In this chapter we sharpen the concept of ‘shape’ into a precise definition of ‘symmetry’, and show that symmetry may be discussed systematically. We see how to classify any molecule according to its symmetry and how to use this classification to discuss molecular properties. After describing the symmetry properties of molecules themselves, we turn to a consideration of the effect of symmetry transformations on orbitals and see that their transformation properties can be used to set up a labelling scheme. These symmetry labels are used to identify integrals that necessarily vanish. One important integral is the overlap integral between two orbitals. By knowing which atomic orbitals may have nonzero overlap, we can decide which ones can contribute to molecular orbitals. We also see how to select linear combinations of atomic orbitals that match the symmetry of the nuclear framework. Finally, by considering the symmetry properties of integrals, we see that it is possible to derive the selection rules that govern spectroscopic transitions.

The systematic discussion of symmetry is called group theory. Much of group theory is a 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. 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. In some cases, though, it leads to unexpected results.

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 certain angles about specific axes, such as 90°, 180°, or 270° about an axis passing through the centres of any of its opposite faces (Fig. 12.1), or by 120° or 240° about an axis passing through any of its opposite corners. Similarly, an NH₃ molecule is ‘more symmetrical’ than an H₂O molecule because NH₃ looks the same after rotations of 120° or 240° about the axis shown in Fig. 12.2, whereas H₂O looks the same only after a rotation of 180°.

An action that leaves an object looking the same after it has been carried out is called a symmetry operation. Typical symmetry operations include rotations, reflections, and inversions. There is a corresponding symmetry element for each symmetry operation, which is the point, line, or plane with respect to which the symmetry operation is performed. For instance, a rotation (a symmetry operation) is carried out around an axis (the corresponding symmetry element). We shall see that we can classify molecules by identifying all their symmetry elements, and grouping together molecules that
possess the same set of symmetry elements. This procedure, for example, puts the trigonal pyramidal species NH$_3$ and SO$_3^{2-}$ into one group and the angular species H$_2$O and SO$_2$ into another group.

### 12.1 Operations and symmetry elements

The classification of objects according to symmetry elements corresponding to operations that leave at least one common point unchanged gives rise to the point groups. There are five kinds of symmetry operation (and five kinds of symmetry element) of this kind. When we consider crystals (Chapter 20), we shall meet symmetries arising from translation through space. These more extensive groups are called space groups.

The identity, $E$, consists of doing nothing; the corresponding symmetry element is the entire object. Because every molecule is indistinguishable from itself if nothing is done to it, every object possesses at least the identity element. One reason for including the identity is that some molecules have only this symmetry element (1); another reason is technical and connected with the detailed 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 $360^\circ/n$. The operation $C_1$ is a rotation through $360^\circ$, and is equivalent to the identity operation $E$. An H$_2$O molecule has one twofold axis, $C_2$. An NH$_3$ molecule has one threefold axis, $C_3$, with which is associated two symmetry operations, one being $120^\circ$ rotation in a clockwise sense and the other $120^\circ$ rotation in a counter-clockwise sense. A pentagon has a $C_5$ axis, with two (clockwise and counterclockwise) rotations through $72^\circ$ associated with it. It also has an axis denoted $C'_{5}$, corresponding to two successive $C_5$ rotations; there are two such operations, one through $144^\circ$ in a clockwise sense and the other through $144^\circ$ in a counterclockwise sense. A cube has three $C_4$ axes, four $C_3$ axes, and six $C_2$ axes. However, even this high symmetry is exceeded by a sphere, which possesses an infinite number of symmetry axes (along any diameter) of all possible integral values of $n$. If a molecule possesses several rotation axes, then the one (or more) with the greatest value of $n$ is called the principal axis. The principal axis of a benzene molecule is the sixfold axis perpendicular to the hexagonal ring (2).
A reflection (the operation) in a mirror plane, \( \sigma \) (the element), may contain the principal axis of a molecule or be perpendicular to it. 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. 12.3) and an \( \text{NH}_3 \) molecule has three. A vertical mirror plane that bisects the angle between two \( C_2 \) axes is called a ‘dihedral plane’ and is denoted \( \sigma_d \) (Fig. 12.4). When the plane of symmetry is perpendicular to the principal axis it is called ‘horizontal’ and denoted \( \sigma_h \). A \( C_6\text{H}_6 \) molecule has a \( C_6 \) principal axis and a horizontal mirror plane (as well as several other symmetry elements).

In an inversion (the operation) through a centre of symmetry, \( i \) (the element), we imagine taking each point in a molecule, moving it to the centre of the molecule, and then moving it out the same distance on the other side; that is, the point \((x, y, z)\) is taken into the point \((-x, -y, -z)\). Neither an \( \text{H}_2\text{O} \) molecule nor an \( \text{NH}_3 \) molecule has a centre of inversion, but a sphere and a cube do have one. A \( C_6\text{H}_6 \) molecule does have a centre of inversion, as does a regular octahedron (Fig. 12.5); a regular tetrahedron and a \( \text{CH}_4 \) molecule do not.

An \( n \)-fold improper rotation (the operation) about an \( n \)-fold axis of improper rotation or an \( n \)-fold improper rotation axis, \( S_n \), (the symmetry element) is composed of two successive transformations. The first component is a rotation through \( 360°/n \), and the second is a reflection through a plane perpendicular to the axis of that rotation; neither operation alone needs to be a symmetry operation. A \( \text{CH}_4 \) molecule has three \( S_4 \) axes (Fig. 12.6).

