

# UNIT 6 APPLICATIONS OF GROUP THEORY

## Structure

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## 6.1 INTRODUCTION

In Unit 5 we have developed the basic concepts of group theory. You have learnt that in physics, groups appear as a set of operations that leave a system unchanged or invariant. This is an expression of symmetry. In this unit we shall illustrate some elementary applications of group theory in expressing symmetry in molecules, crystal structure and quantum mechanics. The idea here is not to make this an exhaustive discussion but to sensitise you to the usefulness of group theory in physics. Some of the concepts regarding molecular and crystal symmetry presented here will be new to you. To grasp them, you will need to visualize rotation of two and three-dimensional figures as well as their reflection in various planes. So we advise you to actually perform these rotations/reflections on objects of appropriate symmetry.

### Objectives

After studying this unit you should be able to:

- identify symmetry operations and construct point groups for simple molecules;
- enumerate crystallographic point groups having one symmetry axis;
- relate the conservation laws of linear momentum, and energy to specific symmetries and symmetry groups of a quantum mechanical system; and
- solve problems involving simple applications of group theory to molecules, crystals and microscopic systems.

## 6.2 SYMMETRY IN MOLECULES

The study of symmetry in molecular structure helps us in understanding various molecular properties such as dipole moment, optical activity, selection rules and spectral characteristics. It also helps us in classifying polyatomic molecules according to groups of appropriate symmetry. Here we shall discuss a few simple symmetry groups which occur in molecular structure.

### Diatomic Molecules

The diatomic molecule is the simplest molecule from symmetry considerations. Examples of such molecules are  $H_2$ ,  $O_2$ ,  $Cl_2$ ,  $CO$ ,  $NH$ ,  $LiH$  etc. Let us first consider a diatomic molecule having two different atoms (Fig. 6.1a).

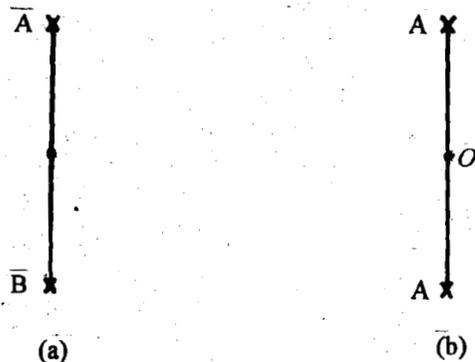


Fig.6.1: Symmetry in diatomic molecules

What operations will leave this system invariant? Recall that such operations are called **symmetry operations**. Let us list them.

1. The *identity* or unit operator  $E$ .
2. *Rotation* by any angle about the line  $AB$  joining the atoms.
3. *Reflection* in any vertical plane passing through  $AB$ .

Thus, the symmetry group for any diatomic molecule comprises  $I$ , rotational symmetry group  $C_\infty$  and reflection symmetry in any vertical plane  $\sigma_v$ . It is denoted by  $C_{\infty v}$ .

If the diatomic molecule has identical atoms (Fig. 6.1b) then it has the following additional symmetries:

- Reflection symmetry in a horizontal plane passing through the centre  $O$  of the molecule denoted by  $\sigma_h$ .
- Two-fold rotational symmetry  $C'_2$  about any horizontal axis passing through the centre of the molecule. The prime is used here to denote that the axis of rotation is different from the main symmetry axis which is the line joining the atoms.

The **complete group of symmetry for diatomic molecules having identical atoms** is denoted by  $D_{\infty h}$ . It contains elements of

- axial rotational symmetry about the line joining the atoms;
- reflection symmetry in any vertical plane passing through the line of atoms;
- two-fold rotational symmetry about any horizontal axis passing through the centre of the molecule ( $C'_2$ ); and
- reflection symmetry in a horizontal plane passing through the centre of the molecule.

Can you list the elements of the **complete group of rotational symmetry** for a diatomic molecule  $AA$ ? It is denoted by  $D_\infty$  and comprises  $C_\infty$  and  $C'_2$ .

In general, the geometrical symmetry transformations of a molecule are of three types: *rotations* about an axis, *reflections* in a plane and *inversions*. In addition, we can have combinations of these three. When the group of transformations of a certain system consists of operations which leave one point of the system undisplaced in position, it is called a **point group**.

$C_\infty$ ,  $C_{\infty v}$ ,  $D_\infty$  and  $D_{\infty h}$  are examples of **molecular point groups**. In all these examples,  $O$  is the point which is left undisplaced in position.

If we choose the point which is invariant under the point group as the origin of a cartesian coordinate system, then a point group would contain only the following types of operations:

- (a) rotations about any axis passing through the origin,
- (b) reflections in planes passing through the origin, and
- (c) inversion.

You must note that the operations of the above three type are not independent of each other. Any one of these operations can be constructed by suitably combining the remaining two types of operations. For example, *inversion can be thought of as a rotation through  $\pi$  about an arbitrary axis passing through the origin followed by a reflection in a plane perpendicular to the axis and passing through the origin.* You can also verify that an inversion followed by  $C_2'$  results in  $\sigma_v$ .

A rotation followed by a reflection, i.e., the inversion is also called an *improper rotation* against a *proper rotation*. The left-handed or right-handed sense of the coordinate system remains unchanged after a proper rotation but it changes from one to the other after an improper rotation (You may like to refer to Unit 1 of PHE-04). You can easily verify that the product of two proper rotations or of two improper rotations is a proper rotation, while the product of a proper rotation with an improper rotation is an improper rotation. It is exactly analogous to the products of +1 and -1 among themselves.

You must also note that the following pairs of point group operations commute with each other:

- (a) inversion and any other operation,
- (b) two rotations about the same axis,
- (c) rotations through  $\pi$  about two perpendicular axes,
- (d) a rotation and a reflection in a plane normal to the axis of rotation,
- (e) a rotation through  $\pi$  and a reflection in a plane passing through the axis of rotation, and
- (f) two reflections in perpendicular planes.

You should verify these statements by performing these operations on a familiar object such as a book or a match box.

An inversion is an operation which takes

$$\begin{aligned} x &\rightarrow -x \\ y &\rightarrow -y \\ z &\rightarrow -z \end{aligned}$$

You have come across this operation in Unit 1 of PHE-04 in the discussion on polar and axial vectors.

### Activity 1

Verify with the help of a book that the operations described in (a) to (f) commute with each other.

Spend 10 min

Let us now consider a system of three identical atoms at the vertices of an equilateral triangle.

### Equilateral Triangle

Refer to Fig. 6.2. What are the symmetry operations for this system?

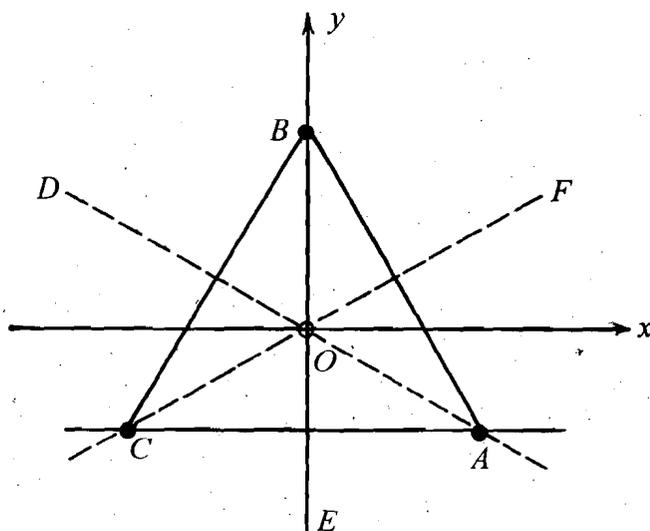


Fig.6.2: Symmetry operations on an equilateral triangle

Note that these are

1. The identity element  $E$ .
2. There is a three-fold rotational symmetry about the axis normal to the plane of the triangle passing through its geometric centre  $O$  which is the centre of symmetry. Thus rotations of the triangle by  $2\pi/3$  and  $4\pi/3$  about this axis (say the  $z$ -axis) will leave the triangle invariant. These are denoted by  $C_3$ .
3. There are three additional symmetries in the plane of the triangle: Two-fold rotational symmetry  $C_2'$  about the **three** horizontal axes ( $AD$ ,  $BE$  and  $CF$ ) passing through each of the vertices and the geometric centre of the triangle (Fig. 6.2). Thus rotation by  $\pi$  about these axes will leave the system invariant.

