

# Symmetry: its description and consequences

# 15

## Check-list of key ideas

1. The significance of *symmetry operations* and of the corresponding *symmetry elements* (Section 15.1).
2. The *classification* of molecules into *point groups* according to the symmetry elements they possess (Section 15.2).
3. The identification of *polar molecules* and *chiral molecules* from their point groups (Section 15.3).
4. The *representation* of symmetry operations by matrices (Section 15.5).
5. The *character* of symmetry operations and the recognition of *classes* of operation (Section 15.5).
6. A representation as a *direct sum of irreducible representations* (Section 15.6).
7. The *character table* of a point group and the recognition of the *symmetry species* of the irreducible representations of the group (Section 15.6).
8. The transformation properties of  $x$ ,  $y$ , and  $z$  and of functions that can be built from them (Section 15.7).
9. The identification of the symmetry properties of functions and products of functions that guarantees that their integral must be zero (Section 15.8 and Examples 15.7 and 15.8).
10. Using symmetry to decide if orbitals have zero overlap (Section 15.8 and Example 15.9).
11. The deduction of *selection rules* from the point group of the molecule (Section 15.8 and Example 15.10).
12. The construction of *symmetry-adapted linear combinations* of atomic orbitals for the construction of molecular orbitals (Section 15.9).

## The symmetry elements of objects

- 15.1 Operations and elements
- 15.2 The symmetry classification of molecules
- 15.3 Some immediate consequences of symmetry

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- 15.9 Symmetry-adapted linear combinations

## Further information: matrices

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In this chapter we sharpen the concept of ‘shape’ into a precise definition of ‘symmetry’, and show that it may be discussed systematically. We shall see how to classify any molecule according to its symmetry, and how to use this classification to discuss molecular properties without the need for detailed calculation. We shall see how to treat systematically many of the topics that we have mentioned in previous chapters. We shall see, for instance, how to select linear combinations of atomic orbitals that match the symmetry of the nuclear framework, and we remarked in Chapter 14 that this grouping of orbitals is one of the central features of molecular orbital theory. We shall see how to judge from its symmetry classification alone whether a molecule is polar or chiral. Through symmetry we shall be able to derive the selection rules that govern the intensities of spectroscopic transitions, not only of the electronic transitions that are responsible for the colours of substances, but also of the rotational and vibrational transitions that give rise to their microwave and infrared spectra.

The detailed discussion of symmetry is called **group theory**. Much of group theory is a systematic summary of common sense about the symmetries of objects. However, because group theory is systematic, its rules can be applied in a straightforward, mechanical way, and in some cases it gives unexpected results. In most cases the theory gives a simple, direct method for arriving at useful conclusions with the minimum of calculation, and this is the aspect we stress here.

## The symmetry elements of objects

Some objects are ‘more symmetrical’ than others. A sphere is more symmetrical than a cube because it looks the same after it has been rotated through any angle about any diameter. A cube looks the same only if it is rotated through  $90^\circ$ ,  $180^\circ$ , or  $270^\circ$  about an axis passing through the centres of any of its opposite faces (Fig. 15.1), or by  $120^\circ$  or  $240^\circ$  about an axis passing through any of its opposite corners. Similarly the  $\text{NH}_3$  molecule is ‘more symmetrical’ than the  $\text{H}_2\text{O}$  molecule because it looks the same after rotations of  $120^\circ$  or  $240^\circ$  about the axis shown in Fig. 15.2, whereas  $\text{H}_2\text{O}$  looks the same only after a rotation of  $180^\circ$ .

An action that leaves an object looking the same after it has been carried out is called a **symmetry operation**. There is a corresponding **symmetry element** for each symmetry operation; this is the point, line, or plane with respect to which the symmetry operation is performed. We shall use the same symbol for the symmetry operation and the corresponding element, but always say which is intended if it is important to distinguish between them. We shall see that we can classify molecules by identifying all their symmetry elements, and grouping together those with identical elements. This procedure puts a sphere into a different group from a cube, and  $\text{NH}_3$  into a different group from  $\text{H}_2\text{O}$ .

### 15.1 Operations and elements

There are five kinds of symmetry operation (and five kinds of symmetry element) that leave at least a single point unchanged and hence give rise to the **point groups**. When we consider crystals (Chapter 21), we shall refer to the symmetries arising from translation through space. These more extensive groups are called **space groups**.

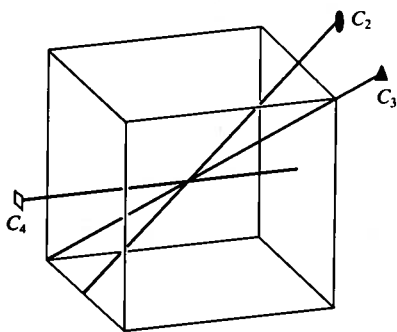


Fig. 15.1 Some of the symmetry elements of a cube. The twofold, threefold, and fourfold axes are labelled with the conventional symbols.

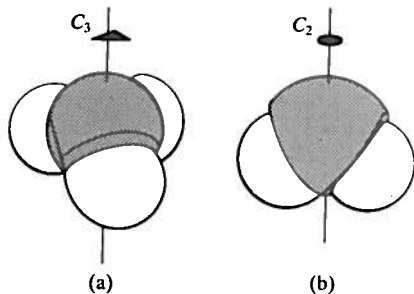


Fig. 15.2 (a) The  $\text{NH}_3$  molecule has a threefold ( $C_3$ ) axis and (b) the  $\text{H}_2\text{O}$  molecule has a twofold ( $C_2$ ) axis.

The **identity**  $E$  consists of doing nothing; the corresponding element is the entire object. Since every molecule is indistinguishable from itself if nothing is done to it, every object possesses at least the identity element. One reason for including it is that some molecules (e.g.  $\text{CHClBrF}$ ) have only this symmetry element; another reason is technical and connected with the formulation of group theory.

An  $n$ -fold rotation (the operation) about an  $n$ -fold axis of symmetry  $C_n$  (the corresponding element) is a rotation through  $360^\circ/n$ . An  $\text{H}_2\text{O}$  molecule has a two-fold axis,  $C_2$ . An  $\text{NH}_3$  molecule has a three-fold  $C_3$  with which are associated two operations, one being  $120^\circ$  rotation in a clockwise sense and the other  $120^\circ$  rotation in a counter-clockwise sense. (There is only one two-fold rotation associated with a  $C_2$  axis because clockwise and counter-clockwise  $180^\circ$  rotations are identical.) A cube has three  $C_4$  axes, four  $C_3$  axes, and six  $C_2$  axes. However, even this high symmetry is capped by a sphere, which possesses an infinite number of symmetry axes (along any diameter) of all possible orders of  $n$ . If a molecule possesses several rotation axes, the one (or more) with the greatest value of  $n$  is called the **principal axis**.

A **reflection** (the operation) in a **plane of symmetry** or a **mirror plane**  $\sigma$  (the element) may be either parallel or perpendicular to a principal axis of a molecule. If the plane is parallel to the principal axis, it is called **vertical** and denoted  $\sigma_v$ . An  $\text{H}_2\text{O}$  molecule has two vertical planes of symmetry (Fig. 15.3) and an  $\text{NH}_3$  molecule has three. When the plane of symmetry is perpendicular to the principal axis it is called **horizontal** and denoted  $\sigma_h$ . The  $\text{C}_6\text{H}_6$  molecule has a  $C_6$  principal axis and a horizontal mirror plane (as well as several other elements). A vertical mirror plane that bisects the angle between two  $C_2$  axes (Fig. 15.4) is called a **dihedral plane** and denoted  $\sigma_d$ .

In an **inversion** (the operation) through a **centre of symmetry**  $i$  (the element) we imagine taking each point in a molecule, moving it to its centre, and then moving it out the same distance on the other side. Neither an  $\text{H}_2\text{O}$  molecule nor an  $\text{NH}_3$  molecule has a centre of inversion, but both the sphere and the cube do have one. A  $\text{C}_6\text{H}_6$  molecule does have a centre of inversion, as does a regular octahedron (Fig. 15.5); a regular tetrahedron and a  $\text{CH}_4$  molecule do not.

An **improper rotation** or a **rotary-reflection** (the operation) about an **axis of improper rotation** or a **rotary-reflection axis**  $S_n$  consists of an  $n$ -fold rotation axis together with a horizontal reflection. A  $\text{CH}_4$  molecule (Fig. 15.6) has three  $S_4$  axes.

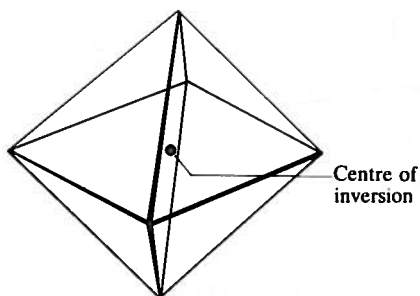


Fig. 15.5

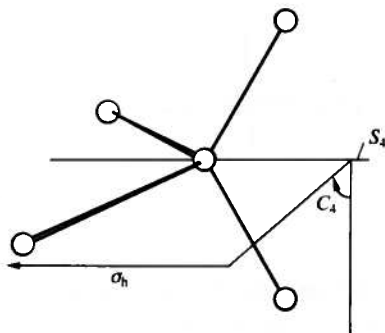


Fig. 15.6

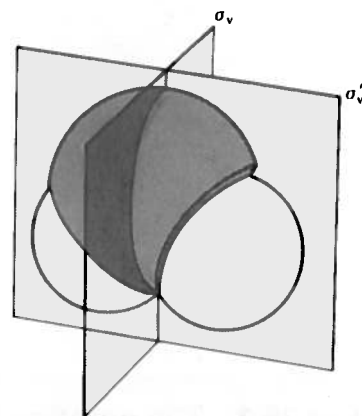
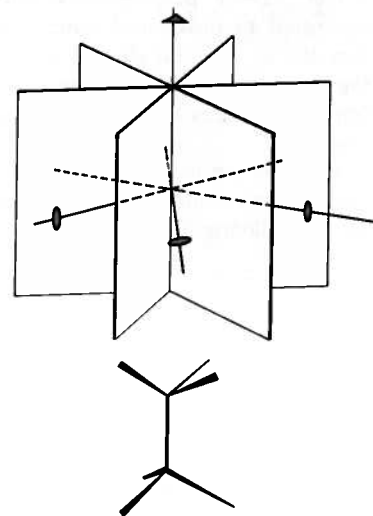
Fig. 15.3 The  $\text{H}_2\text{O}$  molecule has two mirror planes. They are both vertical (i.e. contain the principal axis), and so are denoted  $\sigma_v$  and  $\sigma'_v$ .Fig. 15.4 Dihedral mirror planes ( $\sigma_d$ ) bisect the  $C_2$  axes perpendicular to the principal axis. The staggered conformation of ethane is an example.

Fig. 15.5 A regular octahedron has a centre of inversion; a regular tetrahedron does not.

Fig. 15.6 The  $\text{CH}_4$  molecule has a fourfold rotary-reflection axis ( $S_4$ ): the molecule is indistinguishable after a  $90^\circ$  rotation followed by a reflection across the horizontal plane.

## 15.2 The symmetry classification of molecules

To classify molecules according to their symmetries, we list their symmetry elements and group together those with the same list. This procedure puts  $\text{CH}_4$  and  $\text{CCl}_4$ , which both have the same symmetry as a regular tetrahedron, into the same group, and  $\text{H}_2\text{O}$  into another group.

The name of the group to which a molecule belongs is determined by the symmetry elements it possesses. There are two systems of notation (Box 15.1). The **Schoenflies system** is more common for the discussion of individual molecules, and the **Hermann–Mauguin system**, or **International system**, is used almost exclusively in the discussion of crystal symmetry.

### Box 15.1 The notation for point groups

In the **international system** for point groups, which is also called the **Hermann–Mauguin system**, a number  $n$  denotes the presence of an  $n$ -fold axis and a letter  $m$  denotes a mirror plane. A diagonal line / indicates that the mirror plane is perpendicular to the symmetry axis. It is important to distinguish symmetry elements of the same type but of different classes, as in  $4/mmm$  when there are the three classes of reflection  $\sigma_h$ ,  $\sigma_v$ , and  $\sigma_d$ . A bar over a symbol indicates that that element is combined with an inversion.

The table on the right translates the **Schoenflies system** into the international system. The only groups listed are the crystallographic point groups (Section 21.1).

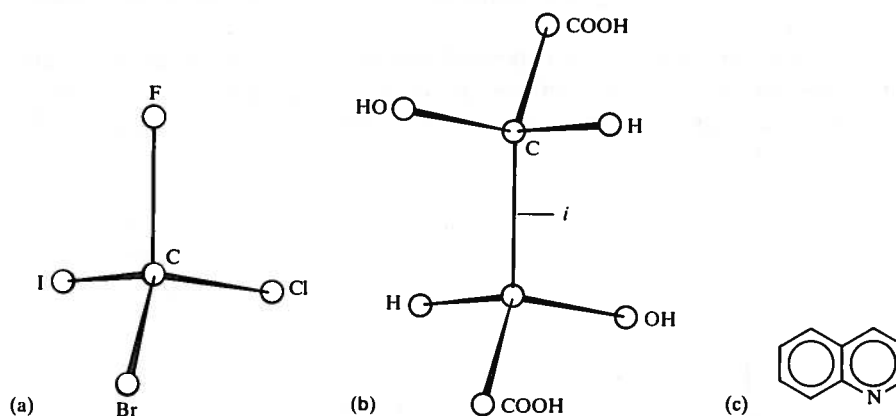
$C_i$	$\bar{1}$								
$C_s$	$m$								
$C_1$	1	$C_2$	2	$C_3$	3	$C_4$	4	$C_6$	6
		$C_{2v}$	$2mm$	$C_{3v}$	$3m$	$C_{4v}$	$4mm$	$C_{6v}$	$6mm$
		$C_{2h}$	$2/m$	$C_{3h}$	$\bar{6}$	$C_{4h}$	$4/m$	$C_{6h}$	$6/m$
		$D_2$	$222$	$D_3$	$32$	$D_4$	$422$	$D_6$	$622$
		$D_{2h}$	$mmm$	$D_{3h}$	$\bar{6}2m$	$D_{4h}$	$4/mmm$	$D_{6h}$	$6/mmm$
		$D_{2d}$	$\bar{4}2m$	$D_{3d}$	$\bar{3}m$	$S_4$	$\bar{4}$	$S_6$	$\bar{3}$
$T$	$23$	$T_d$	$\bar{4}3m$	$T_h$	$m\bar{3}$				
$O$	$432$	$O_h$	$m\bar{3}m$						

The group  $D_2$  ( $222$ ) is sometimes denoted  $V$  and called the *Vierer group* (the 'group of four').