### 12.2 The symmetry classification of molecules

To classify molecules according to their symmetries, we list their symmetry elements and collect together molecules with the same list of elements. This procedure puts \( \text{CH}_4 \) and \( \text{CCl}_4 \), which both possess the same symmetry elements 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 (Table 12.1). The Schoenflies system (in which a name looks like \( C_{vn} \)) is more common for the discussion of individual molecules, and the Hermann–Mauguin system, or International system (in which a name looks like \( 4mm \)), is used almost exclusively in the discussion of crystal symmetry. The identification of a molecule’s point group according to the Schoenflies system is simplified by referring to the flow diagram in Fig. 12.7 and the shapes shown in Fig. 12.8.
Fig. 12.7 A flow diagram for determining the point group of a molecule. Start at the top and answer the question posed in each diamond (Y = yes, N = no).

(a) The groups $C_1$, $C_i$, and $C_s$

A molecule belongs to the group $C_1$ if it has no element other than the identity, as in (1). It belongs to $C_i$ if it has the identity and the inversion alone (3), and to $C_s$ if it has the identity and a mirror plane alone (4).
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 Fig. 12.7.
(b) 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 symbol $C_n$ is now playing a triple role: as the label of a symmetry element, a symmetry operation, and a group. For example, an $\text{H}_2\text{O}_2$ molecule has the elements $E$ and $C_2$ (5), so it belongs to the group $C_2$.

If in addition to the identity and a $C_n$ axis a molecule has $n$ vertical mirror planes $\sigma_v$, then it belongs to the group $C_{nv}$. An $\text{H}_2\text{O}$ molecule, for example, has the symmetry elements $E$, $C_2$, and $2\sigma_v$, so it belongs to the group $C_{2v}$. An $\text{NH}_3$ molecule has the elements $E$, $C_3$, and $3\sigma_v$, so it belongs to the group $C_{3v}$. A heteronuclear diatomic molecule such as HCl belongs to the group $C_{nv}$, because all rotations around the axis and reflections across the axis are symmetry operations. Other members of the group $C_{nv}$ include the linear OCS molecule and 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-CHCl=CHCl (6), which has the elements $E$, $C_2$, and $\sigma_h$, so it belongs to the group $C_{2h}$; the molecule $\text{B(OH)}_3$ in the conformation shown in (7) belongs to the group $C_{3h}$. The presence of certain symmetry elements may be implied by the presence of others: thus, in $C_{2h}$, the operations $C_2$ and $\sigma_h$ jointly imply the presence of a centre of inversion (Fig. 12.9).

(c) The groups $D_{nv}$, $D_{nvh}$, and $D_{nd}$

We see from Fig. 12.7 that a molecule that has an $n$-fold principal axis and $n$ twofold axes perpendicular to $C_n$ belongs to the group $D_{nv}$. A molecule belongs to $D_{nvh}$ if it also possesses a horizontal mirror plane. The planar trigonal BF$_3$ molecule has the elements $E$, $C_3$, $3\sigma_v$, and $\sigma_h$ (with one $C_2$ axis along each B—F bond), so belongs to $D_{3h}$ (8). The $\text{C}_6\text{H}_6$ molecule has the elements $E$, $C_6$, $3C_2$, $3\sigma_v$, and $\sigma_h$ together with some others that these elements imply, so it belongs to $D_{6h}$. All homonuclear diatomic molecules, such as $\text{N}_2$, belong to the group $D_{nv}$ because all rotations around the axis are symmetry operations, as are end-to-end rotation and end-to-end reflection; $D_{nv}$ is also the group of the linear OCO and HCCH molecules and of a uniform cylinder. Other examples of $D_{nv}$ molecules are shown in (9), (10), and (11).

A molecule belongs to the group $D_{nvh}$ if in addition to the elements of $D_{nv}$ it possesses $n$ dihedral mirror planes $\sigma_d$. The twisted, 90° allene (12) belongs to $D_{2d}$, and the staggered conformation of ethane (13) belongs to $D_{3d}$.

(d) The groups $S_n$

Molecules that have not been classified into one of the groups mentioned so far, but that possess one $S_n$ axis, belong to the group $S_{np}$. An example is tetraphenylmethane, which belongs to the point group $S_4$ (14). Molecules belonging to $S_n$ with $n > 4$ are rare. Note that the group $S_2$ is the same as $C_4$, so such a molecule will already have been classified as $C_i$. 

Comment 12.2
The prime on $3C_2'$ indicates that the three $C_2'$ axes are different from the other three $C_2$ axes. In benzene, three of the $C_2$ axes bisect $C—C$ bonds and the other three pass through vertices of the hexagon formed by the carbon framework of the molecule.
A number of very important molecules (e.g. CH$_4$ and SF$_6$) possess more than one principal axis. Most belong to the **cubic groups**. In particular to the **tetrahedral groups** $T$, $T_d$, and $T_h$ (Fig. 12.10a) or to the **octahedral groups** $O$ and $O_h$ (Fig. 12.10b). A few icosahedral (20-faced) molecules belonging to the **icosahedral group**, $I_h$ (Fig. 12.10c), are also known: they include some of the boranes and buckminsterfullerene, C$_{60}$ (15). The groups $T_d$ and $O_h$ are the groups of the regular tetrahedron (for instance, CH$_4$) and the regular octahedron (for instance, 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 $O$ (Fig. 12.11). The group $T_h$ is based on $T$ but also contains a centre of inversion (Fig. 12.12).

**Fig. 12.10** (a) Tetrahedral, (b) octahedral, and (c) icosahedral molecules are drawn in a way that shows their relation to a cube: they belong to the cubic groups $T_d$, $O_h$, and $I_h$, respectively.