The symmetry group of the above system comprising the six elements is called a **dihedral group** of three-fold symmetry. It is denoted by  $D_3$  and has six elements ( $E, 2C_3, 3C_2'$ ). The molecular ion  $[\text{CO} (e_n)_3]$  is an example of  $D_3$ .

Let us consider the symmetries of  $\text{H}_2\text{O}$  as another example.

In SAQ 1 of Unit 5, you have listed the symmetry operations of  $\text{H}_2\text{O}$ , namely,  $E, C_2, \sigma_v, \sigma_v'$  (see Fig. 6.3). The point group for  $\text{H}_2\text{O}$  is denoted by  $C_{2v}$ .

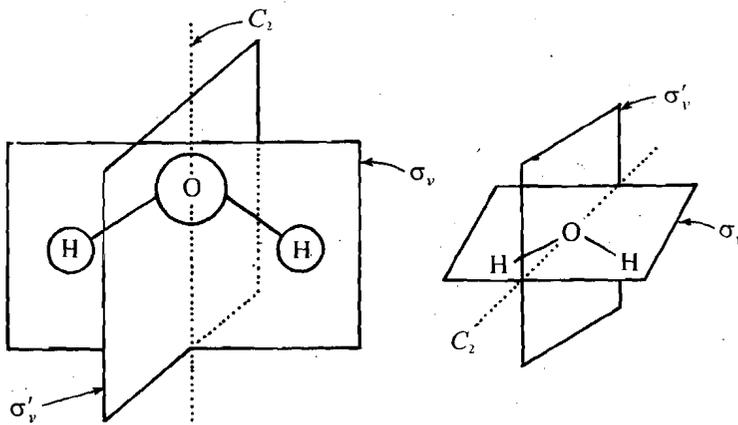


Fig.6.3: The symmetry group for  $\text{H}_2\text{O}$ . There are two vertical planes of symmetry  $\sigma_v$  and  $\sigma_v'$ . These are shown in two orientations of  $\text{H}_2\text{O}$ .

To clarify these concepts further you may like to determine the point group for a simple molecule.

### SAQ 1

List the symmetry operations for the  $\text{NH}_3$  molecule (Fig. 6.4) and construct its point group.

Spend  
10 min

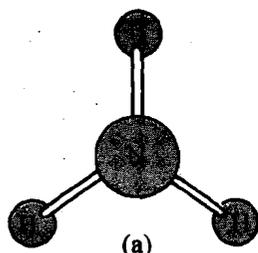


Fig.6.4:  $\text{NH}_3$  molecule

Now that you are familiar with symmetry operations and point groups of some simple molecules, let us see how these ideas find applications in understanding various properties of molecules.

You know that the dipole moment of a molecule characterises it. Therefore, it should remain invariant under any symmetry operation on a molecule. Since it is a vector, the dipole moment must be contained in each symmetry element (rotation, reflection or inversion) of a molecule. As a result, only molecules belonging to  $C_m, C_m'$  and  $C_s$  can possess a dipole moment. Here  $C_s$  is the group having elements  $\sigma$  and  $E$  where  $\sigma$  denotes reflection symmetry in a plane passing through the molecule. (For example, the dipole moment of  $\text{H}_2\text{O}$  is oriented along the  $C_2$  axis and is contained in the  $C_2$  axis, and  $\sigma_v$  and  $\sigma_v'$  planes.) Conversely, the presence and absence of dipole moment tells us about the symmetry of the molecule. The molecule  $\text{CO}_2$  has zero dipole moment — this corresponds to

its linear structure and the point group  $D_{\infty h}$ . Further, only molecules having permanent dipole moment, i.e., molecules having point groups  $C_n$ ,  $C_{nv}$  and  $C_s$  can give rise to pure rotational (or microwave) spectra. We will not go into all the details here.

Similarly, a molecule is optically active only if it does not have inversion symmetry, i.e., only if it changes on inversion. In fact, optical activity arises only if a molecule has distinct left-handed and right-handed forms of mirror image isomers. Lactic acid is an example of an optically active molecule (see Fig. 6.5). Since all molecules possessing a centre of symmetry have the inversion symmetry, they are optically inactive.

Having briefly discussed some symmetry aspects of molecules, we now turn our attention to symmetry in crystals.

### 6.3 CRYSTALS AND SYMMETRY

Crystals are characterised by a regular arrangement of atoms in them. It is therefore possible to say that a crystal consists of a *lattice* (of regularly arranged points) and a *basis* of atoms attached to each lattice point (see Fig. 6.6). Remember that the concept of lattice is purely an abstract geometrical concept. A lattice is a regular arrangement of points in space. The basis attached to each point gives it a physical character.

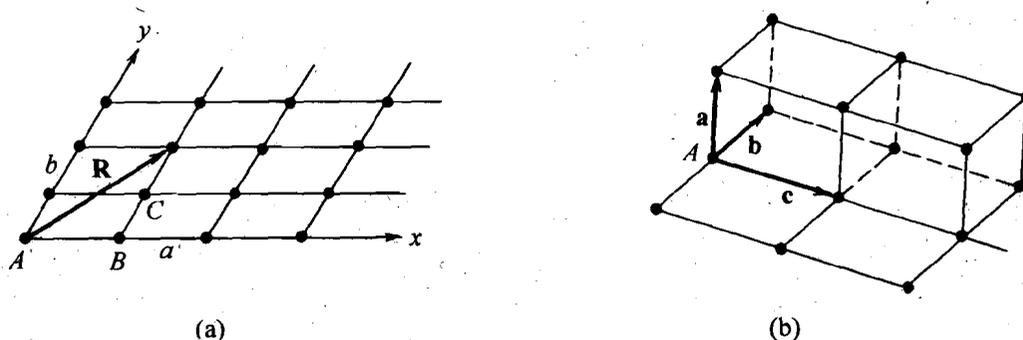


Fig.6.6: (a) A crystal consists of a lattice and a basis; (b) a unit cell in a 3-D crystal.

Due to its regular structure, a crystal possesses many kinds of symmetries. The symmetry of a crystal plays an extremely important role in the study of the properties of crystals such as diffraction of waves from crystals, the electronic structures of crystals, etc. Various other phenomena such as the colours exhibited by crystals having impurities and defects also depend on the symmetry of the environment of the impurity atom. It is but natural, therefore, that group theory is an essential and helpful tool in the study of various phenomena related to solids.

You will study crystal structure in detail in Units 1 to 3 of the course PHE-13 entitled Physics of Solids. Here we will briefly recapitulate the main concepts involving symmetry in crystal structure.

There are two classes of crystal lattices: the **Bravais** and **non-Bravais**. In a *Bravais lattice*, all lattice points are equivalent to each other: The lattice as seen from one lattice point looks exactly the same as viewed from any other lattice point. Here we will consider only the Bravais lattices. There are only 14 distinct Bravais lattices in three dimensions (Fig. 6.7).

The position vector of any lattice point can be written in terms of a set of 3 basis vectors for a 3-D crystal. The parallelepiped formed by the basis vectors as its sides is called a **unit cell** (See Fig. 6.6b). Depending on the shape and symmetry of a unit cell there are seven crystal systems to which a 3-D crystal may belong.

These seven systems are further classified as belonging to one of the 14 Bravais lattices. They are also shown in Fig. 6.7.

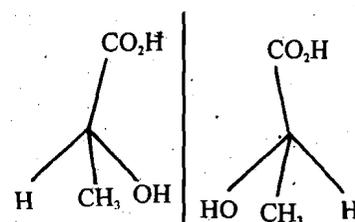


Fig.6.5: Lactic acid does not possess inversion symmetry. Hence it is an optically active molecule.

Several solids, liquids and their solutions cause rotation of the plane of polarisation of linearly polarised light as it passes through them. Such materials are said to be optically active. You can read more about optical activity in Unit 1 of PHE-12(L) and Unit 4 of PHE-09.

Let us now see what possible geometrical transformations would leave a crystal invariant.