### The groups $C_1$ , $C_i$ , $C_s$

A molecule belongs to  $C_1$  if it has no element other than the identity (e.g.  $\text{CBrClFI}$ , Fig. 15.7a), to  $C_i$  if it has the identity and the inversion (e.g. *meso*-tartaric acid, Fig. 15.7b), and to  $C_s$  if it has the identity and a plane of reflection (e.g. the quinoline molecule, Fig. 15.7c).

Fig. 15.7 Examples of molecules belonging to the groups (a)  $C_1$ , (b)  $C_i$ , and (c)  $C_s$ .



### The groups $C_n$ , $C_{nv}$ , and $C_{nh}$

A molecule belongs to the group  $C_n$  if it possesses an  $n$ -fold axis. (Note that  $C_n$  is now playing a triple role: as the label of a symmetry element, a

symmetry operation, and a group.) The  $\text{H}_2\text{O}_2$  molecule (Fig. 15.8) has the elements  $E$  and  $C_2$  and so belongs to the group  $C_2$ .

If in addition to the identity and a  $C_n$  axis a molecule has  $n$  vertical mirror planes  $\sigma_v$ , it belongs to the group  $C_{nv}$ . The  $\text{H}_2\text{O}$  molecule, for example, has the symmetry elements  $E$ ,  $C_2$ , and  $2\sigma_v$ , and so belongs to the group  $C_{2v}$ . The  $\text{NH}_3$  molecule has the elements  $E$ ,  $C_3$ , and  $3\sigma_v$ , and so belongs to the group  $C_{3v}$ . A heteronuclear diatomic molecule such as  $\text{HCl}$  belongs to the group  $C_{\infty v}$  because all rotations around the axis and reflections across it are symmetry operations.  $C_{\infty v}$  is also the group of the linear  $\text{OCS}$  molecule and of a cone.

Objects that in addition to the identity and an  $n$ -fold principal axis also have a horizontal mirror plane  $\sigma_h$  belong to the groups  $C_{nh}$ . An example is *trans*- $\text{CHCl}=\text{CHCl}$  (Fig. 15.9), which has the elements  $E$ ,  $C_2$ , and  $\sigma_h$ , and so belongs to the group  $C_{2h}$ . Sometimes the presence of a symmetry element is implied by others: in this case  $C_2$  and  $\sigma_h$  jointly imply the presence of a centre of inversion (Fig. 15.10).

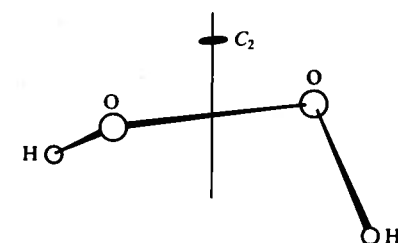
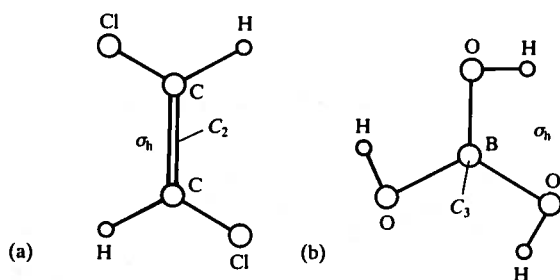


Fig. 15.8 The  $\text{H}_2\text{O}_2$  molecule belongs to the group  $C_2$  when it is in the conformation shown.

Fig. 15.9 (a) *Trans*-dichloroethene belongs to  $C_{2h}$  and (b)  $\text{B(OH)}_3$  belongs to  $C_{3h}$ .

### The groups $D_n$ , $D_{nh}$ , and $D_{nd}$

A molecule that has an  $n$ -fold principal axis and  $n$  two-fold axes perpendicular to  $C_n$  (Fig. 15.11) belongs to the group  $D_n$ . Molecules belong to  $D_{nh}$  if they also possess a horizontal mirror plane (Fig. 15.12). The planar trigonal  $\text{BF}_3$  molecule has the elements  $E$ ,  $C_3$ ,  $3C_2$ , and  $\sigma_h$  (with one  $C_2$  axis along each  $\text{B}-\text{F}$  bond), and so belongs to  $D_{3h}$ . The  $\text{C}_6\text{H}_6$  molecule has the elements  $E$ ,  $C_6$ ,  $6C_2$ , and  $\sigma_h$  together with some others that these imply, and so it belongs to  $D_{6h}$ . All homonuclear diatomic molecules, such as  $\text{N}_2$ , belong to the group  $D_{\infty h}$  since all rotations around the axis are symmetry operations, as are end-to-end rotation and end-to-end reflection;  $D_{\infty h}$  is also the group of the linear  $\text{OCO}$  and  $\text{HC}\equiv\text{CH}$  molecules and of a uniform cylinder.

A molecule belongs to the group  $D_{nd}$  if it has the elements of  $D_n$  and, in addition,  $n$  dihedral mirror planes  $\sigma_d$ . The twisted,  $90^\circ$  allene shown in Fig. 15.13a belongs to  $D_{2d}$ , and the staggered form of ethane (Fig. 15.13b) belongs to  $D_{3d}$ .

### The groups $S_n$

Molecules that have not been classified into one of the groups we have mentioned so far, but which possess *one*  $S_n$  axis, belong to the group  $S_n$ . An example is shown in Fig. 15.14. Molecules belonging to  $S_n$  with  $n > 4$  are rare. Note that the group  $S_2$  is the same as  $C_i$ , so such a molecule will already have been classified as  $C_i$ .

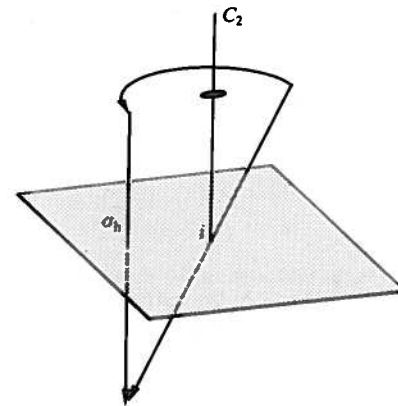


Fig. 15.10 The presence of a twofold axis and a horizontal mirror plane jointly imply the presence of an inversion centre in the molecule.

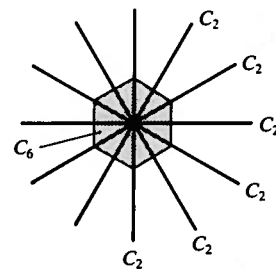
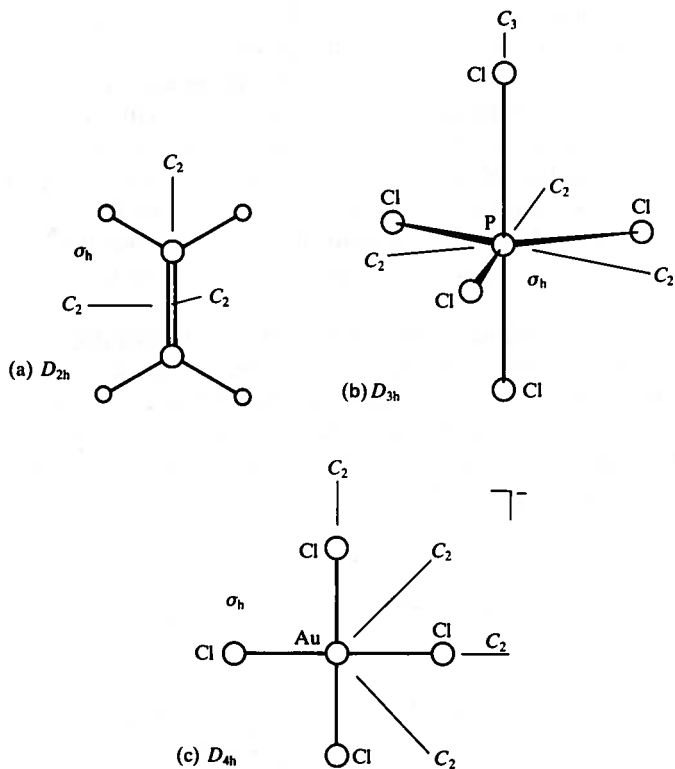
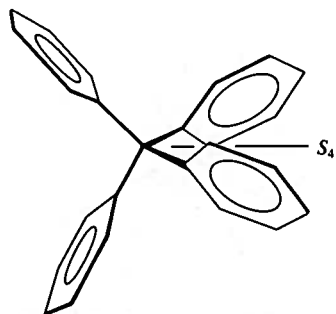
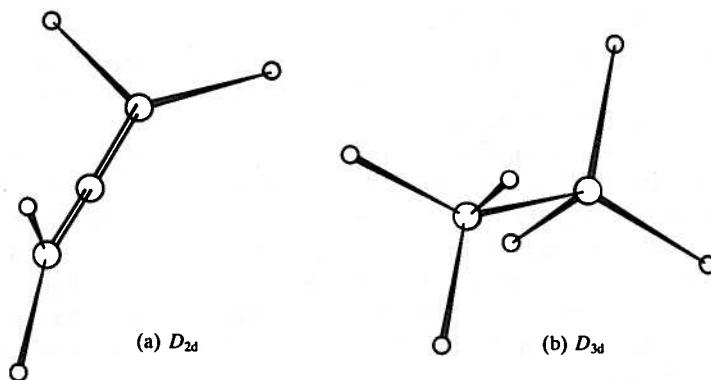


Fig. 15.11 A molecule with  $n$  twofold rotation axes perpendicular to an  $n$ -fold rotation axis belongs to the group  $D_n$ .

**Fig. 15.12** Three examples of molecules belonging to  $D_{nh}$ . (a)  $C_2H_4$  belongs to  $D_{2h}$ , (b)  $PCl_5$ , which has different axial and equatorial bond lengths, belongs to  $D_{3h}$ , and (c) the square-planar complex  $[AuCl_4]^-$  belongs to  $D_{4h}$ .



**Fig. 15.13** (a) The  $90^\circ$  allene molecule belongs to the group  $D_{2d}$  and (b) the staggered conformation of ethane belongs to  $D_{3d}$ .



**Fig. 15.14** Tetraphenylmethane is an example of a molecule that belongs to the group  $S_4$ .

### The cubic groups

A number of very important molecules (e.g.  $CH_4$ ) possess more than one principal axis. They all belong to the **cubic groups**, and in particular to the **tetrahedral groups**  $T$ ,  $T_d$ , and  $T_h$  or to the **octahedral groups**  $O$ ,  $O_h$  (Fig. 15.15). A few icosahedral (twenty-faced) molecules, belonging to the **icosahedral group** are also known: they include some of the boranes.  $T_d$  and  $O_h$  are the groups of the regular tetrahedron (e.g.  $CH_4$ ) and the regular octahedron (e.g.  $SF_6$ ) respectively. If the object possesses the rotational symmetry of the tetrahedron or the octahedron, but none of their planes of reflection, then it belongs to the simpler groups  $T$  or  $O$ . The group  $T_h$  is based on  $T$  but also contains a centre of inversion.

### The full rotation group, $R_3$

The full rotation group consists of an infinite number of rotation axes with all possible values of  $n$ . A sphere and an atom belong to  $R_3$ , but no molecule does. Exploring the consequences of  $R_3$  is a very important way of applying symmetry arguments to atoms and is an alternative approach to the theory of orbital angular momentum.

#### Example 15.1: Identifying a point group of a molecule

Identify the point group to which the sandwich molecule ruthenocene (two eclipsed cyclopentadiene rings) belongs.

**Answer.** The identification of a molecule's group is simplified by referring to the flow diagram in Box 15.2 and the shapes shown in Fig. 15.16. The path we trace through the flow diagram in Box 15.2 is shown by a dotted line; it ends at  $D_{nh}$ . Since the molecule has a fivefold axis, it belongs to the group  $D_{5h}$ .

**Comment.** If the rings were staggered, the horizontal reflection plane would be absent, but dihedral planes would be present.

**Exercise.** Classify (a) the conformation with staggered rings and (b) benzene. [(a)  $D_{5d}$ , (b)  $D_{6h}$ ]

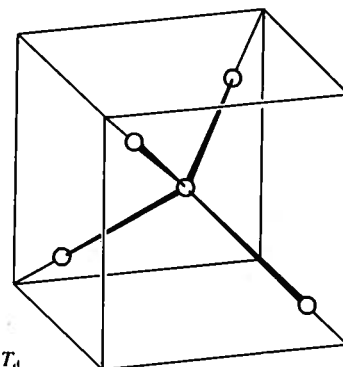
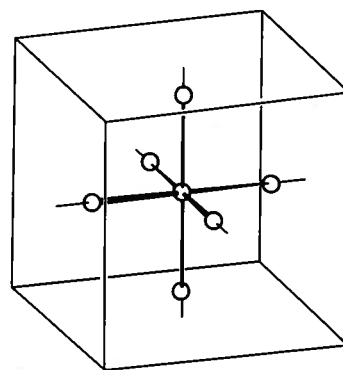
(a)  $T_d$ (b)  $O_h$ 

Fig. 15.15 Tetrahedral and octahedral molecules are best drawn in a way that shows their relation to a cube: they belong to one of the cubic groups. (a)  $\text{CCl}_4$  belongs to  $T_d$  and (b)  $\text{SF}_6$  belongs to  $O_h$ .