(e) **The cubic groups**

A number of very important molecules (e.g. CH$_4$ and SF$_6$) possess more than one principal axis. Most belong to the **cubic groups**, and in particular to the **tetrahedral groups** $T$, $T_d$, and $T_h$ (Fig. 12.10a) or to the **octahedral groups** $O$ and $O_h$ (Fig. 12.10b). A few icosahedral (20-faced) molecules belonging to the **icosahedral group**, $I_h$ (Fig. 12.10c), are also known: they include some of the boranes and buckminsterfullerene, C$_{60}$ (15). The groups $T_d$ and $O_h$ are the groups of the regular tetrahedron (for instance, CH$_4$) and the regular octahedron (for instance, 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 $O$ (Fig. 12.11). The group $T_h$ is based on $T$ but also contains a centre of inversion (Fig. 12.12).
The full rotation group, \( R_3 \) (the 3 refers to rotation in three dimensions), 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 12.1** Identifying a point group of a molecule

Identify the point group to which a ruthenocene molecule (16) belongs.

**Method** Use the flow diagram in Fig. 12.7.

**Answer** The path to trace through the flow diagram in Fig. 12.7 is shown by a green line; it ends at \( D_{5h} \). Because the molecule has a fivefold axis, it belongs to the group \( D_{5h} \). If the rings were staggered, as they are in an excited state of ferrocene that lies 4 kJ mol\(^{-1}\) above the ground state (17), the horizontal reflection plane would be absent, but dihedral planes would be present.

**Self-test 12.1** Classify the pentagonal antiprismatic excited state of ferrocene (17). \([D_{5d}]\)

---

**Comment 12.3**
The web site contains links to interactive tutorials, where you use your web browser to to assign point groups of molecules.
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. 12.13b), and $\text{H}_2\text{O}$ has a dipole moment parallel to its twofold symmetry axis. The same remarks apply generally to the group $C_{nv}$, so molecules belonging to any of the $C_{nv}$ groups may be polar. In all the other groups, such as $C_{3h}$, $D_1$, 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 a permanent electric dipole moment.

For $C_n$ and $C_{nv}$, that dipole moment must lie along the symmetry axis. Thus ozone, $\text{O}_3$, which is angular and belongs to the group $C_{2v}$, may be polar (and is), but carbon dioxide, $\text{CO}_2$, which is linear and belongs to the group $D_{\infty h}$, is not.

(b) Chirality

A chiral molecule (from the Greek word for ‘hand’) is a molecule that cannot be superimposed on its mirror image. An achiral molecule is a molecule that can 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 Appendix 3). A chiral molecule and its mirror-image partner constitute an enantiomeric pair of isomers and rotate the plane of polarization in equal but opposite directions.

A molecule may be chiral, and therefore optically active, only if it does not possess an axis of improper rotation, $S_n$. However, we need to be aware that 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 $C_{nv}$ possess an $S_n$ axis implicitly because they possess both $C_n$ and $\sigma_h$, which are the two components of an improper rotation axis. Any molecule containing a centre of inversion, $i$, also possesses an $S_2$ axis, because $i$ is equivalent to $C_2$ in conjunction with $\sigma_h$, and that combination of elements is $S_2$ (Fig. 12.14). It follows that all molecules with centres of inversion are achiral and hence optically inactive. Similarly, because $S_1 = \sigma$, it follows that any molecule with a mirror plane is achiral.

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 (18), but not with glycine (19). However, a molecule may be achiral even though it does not have a centre of inversion. For example, the $S_4$ species (20) is achiral and optically inactive: though it lacks $i$ (that is, $S_2$) it does have an $S_4$ axis.
Applications to molecular orbital theory and spectroscopy

We shall now turn our attention away from the symmetries of molecules themselves and direct it towards the symmetry characteristics of orbitals that belong to the various atoms in a molecule. This material will enable us to discuss the formulation and labelling of molecular orbitals and selection rules in spectroscopy.

12.4 Character tables and symmetry labels

We saw in Chapter 11 that molecular orbitals of diatomic and linear polyatomic molecules are labelled $\sigma, \pi$, etc. These labels refer to the symmetries of the orbitals with respect to rotations around the principal symmetry axis of the molecule. Thus, a $\sigma$ orbital does not change sign under a rotation through any angle, a $\pi$ orbital changes sign when rotated by 180°, and so on (Fig. 12.15). The symmetry classifications $\sigma$ and $\pi$ can also be assigned to individual atomic orbitals in a linear molecule. For example, we can speak of an individual $p_z$ orbital as having $\sigma$ symmetry if the $z$-axis lies along the bond, because $p_z$ is cylindrically symmetrical about the bond. This labelling of orbitals according to their behaviour under rotations can be generalized and extended to nonlinear polyatomic molecules, where there may be reflections and inversions to take into account as well as rotations.

(a) Representations and characters

Labels analogous to $\sigma$ and $\pi$ are used to denote the symmetries of orbitals in polyatomic molecules. These labels look like $a$, $a_1$, $e$, $e_g$, and we first encountered them in Fig. 11.4 in connection with the molecular orbitals of benzene. As we shall see, these labels indicate the behaviour of the orbitals under the symmetry operations of the relevant point group of the molecule.

A label is assigned to an orbital by referring to the character table of the group, a table that characterizes the different symmetry types possible in the point group. Thus, to assign the labels $\sigma$ and $\pi$, we use the table shown in the margin. This table is a fragment of the full character table for a linear molecule. The entry $+1$ shows that the orbital remains the same and the entry $-1$ shows that the orbital changes sign under the operation $C_2$ at the head of the column (as illustrated in Fig. 12.15). So, to assign the label $\sigma$ or $\pi$ to a particular orbital, we compare the orbital’s behaviour with the information in the character table.