There are three types of geometrical symmetry transformations in a crystal:

- (i) translations,
- (ii) rotations, reflections and inversion, which are known as **point symmetry operations**, and
- (iii) combinations of the above two types of operations.

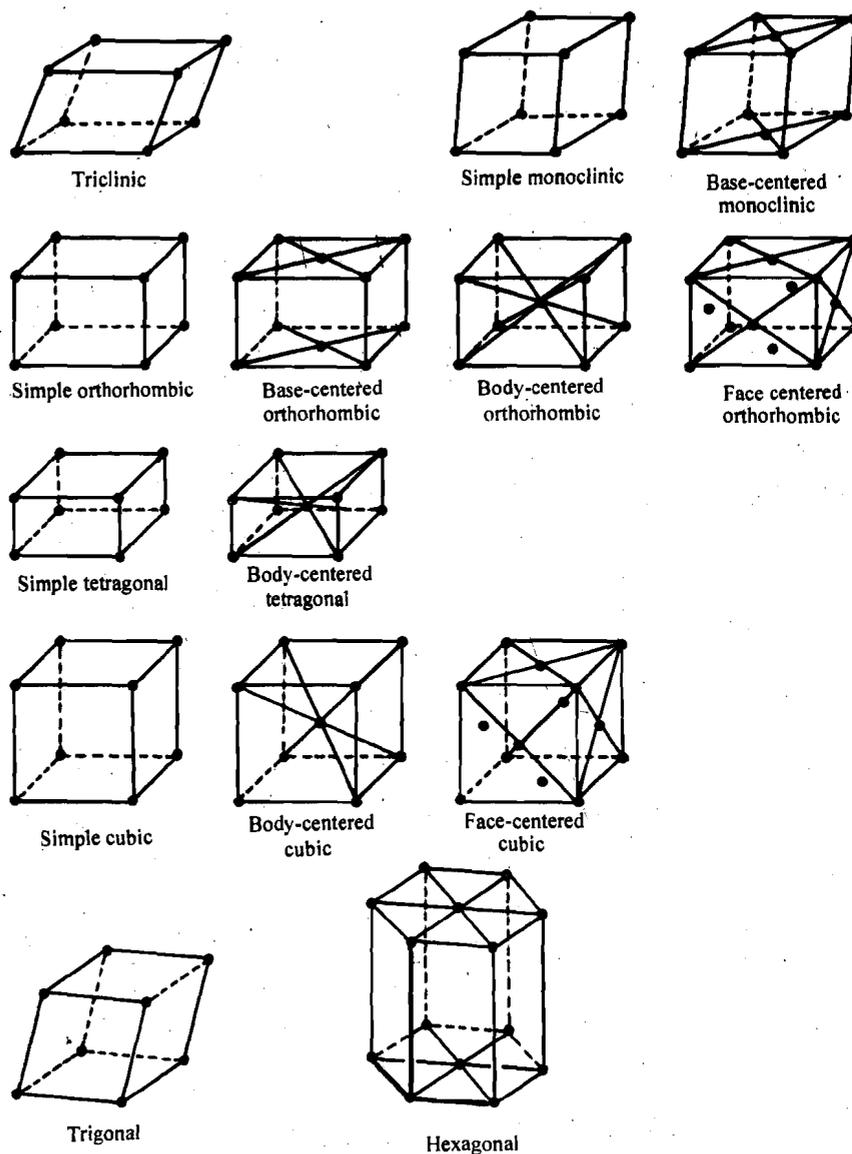


Fig.6.7: Seven crystal systems belonging to 14 Bravais lattices.

You know that when the group of transformations of a certain system consists of operations like rotation, reflection or inversion which leave one point of the system undisplaced in position, it is called a *point group*. Groups containing space translations are not point groups. The crystal symmetry groups can therefore be divided into two categories:

- (a) the **crystallographic point groups**, which leave at least one point of the crystal undisplaced, and
- (b) the **crystallographic space groups**, which include the translational symmetry of the crystals.

As you have seen, molecules possess only point symmetries, except in the case of very long-chain polymer molecules.

Let us now study some of the simpler crystallographic point groups involving one symmetry axis, in some detail.

### 6.3.1 Some Crystallographic Point Groups

The first question that may have come to your mind is: How many crystallographic point groups are possible? And how are they obtained? The requirement of translational symmetry in the crystals puts a limit on the number of possible crystallographic point groups. You can easily see this as follows. Recall that all the lattice points in a Bravais lattice are equivalent to each other. This means that if the lattice is invariant under a rotation of  $2\pi/n$  ( $n$  being a positive integer) about some axis passing through a lattice point, then a rotation of  $2\pi/n$  about a parallel axis passing through any other lattice point is also a symmetry transformation of the lattice.

This condition imposes severe restrictions on the possible point groups. In fact, it is an elementary problem of solid state physics to show that the only  $n$ -fold rotations consistent with translational symmetry are  $n = 1, 2, 3, 4$  and  $6$ . What this means essentially is that you cannot have translational symmetry with a pentagon (having 5-fold rotational symmetry). To verify this, try translating a pentagon repeatedly in a plane and see if you can fill it up. You will find that the resulting figure does not retain its symmetry! Similar situation exists for polygons with 7, 8 or more sides (see Fig. 6.8).

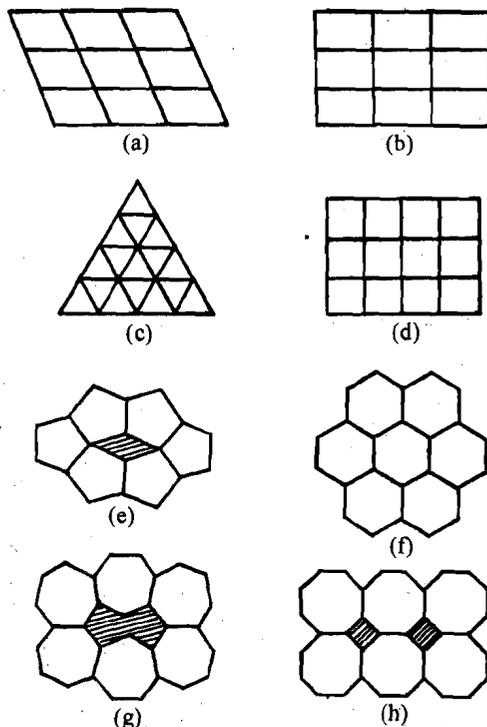


Fig.6.8: Only 1, 2, 3, 4 and 6-fold symmetry axes exist in crystals. Notice that in (e), (g) and (h) space cannot be filled without leaving gaps (shaded)

In Unit 5, we have introduced the concept of a group by considering the example of a square. You know that, in general, if we have a regular polygon of  $n$  sides, a rotation through  $2\pi/n$  about an axis normal to the plane of the polygon passing through its centre is a symmetry operation for it. This axis is known as its **principal axis** or **symmetry axis**. The cyclic group consisting of the  $n$  rotations ( $C_n, C_n^2, \dots, C_n^n = E$ ) is usually denoted by (the same symbol)  $C_n$ . This is the Schoenflies notation for the point groups which we shall be using in this unit. There are five crystallographic point groups having only *one axis of rotational symmetry*.

#### Five Point Groups with One Symmetry Axis

The groups having only one axis of rotational symmetry and consistent with translational symmetry in crystals are  $C_1, C_2, C_3, C_4$  and  $C_6$ .

For example, consider the simple monoclinic and orthorhombic crystal systems (Fig. 6.7). Both these have a two fold rotational symmetry about the principal 2-fold axis (which we have chosen as the vertical). Therefore, the point group corresponding to these systems is  $C_2$ . The triclinic system has only one-fold rotational symmetry corresponding to  $C_1$ . Similarly, the trigonal system corresponds to  $C_3$ , the cubic and the tetragonal to  $C_2$  and  $C_4$  and the hexagonal to  $C_6$  about their principal axes. You should verify these results from Fig. 6.7 before studying further.

The 2-D geometrical patterns having these symmetry groups are shown in Fig. 6.9. Such figures, which show the projection of the atoms on a plane, are called *stereographic projections*. In this figure, and in the following figures showing stereographic projections in this unit, we shall denote a point above the plane by + and a point below the plane by o. The nature of the rotation axis is denoted by a symbol in the centre of the circle. Thus, a filled ellipse denotes a two-fold axis, a filled triangle a three-fold axis, a filled square a four-fold axis and a filled hexagon a six-fold axis of proper rotations.