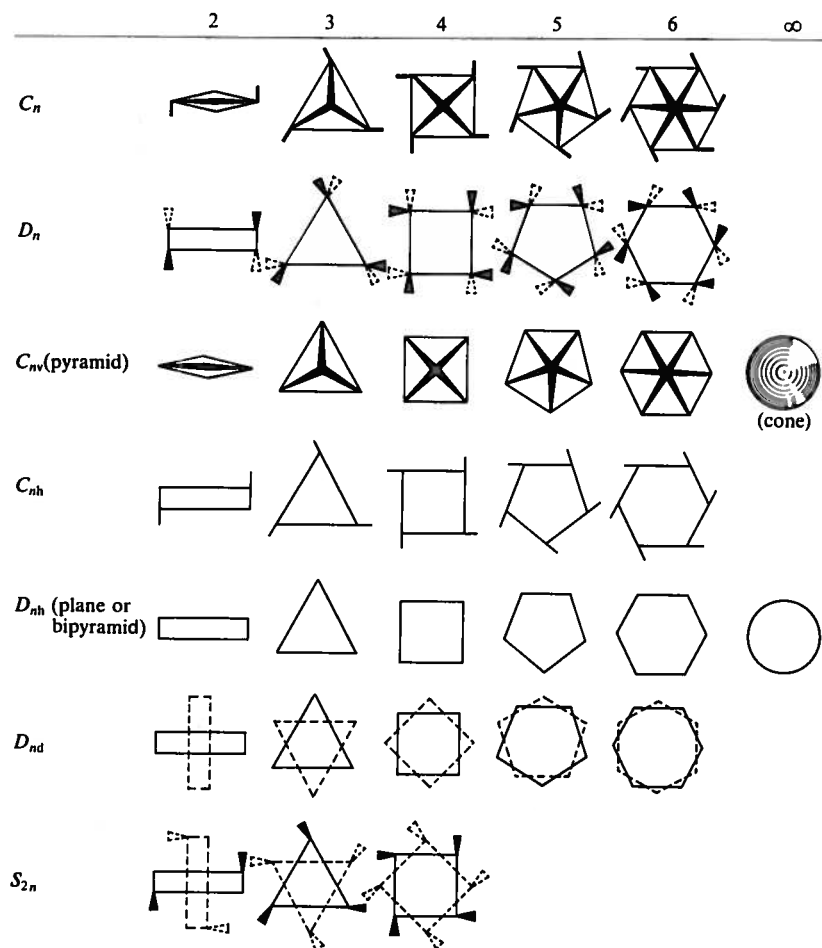
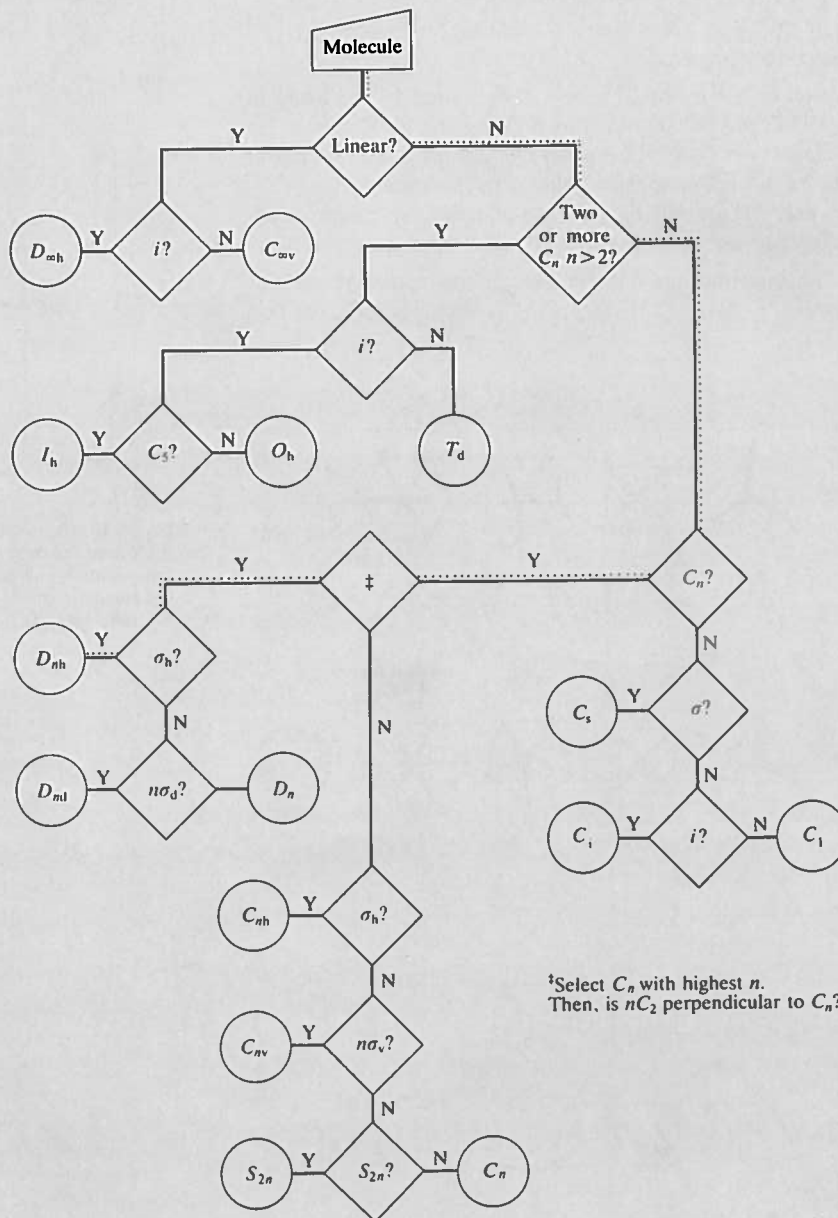


Fig. 15.16 A summary of the shapes corresponding to different point groups. The group to which a molecule belongs can often be identified from this diagram without going through the formal procedure in Box 15.2.

**Box 15.2 The determination of a point group**

To arrive at the point group of a given molecule, work through the following table. The use of a subgroup (i.e. not travelling to the end of a route) is permissible but gives less complete information. The dotted line shows the path through the following table. The use of a subgroup (i.e. used in Example 15.1.)





### 15.3 Some immediate consequences of symmetry

We can make some statements about the properties of a molecule as soon as we have identified its point group.

#### Polarity

A **polar molecule** is one with a permanent electric dipole moment (HCl,  $O_3$ , and  $NH_3$  are examples). If the molecule belongs to the group  $C_n$  with  $n > 1$ , it cannot possess a charge distribution corresponding to a dipole moment perpendicular to the axis. However, as the group makes no reference to operations relating the two ends of the molecule, a charge distribution may exist that results in a dipole along the axis (Fig. 15.17). The same remarks apply to  $C_{nv}$ , so molecules belonging to any of the  $C_{nv}$  groups may be polar. In all the other groups, such as  $C_{3h}$ ,  $D$ , etc, there are symmetry operations that take one end of the molecule into the other. Therefore, as well as having no dipole perpendicular to the axis, such molecules can have none along the axis, for otherwise these additional operations would not be symmetry operations.

We can conclude that only molecules belonging to the groups  $C_n$ ,  $C_{nv}$ , and  $C_s$  may have an electric dipole moment, and in the case of  $C_n$  and  $C_{nv}$  that that dipole must lie along the rotation axis. Thus  $O_3$ , which is angular and belongs to the group  $C_{2v}$ , may be polar, but  $CO_2$ , which is linear and belongs to the group  $D_{\infty h}$ , is not.

#### Chirality

A **chiral molecule** (from the Greek word for hand) is a molecule that cannot be superimposed on its mirror image. Chiral molecules are **optically active** in the sense that they rotate the plane of polarized light (a property discussed in more detail in Section 22.2). A chiral molecule and its mirror-image partner constitute an **enantiomeric pair**.

A molecule may be chiral only if it does not possess an axis of improper rotation,  $S_n$ . However, such an axis may be present under a different name and be implied by other symmetry elements that are present. For example, molecules belonging to the groups  $C_{nh}$  include  $S_n$  implicitly because they possess both  $C_n$  and  $\sigma_h$ . Any molecule containing a centre of inversion  $i$  also possesses an  $S_2$  axis because  $i$  is equivalent to  $C_2$  in conjunction with  $\sigma_h$ , which is  $S_2$  (Fig. 15.18). It follows that all molecules with centres of inversion are non-chiral and hence optically inactive.

A molecule may be chiral if it does not have a centre of inversion or a mirror plane, which is the case with the amino acid alanine  $CH_3CH(NH_2)COOH$  but not with glycine  $CH_2(NH_2)COOH$ . However, a molecule may be non-chiral even though it does not have a centre of inversion. For example, an  $S_4$  molecule (Fig. 15.19) is non-chiral and optically inactive, for though it lacks  $i$  it does have an  $S_4$  axis.

### Groups, representations, and characters

Many properties may be analysed once the point group of a molecule is known, but to extract them we often need to use numerical aspects of group theory. We introduce these here, but we shall do no more than skim the surface of this very subtle and powerful subject.

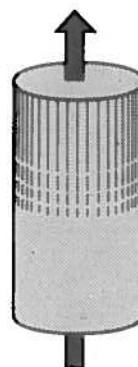


Fig. 15.17 A molecule with a  $C_n$  axis cannot have a dipole perpendicular to the axis, but it may have one parallel to the axis.

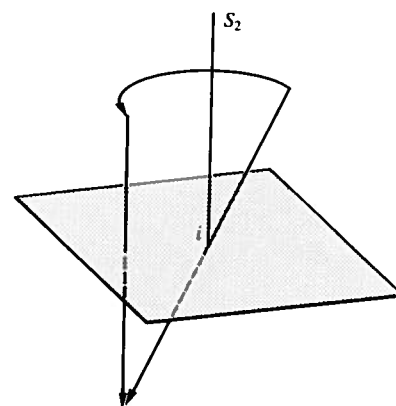


Fig. 15.18 Some elements are implied by the other elements in a group. Any molecule containing an inversion also possesses at least an  $S_2$  element because  $i$  and  $S_2$  are equivalent.

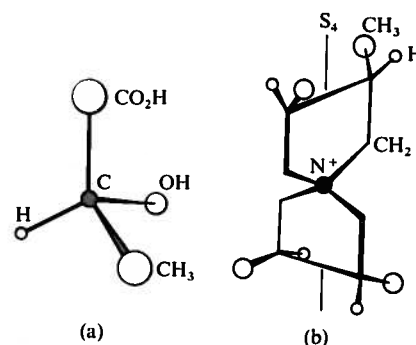


Fig. 15.19 (a) An optically active molecule without a centre of inversion. (b) Although this molecule has no centre of inversion (i.e. no  $S_2$  axis) it is not optically active because it has an  $S_4$  axis.

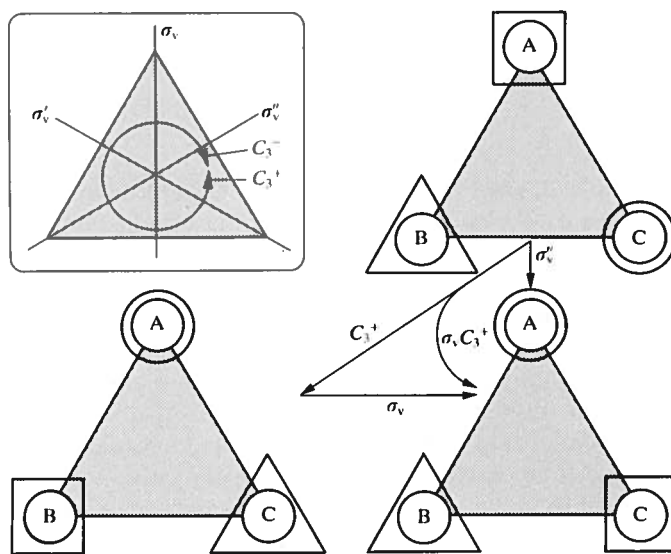


Fig. 15.20 The symmetry operations of the group  $C_{3v}$  are shown in the box, and the equivalence  $\sigma_v C_3^+ = \sigma'_v$  is constructed by considering the effect of successive operations.

## 15.4 Group multiplication

Consider  $\text{NH}_3$ , which belongs to  $C_{3v}$  and is symmetrical under the operations  $E$ ,  $C_3^+$ ,  $C_3^-$ ,  $\sigma_v$ ,  $\sigma'_v$ , and  $\sigma''_v$  (Fig. 15.20).  $C_3^+$  is a counter-clockwise  $120^\circ$  rotation as seen from above,  $C_3^-$  the corresponding clockwise rotation.<sup>1</sup> It should be obvious that the operation  $C_3^+$  followed by  $C_3^-$  is the identity. We can express this symbolically by writing

$$C_3^- C_3^+ = E$$

Similarly, two successive counter-clockwise rotations by  $120^\circ$  are equivalent to one clockwise rotation:

$$C_3^+ C_3^+ = C_3^-$$

We can see from Fig. 15.20 that  $C_3^+$  followed by  $\sigma_v$  is equivalent to  $\sigma'_v$ , and so we can write

$$\sigma_v C_3^+ = \sigma'_v$$

Note that in working out these relations, all the operations refer to some *fixed* arrangement of symmetry elements. That is, the planes and axes remain where they were first drawn on the page, and are unaffected by the performance of an operation. Note, too, that the second operation is written to the left of the first, so in the last example  $\sigma_v$  is carried out after  $C_3^+$ .

<sup>1</sup> This sign convention may seem odd, but it matches the convention used for angular momentum, when a clockwise rotation as seen from below (i.e. counter-clockwise as seen from above) is associated with positive values of  $m_l$ .