The entries in a complete character table are derived by using the formal techniques of group theory and are called characters, $\chi$ (chi). These numbers characterize the essential features of each symmetry type in a way that we can illustrate by considering the $C_2v$ molecule $SO_2$ and the valence $p_x$ orbitals on each atom, which we shall denote $p_S, p_A, p_B$ (Fig. 12.16).

Under $\sigma_v$, the change $(p_S, p_B, p_A) \leftrightarrow (p_S, p_A, p_B)$ takes place. We can express this transformation by using matrix multiplication:

\[
(P_S, P_B, P_A) = (P_S, P_A, P_B) \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix} = (P_S, P_A, P_B)D(\sigma_v)
\]

(12.1)

The matrix $D(\sigma_v)$ is called a representative of the operation $\sigma_v$. Representatives take different forms according to the basis, the set of orbitals, that has been adopted.

---

**Comment 12.4**

See Appendix 2 for a summary of the rules of matrix algebra.
We can use the same technique to find matrices that reproduce the other symmetry operations. For instance, $C_2$ has the effect $(-p_S, -p_B, -p_A) \leftrightarrow (p_S, p_A, p_B)$, and its representative is

$$D(C_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 0 & -1 \\ 0 & -1 & 0 \end{pmatrix} \quad (12.2)$$

The effect of $\sigma_v'$ is $(-p_S, -p_A, -p_B) \leftrightarrow (p_S, p_A, p_B)$, and its representative is

$$D(\sigma_v') = \begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \quad (12.3)$$

The identity operation has no effect on the basis, so its representative is the $3 \times 3$ unit matrix:

$$D(E) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad (12.4)$$

The set of matrices that represents all the operations of the group is called a matrix representation, $\Gamma$ (uppercase gamma), of the group for the particular basis we have chosen. We denote this three-dimensional representation by $\Gamma^{(3)}$. The discovery of a matrix representation of the group means that we have found a link between symbolic manipulations of operations and algebraic manipulations of numbers.

The character of an operation in a particular matrix representation is the sum of the diagonal elements of the representative of that operation. Thus, in the basis we are illustrating, the characters of the representatives are

$$\begin{array}{cccc}
D(E) & D(C_2) & D(\sigma_v) & D(\sigma_v') \\
3 & -1 & 1 & -3 
\end{array}$$

The character of an operation depends on the basis.

Inspection of the representatives shows that they are all of block-diagonal form:

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

The block-diagonal form of the representatives show us that the symmetry operations of $C_{2v}$ never mix $p_S$ with the other two functions. Consequently, the basis can be cut into two parts, one consisting of $p_S$ alone and the other of $(p_A, p_B)$. It is readily verified that the $p_S$ orbital itself is a basis for the one-dimensional representation

$$D(E) = 1 \quad D(C_2) = -1 \quad D(\sigma_v) = 1 \quad D(\sigma_v') = -1$$

which we shall call $\Gamma^{(1)}$. The remaining two basis functions are a basis for the two-dimensional representation $\Gamma^{(2)}$:

$$D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad D(C_2) = \begin{pmatrix} 0 & -1 \\ -1 & 0 \end{pmatrix} \quad D(\sigma_v) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad D(\sigma_v') = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}$$

These matrices are the same as those of the original three-dimensional representation, except for the loss of the first row and column. We say that the original three-dimensional representation has been reduced to the 'direct sum' of a one-dimensional representation 'spanned' by $p_S$, and a two-dimensional representation spanned by $(p_A, p_B)$. This reduction is consistent with the common sense view that the central
orbital plays a role different from the other two. We denote the reduction symbolically by writing
\[ \Gamma^{(3)} = \Gamma^{(1)} + \Gamma^{(2)} \] (12.5)

The one-dimensional representation \( \Gamma^{(1)} \) cannot be reduced any further, and is called an irreducible representation of the group (an ‘irrep’). We can demonstrate that the two-dimensional representation \( \Gamma^{(2)} \) is reducible (for this basis in this group) by switching attention to the linear combinations \( p_1 = p_A + p_B \) and \( p_2 = p_A - p_B \). These combinations are sketched in Fig. 12.17. The representatives in the new basis can be constructed from the old by noting, for example, that under \( \sigma_v \), \((p_B, p_A) \leftarrow (p_A, p_B)\). In this way we find the following representation in the new basis:
\[
D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D(C_2) = \begin{pmatrix} -1 & 0 \\ 0 & 1 \end{pmatrix}, \quad D(\sigma_v) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}, \quad D(\sigma_v') = \begin{pmatrix} -1 & 0 \\ 0 & -1 \end{pmatrix}
\]
The new representatives are all in block-diagonal form, and the two combinations are not mixed with each other by any operation of the group. We have therefore achieved the reduction of \( \Gamma^{(2)} \) to the sum of two one-dimensional representations. Thus, \( p_1 \) spans
\[
D(E) = 1, \quad D(C_2) = -1, \quad D(\sigma_v) = 1, \quad D(\sigma_v') = -1
\]
which is the same one-dimensional representation as that spanned by \( p_2 \), and \( p_2 \) spans
\[
D(E) = 1, \quad D(C_2) = 1, \quad D(\sigma_v) = -1, \quad D(\sigma_v') = -1
\]
which is a different one-dimensional representation; we shall denote it \( \Gamma^{(1)'} \).