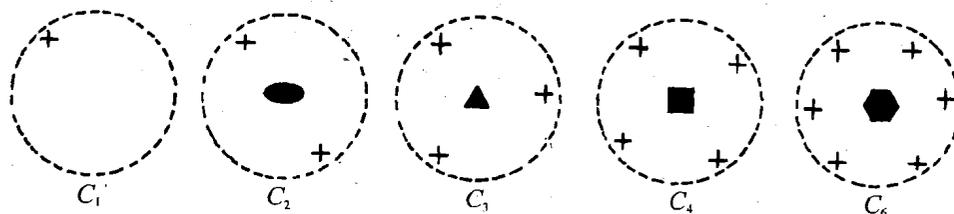


Fig.6.9: Stereographic projections for the point groups  $C_n$ .

#### Five Point Groups with $n$ fold Rotational Symmetry and Reflection Symmetry in Horizontal Plane

We can obtain five more point groups by introducing an additional symmetry element to the above rotations – **reflection in the horizontal plane** (the plane perpendicular to the principal axis) denoted by  $\sigma_h$ . We denote the group of order two,  $(E, \sigma_h)$ , by  $C_{1h}$ . You can verify that  $\sigma_h$  commutes with a rotation about the vertical axis. Noting this fact we see that the resulting groups, denoted by  $C_{nh}$  will contain all elements of  $C_n$  once and again all these elements multiplied by  $\sigma_h$ , that is

$$C_{nh} = \{ \{C_n\}, \{C_n\}\sigma_h \}, \quad (6.1)$$

where  $\{C_n\}$  stands for the elements of the group  $C_n$ . Thus, the group  $C_{nh}$  contains  $2n$  elements. You can verify from Fig. 6.7 that the monoclinic system has the point group  $C_{2h}$ , the tetragonal  $C_{4h}$ , the hexagonal  $C_{3h}$  and  $C_{6h}$ . The geometrical patterns having these symmetry groups are shown in Fig. 6.10. Notice that the symbol used is indicating a rotation followed by reflection. The points finally lie below the plane after the reflection. The presence of a horizontal reflection plane is indicated by drawing a full outer circle rather than a broken circle.

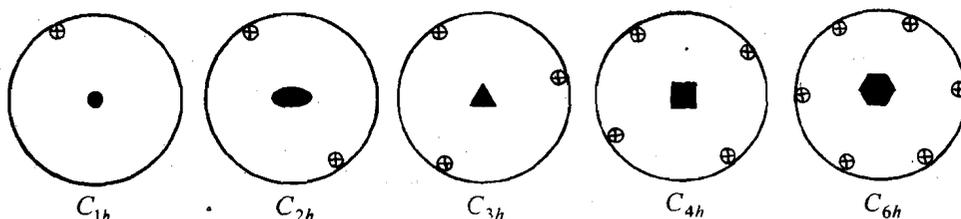


Fig.6.10: Stereographic projections for the point groups  $C_{nh}$ .

#### Four Point Groups with $n$ fold Rotational Symmetry and Reflection Symmetry in a Vertical Plane

Four more point groups can be obtained by adding a vertical reflection plane (passing through the  $n$ -fold axis) to the last four groups of Fig. 6.9. Such a reflection plane, passing through the axis of  $n$ -fold rotational symmetry, implies the existence of  $n - 1$  other vertical reflection planes, all passing through the axis of rotation. These groups as you know from Sec. 6.2 are denoted by  $C_{nv}$ . Examples of crystal systems having such point groups are

orthorhombic ( $C_{2v}$ ), tetragonal ( $C_{4v}$ ), trigonal ( $C_{3v}$ ), hexagonal ( $C_{6v}$ ) etc. The stereographs of  $C_m$  are shown in Fig. 6.11.

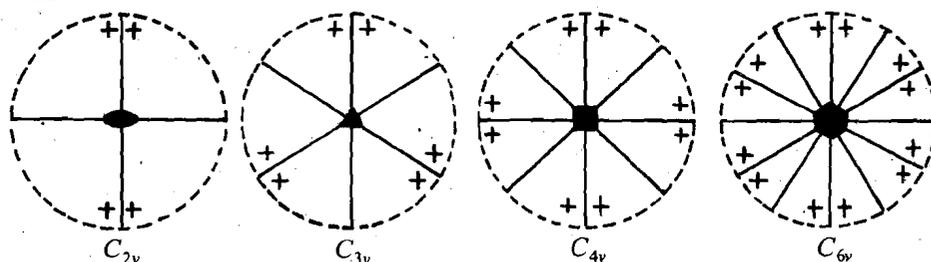


Fig.6.11: Stereographic projections for point groups  $C_m$ .

The reflection planes are shown by solid lines. You can see that a reflection does not commute with a rotation about an axis in the plane of the reflection. You should verify this before studying further.

### Activity 2

- Verify with the help of a book that a reflection in the horizontal plane ( $\sigma_h$ ) commutes with a rotation about the vertical axis.
- Verify that a reflection does not commute with a rotation about an axis in the plane of reflection.

Spend  
15 min

In the above case, since the 'vertical' and the 'horizontal' are not distinguishable for  $C_1$ , we do not have a new group such as  $C_{1v}$ . In other words, the group is identical to  $C_{1h}$ .

### Three Point Groups with $n$ fold Rotational Symmetry and Inversion

We may now add the inversion symmetry  $J$  to the first five groups of  $n$  fold rotational symmetry ( $n = 1, 2, 3, 4, 6$ ). Let us denote the group of order two,  $(E, J)$ , by the symbol  $S_2$ . Since inversion commutes with all the rotations we could have five groups, each with  $2n$  elements of the form

$$S_{2n} = \{C_n, C_n^2, \dots, C_n^{n-1}, C_n^n, S_2, C_n S_2, \dots, C_n^{n-1} S_2\} \quad (6.2)$$

But not all of these are new groups. In fact, you can verify that if  $n$  is even ( $n = 2, 4$  or  $6$ ), then  $S_{2n}$  is identical to  $C_{2n}$ . In the remaining two cases ( $n = 1$  and  $3$ ), we have two new groups  $S_2$  and  $S_6$ . A third group  $S_4$ , which is distinct from all the point groups hitherto considered, consists of four elements which are powers of the element  $J C_4 = S_4$ , i.e.,

$S_4 = \{E, S_4, C_4^2, S_4^3\}$  noting that  $J^2 = E$ . The stereographic projections for these groups are shown in Fig. 6.12.

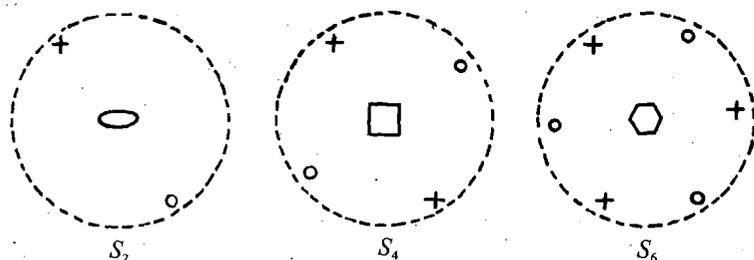


Fig.6.12: Stereographic projections for the point groups  $S_n$ .

The patterns with the symmetry groups  $S_2$  and  $S_6$  have inversion symmetry whereas the one with the group  $S_4$  does not. The triclinic system has  $S_2$  point group, tetragonal corresponds to  $S_4$  and trigonal to  $S_6$ .

You may now like to stop for a while and review what you have studied so far. The following SAQ will also help you clarify your ideas.

Spend  
10 min

SAQ 2

Consider the stereographic projection of  $C_1$ , the first part of Fig. 6.9, with only one point about the plane. Operate on this by the elements of group  $S_4$  and label all the points thus obtained. Show that it is identical to the one in Fig. 6.12.