The table of all such combinations is called the **group multiplication table**, and for  $C_{3v}$  is as follows:

Second	First					
	$E$	$C_3^+$	$C_3^-$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
$E$	$E$	$C_3^+$	$C_3^-$	$\sigma_v$	$\sigma_v'$	$\sigma_v''$
$C_3^+$	$C_3^+$	$C_3^-$	$E$	$\sigma_v'$	$\sigma_v''$	$\sigma_v$
$C_3^-$	$C_3^-$	$E$	$C_3^+$	$\sigma_v''$	$\sigma_v$	$\sigma_v'$
$\sigma_v$	$\sigma_v$	$\sigma_v''$	$\sigma_v'$	$E$	$C_3^-$	$C_3^+$
$\sigma_v'$	$\sigma_v'$	$\sigma_v$	$\sigma_v''$	$C_3^+$	$E$	$C_3^-$
$\sigma_v''$	$\sigma_v''$	$\sigma_v'$	$\sigma_v$	$C_3^-$	$C_3^+$	$E$

A glance at the group multiplication table shows that the outcome of successive symmetry operations is always equivalent to a single symmetry operation of the group, which is called the **group property**. The group property is the main feature of the structure of groups: a set of operations form a group if they satisfy the group property together with some other mild conditions (Box 15.3). All symmetry operations on molecules satisfy the conditions in Box 15.3, which is why the theory of the symmetry of molecules is called group theory.

### Box 15.3 The definition of a group

A group  $G$  of order  $h$  is a set of  $h$  elements (such as the symmetry operations of a molecule)

$$G = \{g_1, g_2, \dots, g_h\}$$

together with a rule of combination that gives the symbol  $g_i g_j$  a meaning (such as the symmetry operation  $g_j$  followed by the symmetry operation  $g_i$ ) and which satisfy the following criteria:

(1)  $G$  includes the **identity**  $E$ , the element for which  $Eg_i = g_i E = g_i$  for all the elements of the group

(2)  $G$  includes the **inverse** ( $g_i^{-1}$ ) of each element, the element for which

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

(3) The rule of combination is **associative**, so

$$g_i(g_j g_k) = (g_i g_j)g_k$$

(4) The elements satisfy the **group property** that the combination of any pair of elements is itself an element:

$$g_i g_j = g_k$$

The definition of a group does not require the elements to **commute**:

$$g_i g_j = g_j g_i \text{ is not required}$$

However, if all the elements of a group do commute, the group is called **Abelian**.

## 15.5 The representation of transformations

Expressions like  $C_3^- C_3^+ = E$  are symbolic ways of writing what happens when various physical operations are carried out in succession. However, it is possible to give them an actual algebraic significance, which means that we can deal with numbers instead of abstract symbols for operations. By dealing with numbers we shall arrive at precise conclusions.

The remainder of this section establishes the language and sets out the background of group theory. It makes use of the properties of matrices, which are reviewed in the *Further information* section at the end of the chapter. The rules needed for applying group theory are set out in Sections

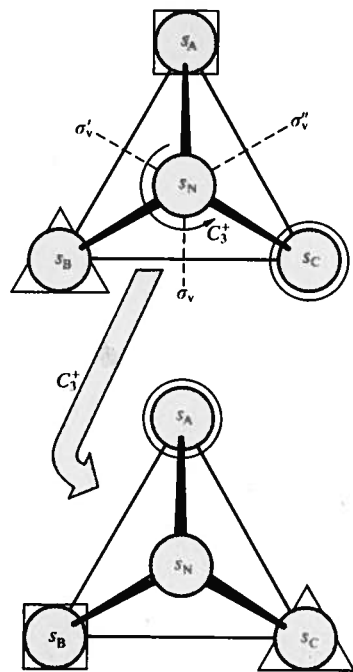


Fig. 15.21 The basis used for the discussion of the transformation properties of a  $C_{3v}$  molecule. We use the convention that the basis is always written in the order  $\{\square, \triangle, \circ\}$  and that the operations move the shapes on the diagram without affecting the N, A, B, C labels. The interpretation of the effect of  $C_3^+$  is shown.

15.8 and 15.9. Most of them can be used simply as recipes without needing to work through the background material presented in this section.

### Matrix representatives

Consider a  $C_{3v}$  molecule (such as  $\text{NH}_3$ ) with  $s$  orbitals on each atom (Fig. 15.21) and think about what happens to these functions under a symmetry operation. Under  $\sigma_v$ , the change

$$(s_N, s_A, s_C, s_B) \leftarrow (s_N, s_A, s_B, s_C)$$

takes place. We can express this transformation using matrix multiplication:

$$(s_N, s_A, s_C, s_B) = (s_N, s_A, s_B, s_C) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_A, s_B, s_C) D(\sigma_v)$$

The matrix  $D(\sigma_v)$  is called a **representative** of the operation  $\sigma_v$ .

We can use the same technique to find matrices that reproduce the other symmetry operations. For instance,  $C_3^+$  has the effect

$$(s_N, s_B, s_C, s_A) \leftarrow (s_N, s_A, s_B, s_C)$$

and we can express the transformation as

$$(s_N, s_B, s_C, s_A) = (s_N, s_A, s_B, s_C) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (s_N, s_A, s_B, s_C) D(C_3^+)$$

The operation  $\sigma_v''$ , which causes

$$(s_N, s_C, s_B, s_A) \leftarrow (s_N, s_A, s_B, s_C)$$

is represented by the matrix multiplication

$$(s_N, s_C, s_B, s_A) = (s_N, s_A, s_B, s_C) \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = (s_N, s_A, s_B, s_C) D(\sigma_v'')$$

Since the identity leaves  $(s_N, s_A, s_B, s_C)$  unchanged,

$$D(E) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}$$

**Example 15.2: Finding a matrix representative of an operation**

Consider the four  $1s$  orbitals of  $\text{CH}_4$ . Find matrix representatives for the operations  $C_3^+$  and  $S_4^+$ .

**Answer.**  $\text{CH}_4$  belongs to the group  $T_d$ . The axis corresponding to  $C_3^+$  runs along a  $\text{C}-\text{H}$  bond (e.g.  $\text{C}-\text{H}_D$ ), and so it rotates the other three  $\text{H}$  atoms into each other in a counterclockwise sense seen from above. A good plan is to put different shaped receptacles on each atom location (the shapes in Fig. 15.22) and to allow the operations to move them (the letters remaining stationary): the row vector representing the basis is then determined by writing the appropriate letter in the receptacle always written in the same order ( $\square, \diamond, \triangle, \square$ ). The effect of  $C_3^+(D)$  is

$$\begin{aligned} C_3^+(H_A, H_B, H_C, H_D) &= (H_C, H_A, H_B, H_D) \\ &= (H_A, H_B, H_C, H_D) \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = (H_A, H_B, H_C, H_D) D(C_3^+) \end{aligned}$$

$S_4^+$  rotates counterclockwise by  $90^\circ$  about a bisector of a  $\text{CH}_2$  angle (e.g.  $\text{H}_A\text{CH}_C$ ) and then reflects across the perpendicular plane:

$$\begin{aligned} S_4^+(H_A, H_B, H_C, H_D) &= (H_B, H_C, H_D, H_A) \\ &= (H_A, H_B, H_C, H_D) \begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = (H_A, H_B, H_C, H_D) D(S_4^+) \end{aligned}$$

**Comment.** The representation depends on the basis selected: in this case it is four-dimensional because the basis has four members.

**Exercise.** Find the representatives for  $S_4^-(CD)$ , where the four-fold axis bisects the  $\text{H}_C\text{H}_D$  angle, and  $C_3^+(B)$ .

$$D(S_4^-) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}, \quad D(C_3^+) = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

**Matrix representations**

A very important property of the  $D$  matrices may now be identified. Using the rules of matrix multiplication gives

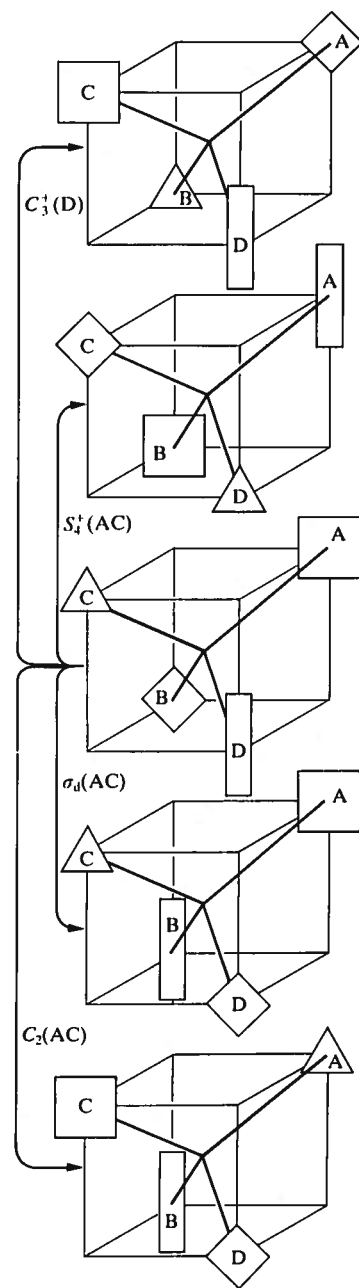
$$D(\sigma_v)D(C_3^+) = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix} = D(\sigma_v'')$$

The importance of this result is that its structure

$$D(\sigma_v)D(C_3^+) = D(\sigma_v'')$$

has exactly the same form as the group multiplication rule

$$\sigma_v C_3^+ = \sigma_v''$$



**Fig. 15.22** The symmetry transformations used in Example 15.2. Note that we are using the convention defined in Fig. 15.21.

Whichever operations of a group we chose, we find that the matrix representatives multiply in an analogous way. We say that the multiplications are **homomorphous**. Therefore, the whole of the group multiplication table is reproduced by the matrix multiplication of the representatives. The set of six matrices is called a **matrix representation** of the  $C_{3v}$  group for the particular **basis** we have chosen, which in this case consists of the four orbitals  $s_N, s_A, s_B,$  and  $s_C$ . We denote the representation by the symbol  $\Gamma$ , and since it is four-dimensional, more specifically as  $\Gamma^{(4)}$ . The discovery of a matrix representation of the group means that we have found a link between the symbolic manipulations of the operations and algebraic manipulations involving numbers.

**Example 15.3: Verifying the matrix representation of a group**

Confirm that the matrix representatives found in Example 15.2 satisfy the group multiplication property.

**Answer.** Identify  $C_3^+S_4^+$  by assessing the effect on the basis of successive symmetry operations, and confirm the homomorphism by multiplying the representatives. The effect of the joint operation  $S_4^+C_3^+$  is

$$S_4^+C_3^+(H_A, H_B, H_C, H_D) = (H_D, H_B, H_C, H_A) = \sigma(H_A, H_B, H_C, H_D)$$

where the plane of the operation  $\sigma$  bisects  $H_ACH_D$ . The product of the representatives is

$$\begin{pmatrix} 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{pmatrix} \begin{pmatrix} 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix}$$

which is the representative of  $\sigma$ .

**Exercise.** Confirm that the representatives for  $S_4^-(CD)$  and  $C_3^+(B)$  multiply homomorphously with the elements of the group.  $[S_4^-C_3^+ = S_4^-(AC)]$

### The character of symmetry operations

In common parlance, the rotations  $C_3^+$  and  $C_3^-$  of the group  $C_{3v}$  have the same 'character' but differ in direction. Likewise, the three reflections have the same character, but are different from the rotations. We say that the two rotations belong to the same **class** of operation, and that the three reflections form another class. This notion of class can be given precise, numerical significance.

Inspection of the matrix representation of  $C_{3v}$  for the  $s$ -orbital basis of Fig. 15.21 shows a remarkable fact. If we form the **trace** of each matrix, that is, sum the diagonal elements of each matrix, we get the following numbers:

$$\begin{array}{cccccc} D(E) & D(C_3^+) & D(C_3^-) & D(\sigma_v) & D(\sigma_v') & D(\sigma_v'') \\ \text{Trace:} & 4 & 1 & 1 & 2 & 2 & 2 \end{array}$$

We see that the matrices representing operations of the same class have identical diagonal sums. We call the trace of the representative the **character**  $\chi$  of the operation; hence we can conclude that symmetry operations in the same class have the same character.

**Example 15.4: Calculating the character of an operation**

Calculate the characters of the operations  $C_3^+$ ,  $S_4^+$ , and  $\sigma_4^-$  in the basis used in Example 15.3.

**Answer.** We refer to the representatives calculated in the example, and sum their diagonal elements.

$$\chi(C_3^+) = 0 + 0 + 0 + 1 = 1$$

$$\chi(S_4^+) = 0 + 0 + 0 + 0 = 0$$

$$\chi(\sigma) = 0 + 1 + 1 + 0 = 2$$

**Comment.** A quick rule for determining the character without first having to set up the matrix representation is to count 1 each time a basis function is left unchanged by the operation, because only these functions give a non-zero entry on the diagonal of the matrix representative. In some cases there is a sign change,  $(\dots -f \dots) \leftarrow (\dots f \dots)$ ; then  $-1$  occurs on the diagonal, and so count  $-1$ . The character of the identity is always equal to the dimension of the basis since each function contributes 1 to the trace.

**Exercise.** Calculate the character of (a)  $C_2$  and (b)  $S_4^-$  in the same basis.

[(a) 0, (b) 0]

The character of an operation depends on the basis. For example, if instead of considering the four  $s$  orbitals, we used only  $s_N$  as the basis, then since each operation results in  $s_N \leftarrow s_N$ , which may be written  $s_N = s_N \times \mathbf{1}$ , with  $\mathbf{1}$  a  $1 \times 1$  matrix, the characters of the operations would be

$$\begin{array}{cccccc} & D(E) & D(C_3^+) & D(C_3^-) & D(\sigma_v) & D(\sigma_v') & D(\sigma_v'') \\ \chi = & 1 & 1 & 1 & 1 & 1 & 1 \end{array}$$

We shall write this representation  $\Gamma^{(1)}$  because it is one-dimensional. It is still true that the characters of the operations of the same class are equal; however, we also see that the characters of different classes may be the same. Furthermore, it is obvious that because  $1 \times 1 = 1$ , the matrices do reproduce the group multiplication table. However, as they do so in a trivial and uninformative way, the representation in which 1 represents each element is called the **unfaithful representation** of the group.