At this point we have found two irreducible representations of the group \( C_{2v} \) (Table 12.2). The two irreducible representations are normally labelled \( B_1 \) and \( A_2 \), respectively. An \( A \) or a \( B \) is used to denote a one-dimensional representation; \( A \) is used if the character under the principal rotation is +1, and \( B \) is used if the character is −1. Subscripts are used to distinguish the irreducible representations if there is more than one of the same type: \( A_1 \) is reserved for the representation with character 1 for all operations. When higher dimensional irreducible representations are permitted, \( E \) denotes a two-dimensional irreducible representation and \( T \) a three-dimensional irreducible representation; all the irreducible representations of \( C_{2v} \) are one-dimensional.

There are in fact only two more species of irreducible representations of this group, for a surprising theorem of group theory states that
\[
\text{Number of symmetry species} = \text{number of classes} \quad (12.6)
\]
Symmetry operations fall into the same class if they are of the same type (for example, rotations) and can be transformed into one another by a symmetry operation of the

<table>
<thead>
<tr>
<th>Table 12.2*</th>
<th>The ( C_{2v} ) character table</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{2v} ) 2mm</td>
<td>( E )</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
</tr>
</tbody>
</table>

* More character tables are given at the end of the Data section.
In $C_{2v}$, for instance, there are four classes (four columns in the character table), so there are only four species of irreducible representation. The character table in Table 12.2 therefore shows the characters of all the irreducible representations of this group.

(b) The structure of character tables

In general, the columns in a character table are labelled with the symmetry operations of the group. For instance, for the group $C_{3v}$, the columns are headed $E$, $C_3$, and $\sigma_v$ (Table 12.3). The numbers multiplying each operation are the numbers of members of each class. In the $C_{3v}$ character table we see that the two threefold rotations (clockwise and counter-clockwise rotations by 120°) belong to the same class: they are related by a reflection (Fig. 12.18). The three reflections (one through each of the three vertical mirror planes) also lie in the same class: they are related by the three-fold rotations. The two reflections of the group $C_{2v}$ fall into different classes: although they are both reflections, one cannot be transformed into the other by any symmetry operation of the group.

The total number of operations in a group is called the order, $h$, of the group. The order of the group $C_{3v}$, for instance, is 6.

The rows under the labels for the operations summarize the symmetry properties of the orbitals. They are labelled with the symmetry species (the analogues of the labels $\sigma$ and $\pi$). More formally, the symmetry species label the irreducible representations of the group, which are the basic types of behaviour that orbitals may show when subjected to the symmetry operations of the group, as we have illustrated for the group $C_{2v}$. By convention, irreducible representations are labelled with upper case Roman letters (such as $A_1$ and $E$) but the orbitals to which they apply are labelled with the lower case italic equivalents (so an orbital of symmetry species $A_1$ is called an $a_1$ orbital). Examples of each type of orbital are shown in Fig. 12.19.

(c) Character tables and orbital degeneracy

The character of the identity operation $E$ tells us the degeneracy of the orbitals. Thus, in a $C_{3v}$ molecule, any orbital with a symmetry label $a_1$ or $a_2$ is nondegenerate. Any doubly degenerate pair of orbitals in $C_{3v}$ must be labelled $e$ because, in this group, only $E$ symmetry species have characters greater than 1.

Because there are no characters greater than 2 in the column headed $E$ in $C_{3v}$, we know that there can be no triply degenerate orbitals in a $C_{3v}$ molecule. This last point is a powerful result of group theory, for it means that, with a glance at the character table of a molecule, we can state the maximum possible degeneracy of its orbitals.

Comment 12.5

Note that care must be taken to distinguish the identity element $E$ (italic, a column heading) from the symmetry label $E$ (roman, a row label).
Example 12.2 Using a character table to judge degeneracy

Can a trigonal planar molecule such as BF₃ have triply degenerate orbitals? What is the minimum number of atoms from which a molecule can be built that does display triple degeneracy?

Method First, identify the point group, and then refer to the corresponding character table in the Data section. The maximum number in the column headed by the identity $E$ is the maximum orbital degeneracy possible in a molecule of that point group. For the second part, consider the shapes that can be built from two, three, etc. atoms, and decide which number can be used to form a molecule that can have orbitals of symmetry species $T$.

Answer Trigonal planar molecules belong to the point group $D_{3h}$. Reference to the character table for this group shows that the maximum degeneracy is 2, as no character exceeds 2 in the column headed $E$. Therefore, the orbitals cannot be triply degenerate. A tetrahedral molecule (symmetry group $T$) has an irreducible representation with a $T$ symmetry species. The minimum number of atoms needed to build such a molecule is four (as in $P₄$, for instance).

Self-test 12.2 A buckminsterfullerene molecule, $C_{60}$ (15), belongs to the icosahedral point group. What is the maximum possible degree of degeneracy of its orbitals?

(d) Characters and operations

The characters in the rows labelled A and B and in the columns headed by symmetry operations other than the identity $E$ indicate the behaviour of an orbital under the corresponding operations: a $+1$ indicates that an orbital is unchanged, and a $-1$ indicates that it changes sign. It follows that we can identify the symmetry label of the orbital by comparing the changes that occur to an orbital under each operation, and then comparing the resulting $+1$ or $-1$ with the entries in a row of the character table for the point group concerned.

For the rows labelled $E$ or $T$ (which refer to the behaviour of sets of doubly and triply degenerate orbitals, respectively), the characters in a row of the table are the sums of the characters summarizing the behaviour of the individual orbitals in the basis. Thus, if one member of a doubly degenerate pair remains unchanged under a symmetry operation but the other changes sign (Fig. 12.20), then the entry is reported as $\chi = 1 - 1 = 0$. Care must be exercised with these characters because the transformations of orbitals can be quite complicated; nevertheless, the sums of the individual characters are integers.