Point Groups with Two or More Symmetry Axes

The 17 point groups discussed above contain only one axis of  $n$ -fold symmetry. We can obtain new point groups of order  $2n$  by adding  $n$  two-fold axes of symmetry in a plane perpendicular to the principal  $n$ -fold axis. These are the four dihedral groups  $D_n$  ( $n = 2, 3, 4, 6$ ). You have already studied about  $D_3$  in Sec. 6.2. For the group  $D_2$ , we have one principal axis of 2-fold symmetry and two horizontal axes of 2-fold symmetry (see Fig. 6.13). The group  $D_2$  therefore consists of the four elements ( $E, C_{2x}, C_{2y}, C_{2z}$ ). Here  $C_{2j}$  denotes two-fold rotational symmetry about  $Oj$  ( $j = x, y, z$ ) axis.

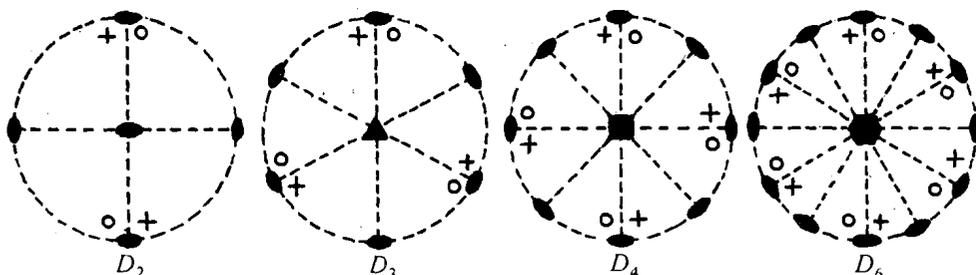


Fig.6.13: Stereographic projections for the point groups  $D_n$ .

The group  $D_1$  is identical to the group  $C_{1h}$  as you can work out in the following SAQ.

Spend  
5 min

SAQ 3

Show that the group  $D_1$  is not a new group but is identical to the group  $C_{1h}$ .

Can you write down the elements of the groups  $D_4$  and  $D_6$ ? The group  $D_4$  consists of 8 elements:  $E, 2C_4, C_4^2$  corresponding to the 4-fold principal axis;  $2C_2'$  and  $2C_2''$  corresponding to the 4 two-fold axes perpendicular to the principal axis. Similarly,  $D_6$  consists of 12 elements:  $E, 2C_6, 2C_6^2, C_6^3, 3C_2', 3C_2''$ . You should verify this statement from Fig. 6.13 before proceeding further.

All the 21 point groups mentioned so far have one principal  $n$ -fold axis (which we have chosen as the vertical) and the last 4 have  $n$  two-fold axes in the horizontal plane. These are known as the *simple point groups* and we have discussed some of them in increasing order of complexity. We can obtain six more simple point groups which we state below, without going into details:

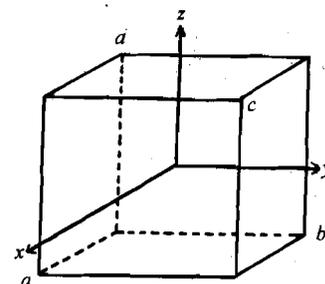
- 4 groups ( $D_{nh}, n = 2, 3, 4, 6$ ) by adding horizontal two-fold axes to the five groups  $C_{nh}$ ;
- 2 groups ( $D_{nd}, n = 2, 3$ ) by adding diagonal reflection planes bisecting the angles between the horizontal two-fold axes to the groups  $D_n$ .

These as you have seen are the point groups that occur in two and three-dimensional crystals. There are five more groups of higher symmetry in which there is no unique principal axis of higher symmetry. We shall not go into their details here.

The largest point group, known as  $O_h$  is the full symmetry group of a cube (Fig. 6.14). It has 48 elements; of these 24 are proper rotations and 24 are improper rotations. The 24 proper rotations, which themselves constitute a subgroup of  $O_h$ , are denoted by  $O$  and called the cubic group of proper rotations. These are listed in Table 6.1. Their effect on a cartesian coordinate system ( $x, y, z$ ) is also indicated in the last column of the table.

**Table 6.1: The elements of group  $O$  listed classwise along with their operation on a coordinate system  $(x, y, z)$** 

Class	Operation	$x, y, z$ change to
$(E)$	Identity operation (1 element)	$(x, y, z)$
$(3C_4, 3C_4^3)$ or $(6C_4)$	Rotations through $\pi/2$ and $3\pi/2$ about $x, y,$ and $z$ (6 elements)	$(y, -x, z), \text{ etc.}$
$(3C_2^2)$	Rotations through $\pi$ about $x, y$ and $z$ (3 elements)	$(-x, -y, z), \text{ etc.}$
$(6C_2)$	Rotations through $\pi$ about a line joining centres of any pair of opposite edges (6 elements)	$(y, x, -z), \text{ etc.}$
$(4C_3, 4C_3^2)$ or $(8C_3)$	Rotations through $2\pi/3$ and $4\pi/3$ about the four cube diagonals (8 elements)	$(y, z, x), \text{ etc.}$


**Fig.6.14: Symmetries of a cube.**

The remaining 24 elements of  $O_h$  are obtained by combining the 24 elements of  $O$  with the inversion operator  $J$ , which has the effect of changing  $(x, y, z)$  to  $(-x, -y, -z)$ . The composite operations are denoted by  $JC_4^2, JC_3$ , etc. Note that  $J$  itself is a symmetry operation of the cube. Thus, the group  $O_h$  consists of 48 elements, 24 belonging to  $O$  and 24 those of  $O$  multiplied by the inversion:

$$O_h = \{O\}, \{O\}J \quad (6.3)$$

It is interesting to note that the number of permutations of  $(x, y, z)$  among themselves is six, and we can attach a positive or a negative sign to each of them in eight different ways (Fig. 6.14); the total number of arrangements of  $\pm x, \pm y, \pm z$  is thus 48. In other words, 48 is the number of ways in which we can choose a cartesian coordinate system with axes parallel to the edges of a cube.

Before closing this section, we list in Table 6.2 the point groups which can occur in the seven three-dimensional lattice systems in increasing order of symmetry. A system can also have point groups of the systems which have preceded it in Table 6.2. The last entry for each system shows the point group with the highest symmetry for the system.

**Table 6.2: The point groups corresponding to the seven lattice systems**

System	Point Groups
Triclinic	$C_1, S_2;$
Monoclinic	$C_{1h}, C_2, C_{2h};$
Orthorhombic	$C_{2v}, D_2, D_{2h};$
Trigonal	$C_3, S_6, C_{3v}, D_3, D_{3d};$
Tetragonal	$S_4, D_{2d}, C_4, C_{4h}, C_{4v}, D_4, D_{4h};$
Hexagonal	$C_6, C_{3h}, D_{3h}, C_{6h}, C_{6v}, D_6, D_{6h};$
Cubic	$T, T_h, T_d, O, O_h.$

Apart from the point groups, certain groups are associated with the translational symmetry of crystals. We will consider them very briefly.

### 6.3.2 Translation Group

We now consider the translation group for crystals. We shall first illustrate the situation for a linear (1-D) crystal for simplicity.

Consider a linear lattice of  $N$  lattice points with the lattice constant  $a$  (Fig. 6.15). We employ the periodic boundary conditions so that  $x - Na \equiv x$ , where  $x$  is the coordinate measured along the linear lattice. Such a lattice is invariant under translations by multiples of  $a$  along the lattice.

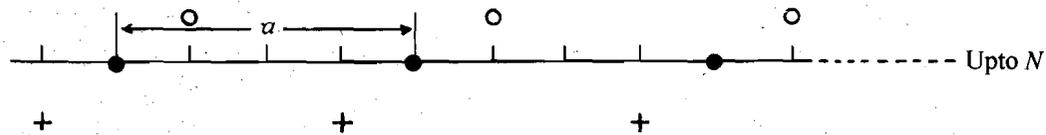


Fig.6.15: Translational symmetry in a linear lattice of  $N$  points

Let  $T_1$  denote the operator for translation to the right by  $a$  and let  $T_n$  denote the operator for translation by a distance  $na$ . Then

$$T_1 x = x + a, \quad T_n x = (T_1)^n x = x + na. \quad (6.4a)$$

Owing to the periodic boundary conditions, we have

$$T_N x = (T_1)^N x = x + Na = x. \quad (6.4b)$$

The powers of  $T_1$  clearly generate a cyclic group of order  $N$ . We shall denote this group, known as the *translation group*, by

$$T = \{T_N \equiv E, T_1, T_2, \dots, T_{N-1}\}. \quad (6.5)$$

Note that each element of  $T$  is a class by itself since  $T$  is an abelian group (recall Sec. 5.3, Unit 5). We can generalise these results to three-dimensions.