## 15.6 Irreducible representations

The unfaithful representation of the group, although apparently trivial, is a representation, and should not be discarded as being of no importance. In the next few sections, in fact, we shall see that it is the most important representation for many chemical applications.

### The direct sum

The representatives in the basis  $(s_N, s_A, s_B, s_C)$  are four-dimensional (i.e. they are  $4 \times 4$  matrices), but inspection shows that they are all of the form

$$\begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & \blacksquare & & \\ 0 & & \blacksquare & \\ 0 & & & \blacksquare \end{pmatrix}$$

and that the symmetry operations never mix  $s_N$  with the other three basis functions. This suggests that the basis can be cut into two parts, one consisting of  $s_N$  alone and the other of  $(s_A, s_B, s_C)$ . The  $s_N$  orbital is a basis for the unfaithful representation, as we have seen, and we now see that the other three orbitals are a basis for a three-dimensional representation  $\Gamma^{(3)}$  consisting of the following matrices:

$$\begin{array}{cccccc} D(E) & D(C_3^+) & D(C_3^-) & D(\sigma_v) & D(\sigma'_v) & D(\sigma''_v) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} & \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix} \\ \chi = 3 & 0 & 0 & 1 & 1 & 1 \end{array}$$

The characters still satisfy the rule about symmetry operations of the same class. The matrices of  $\Gamma^{(3)}$  are the same as those of the four-dimensional representation, except for the loss of the first row and column. We say that the original four-dimensional representation has been **reduced** to the **direct sum** of a one-dimensional representation **spanned** by  $s_N$  and a three-dimensional representation spanned by  $(s_A, s_B, s_C)$ . This reduction is consistent with the common sense view that the central orbital plays a role different from the other three. The reduction is denoted symbolically by

$$\Gamma^{(4)} = \Gamma^{(1)} + \Gamma^{(3)}$$

### The reduction of a representation

The one-dimensional representation  $\Gamma^{(1)}$ , which consists of the six  $1 \times 1$  matrices 1, 1, 1, 1, 1, 1, obviously cannot be reduced any further, and is called an **irreducible representation** (or 'irrep') of the group.

We can demonstrate that  $\Gamma^{(3)}$  is reducible by switching attention from  $s_A$ ,  $s_B$ , and  $s_C$  to the linear combinations

$$s_1 = s_A + s_B + s_C \quad s_2 = 2s_A - s_B - s_C \quad s_3 = s_B - s_C$$

These are sketched in Fig. 15.23 (their form is justified later). Even at this stage it is clear that, because of the presence of the node in  $s_2$  and  $s_3$ , these two have different symmetry from  $s_1$ . The decomposition

$$\Gamma^{(3)} = \Gamma^{(1)} + \Gamma^{(2)}$$

is beginning to emerge.

The representatives in the new basis can be constructed from the old. For example, since under  $\sigma_v$ ,

$$(s_A, s_C, s_B) \leftarrow (s_A, s_B, s_C)$$

it follows (by applying these transformations to the linear combinations) that

$$(s_1, s_2, -s_3) \leftarrow (s_1, s_2, s_3)$$

The transformation is achieved by writing

$$(s_1, s_2, -s_3) = (s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

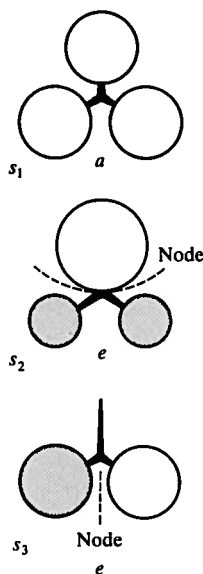


Fig. 15.23 Three linear combinations of three  $s$  orbitals in a  $C_{3v}$  molecule. The symmetry species they span (see later) have been added.



which gives us the representative  $D(\sigma_v)$  in the new basis. The representative of  $C_3^+$  takes a little more calculation, but depends on the transformation

$$(s_B, s_C, s_A) \leftarrow (s_A, s_B, s_C)$$

We know how the individual  $s_Q$  transform (with  $Q = A, B,$  and  $C$ ), and so by substitution in the expressions defining the new basis gives the transformation of the  $s_n$  (with  $n = 1, 2,$  and  $3$ ):

$$(s_1, -\frac{1}{2}s_2 + \frac{3}{2}s_3, -\frac{1}{2}s_2 - \frac{1}{2}s_3) \leftarrow (s_1, s_2, s_3)$$

This transformation is reproduced by

$$(s_1, -\frac{1}{2}s_2 + \frac{3}{2}s_3, -\frac{1}{2}s_2 - \frac{1}{2}s_3) = (s_1, s_2, s_3) \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{3}{2} & -\frac{1}{2} \end{pmatrix}$$

so giving  $D(C_3^+)$ . The complete representation and its characters may be found similarly, and are

$$\chi = \begin{array}{ccc} \begin{matrix} D(E) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ 3 \end{matrix} & \begin{matrix} D(C_3^+) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & \frac{3}{2} & -\frac{1}{2} \end{pmatrix} \\ 0 \end{matrix} & \begin{matrix} D(C_3^-) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & -\frac{3}{2} & -\frac{1}{2} \end{pmatrix} \\ 0 \end{matrix} \\ \\ \begin{matrix} D(\sigma_v) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \\ 1 \end{matrix} & \begin{matrix} D(\sigma'_v) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & \frac{3}{2} & \frac{1}{2} \end{pmatrix} \\ 1 \end{matrix} & \begin{matrix} D(\sigma''_v) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & -\frac{3}{2} & \frac{1}{2} \end{pmatrix} \\ 1 \end{matrix} \end{array}$$

The new representatives are all in **block diagonal form**

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & \blacksquare & \\ 0 & & \blacksquare \end{pmatrix}$$

and the  $s_1$  combination is not mixed with the other two by any operation of the group. We have therefore achieved the reduction of  $\Gamma^{(3)}$  to  $\Gamma^{(1)} + \Gamma^{(2)}$ , with  $s_1$  a basis for the same one-dimensional irreducible representation  $(1, 1, 1, 1, 1, 1)$  as before and  $(s_2, s_3)$  a basis for a two-dimensional representation  $\Gamma^{(2)}$ :

$$\chi = \begin{array}{cccccc} D(E) & D(C_3^+) & D(C_3^-) & D(\sigma_v) & D(\sigma'_v) & D(\sigma''_v) \\ \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} \\ \frac{3}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} \\ -\frac{3}{2} & -\frac{1}{2} \end{pmatrix} & \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{1}{2} \\ \frac{3}{2} & \frac{1}{2} \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2} \\ -\frac{3}{2} & \frac{1}{2} \end{pmatrix} \\ 2 & -1 & -1 & 0 & 0 & 0 \end{array}$$

It is easy to check that these matrices are a representation by multiplying pairs together and seeing that they reproduce the original group multiplication table.

### The irreducibility of some representations

No linear combination of  $s_2$  and  $s_3$  exists that reduces  $\Gamma^{(2)}$  to two one-dimensional representations, and so the  $\Gamma^{(2)}$  representation is ir-

reducible. We can conclude that while  $s_N$  and  $s_1$  'have the same symmetry'—technically, are the bases for the same irreducible representation of the group—the pair  $s_2, s_3$  'have different symmetry'—they span a different irreducible representation and must be treated as a pair (because that representation is two-dimensional). These features agree with what common sense tells us by inspection of the diagrams in Fig. 15.23.

But how do we know that  $\Gamma^{(2)}$  is irreducible? This information, together with a great deal more, is included in one of the principal tools of group theory, the 'character tables' of the point groups.

### Character tables

The **character table** of a group is the list of the characters of all its irreducible representations. The  $C_{3v}$  character table is shown below.

$C_{3v}$	$E$	$2C_3$	$3\sigma_v$	← Symmetry operations, class by class
$A_1$	1	1	1	← Characters
$A_2$	1	1	-1	
$E$	2	-1	0	

Name of group (points to  $C_{3v}$ )  
 Number of elements in the class (points to  $3\sigma_v$ )  
 Symmetry species (name of irreducible representation) (points to  $A_1, A_2, E$ )  
 Denotes one-dimensional representation (points to  $A_1, A_2$ )  
 Denotes two-dimensional representation (points to  $E$ )

The columns in the table are labelled by the symmetry operations: it is not necessary to show the character for every individual operation because all those in the same class have the same value. The number of operations in each class is given (e.g. the 2 in  $2C_3$ , showing that there are two threefold rotations). The total number of operations in the group is called its **order**: the order of the  $C_{3v}$  group is 6.

The column on the left labels the **symmetry species** of the irreducible representations of the group. An A or B signifies a one-dimensional representation; A is used when the character is +1 under a principal rotation and B when it is -1. There are two species of one-dimensional representation in  $C_{3v}$ , and both have +1 for the character of the principal rotation; they are therefore labelled  $A_1$  and  $A_2$ .  $A_1$  and  $A_2$  are distinguished by the character under a vertical reflection, and in some cases by their behaviour under a  $C_2$  rotation perpendicular to the principal axis. An E denotes a two-dimensional representation, and T denotes a three-dimensional representation (there is none in  $C_{3v}$ ).

The characters of the  $\Gamma^{(2)}$  representation spanned by  $(s_2, s_3)$  are those of E. Since E is an irreducible representation, we know at once that  $\Gamma^{(2)}$  is irreducible too.

Perhaps the most surprising feature of the character table is that there are so few allowed symmetry species. That the three given exhaust all possibilities is confirmed by an elegant theorem in group theory which states

that

Number of symmetry species = Number of classes

In  $C_{3v}$  there are three classes (three columns in the character table), and so there are only three species of irreducible representation.

Although we have introduced these points through the group  $C_{3v}$ , they are entirely general, and the characters of all possible species of irreducible representation of any group may be listed. A selection of these very important tables is given at the end of the *Data section*.

## 15.7 Transformations of other bases

We shall now show that the three  $p$  orbitals on the central atom are a basis for another three-dimensional (reducible) representation. Each orbital has the form

$$p_x = xf \quad p_y = yf \quad p_z = zf$$

where  $f$  is a function of distance from the nucleus. Since the distance of a point from the nucleus does not change when the molecule is rotated and reflected, we can ignore  $f$  and use the basis  $(x, y, z)$ .

Under the reflection  $\sigma_v$  in  $C_{3v}$  (Fig. 15.24),

$$(-x, y, z) \leftarrow (x, y, z)$$

That is, the  $p_x$  orbital changes sign. (Note that the coordinate system is an unchanging background on which these transformations are played out.) We can express the transformation as a matrix equation:

$$(-x, y, z) = (x, y, z) \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = (x, y, z) \mathbf{D}(\sigma_v)$$

Similarly, under  $C_3^+$ ,

$$\left(-\frac{1}{2}x + \frac{1}{2}\sqrt{3}y, -\frac{1}{2}\sqrt{3}x - \frac{1}{2}y, z\right) \leftarrow (x, y, z)$$

which can be expressed as

$$\left(-\frac{1}{2}x + \frac{1}{2}\sqrt{3}y, -\frac{1}{2}\sqrt{3}x - \frac{1}{2}y, z\right) = (x, y, z) \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} = (x, y, z) \mathbf{D}(C_3^+)$$

All the representatives can be compiled in this way, and the complete representation is

$$\chi = \begin{matrix} \mathbf{D}(E) & \mathbf{D}(C_3^+) & \mathbf{D}(C_3^-) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -\frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ 3 & 0 & 0 \end{matrix}$$

$$\chi = \begin{matrix} \mathbf{D}(\sigma_v) & \mathbf{D}(\sigma_v') & \mathbf{D}(\sigma_v'') \\ \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & -\frac{1}{2}\sqrt{3} & 0 \\ \frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} \frac{1}{2} & \frac{1}{2}\sqrt{3} & 0 \\ -\frac{1}{2}\sqrt{3} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \\ 1 & 1 & 1 \end{matrix}$$

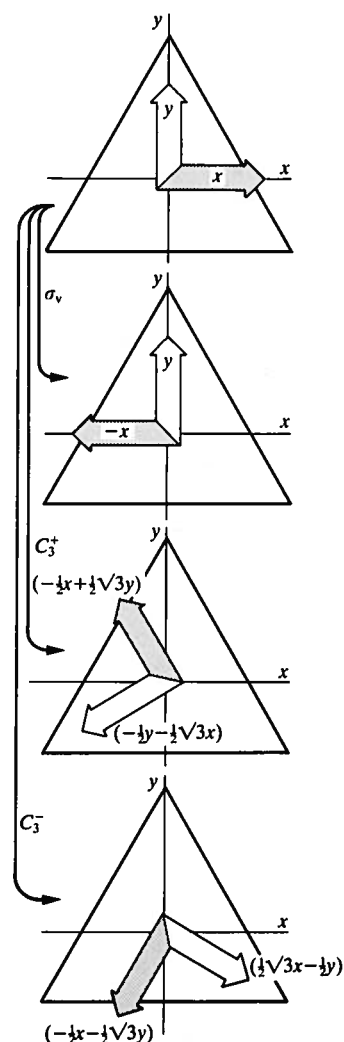


Fig. 15.24 The transformations of the functions  $x$  and  $y$  under the operations of the group  $C_{3v}$ . Notice that they take place against a fixed coordinate system (just as the N, A, B, C are fixed in Fig. 15.21).

## 15.7 | Symmetry: its description and consequences

The representation is reducible because all the matrices have block-diagonal form and the parts relating to  $z$  may be sliced off. The characters of the matrices for the remaining functions in the basis  $(x, y)$  are

$$2 \quad -1 \quad -1 \quad 0 \quad 0 \quad 0$$

By comparing this with the  $C_{3v}$  character table it is clear that  $(x, y)$  spans an irreducible representation of symmetry species  $E$ .