As an example, consider the $2p_\sigma$ orbital in $H_2O$. Because $H_2O$ belongs to the point group $C_{3v}$, we know by referring to the $C_{3v}$ character table (Table 12.2) that the labels available for the orbitals are $a_1$, $a_2$, $b_1$, and $b_2$. We can decide the appropriate label for $2p_\sigma$ by noting that under a $180^\circ$ rotation ($C_2$) the orbital changes sign (Fig. 12.21), so it must be either $b_1$ or $b_2$, as only these two symmetry types have character $-1$ under $C_2$. The $2p_\sigma$ orbital also changes sign under the reflection $\sigma'_x$, which identifies it as $b_1$. As we shall see, any molecular orbital built from this atomic orbital will also be a $b_1$ orbital. Similarly, $2p_\gamma$ changes sign under $C_2$ but not under $\sigma'_x$; therefore, it can contribute to $b_2$ orbitals.

The behaviour of $s$, $p$, and $d$ orbitals on a central atom under the symmetry operations of the molecule is so important that the symmetry species of these orbitals...
are generally indicated in a character table. To make these allocations, we look at the symmetry species of \( x, y, \) and \( z \), which appear on the right-hand side of the character table. Thus, the position of \( z \) in Table 12.3 shows that \( p_z \) (which is proportional to \( z f(r) \)), has symmetry species \( A_1 \) in \( C_{3v} \), whereas \( p_x \) and \( p_y \) (which are proportional to \( x f(r) \) and \( y f(r) \), respectively) are jointly of \( E \) symmetry. In technical terms, we say that \( p_x \) and \( p_y \) jointly span an irreducible representation of symmetry species \( E \). An \( s \) orbital on the central atom always spans the fully symmetrical irreducible representation (typically labelled \( A_1 \) but sometimes \( A_1' \)) of a group as it is unchanged under all symmetry operations.

The five \( d \) orbitals of a shell are represented by \( xy \) for \( d_{xy} \), etc, and are also listed on the right of the character table. We can see at a glance that in \( C_{3v} \), \( d_{xy} \) and \( d_{x^2-y^2} \) on a central atom jointly belong to \( E \) and hence form a doubly degenerate pair.

(e) The classification of linear combinations of orbitals

So far, we have dealt with the symmetry classification of individual orbitals. The same technique may be applied to linear combinations of orbitals on atoms that are related by symmetry transformations of the molecule, such as the combination \( \psi_1 = \psi_A + \psi_B + \psi_C \) of the three \( H_1 \) orbitals in the \( C_{3v} \) molecule \( \text{NH}_3 \) (Fig. 12.22). This combination remains unchanged under a \( C_3 \) rotation and under any of the three vertical reflections of the group, so its characters are

\[
\chi(E) = 1 \quad \chi(C_3) = 1 \quad \chi(\sigma_v) = 1
\]

Comparison with the \( C_{3v} \) character table shows that \( \psi_1 \) is of symmetry species \( A_1 \), and therefore that it contributes to an \( a_1 \) molecular orbitals in \( \text{NH}_3 \).

Example 12.3 Identifying the symmetry species of orbitals

Identify the symmetry species of the orbital \( \psi = \psi_A - \psi_B \) in a \( C_{2v} \) \( \text{NO}_2 \) molecule, where \( \psi_A \) is an \( O2p_x \) orbital on one \( O \) atom and \( \psi_B \) that on the other \( O \) atom.

Method The negative sign in \( \psi \) indicates that the sign of \( \psi_B \) is opposite to that of \( \psi_A \). We need to consider how the combination changes under each operation of the group, and then write the character as \(+1, -1, \) or \( 0 \) as specified above. Then we compare the resulting characters with each row in the character table for the point group, and hence identify the symmetry species.

Answer The combination is shown in Fig. 12.23. Under \( C_2 \), \( \psi \) changes into itself, implying a character of \(+1\). Under the reflection \( \sigma_v \), both orbitals change sign, so \( \psi \to -\psi \), implying a character of \(-1\). Under \( \sigma_v' \), \( \psi \to -\psi \), so the character for this operation is also \(-1\). The characters are therefore

\[
\chi(E) = 1 \quad \chi(C_2) = 1 \quad \chi(\sigma_v) = -1 \quad \chi(\sigma_v') = -1
\]

These values match the characters of the \( A_2 \) symmetry species, so \( \psi \) can contribute to an \( a_2 \) orbital.

Self-test 12.3 Consider \( \text{PtCl}_4^- \), in which the \( \text{Cl} \) ligands form a square planar array of point group \( D_{4h} \) (21). Identify the symmetry type of the combination \( \psi_A - \psi_B + \psi_C - \psi_D \).
12.5 Vanishing Integrals and Orbital Overlap

Suppose we had to evaluate the integral

\[ I = \int f_1 f_2 \, d\tau \]  

(12.7)

where \( f_1 \) and \( f_2 \) are functions. For example, \( f_1 \) might be an atomic orbital \( A \) on one atom and \( f_2 \) an atomic orbital \( B \) on another atom, in which case \( I \) would be their overlap integral. If we knew that the integral is zero, we could say at once that a molecular orbital does not result from \((A,B)\) overlap in that molecule. We shall now see that character tables provide a quick way of judging whether an integral is necessarily zero.