The translation symmetry operators of a three-dimensional lattice also constitute a group. Let the lattice be generated by the three primitive translation vectors  $\mathbf{a}_1$ ,  $\mathbf{a}_2$  and  $\mathbf{a}_3$ . We use the following periodic boundary conditions:

$$\mathbf{r} - N_1 \mathbf{a}_1 = \mathbf{r}, \quad \mathbf{r} - N_2 \mathbf{a}_2 = \mathbf{r}, \quad \mathbf{r} - N_3 \mathbf{a}_3 = \mathbf{r}, \quad (6.6)$$

where  $\mathbf{r}$  is the position vector of some point in the lattice and the number of primitive cells is  $N_1 N_2 N_3$ .

Let the operator  $T(n_1, n_2, n_3)$  denote a translation through a vector  $\mathbf{t}(n_1, n_2, n_3)$  given by

$$T(n_1, n_2, n_3) \mathbf{r} = \mathbf{r} + n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2 + n_3 \mathbf{a}_3 = \mathbf{r} + \mathbf{t}(n_1, n_2, n_3), \quad (6.7)$$

where  $1 \leq n_i \leq N_i$ . It can be seen that the successive application of two translation operators is equivalent to another translation operator. Thus;

$$T(m_1, m_2, m_3) T(n_1, n_2, n_3) \mathbf{r} = T(m_1 + n_1, m_2 + n_2, m_3 + n_3) \mathbf{r}. \quad (6.8)$$

All such operators constitute a group which is of order  $N_1 N_2 N_3$ . This is the **full translation group**  $T$  of a three-dimensional lattice. The identity element is  $T(0, 0, 0) = T(N_1, N_2, N_3)$ . All the translations of the group  $T$  commute with each other; the group is therefore again abelian though not cyclic.

An actual three-dimensional lattice will be invariant under both the point group transformations and the translations of groups. This brings us to the concept of space groups.

### 6.3.3 Space Groups

The full symmetry group of a crystal is called its **space group**. The elements of a space group are combinations of the point group operations and translations.

A general element of the space group may therefore be denoted by  $\{A/\tau\}$ , where  $A$  is a point group operation and  $\tau$  is a translation, which is not necessarily an element of the translation group of the crystal. The operation  $\{A/\tau\}$  on the position vector  $\mathbf{r}$  is defined as

$$\{A/\tau\} \mathbf{r} = A\mathbf{r} - \tau.$$

All such operations which leave the crystal invariant make the space group. There are altogether 230 possible space groups and their study is beyond the scope of this course.

Let us now study how symmetry in the microscopic world is expressed in terms of group theory.

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## 6.4 SYMMETRY AND CONSERVATION LAWS IN QUANTUM MECHANICS

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As you are well aware from your study of Blocks 2 and 3 of PHE-11, the fundamental problem of quantum mechanics is to investigate the Schrodinger equation for a given physical system:

$$H\psi = E\psi \quad (6.9)$$

where  $H$  is the Hamiltonian operator of the system and  $\psi$  and  $E$  are its eigenfunction and eigenvalue, respectively. The Hamiltonian operator of a physical system plays two major roles in quantum mechanics. Firstly its eigenvalues  $E$  given by Eq. (6.9) are the only allowed values of the energy of the system. Secondly, the time development of the system is determined by the wavefunction  $\psi(t)$  which satisfies the time-dependent Schrodinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (6.10)$$

Thus, a considerable amount of information about the system can be obtained by simply examining the set of transformations which leave the Hamiltonian invariant. Indeed one of the main applications of group theory in quantum mechanics is to extract as much information as possible from this set of transformations.

To present the essential features as clearly as possible, we will consider an isolated single particle system with a typical Hamiltonian given by

$$H(\mathbf{r}) = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (6.11)$$

where  $m$  is the mass of the particle and  $V(\mathbf{r})$  is the potential experienced by it.

Let us consider the operation of  $P_R$ , which corresponds to some coordinate transformation  $R$ , on the Schrödinger equation (6.9):

$$P_R H\psi = P_R E\psi$$

Notice that both  $\psi$  and  $P_R \psi$  belong to the same eigenvalue  $E$ . Hence  $E$  is degenerate.

or

$$(P_R H P_R^{-1})(P_R \psi) = E P_R \psi$$

or

$$H'(P_R \psi) = E(P_R \psi)$$

where

$$H' = P_R H P_R^{-1}$$

is the Hamiltonian with respect to the transformed coordinate system.

If the operator  $P_R$  is such that

$$H' = P_R H P_R^{-1} = H \quad (6.12)$$

then the coordinate transformation is said to leave the **Hamiltonian invariant**. From Eq. (6.12) it follows that

$$H P_R = P_R H \quad (6.13)$$

This shows that the Hamiltonian commutes with all the operators under which it is invariant.

The set of all transformations  $R$  which leave the physical system invariant forms a group. The set of corresponding transformations which leave the Hamiltonian invariant also constitutes a group known as the **symmetry group of the Hamiltonian** or the **group of the Schrodinger equation**. Why don't you verify this statement before studying further?

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#### SAQ 4

Spend  
10 min

Prove that the set of coordinate transformations that leaves the Hamiltonian invariant forms a group.

---

In this section we will focus on the connection between symmetry and conservation laws in quantum mechanics. We have to look for the symmetry operations that leave the time-independent Hamiltonian operator of an **isolated system** invariant. We shall now show that for each symmetry operation that leaves the Hamiltonian invariant, there is a corresponding physical quantity that is conserved.

#### 6.4.1 Symmetry under Spatial Translations : Conservation of Linear Momentum

Consider a physical system represented by a wave function  $\psi(\mathbf{r})$ . Let the system be translated in space by an arbitrary displacement  $\mathbf{a}$ . Such a translation is equivalent to displacing the coordinate system through  $-\mathbf{a}$ . Thus the new position vector  $\mathbf{r}'$  of a point is related to the old one  $\mathbf{r}$ , by

$$\mathbf{r}' = T(\mathbf{a}) \mathbf{r} = \mathbf{r} + \mathbf{a} \quad (6.14a)$$

where  $T(\mathbf{a})$  is the operator effecting the translation in space. The inverse translation is defined by

$$\mathbf{r} = T^{-1}(\mathbf{a}) \mathbf{r}' = \mathbf{r}' - \mathbf{a} \quad (6.14b)$$

Let the wave function  $\psi'(\mathbf{r})$  describe the system after the translation. The two wavefunctions can be connected by an operator  $P_r(\mathbf{a})$  defined so that

$$P_r(\mathbf{a}) \psi(\mathbf{r}) = \psi'(\mathbf{r}) \equiv \psi(\mathbf{r} - \mathbf{a}) \quad (6.15)$$

Note that  $T(\mathbf{a})$  and  $P_r(\mathbf{a})$  are different operators. While  $T(\mathbf{a})$  operates on the coordinates of the system,  $P_r(\mathbf{a})$  operates on the wavefunction. We would now like to obtain an expression for the translation operator  $P_r(\mathbf{a})$ . Since  $\psi(\mathbf{r})$  is continuous and differentiable at all points in space, we can expand  $\psi(\mathbf{r} - \mathbf{a})$  in a Taylor series. Let us consider the effect of an infinitesimal translation  $\delta\mathbf{a}$  and retain terms to the first order in  $\delta\mathbf{a}$ :

$$\begin{aligned}\psi'(\mathbf{r}) &= \psi(\mathbf{r} - \delta\mathbf{a}) = \psi(\mathbf{r}) - \delta a_x \frac{\partial\psi(\mathbf{r})}{\partial x} - \delta a_y \frac{\partial\psi(\mathbf{r})}{\partial y} - \delta a_z \frac{\partial\psi(\mathbf{r})}{\partial z} \\ &= (I - \delta\mathbf{a}\cdot\nabla) \psi(\mathbf{r})\end{aligned}\quad (6.16)$$

Comparing Eqs. (6.15) and (6.16) we can write

$$\begin{aligned}P_r(\delta\mathbf{a}) &= I - \delta\mathbf{a}\cdot\nabla \\ &= I - \frac{i}{\hbar} \delta\mathbf{a}\cdot\mathbf{p}_{op}\end{aligned}$$

where  $\mathbf{p}_{op} = -i\hbar\nabla$  is the linear momentum operator of the particle.