### Example 15.5: Finding the symmetry species of a representation

Find the symmetry species of the irreducible representations spanned by  $(x, y, z)$  in the group  $C_{2v}$ .

**Answer.** We need to establish the effect of the operations  $E$ ,  $C_2$ ,  $\sigma_v$ , and  $\sigma'_v$  on the three functions. To do so, we write the matrix representation in the basis, and identify the symmetry species from the characters. The four transformations are

$$\begin{aligned} E: (x, y, z) &\leftarrow (x, y, z) & C_2: (-x, -y, z) &\leftarrow (x, y, z) \\ \sigma_v: (-x, y, z) &\leftarrow (x, y, z) & \sigma'_v: (x, -y, z) &\leftarrow (x, y, z) \end{aligned}$$

The matrix representation is therefore

$$\begin{matrix} D(E) & D(C_2) & D(\sigma_v) & D(\sigma'_v) \\ \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} & \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \end{matrix}$$

This representation is in block-diagonal form, and may be decomposed into the following one-dimensional irreducible representations

$$\begin{aligned} x: & 1 & -1 & -1 & 1 \\ y: & 1 & -1 & 1 & -1 \\ z: & 1 & 1 & 1 & 1 \end{aligned}$$

The characters of the representatives are the numbers themselves (because they are  $1 \times 1$  matrices), and so the symmetry species of the irreducible representations spanned by  $x$ ,  $y$ , and  $z$  are  $B_1$ ,  $B_2$ , and  $A_1$  respectively.

**Exercise.** What symmetry species does  $xy$  span in  $C_{2v}$ ?

[A<sub>2</sub>]

The conclusion of the analysis given above is that in  $C_{3v}$ ,  $z$  spans an irreducible representation of symmetry species  $A_1$  and  $(x, y)$  spans one of symmetry species  $E$ . Information like this will turn out to be so important that the symmetry species of the irreducible representations spanned by  $x$ ,  $y$ , and  $z$  are normally reported in the character table. The same technique may be applied to the **quadratic forms**  $x^2$ ,  $xy$ ,  $xz$ ,  $\dots$ ,  $z^2$  which represent the shapes of the  $d$  orbitals, and the symmetry species of the irreducible representations they span are also usually listed. A complete character table therefore looks something like the following:

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

The  $R_x$ , etc, in the final column denote rotations, and their listing shows how they transform under the operations of the group. The transformation properties of rotations can be deduced from those of angular momentum; for instance,  $R_z$  transforms as  $l_z = xp_y - yp_x$  (Section 12.6), and the linear momentum components transform like  $x, y, z$ .

**Example 15.6: Deducing the transformation properties of a rotation**

Decide how a rotation around the  $z$ -axis transforms in the group  $C_{2v}$ .

**Answer.** We need to consider the transformation properties of the angular momentum operator

$$l_z = xp_y - yp_x$$

Under a  $C_2$  rotation both  $x$  and  $y$  and  $p_x$  and  $p_y$  change sign, so  $l_z$  is unchanged. We know, therefore, that the rotation is the basis for either  $A_1$  or  $A_2$ . Under a reflection in the  $yz$ -plane,  $x$  and  $p_x$  both change sign but neither  $y$  nor  $p_y$  does; therefore  $l_z$  does change sign, and its character is  $-1$ . It has the same character for reflection in the  $xz$ -plane. Hence, from the  $C_{2v}$  character table we can identify the irreducible representation spanned by rotation around the  $z$ -axis as  $A_2$ .

**Exercise.** Identify the irreducible representation spanned by a rotation around the  $x$ -axis in  $C_{2v}$ . [B.]

## Using character tables

Although the characters do not carry all the information contained in the representatives (they are, after all, only the diagonal sums), they do contain enough to make them of central importance in chemistry. One of the reasons for the importance of character tables is that they let us say, almost at a glance, whether an integral is zero. Integrals of interest to chemists include overlap integrals and 'transition dipole moments', which, as we shall see, govern the intensities of spectroscopic transitions. Thus group theory enables us to make powerful statements about chemical bonding and the appearance of spectra.

### 15.8 Vanishing integrals

Suppose we had to evaluate the integral

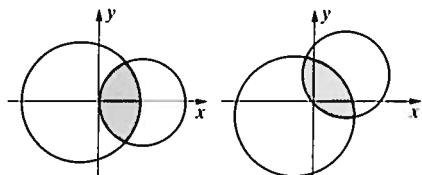
$$I = \int f_1 f_2 \, d\tau \quad (1)$$

where  $f_1$  and  $f_2$  are wavefunctions. For example,  $f_1$  might be an atomic orbital on one atom and  $f_2$  an atomic orbital on another atom, in which case  $I$  would be their overlap integral  $S$ . If we knew that the integral is zero, we could say at once that a molecular orbital does not result from  $(f_1, f_2)$  overlap in that molecule.

#### Integrals over the product of two functions

The key point in dealing with  $I$  is that the value of any integral, and of an overlap integral in particular, is independent of the orientation of the

## 15.8 | Symmetry: its description and consequences



**Fig. 15.25** The value of an integral  $I$  (e.g. an area) is independent of the coordinate system used to evaluate it. That is,  $I$  is a basis of a representation of symmetry species  $A_1$ .

molecule (Fig. 15.25). In group theoretical language we express this by saying that  $I$  is unchanged by any symmetry operation of the molecule, and that each operation brings about the trivial transformation

$$I \leftarrow I$$

Since the volume element  $d\tau$  is unchanged by a symmetry operation, it follows that the integral is non-zero only if the product  $f_1 f_2$  is unchanged by any symmetry operation of the molecular point group. If the product of functions changed sign under a symmetry operation, the integral would be the sum of equal and opposite contributions, and hence would be zero. It follows that the only contribution to a non-zero integral comes from functions for which under any symmetry operation of the molecular point group

$$f_1 f_2 \leftarrow f_1 f_2$$

and hence for which the representatives, and the characters, are all equal to 1. Therefore, for  $I$  not to be zero, the integrand  $f_1 f_2$  must be a basis for the totally symmetric  $A_1$  irreducible representation of the molecular point group.

We use the following procedure<sup>2</sup> to deduce the symmetry species spanned by the product  $f_1 f_2$  and hence to see whether it does indeed span  $A_1$ .

- (1) Decide on the symmetry species of the functions by reference to the character table, and write the characters in two rows in the same order as in the table.

For example, if  $f_1$  is the  $s_N$  orbital in  $\text{NH}_3$  and  $f_2$  is the linear combination  $s_3$  (Fig. 15.23), then since  $s_N$  spans  $A_1$  and  $s_3$  is a member of the basis spanning  $E$ , we write

$$\begin{array}{ccc} f_1: & 1 & 1 & 1 \\ f_2: & 2 & -1 & 0 \end{array}$$

- (2) Multiply the numbers in each column, writing the results in the same order.

For the  $\text{NH}_3$  calculation,

$$f_1 f_2: \quad 2 \quad -1 \quad 0$$

- (3) Inspect the row so produced, and see if it can be expressed as a sum of characters of the irreducible representations of the group. If this sum does not contain  $A_1$ , the integral must be zero.

<sup>2</sup> The procedure here and in the rest of the chapter is based on a very important theorem in group theory known as the 'little orthogonality theorem' which states that

$$\sum_C g(C) \chi^{(\Gamma)}(C) \chi^{(\Gamma')}(C) = 0$$

where the sum is over the classes of the group (the columns in the character table),  $g$  is the number of elements in each class, and  $\Gamma$  and  $\Gamma'$  are two *different* irreducible representations.

In  $C_{3v}$ , for instance, the character of each operation can always be expressed as

$$\chi = c_1\chi(A_1) + c_2\chi(A_2) + c_3\chi(E)$$

and the integral must be zero if  $c_1 = 0$ . In the present example, the characters 2, -1, 0 are those of E alone, and so the integral must be zero. Inspection of the form of the functions (Fig. 15.23) shows why this is so:  $s_3$  has a node running through  $s_N$ . Had we taken  $f_1 = s_N$  and  $f_2 = s_1$  instead, then since each spans  $A_1$  with characters 1, 1, 1,

$$f_1: \quad 1 \quad 1 \quad 1$$

$$f_2: \quad 1 \quad 1 \quad 1$$

$$f_1 f_2: \quad 1 \quad 1 \quad 1$$

The characters of the product are those of  $A_1$  itself. Therefore,  $s_1$  and  $s_N$  may have non-zero overlap.

It is important to note that group theory is specific about when an integral must be zero, but integrals that it allows to be non-zero may be zero for reasons unrelated to symmetry. For example, the N—H distance may be so great that the  $s_1, s_N$  overlap integral is zero simply because the orbitals are so far apart.

**Example 15.7:** *Deciding if an integral must be zero (1)*

May the integral of the function  $f = xy$  be non-zero when evaluated over a region the shape of an equilateral triangle centred on the origin?

**Answer.** An equilateral triangle has the point-group symmetry  $C_{3v}$ . If we refer to the character table of the group, we see that  $xy$  is a member of a basis that spans the irreducible representation E. Therefore, its integral must be zero, since the integrand has no component that spans  $A_1$ .

**Comment.** In this case we have used a special case of the argument given above in which the integrand is expressed as a single function. We can regard  $f_2$  as present, but as equal to 1.

**Exercise.** Can the function  $x^2 + y^2$  have a non-zero integral when integrated over a regular pentagon centred on the origin? [Yes, spans  $A_1$ ]

### Integrals over the product of three functions

The same technique may be used to decide whether integrals of the form

$$I = \int f_1 f_2 f_3 d\tau \quad (2)$$

necessarily disappear. In this case the triple product  $f_1 f_2 f_3$  must contain a component that spans  $A_1$ . To test whether this is so, the characters of all three functions are multiplied together in the same way as in the rules set out above.

**Example 15.8: Deciding if an integral must be zero (2)**

Does the integral  $\int (3d_{z^2})x(3d_{xy}) d\tau$  vanish in a tetrahedral molecule?

**Answer.** We must refer to the  $T_d$  character table (at the end of the *Data section*) and find the characters of the irreducible representations spanned by  $3z^2 - r^2$  (the form of the  $d_{z^2}$  orbital),  $x$ , and  $xy$ ; then we can use the procedure set out above (with one more row of multiplication). Note that  $3z^2 - r^2 = 2z^2 - x^2 - y^2$ . We then draw up the following table:

	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$f_3 = d_{xy}$	3	0	-1	-1	1	( $T_2$ )
$f_2 = x$	3	0	-1	-1	1	( $T_2$ )
$f_1 = d_{z^2}$	2	-1	2	0	0	( $E$ )
$f_1 f_2 f_3$	18	0	2	0	0	

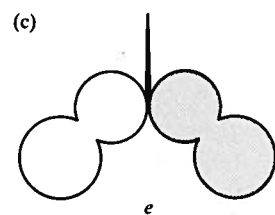
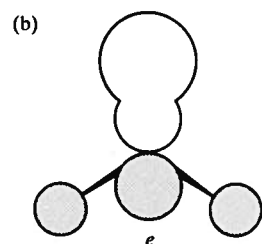
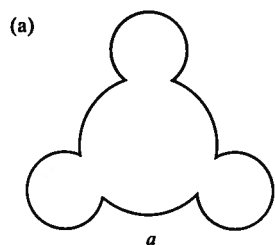
The characters are the sum of  $A_1 + A_2 + 2E + 2T_1 + 2T_2$ . Therefore, the integral is not necessarily zero.

**Comment.** Closer inspection of the integral (e.g. using the representation itself, not just the characters) show that the integral must in fact vanish. This is a warning that arguments based on the character tables, since they carry only incomplete information in general, show only when an integral is necessarily zero. A second point is that the decomposition of the result to discover if  $A_1$  is included is sometimes a lengthy job. The following procedure<sup>3</sup> can always be used if the answer is not obvious:

- (1) Multiply the characters (18, 0, ...) by the number of elements in each class (1, 8, ...).
- (2) Add together the numbers this produces (18 + 0 + ... = 24).
- (3) Divide the sum by the order of the group (the number of elements, 24).

This gives the number of times  $A_1$  appears in the reducible representation (1).

**Exercise.** Does the integral  $\int (2p_x)(2p_y)(2p_z) d\tau$  necessarily vanish in an octahedral environment? [No; spans  $A_1$ ]



**Fig. 15.26** Orbitals of the same symmetry species may have non-vanishing overlap. This diagram illustrates the three bonding orbitals that may be constructed from  $(N2s, H1s)$  and  $(N2p, H1s)$  overlap in a  $C_{3v}$  molecule, and their symmetry labels. (There are also three antibonding orbitals of the same species.)

**Orbitals with non-zero overlap**

The rules just given let us decide which atomic orbitals may have non-zero overlap in a molecule. We have seen that  $s_N$  may have non-zero overlap with  $s_1$  (the combination  $1s_A + 1s_B + 1s_C$ ), and so  $(s_N, s_1)$  overlap bonding and antibonding molecular orbitals can form (Fig. 15.26a). The general rule is that:

Only orbitals of the same symmetry species may have non-zero overlap, and so only orbitals of the same symmetry species form bonding and antibonding combinations.

<sup>3</sup> The procedure is based on an orthogonality theorem like that given in the previous footnote. The number of times  $c_1$  that the irreducible representation  $A_1$  appears in a representation  $\Gamma$  with characters  $\chi^{(\Gamma)}$  is:

$$c_1 = \frac{1}{h} \sum_C g(C) \chi^{(\Gamma)}(C)$$

where  $h$  is the order of the group and  $g$  is the number of elements in each class  $C$ .



It should be recalled from Chapter 14 that the selection of atomic orbitals that had mutual non-zero overlap is the central and initial step in the construction of molecular orbitals by the LCAO procedure. We are therefore at the point of contact between group theory and the material introduced in that chapter. The molecular orbitals formed from a particular set of atomic orbitals with non-zero overlap are labelled with the lower-case letter corresponding to the symmetry species. Thus, the  $(s_N, s_1)$ -overlap orbitals are called  $a_1$  orbitals (and  $a_1^*$  if we wish to emphasize that they are antibonding).