(a) The Criteria for Vanishing Integrals

The key point in dealing with the integral \( I \) is that the value of any integral, and of an overlap integral in particular, is independent of the orientation of the molecule (Fig. 12.24). In group theory we express this point by saying that \( I \) is invariant under any symmetry operation of the molecule, and that each operation brings about the trivial transformation \( I \to I \). Because the volume element \( d\tau \) is invariant under any symmetry operation, it follows that the integral is nonzero only if the integrand itself, the product \( f_1 f_2 \), is unchanged by any symmetry operation of the molecular point group. If the integrand 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 nonzero integral comes from functions for which under any symmetry operation of the molecular point group \( f_1 f_2 \to f_1 f_2 \), and hence for which the characters of the operations are all equal to +1. Therefore, for \( I \) not to be zero, the integrand \( f_1 f_2 \) must have symmetry species \( A_1 \) (or its equivalent in the specific molecular point group).

We use the following procedure 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 individual functions \( f_1 \) and \( f_2 \) by reference to the character table, and write their characters in two rows in the same order as in the table.

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

3. Inspect the row so produced, and see if it can be expressed as a sum of characters from each column of the group. The integral must be zero if this sum does not contain \( A_1 \).

For example, if \( f_1 \) is the \( s_N \) orbital in \( \text{NH}_3 \) and \( f_2 \) is the linear combination \( s_3 = s_B - s_C \) (Fig. 12.25), then, because \( s_N \) spans \( A_1 \) and \( s_3 \) is a member of the basis spanning \( E \), we write

\[
\begin{align*}
f_1 &: 1 \quad 1 \quad 1 \\
f_2 &: 2 \quad -1 \quad 0 \\
f_1 f_2 &: 2 \quad -1 \quad 0
\end{align*}
\]

The characters 2, -1, 0 are those of \( E \) alone, so the integrand does not span \( A_1 \). It follows that the integral must be zero. Inspection of the form of the functions (see Fig. 12.25) 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, where \( s_1 = x_A + s_B + s_C \), then because each spans \( A_1 \) with characters 1, 1, 1:

\[
\begin{align*}
f_1 &: 1 \quad 1 \quad 1 \\
f_2 &: 1 \quad 1 \quad 1 \\
f_1 f_2 &: 1 \quad 1 \quad 1
\end{align*}
\]
The characters of the product are those of $A_1$ itself. Therefore, $s_1$ and $s_N$ may have nonzero overlap. A shortcut that works when $f_1$ and $f_2$ are bases for irreducible representations of a group is to note their symmetry species: if they are different, then the integral of their product must vanish; if they are the same, then the integral may be nonzero.

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

**Example 12.4 Deciding if an integral must be zero (1)**

May the integral of the function $f = xy$ be nonzero when evaluated over a region the shape of an equilateral triangle centred on the origin (Fig. 12.26)?

**Method** First, note that an integral over a single function $f$ is included in the previous discussion if we take $f_1 = f$ and $f_2 = 1$ in eqn 12.7. Therefore, we need to judge whether $f$ alone belongs to the symmetry species $A_1$ (or its equivalent) in the point group of the system. To decide that, we identify the point group and then examine the character table to see whether $f$ belongs to $A_1$ (or its equivalent).

**Answer** An equilateral triangle has the point-group symmetry $D_{3h}$. 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, because the integrand has no component that spans $A_1$.

**Self-test 12.4** Can the function $x^2 + y^2$ have a nonzero integral when integrated over a regular pentagon centred on the origin? [Yes, Fig. 12.27]

In many cases, the product of functions $f_1$ and $f_2$ spans a sum of irreducible representations. For instance, in $C_{2v}$ we may find the characters $2, 0, 0, -2$ when we multiply the characters of $f_1$ and $f_2$ together. In this case, we note that these characters are the sum of the characters for $A_2$ and $B_1$:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_{2v}$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$A_2 + B_1$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-2</td>
</tr>
</tbody>
</table>

To summarize this result we write the symbolic expression $A_2 \times B_1 = A_2 + B_1$, which is called the **decomposition of a direct product**. This expression is symbolic. The $\times$ and + signs in this expression are not ordinary multiplication and addition signs: formally, they denote technical procedures with matrices called a ‘direct product’ and a ‘direct sum’. Because the sum on the right does not include a component that is a basis for an irreducible representation of symmetry species $A_1$, we can conclude that the integral of $f_1 f_2$ over all space is zero in a $C_{2v}$ molecule.

Whereas the decomposition of the characters 2, 0, 0, −2 can be done by inspection in this simple case, in other cases and more complex groups the decomposition is often far from obvious. For example, if we found the characters 8, −2, −6, 4, it would not be obvious that the sum contains $A_1$. Group theory, however, provides a systematic way of using the characters of the representation spanned by a product to find the symmetry species of the irreducible representations. The recipe is as follows:
12.5 VANISHING INTEGRALS AND ORBITAL OVERLAP

1 Write down a table with columns headed by the symmetry operations of the group.
2 In the first row write down the characters of the symmetry species we want to analyse.
3 In the second row, write down the characters of the irreducible representation \( \Gamma \) we are interested in.
4 Multiply the two rows together, add the products together, and divide by the order of the group.

The resulting number is the number of times \( \Gamma \) occurs in the decomposition.

**Illustration 12.1** To find whether \( A_1 \) occurs in a direct product

To find whether \( A_1 \) does indeed occur in the product with characters 8, \(-2\), \(-6\), 4 in \( C_{2v} \), we draw up the following table:

<table>
<thead>
<tr>
<th>( E )</th>
<th>( C_{2v} )</th>
<th>( \sigma_y )</th>
<th>( \sigma_y' )</th>
<th>( h = 4 ) (the order of the group)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( f_1, f_2 )</td>
<td>8</td>
<td>(-2)</td>
<td>(-6)</td>
<td>4 (the characters of the product)</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1 (the symmetry species we are interested in)</td>
</tr>
<tr>
<td>8</td>
<td>(-2)</td>
<td>(-6)</td>
<td>4 (the product of the two sets of characters)</td>
<td></td>
</tr>
</tbody>
</table>

The sum of the numbers in the last line is 4; when that number is divided by the order of the group, we get 1, so \( A_1 \) occurs once in the decomposition. When the procedure is repeated for all four symmetry species, we find that \( f_1 f_2 \) spans \( A_1 \) + 2\( A_2 \) + 3\( B_2 \).