A finite translation  $\mathbf{a}$  can be obtained by performing successive infinitesimal translations (each step corresponding to matrix multiplication) in steps of  $\delta\mathbf{a}$ . We can write  $\delta\mathbf{a} = \frac{\mathbf{a}}{n}$  and take the limit  $n \rightarrow \infty$ . We then have

$$P_r(\mathbf{a}) = \lim_{n \rightarrow \infty} \left( I - \frac{i}{\hbar} \frac{\mathbf{a}\cdot\mathbf{p}_{op}}{n} \right)^n$$

or

$$P_r(\mathbf{a}) = \exp\left(-\frac{i}{\hbar} \mathbf{a}\cdot\mathbf{p}_{op}\right) \quad (6.17)$$

Since  $\mathbf{a}$  is real and  $\mathbf{p}_{op}$  is hermitian,  $P_r(\mathbf{a})$  is a unitary operator (see Unit 2 of this block).

Let us see if  $\psi'(\mathbf{r})$  still characterizes a possible state of the system. For this we consider the time dependent Schrödinger equation

$$i\hbar \frac{\partial\psi'(\mathbf{r})}{\partial t} = i\hbar P_r(\mathbf{a}) \frac{\partial\psi(\mathbf{r})}{\partial t} = P_r(\mathbf{a}) H\psi(\mathbf{r})$$

Since

$$\psi'(\mathbf{r}) = P_r(\mathbf{a})\psi(\mathbf{r}) \quad \text{and} \quad P_r^\dagger(\mathbf{a})P_r = I$$

we have

$$\begin{aligned}P_r^\dagger(\mathbf{a})\psi'(\mathbf{r}) &= P_r^\dagger(\mathbf{a})P_r(\mathbf{a})\psi(\mathbf{r}) \\ &= \psi(\mathbf{r}),\end{aligned}$$

Thus we have

$$i\hbar \frac{\partial\psi'(\mathbf{r})}{\partial t} = P_r(\mathbf{a}) H P_r^\dagger(\mathbf{a})\psi'(\mathbf{r})$$

Thus  $\psi'(\mathbf{r})$  satisfies the time-dependent equation with the same Hamiltonian if and only if

$$H' = P_r(\mathbf{a}) H P_r^\dagger(\mathbf{a}) = H$$

or

$$P_r(\mathbf{a}) H = H P_r(\mathbf{a}) \tag{6.18}$$

In Unit 7 of PHE-11, you have obtained the following relation for the time variation of the average value of an operator  $D$ :

$$\frac{d\langle D \rangle}{dt} = \langle [D, H] \rangle$$

Thus if  $[D, H] = 0$ ,

$$\frac{d\langle D \rangle}{dt} = 0$$

and  $\langle D \rangle$  is a constant of motion.

Using the definition of  $P_r(\mathbf{a})$  from Eq. (6.17) we can see that Eq. (6.18) will hold for all vectors  $\mathbf{a}$  if and only if  $[p_{op}, H] = 0$ , i.e.,  $p_{op}$  commutes with  $H$ , implying that linear momentum is a constant of motion and is conserved (see margin remark). Thus we can conclude that

If the Hamiltonian of an isolated physical system is invariant under all space translations, its linear momentum is conserved.

The set of all translation operators  $P_r(\mathbf{a})$  with the law of composition  $P_r(\mathbf{a}) P_r(\delta\mathbf{a}) = P_r(\delta\mathbf{a}) P_r(\mathbf{a}) = P_r(\mathbf{a} + \delta\mathbf{a})$  constitutes a symmetry group of the physical system.

Let us apply these ideas to two simple examples.

### Free Particle System

The Hamiltonian of a free particle is given by

$$H = -\frac{\hbar^2 \nabla^2}{2m} = \frac{\mathbf{p}^2}{2m}$$

Its wavefunction is of the form of the plane wave  $\exp(i \mathbf{k} \cdot \mathbf{r})$  where  $\mathbf{k}$  denotes the wave vector of the particle. If we displace the system through a vector  $\mathbf{a}$ , the new wavefunction  $\exp[i \mathbf{k} \cdot (\mathbf{r} - \mathbf{a})]$  also represents a possible state of the free particle. It satisfies  $H\Psi = E\Psi$ . This is true for any vector  $\mathbf{a}$  since  $\mathbf{p}$  commutes with the Hamiltonian and is therefore a constant of motion ( $\mathbf{p} = \hbar \mathbf{k}$ ).

### Electron in the Hydrogen Atom

The position vector  $\mathbf{r}$  of the electron is measured in a coordinate system whose origin is at the nucleus. In this system the wavefunction is of the form  $R_{nl}(r)Y_{lm}(\theta, \phi)$  (see Unit 9 of PHE-11). If we displace the system through some vector  $\mathbf{a}$ , the nucleus is no longer at the origin of coordinates. The displaced wavefunction cannot be put in the standard form and hence does not denote a possible state of the system.  $H$  does not commute with  $\mathbf{p}$  and hence the linear momentum of an electron in a hydrogen atom is not a constant of motion.

## 6.4.2 Time Translations and Conservation of Energy

Let  $\psi(t)$  be the wave function of a physical system and let  $P_t(\tau)$  denote the operator for translating the function of time by an amount  $\tau$ . We then have

$$P_t(\tau) \psi(t) = \psi'(t) = \psi(t - \tau) \tag{6.19}$$

Expanding  $\psi(t - \tau)$  in a Taylor series about the point  $t$ , we get

$$\psi(t - \tau) = \left\{ 1 - \tau \frac{\partial}{\partial t} + \frac{\tau^2}{2!} \frac{\partial^2}{\partial t^2} - \dots \right\} \psi(t) = \exp(-\tau \partial / \partial t) \psi(t)$$

and

$$P_t(\tau) \psi(t) = \exp(-\tau \partial / \partial t) \psi(t)$$

Thus

$$P_t(\tau) = \exp\left(-\tau \frac{\partial}{\partial t}\right) \quad (6.20)$$

Now we know that the quantum mechanical energy operator is given by  $H = i \hbar \partial/\partial t$ . Hence

$$P_t(\tau) = \exp(i\tau H / \hbar) \quad (6.21)$$

which is a unitary operator since  $\tau$  is real and  $H$  is hermitian. Once again

$$P_t H \psi = P_t E \psi$$

or

$$P_t H P_t^{-1} P_t \psi = E P_t \psi$$

$$H'(P_t \psi) = E(P_t \psi)$$

where  $H' = P_t H P_t^{-1}$ .

If  $H' = H$ , i.e. if  $H$  is invariant under all time translations then

$$P_t H = H P_t$$

or

$$[H, P_t] = 0 \text{ for all } \tau \quad (6.22)$$

Using the expression for  $P_t$  from Eq. (6.21) we can say that  $H$  and hence energy is a constant of motion.

Thus if the Hamiltonian of a physical system is invariant under all time translations, then the energy of the system is a constant of motion. The set of all time translations is again a symmetry group of the physical system.

Once again let us consider the example of an isolated hydrogen atom with no perturbations. Then its Hamiltonian is invariant under all time translations. If the atom is in a given state at any instant of time, it will continue to remain in the state for all time, and its total energy will be conserved. On the other hand, if we apply time-dependent perturbations to the atom, its Hamiltonian is no longer invariant under time translations and its energy is not conserved any more.

We can similarly relate the rotational symmetry of the Hamiltonian to the conservation of angular momentum. However, we will not go into these details here.

Let us now summarise what you have studied in this unit.