The  $s_2$  and  $s_3$  linear combinations span an irreducible representation of symmetry species E. Does the N atom have orbitals that have non-zero overlap with them (and give rise to an  $e$  orbital)? Intuition (Fig. 15.26b and c) suggests that  $N2p_x$  and  $N2p_y$  should be suitable. We can confirm this conclusion by noting that the character table shows that in  $C_{3v}$ ,  $x$  and  $y$  jointly span an irreducible representation of symmetry species E. Therefore,  $N2p_x$  and  $N2p_y$  also span E, and so may have non-zero overlap with  $s_2$  and  $s_3$  (verify this by multiplying the characters:  $E \times E = A_1 + A_2 + E$  in  $C_{3v}$ ). The two  $e$  orbitals that result are shown in Fig. 15.26 (there are also two antibonding  $e$  orbitals).

The power of the method can be illustrated by exploring whether any  $d$  orbitals on the central atom can take part in bonding. The  $d$  orbitals have the forms

$$\begin{aligned}d_{z^2} &= (3z^2 - r^2)f & d_{x^2-y^2} &= (x^2 - y^2)f \\d_{xy} &= xyf & d_{yz} &= yzf & d_{zx} &= zxf\end{aligned}$$

Their symmetries can be taken from the character tables by noting how the quadratic forms  $xy$ ,  $yz$ , etc, transform. Reference to the  $C_{3v}$  table shows that  $d_{z^2}$  has  $A_1$  symmetry and that the pairs  $(d_{x^2-y^2}, d_{xy})$  and  $(d_{yz}, d_{zx})$  each transform as E. It follows that molecular orbitals may be formed by  $s_1, d_{z^2}$  overlap and by overlap of the  $s_2, s_3$  combinations with the E  $d$  orbitals. Whether or not the  $d$  orbitals are in fact important is a question group theory cannot answer because that depends on energy considerations, not symmetry.

Although we have illustrated the technique with the group  $C_{3v}$ , it is entirely general, and the importance of knowing which  $s$ ,  $p$ , and  $d$  orbitals overlap is one of the reasons why the transformation properties of  $x$ ,  $xz$ , etc, are listed in the character tables.

**Example 15.9:** *Determining which orbitals can contribute to bonding*

The four H1s orbitals of methane span  $A_1 + T_2$ . With which of the C atom orbitals can they overlap? What if the C atom had  $d$  orbitals available?

**Answer.** We need to refer to the  $T_d$  character table (at the end of the *Data section*) and look for  $s$ ,  $p$ , and  $d$  orbitals spanning  $A_1$  or  $T_2$ . An  $s$  orbital spans  $A_1$ , and so it may have non-zero overlap with the  $A_1$  combination of H1s orbitals. The  $C2p$  orbitals span  $T_2$ , and so they may have non-zero overlap with the  $T_2$  combination. The  $d_{xy}$ ,  $d_{yz}$ , and  $d_{zx}$  orbitals span  $T_2$ , and so may overlap the same combination. Neither of the other two  $d$  orbitals span  $A_1$  (they span E), and so they remain nonbonding orbitals.

**Comment.** It follows that in methane, there are ( $C_{2s}, H1s$ )-overlap  $a_1$  orbitals and ( $C_{2p}, H1s$ )-overlap  $t_2$  orbitals. The  $C3d$  orbitals might contribute to the latter. The lowest energy configuration is probably  $a_1^7 t_2^6$ , with all bonding orbitals occupied.

**Exercise.** Consider the octahedral  $SF_6$  molecule, with the bonding arising from overlap of  $S$  orbitals and a  $2p$  orbital on each  $F$  directed towards the central  $S$ . The latter span  $A_{1g} + E_g + T_{1u}$ . What  $S$  orbitals have non-zero overlap? Suggest what the ground configuration is likely to be.

$$[3s(A_{1g}), 3p(T_{1u}), 3d(E_g); a_{1g}^2 t_{1u}^6 e_g^4]$$

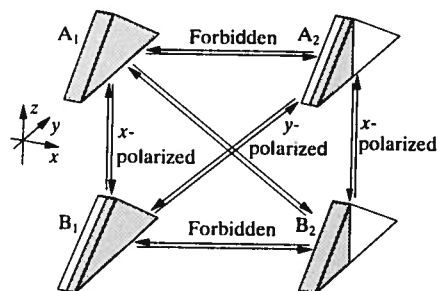
### Selection rules

In Chapters 16 and 17 we shall see that the intensity of a spectral line arising from a molecular transition between some initial state with wavefunction  $\psi_i$  and a final state with wavefunction  $\psi_f$  depends on the (electric) **transition dipole moment**  $\mu$ . The  $z$ -component of this vector is defined through

$$\mu_z = -e \int \psi_f^* z \psi_i d\tau \quad (3)$$

where  $-e$  is the charge of the electron. Stating the conditions for this quantity (and the  $x$ - and  $y$ -components) to be zero amounts to specifying the **selection rules** for the transition, the statement of which transitions are possible. The transition moment has the form of the integral in eqn 2, and so, once we know the symmetry species of the states, we can use group theory to decide which transitions have zero transition dipole moment and therefore cannot occur.

As an example, we investigate whether an  $a_1$  electron in  $H_2O$  (which belongs to  $C_{2v}$ ) can make an electric dipole transition to a  $b_1$  orbital (Fig. 15.27). We must examine all three components of the transition dipole, and take  $f_2$  in eqn 2 as  $x$ ,  $y$ , and  $z$  in turn. Reference to the  $C_{2v}$  character table shows that these transform as  $B_1$ ,  $B_2$ , and  $A_1$  respectively. The three calculations run as follows:



**Fig. 15.27** The polarizations of the allowed transitions in a  $C_{2v}$  molecule. The shading indicates the structure of the orbitals of the specified symmetry species.

	x-component				y-component				z-component				
$f_1$ :	1	1	1	1	1	1	1	1	1	1	1	1	( $A_1$ )
$f_2(x, y, \text{ or } z)$ :	1	-1	1	-1	1	-1	-1	1	1	1	1	1	( $B_1$ )
$f_3$ :	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1	( $B_1$ )
$f_1 f_2 f_3$ :	1	1	1	1	1	1	-1	-1	1	-1	1	-1	$A_1$ $A_2$ $B_1$

Only the first product (with  $f_2 = x$ ) spans  $A_1$ , and so only the  $x$ -component of the transition dipole may be non-zero. Therefore, we conclude that the electric dipole transition  $a_1 \leftarrow b_1$  (and  $a_1 \rightarrow b_1$ ) is allowed. We can go on to state that the radiation emitted (or absorbed) is **x-polarized** and has its electric field vector in the  $x$ -direction, because that form of radiation couples with the  $x$ -component of a transition dipole.

**Example 15.10: Deducing a selection rule**

Is  $p_x \leftarrow p_y$  an allowed transition in a tetrahedral molecule?

**Answer.** We must decide whether the product  $p_y q p_x$ , with  $q = x, y$ , or  $z$ , spans  $A_1$  using the  $T_d$  character table. The procedure works out as follows:

$$\begin{array}{l} f_3(p_y): \quad 3 \quad 0 \quad -1 \quad -1 \quad 1 \quad (T_2) \\ f_2(q): \quad 3 \quad 0 \quad -1 \quad -1 \quad 1 \quad (T_2) \\ f_1(p_x): \quad 3 \quad 0 \quad -1 \quad -1 \quad 1 \quad (T_2) \\ f_1 f_2 f_3: \quad 27 \quad 0 \quad -1 \quad -1 \quad 1 \end{array}$$

$A_1$  occurs (once) in this set of characters, and so  $p_x \rightarrow p_y$  is allowed.

**Comment.** Closer analysis (using the representatives) shows that only  $q = z$  gives a non-zero integral, and so the transition is  $z$ -polarized.

**Exercise.** What are the allowed transitions, and their polarizations, of a  $b_1$  electron in a  $C_{4v}$  molecule? [ $b_1 \rightarrow b_1(z); b_1 \rightarrow e(x, y)$ ]

## 15.9 Symmetry-adapted linear combinations

So far we have only asserted the forms of the linear combinations (such as  $s_1$ , etc) that act as bases for irreducible representations. Group theory also provides machinery that takes an arbitrary basis ( $s_A$ , etc) as input and generates combinations of the specified symmetry. Because these combinations are adapted to the symmetry of the molecule, they are called **symmetry-adapted linear combinations** (SALC). Symmetry-adapted linear combinations are the building blocks of LCAO molecular orbitals, for they include combinations such as the  $\psi_{1s}(A) \pm \psi_{1s}(B)$  used to construct molecular orbitals in  $H_2O$  (Section 14.8) and some of the complex examples that we have seen since then. The selection of symmetry-adapted linear combinations of atomic orbitals is the first step in any molecular orbital treatment of molecules, and is central, for instance, to the construction and analysis of Walsh diagrams and to the description of  $d$ -metal complexes.

The technique for building symmetry-adapted linear combinations is derived using the full power of group theory. We shall not show the derivation, which is very lengthy, but present the main conclusions as a set of rules:<sup>4</sup>

(1) Construct a table showing the effect of each operation on each orbital of the original basis.

For example, from the  $(s_N, s_A, s_B, s_C)$  basis in  $NH_3$  we form the following table:

<sup>4</sup> Once again, it is possible to express the rules given here in a succinct formula derived from group theory. In this case, to form an orbital of symmetry species  $\Gamma$  we form  $P\psi$ , where

$$P\psi = \frac{1}{h} \sum_R \chi^{(\Gamma)}(R) R\psi$$

where  $R$  is an operation of the group. The implementation of this formula is described in the following remarks. Note that the actual operations occur in the formula, not the classes as in the earlier expressions.

Original basis:	$s_N$	$s_A$	$s_B$	$s_C$
Under $E$	$s_N$	$s_A$	$s_B$	$s_C$
$C_3^+$	$s_N$	$s_B$	$s_C$	$s_A$
$C_3^-$	$s_N$	$s_C$	$s_A$	$s_B$
$\sigma_v$	$s_N$	$s_A$	$s_C$	$s_B$
$\sigma'_v$	$s_N$	$s_B$	$s_A$	$s_C$
$\sigma''_v$	$s_N$	$s_C$	$s_B$	$s_A$

- (2) To generate the combination of a specified symmetry species, take each column in turn and:
- Multiply each member of the column by the character of the corresponding operation.
  - Add together all the orbitals in each column with the factors as determined in (i).
  - Divide the sum by the order of the group.

In our example, in order to generate the  $A_1$  combination we take the characters for  $A_1$  (1, 1, 1, 1, 1, 1), and so rules (i) and (ii) lead to

$$\psi \propto s_N + s_N + \dots = 6s_N$$

The order of the group (the number of elements) is 6, and so the combination of  $A_1$  symmetry that can be generated from  $s_N$  is  $s_N$  itself. Applying the same technique to the column under  $s_A$  gives

$$\psi = \frac{1}{6}(s_A + s_B + s_C + s_A + s_B + s_C) = \frac{1}{3}(s_A + s_B + s_C)$$

The same combination is built from the other two columns, and so they give no further information. The combination we have just formed is the  $s_1$  combination we used before (apart from the numerical factor).

We now form the overall molecular orbital by forming a linear combination of all the symmetry-adapted linear combinations of the specified symmetry species. In this case, therefore, the  $a_1$  molecular orbital is

$$\psi = c_N s_N + c_1 s_1$$

This is as far as group theory can take us. The coefficients must be found by solving the Schrödinger equation because they do not come directly from the symmetry of the system.

Suppose we try to generate a symmetry-adapted linear combination of species  $A_2$  despite the fact that the previous work has shown that there is no such combination. The characters for  $A_2$  are 1, 1, 1, -1, -1, -1. The column under  $s_N$  generates zero, and so do the other three. Therefore, we find that we generate no combination of  $A_2$  symmetry.

When we try to generate the  $E$  symmetry-adapted combinations we run into a problem because, for representations of dimension 2 or more, where the characters are the sums of the diagonal elements, the rules generate sums of the symmetry-adapted combinations. (A more detailed rule based on the representatives themselves gives the individual combinations.) This can be seen as follows. The  $E$  characters are 2, -1, -1, 0, 0, 0, and so the

column under  $s_N$  gives

$$\psi = 2s_N - s_N - s_N + 0 + 0 + 0 = 0$$

The other columns give

$$\frac{1}{6}(2s_A - s_B - s_C) \quad \frac{1}{6}(2s_B - s_A - s_C) \quad \frac{1}{6}(2s_C - s_B - s_A)$$

However, any one can be expressed as a sum of the other two (they are not linearly independent). The difference of the second and third gives  $\frac{1}{6}(s_B - s_C)$ , and this and the first,  $\frac{1}{6}(2s_A - s_B - s_C)$ , are the two linearly independent symmetry-adapted combinations we have used in the discussion of  $e$  orbitals.

The following chapters will show many more examples of how the systematic use of symmetry using the techniques of group theory can greatly simplify the analysis of molecular structure and spectra.

## Further information: matrices

Matrices are arrays of numbers with special rules for combining them together. We shall consider  $n \times n$  square matrices  $M$  with  $n^2$  elements  $M_{rc}$ :

$$M = \begin{pmatrix} M_{11} & M_{12} & \dots & M_{1n} \\ M_{21} & M_{22} & \dots & M_{2n} \\ \dots & \dots & \dots & \dots \\ M_{n1} & M_{n2} & \dots & M_{nn} \end{pmatrix}$$

$M_{rc}$  is the element in row  $r$ , column  $c$  ( $r, c$  is a map reference). Two matrices  $M$  and  $N$  are equal (written  $M = N$ ) only if all corresponding elements are equal:  $M_{rc} = N_{rc}$  for all  $r, c$ .

