which also transforms according to one of the irreducible representations of the group. The transformation of the specific ith operator O_i^n of a set of n operators is expressed as

$$AO_i^n A^{-1} = \sum_j O_j^n \Gamma_n(A)_{ji}, \tag{2.23}$$

where A is an element of the group of the Hamiltonian and Γ_n is a representation of this group.

The physical process may cause the system to undergo transitions from one eigenstate to another or to split degenerate energy states into several states with lower degeneracies. The qualitative features of these effects can be determined by using group theory techniques such as the direct products and decompositions of representations to evaluate matrix elements. In general the quantum mechanical description of these physical processes involves evaluating matrix elements

$$\langle \psi_{\rm f} | O | \psi_{\rm i} \rangle$$

where i and f designate initial and final states of the system and O represents the physical operator. The matrix element represents an integral over all space and to be nonzero the integrand must be symmetric. Instead of evaluating the complete mathematical expression for the integral of the products of the operator and eigenfunctions, we can rewrite this as the product of the group theory representations of the functions

$$\langle \psi_{\rm f} | O | \psi_{\rm i} \rangle \neq 0, \quad \text{if } \Gamma_{\rm f} \times \Gamma_O \times \Gamma_{\rm i} = A_{1{\rm g}} + \cdots \tag{2.24}$$

and

$$\langle \psi_{\rm f} | O | \psi_{\rm i} \rangle = 0, \quad \text{if } \Gamma_{\rm f} \times \Gamma_O \times \Gamma_{\rm i} \neq A_{1{\rm g}} + \cdots.$$

Thus the matrix element is nonzero if the decomposition of the triple direct product representation $\Gamma_{\rm f} \times \Gamma_{\rm o} \times \Gamma_{\rm i}$ contains the totally symmetric $A_{1{\rm g}}$ representation. This is called an *allowed transition*. The matrix element is zero if it does not contain $A_{1{\rm g}}$. This is called a *forbidden transition*. This can be stated in a different way knowing that $A_{1{\rm g}}$ will only appear in the decomposition of the direct product of a representation with itself. Thus for a nonzero matrix element the decomposition of the direct product representation of the initial and final states must contain the irreducible representation of the operator causing the transition.

These concepts can be visualized using a simple example of rectangular symmetry. If the square symmetry shown in Fig. 1.2 is stretched along the x direction the symmetry group is lowered from D_{4h} to D_{2h} with the character table given in Table 2.8. A quantum mechanical state of the system is designated by one of the eight irreducible representations listed in the character table. The signs of the eigenfunctions transforming as some of these representations within the rectangular space are shown in Fig. 2.4. The effect of a symmetry operation on the sign of the function is given by the character of the operation. A positive character leaves the sign unchanged while a negative character changes the sign. For example, the function transforming as the totally symmetric irreducible representation $A_{\rm g}$ is positive throughout the rectangular space and does not change when it undergoes under any of the symmetry operations. The function transforming as $B_{1{\rm g}}$ changes sign under the $C_2(y)$, $C_2(x)$, $\sigma(xz)$, and $\sigma(yz)$ operations, all of which have characters of -1, and remains unchanged under the other four operations which have characters of $+1$. The function transforming as $B_{2{\rm g}}$ changes sign under the $C_2(y)$, $C_2(z)$,

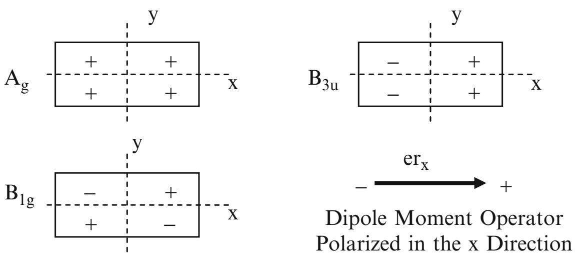


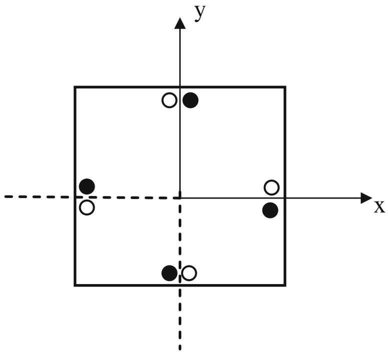
Fig. 2.4 Signs of the basis functions for some of the irreducible representations in a system with rectangular symmetry

$\imath$, and $\sigma(yz)$ operations. The triple product of the three irreducible representations shown in Fig. 2.4 is a function that has positive values in the two upper quadrants and negative values in the two lower quadrants. This forms the basis of a B_{2u} representation. Integrating this function over the area of the rectangle is identically zero since there are equal positive and negative areas. The dipole moment operator polarized in the x direction is also shown in Fig. 2.4. Applying the symmetry operations of the D_{2h} point group shows that this transforms according to the B_{3u} representation as indicated in the character table for the group. The fact that the reduction of the triple direct product $A_g \times B_{3u} \times B_{1g} = B_{2u}$ does not contain A_g is consistent with the fact that the matrix element is zero and the electric dipole induced transition between states A_g and B_{1g} is forbidden. The determination of transition matrix elements in this way is discussed further in later chapters.

Using these concepts of group theory, the irreducible representations of the group of symmetry operations that leave the Hamiltonian of the quantum mechanical system invariant provide information about the degrees of degeneracy of the eigenfunctions of the system and the transformation properties of these eigenfunctions. The group theory procedure of forming and decomposing direct products of representations is useful in quickly determining qualitatively whether a transition is allowed or forbidden, or how many states occur in the splitting of an energy level. However, it can not provide quantitative information about these processes.

2.5 Problems

Consider the thin, square object with the basis set shown in the figure. (○ represents objects above the plane of the square and • represents objects below this plane.) The z-axis is directed out of the paper from the center of the square. Answer the following questions:



1. Identify the symmetry elements for the point group of this object.
2. Develop the multiplication table for the symmetry elements.
3. Derive the classes of elements for this symmetry group. What is the order of the group?
4. Derive the transition matrices for the group elements operating on the x,y,z coordinates and find the character of each of these.
5. Derive the character table for this group using the concepts of box diagonalization and the properties of characters (especially (2.11) and (1.12)).

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