## 6.5 SUMMARY

- Group theory finds several applications in the study of symmetry in molecules and crystals, such as molecular spectra, their properties like dipole moment, optical activity etc. and electronic structure of crystals, point impurities in crystals, lattice vibrations etc.
- The symmetry group of a molecule is called a **molecular point group**.
- The complete symmetry group of an ideal crystal is called its **space group**. There are altogether 230 space groups.
- Those symmetry elements, under which at least one point of the crystal remains at the same position, make a group called the **point group** of the crystal. There are altogether

32 point groups. Among these, 27 point groups can also occur in two-dimensional crystals, and the other five refer to cubic systems.

- When a physical system possesses a certain symmetry, i.e., its Hamiltonian is invariant under a certain transformation, there is a corresponding physical observable which is a constant of motion.
- The conservation of linear momentum, angular momentum and energy of an isolated system are a consequence of the invariance of the Hamiltonian under space translations, rotations and time translations, respectively.

## 6.6 TERMINAL QUESTIONS

Spend 20 min

1. Construct the point symmetry groups of the molecules  $C_2H_2$ , mesotartaric acid and HBr shown in Fig. 6.16.
2. You have studied in Sec. 6.3.1 that the 48 elements of the cubic group  $O_h$  correspond to the 48 ways in which we can choose a 3-D cartesian coordinate system with axes parallel to the cube edges. In a similar manner, show that the 8 elements of  $C_{4v}$ , the group of a square which you studied in Unit 5, correspond to the 8 distinct ways of choosing a cartesian coordinate system with  $x$  and  $y$  axes parallel to the edges of the square.

## 6.7 SOLUTIONS AND ANSWERS

### Self-Assessment Questions

1.  $NH_3$  has a three-fold rotational symmetry and reflection symmetry in the vertical planes shown in Fig. 6.17. Hence its point group is  $C_{3v}$ .

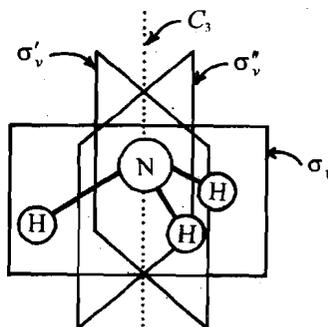


Fig.6.17: The symmetry group of  $NH_3$

2. The group elements of  $S_4$  are  $(E, S_4, S_4^2, S_4^3)$  where  $S_4$  denotes a rotation through  $\pi/2$  (in the clockwise sense) about a vertical axis ( $C_4$ ) followed by inversion in the origin. Let us label the initial point in the stereographic projection of  $C_1$  as  $P$  which is above the plane of the circle. The origin is supposed to be at the centre of the circle.  $E$  is the identity operator and when it operates on point  $P$ ,  $P$  remains where it is. To operate by  $S_4$ , we rotate the point  $P$  about the vertical axis through  $\pi/2$  so that it goes near  $S$  but above the plane, and then invert it in the origin so that it goes to point  $Q$  below the plane. See Fig. 6.18. One more operation of  $S_4$  on  $Q$  brings it to point  $R$  above the plane, and finally to point  $S$ . One more operation of  $S_4$  brings it back to point  $P$ ; thus there is no new point. This gives the stereographic projection for  $S_4$  shown in Fig. 6.12.

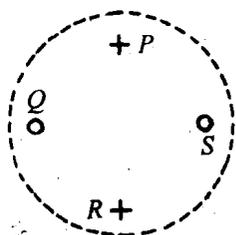


Fig.6.18

3. We start with the stereographic projection of group  $C_1$ , with just one point  $A$  above the plane. The presence of a horizontal reflection plane gives rise to another point, and the stereographic projection of the resulting group  $C_{1h}$  is shown in Fig. 6.10. On the other hand, let us see the effect of having a two-fold rotation symmetry axis in the horizontal plane, such as  $PQ$  in Fig. 6.19. A rotation of  $A$  about  $PQ$  through  $\pi$  would give rise to a point  $B$  below the plane. That means here also there are just two points  $A$  and  $B$ . Now we may choose the plane which is the perpendicular bisector of the line  $AB$  and call it

the reflection plane. Looking perpendicular to this plane, we see that the point  $B$  would be below  $A$ , which is exactly the case in the group  $C_{1h}$ .

4. Let us see whether the four groups axioms are satisfied:

- i. If the Hamiltonian is invariant under two transformations  $P_R$  and  $P_S$  then it is invariant under their product  $P_R \cdot P_S$ ;
- ii. The associative law is valid for all coordinate transformations;
- iii. The identity transformation leaves the Hamiltonian invariant;
- iv. Finally, if  $P_R$  leaves the Hamiltonian invariant, then  $P_R^{-1}$  also leaves  $H$  invariant because (if  $P_R H P_R^{-1} = H$ , then it follows that  $H = P_R^{-1} H P_R$ ) Hence the inverse also exists.

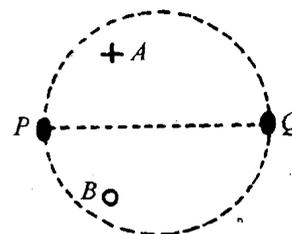


Fig.6.19

Thus the set of all transformations  $P_R$  which leave the Hamiltonian invariant forms a group.

### Terminal Questions

1.  $C_2H_2$  is a linear molecule having the point symmetry group  $D_{\infty h}$ . The mesotartaric acid has the point symmetry group  $S_2$  containing the elements  $E$  and  $J$ . The point symmetry group of  $HBr$  is  $C_{\infty v}$ .
2. The eight elements of  $C_{4v}$  correspond to the eight ways of choosing the  $x$  and  $y$  axes parallel to the edges of a square, as shown in Fig. 6.20.

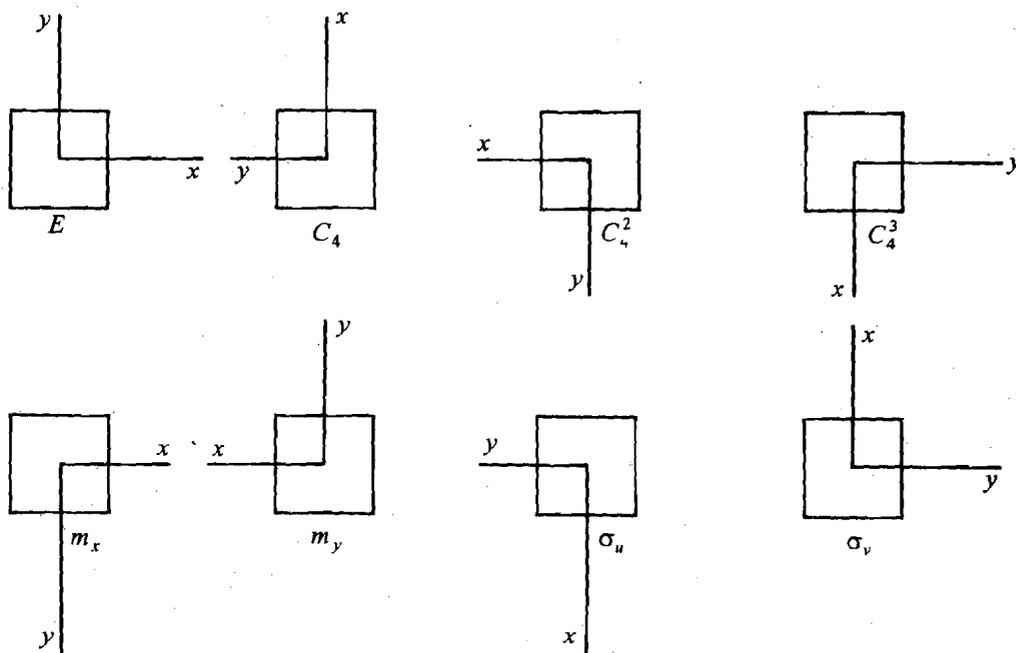


Fig.6.20

### FURTHER READING

1. Matrices and Tensors in Physics, A.W. Joshi, New Age International, 3<sup>rd</sup> Edition, 1995.
2. Elements of Group Theory for Physicists, A.W. Joshi, New Age International, 4<sup>th</sup> Edition, 1997.
3. Mathematics A Textbook for Class XII, Part I, NCERT, 1989.

# NOTES