The addition of two matrices,

$$M + N = P$$

is defined through

$$P_{rc} = M_{rc} + N_{rc}$$

That is, add corresponding elements. For example,

$$M = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \quad N = \begin{pmatrix} 5 & 6 \\ 7 & 8 \end{pmatrix} \quad M + N = \begin{pmatrix} 1+5 & 2+6 \\ 3+7 & 4+8 \end{pmatrix} = \begin{pmatrix} 6 & 8 \\ 10 & 12 \end{pmatrix}$$

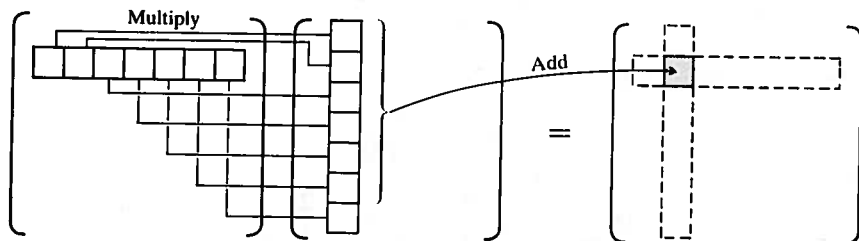
The multiplication of two matrices is written

$$MN = P$$

and defined through

$$P_{rc} = \sum_q M_{rq} N_{qc}$$

This rule can be remembered in terms of the following diagram:



## 15.9 | Symmetry: its description and consequences

For example, using the same matrices as above,

$$MN = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \begin{pmatrix} 5 & 6 \\ 7 & 8 \end{pmatrix} = \begin{pmatrix} 1 \times 5 + 2 \times 7 & 1 \times 6 + 2 \times 8 \\ 3 \times 5 + 4 \times 7 & 3 \times 6 + 4 \times 8 \end{pmatrix} = \begin{pmatrix} 19 & 22 \\ 43 & 50 \end{pmatrix}$$

In this case  $NM \neq MN$ , and so matrix multiplication is 'noncommutative' and depends on the order of multiplication in general.

Several types of matrix have special names or properties. Among them are the following:

A **diagonal matrix** is one in which all  $M_{rc} = 0$  unless  $r = c$ . For example,

$$\begin{pmatrix} 1 & 0 \\ 0 & 5 \end{pmatrix} \text{ is diagonal}$$

$$\begin{pmatrix} 0 & 1 \\ 5 & 0 \end{pmatrix} \text{ is not diagonal}$$

The **unit matrix**  $\mathbf{1}$  diagonal with all diagonal elements equal to 1. Thus, the  $2 \times 2$  unit matrix is

$$\mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

The **transpose** of a matrix  $M^T$  is related to  $M$  by interchange of rows and columns:

$$M = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \quad M^T = \begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}$$

The **inverse** of a matrix  $M^{-1}$  satisfies

$$MM^{-1} = M^{-1}M = \mathbf{1}$$

The inverse can be constructed as follows:

(1) Calculate the **determinant**,  $\det M$ , of the matrix  $M$ :

$$M = \begin{pmatrix} 1 & 2 \\ 3 & 4 \end{pmatrix} \quad \det M = \begin{vmatrix} 1 & 2 \\ 3 & 4 \end{vmatrix} = 1 \times 4 - 2 \times 3 = -2$$

If  $\det M = 0$  the matrix is **singular** and  $M^{-1}$  does not exist (just as  $0^{-1}$  is not defined in ordinary arithmetic).

(2) Form the transpose of  $M$ :

$$M^T = \begin{pmatrix} 1 & 3 \\ 2 & 4 \end{pmatrix}$$

(3) Form the matrix  $M'$  of **cofactors** of  $M^T$ , where a cofactor of an element is the determinant formed from the matrix with row  $r$ , column  $c$  struck out and multiplied by  $(-1)^{r+c}$ :

$$M' = \begin{pmatrix} 4 & -2 \\ -3 & 1 \end{pmatrix}$$

(4) The inverse is then

$$M^{-1} = \frac{M'}{\det M}$$

$$M^{-1} = -\frac{1}{2} \begin{pmatrix} 4 & -2 \\ -3 & 1 \end{pmatrix} = \begin{pmatrix} -2 & 1 \\ \frac{3}{2} & -\frac{1}{2} \end{pmatrix}$$

An important application of matrices (apart from their role as representatives of symmetry operations) is in the solution of simultaneous equations. A set of equations

$$\begin{aligned}M_{11}x_1 + M_{12}x_2 + \dots + M_{1n}x_n &= c_1 \\M_{21}x_1 + M_{22}x_2 + \dots + M_{2n}x_n &= c_2 \\&\dots\dots\dots \\M_{n1}x_1 + M_{n2}x_2 + \dots + M_{nn}x_n &= c_n\end{aligned}$$

can be expressed in the compact form

$$Mx = c$$

where  $M$  is the matrix of coefficients and  $x$  and  $c$  are the  $1 \times n$  matrices (or 'column vectors')

$$x = \begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_n \end{pmatrix} \quad c = \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_n \end{pmatrix}$$

Then, on multiplying both sides of the matrix equation by  $M^{-1}$  we obtain

$$x = M^{-1}c$$

Hence, solving the set of equations amounts to finding the inverse of the matrix of coefficients.

## Further reading

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## Exercises

**15.1** The point group  $D_3$  has four symmetry species of irreducible representation. How many classes of symmetry operations does it contain?

**15.2** The  $\text{CH}_3\text{Cl}$  molecule belongs to the point group  $C_{3v}$ . List the symmetry elements of the group and locate them in the molecule.

**15.3** Which of the following molecules may be polar? (a) pyridine ( $C_{2v}$ ), (b) nitroethane ( $C_s$ ), (c) gas-phase  $\text{HgBr}_2$  ( $D_{\infty h}$ ), (d)  $\text{B}_3\text{N}_3\text{H}_6$  ( $D_{3h}$ ), (e)  $\text{CH}_3\text{Cl}$  ( $C_{3v}$ ), (f)  $\text{HW}_2(\text{CO})_{10}$  ( $D_{4h}$ ), (g)  $\text{SnCl}_4$  ( $T_d$ ).

**15.4** Use symmetry properties to determine whether or not

the integral  $\int p_x z p_z \, d\tau$  is necessarily zero in a molecule with symmetry  $C_{4v}$ .

**15.5** Show that the transition  $A_1 \rightarrow A_2$  is forbidden for electric dipole transitions in a  $C_{3v}$  molecule.

**15.6** Show that a set of five hybrid orbitals in a molecule of  $C_{4v}$  symmetry and the characters

$$\begin{array}{ccccc} E & 2C_4 & C_2 & 2\sigma_v & 2\sigma_d \\ 5 & 1 & 1 & 3 & 1 \end{array}$$

may have the composition  $p^1 d^4$ .

## 15 | Symmetry: its description and consequences

**15.7** Show that the function  $xy$  has symmetry species  $B_2$  in the group  $C_{4v}$ .

**15.8** Molecules belonging to the point groups  $D_{2h}$ ,  $C_{3h}$ ,  $T_h$ , and  $T_d$  cannot be chiral. Which elements of these groups rule out chirality?

**15.9** The group  $D_{2d}$  consists of the elements  $E$ ,  $C_2$ ,  $C_2'$ , and  $C_2''$ , where the three twofold rotations are around mutually perpendicular axes. Construct the group multiplication table.

**15.10** Identify the point groups to which the following objects belong: (a) a sphere, (b) an isosceles triangle, (c) an equilateral triangle, (d) an unsharpened cylindrical pencil, (e) a sharpened cylindrical pencil, (f) a three-bladed propellor, (g) a four-legged table, (h) yourself (approximately).

**15.11** List the symmetry elements of the following molecules and name the point groups to which they belong: (a)  $\text{NO}_2$ , (b)  $\text{N}_2\text{O}$ , (c)  $\text{CHCl}_3$ , (d)  $\text{CH}_2=\text{CH}_2$ , (e) *cis*- $\text{CHCl}=\text{CHCl}$ , (f) *trans*- $\text{CHCl}=\text{CHCl}$ .

**15.12** List the symmetry elements of the following molecules and name the point groups to which they belong: (a) naphthalene, (b) anthracene, (c) the three dichlorobenzenes.

**15.13** Which of the molecules in Exercises 15.11 and 15.12 can be (a) polar, (b) chiral?

**15.14** Consider the  $C_{2v}$  molecule  $\text{NO}_2$ . The combination

$p_x(\text{A}) - p_x(\text{B})$  of the two O atoms (with  $x$  perpendicular to the plane) spans  $A_2$ . Is there any orbital of the central N atom that can have a non-zero overlap with that combination of O orbitals? What would be the case in  $\text{SO}_2$ , where  $3d$  orbitals might be available?

**15.15** The ground state of  $\text{NO}_2$  is  $A_1$  in the group  $C_{2v}$ . To what excited states may it be excited by electric-dipole transitions, and what polarization of light is it necessary to use?

**15.16** The  $\text{ClO}_2$  molecule (which belongs to the group  $C_{2v}$ ) was trapped in a solid. Its ground state is known to be  $B_1$ . Light polarized parallel to the  $y$  axis (parallel to the OO separation) excited the molecule to an upper state. What is the symmetry of that state?

**15.17** What states of (a) benzene, (b) naphthalene may be reached by electric dipole transitions from their (totally symmetrical) ground states?

**15.18** Confirm that the  $z$  component of orbital angular momentum is a basis for an irreducible representation of  $A_2$  symmetry in  $C_{3v}$ .

**15.19** Write  $f_1 = \sin \theta$  and  $f_2 = \cos \theta$ , and show by symmetry arguments using the group  $C_\infty$  that the integral of their product over a symmetrical range around the origin is zero.

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## Problems

**15.1** List the symmetry elements of the following molecules and name the point groups to which they belong: (a) staggered  $\text{CH}_3\text{CH}_3$ , (b) chair and boat cyclohexane, (c)  $\text{B}_2\text{H}_6$ , (d)  $[\text{Co}(\text{en})_3]^{3+}$  where en is ethylenediamine (ignore its detailed structure), (e) crown-shaped  $\text{S}_8$ . Which of these molecules can be (i) polar, (ii) chiral?

**15.2** The group  $C_{2h}$  consists of the elements  $E$ ,  $C_2$ ,  $\sigma_h$ ,  $i$ . Construct the group multiplication table and find an example of a molecule that belongs to the group.

**15.3** The group  $D_{2h}$  has a  $C_2$  axis perpendicular to the principal axis and a horizontal mirror plane. Show that the group must therefore have a centre of inversion.

**15.4** Consider the  $\text{H}_2\text{O}$  molecule, which belongs to the group  $C_{2v}$ . Take as a basis the two  $1s$  orbitals and the four valence orbital of the O atom and set up the  $6 \times 6$  matrices that represent the group in this basis. Confirm by explicit matrix multiplication that the group multiplications (a)  $C_2\sigma_v = \sigma_v'$  and (b)  $\sigma_v\sigma_v' = C_2$ . Confirm, by calculating the traces of the matrices, (a) that the representation is reducible, and (b) that the basis spans  $3A_1 + B_1 + 2B_2$ .

**15.5** The (one-dimensional) matrices  $\mathbf{D}(C_3) = 1$  and  $\mathbf{D}(C_2) = 1$ , and  $\mathbf{D}(C_3) = 1$  and  $\mathbf{D}(C_2) = -1$  both represent the group multiplication  $C_3C_2 = C_6$  in the group  $C_{6v}$  with  $\mathbf{D}(C_6) = +1$  and  $-1$  respectively. Use the character table to

confirm these remarks. What are the representatives of  $\sigma_v$  and  $\sigma_d$  in each case?

**15.6** What irreducible representations do the four  $1s$  orbitals of  $\text{CH}_4$  span? Are there  $s$  and  $p$  orbitals of the central C atom that may form molecular orbitals with them? Could  $d$  orbitals, even if they were present on the C atom, play a role in orbital formation in  $\text{CH}_4$ ?

**15.7** Suppose that a methane molecule became distorted to (a)  $C_{3v}$  symmetry by the lengthening of one bond, (b)  $C_{2v}$  symmetry, by a kind of scissors action in which one bond angle opened and another closed slightly. Would more  $d$  orbitals become available for bonding?

**15.8** The algebraic forms of the  $f$  orbitals are a radial function multiplied by one of the factors

$$(a) z(5z^2 - 3r^2), (b) y(5y^2 - 3r^2), (c) x(5x^2 - 3r^2) \\ (d) z(x^2 - y^2), (e) y(x^2 - z^2), (f) x(z^2 - y^2), (g) xyz$$

Identify the irreducible representations spanned by these orbitals in (a)  $C_{2v}$ , (b)  $C_{3v}$ , (c)  $T_d$ , (d)  $O_h$ . Consider a lanthanide ion at the center of (a) a tetrahedral complex, (b) an octahedral complex. What sets of orbitals do the seven  $f$  orbitals split into?

**15.9** Which of the following transitions is allowed in (a) a



tetrahedral complex, (b) an octahedral complex: (i)  $d_{xy} \rightarrow d_{z^2}$ , (ii)  $d_{xy} \rightarrow f_{xyz}$ ?

**15.10** Does the product  $xyz$  necessarily vanish when integrated over (a) a cube, (b) a tetrahedron, (c) a hexagonal prism, each centred on the origin?

**15.11** Treat the naphthalene molecule as belonging to the group  $C_{2v}$  with the  $C_2$  axis perpendicular to the plane. Classify the irreducible representations spanned by the carbon  $2p_z$  orbitals and find their symmetry-adapted linear combinations.

**15.12** The  $\text{NO}_2$  molecule belongs to the group  $C_{2v}$ , with the

$C_2$  axis bisecting the  $\text{ONO}$  angle. Taking as a basis the  $\text{N}2s$ ,  $\text{N}2p$ , and  $\text{O}2p$  orbitals, identify the irreducible representations they span, and construct the symmetry-adapted linear combinations.

**15.13** Construct the symmetry-adapted linear combinations of  $C2p_z$  orbitals for benzene, and use them to calculate the Hückel secular determinant. This procedure leads to equations that are much easier to solve than using the original orbitals, and show that the Hückel orbitals are those specified in Section 14.10.

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