**Self-test 12.5** Does \( A_2 \) occur among the symmetry species of the irreducible representations spanned by a product with characters 7, \(-3\), \(-1\), 5 in the group \( C_{2v} \)?

[No]

(b) Orbitals with nonzero overlap

The rules just given let us decide which atomic orbitals may have nonzero overlap in a molecule. We have seen that \( s_N \) may have nonzero overlap with \( s_1 \) (the combination \( s_N + s_R + s_C \) ), so bonding and antibonding molecular orbitals can form from \( (s_N, s_1) \) overlap (Fig. 12.28). The general rule is that **only orbitals of the same symmetry species may have nonzero overlap**, so only orbitals of the same symmetry species form bonding and antibonding combinations. It should be recalled from Chapter 11 that the selection of atomic orbitals that had mutual nonzero 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 nonzero overlap are labelled with the lowercase letter corresponding to the symmetry species. Thus, the \((s_N, s_1)\)-overlap orbitals are called \( a_1 \) orbitals (or \( a_1^* \), if we wish to emphasize that they are antibonding).

The linear combinations \( s_2 = 2s_N - s_R - s_C \) and \( s_3 = s_R - s_C \) have symmetry species E. Does the N atom have orbitals that have nonzero overlap with them (and give rise to e molecular orbitals)? Intuition (as supported by Figs. 12.28b and c) suggests that \( N_2p_x \) and \( N_2p_y \) should be suitable. We can confirm this conclusion by noting that the character table shows that, in \( C_{3v} \), the functions \( x \) and \( y \) jointly belong to the symmetry species E. Therefore, \( N_2p_x \) and \( N_2p_y \) also belong to E, so may have nonzero overlap with \( s_2 \) and \( s_3 \). This conclusion can be verified by multiplying the characters...
and finding that the product of characters can be expressed as the decomposition $E \times E = A_1 + A_2 + E$. The two $e$ orbitals that result are shown in Fig. 12.28 (there are also two antibonding $e$ orbitals).

We can see the power of the method by exploring whether any $d$ orbitals on the central atom can take part in bonding. As explained earlier, reference to the $C_{3v}$ character 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 $(s, d_{z^2})$ overlap and by overlap of the $s, d_{z^2}$ combinations with the $E$ $d$ orbitals. Whether or not the $d$ orbitals are in fact important is a question group theory cannot answer because the extent of their involvement depends on energy considerations, not symmetry.

**Example 12.5 Determining which orbitals can contribute to bonding**

The four H1$s$ orbitals of methane span $A_1 + T_2$. With which of the C atom orbitals can they overlap? What bonding pattern would be possible if the C atom had $d$ orbitals available?

**Method** Refer to the $T_d$ character table (in the Data section) and look for $s$, $p$, and $d$ orbitals spanning $A_1$ or $T_2$.

**Answer** An $s$ orbital spans $A_1$, so it may have nonzero overlap with the $A_1$ combination of H1$s$ orbitals. The $C_2p$ orbitals span $T_2$, so they may have nonzero overlap with the $T_2$ combination. The $d_{x^2}$, $d_{y^2}$, and $d_{xy}$ orbitals span $T_2$, so they may overlap the same combination. Neither of the other two $d$ orbitals span $A_1$ (they span $E$), so they remain nonbonding orbitals. It follows that in methane there are ($C_2s$, H1$s$)-overlap $a_1$ orbitals and ($C_2p$, H1$s$)-overlap $t_2$ orbitals. The $C_3d$ orbitals might contribute to the latter. The lowest energy configuration is probably $a_1^2t_2^6$, with all bonding orbitals occupied.

**Self-test 12.6** Consider the octahedral SF$_6$ molecule, with the bonding arising from overlap of S orbitals and a 2$p$ orbital on each F directed towards the central S atom. The latter span $A_{1g} + E_g + T_{1u}$. What $s$ orbitals have nonzero overlap? Suggest what the ground-state configuration is likely to be.

$[3s(A_{1g}), 3p(T_{1u}), 3d(E_g); a_1^2 t_2^6, e^4]$.

**(c) Symmetry-adapted linear combinations**

So far, we have only asserted the forms of the linear combinations (such as $s_1$, etc.) that have a particular symmetry. Group theory also provides machinery that takes an arbitrary basis, or set of atomic orbitals ($s_A$, 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 those used to construct molecular orbitals in benzene. The construction of SALCs is the first step in any molecular orbital treatment of molecules.

The technique for building SALCs is derived by using the full power of group theory. We shall not show the derivation (see Further reading), which is very lengthy, but present the main conclusions as a set of rules:

1. Construct a table showing the effect of each operation on each orbital of the original basis.
2 To generate the combination of a specified symmetry species, take each column in turn and:

(i) Multiply each member of the column by the character of the corresponding operation.

(ii) Add together all the orbitals in each column with the factors as determined in (i).

(iii) Divide the sum by the order of the group.

For example, from the \((s_N, s_A, s_B, s_C)\) basis in \(\text{NH}_3\) we form the table shown in the margin. To generate the \(A_1\) combination, we take the characters for \(A_1\) (1,1,1,1,1,1); then rules (i) and (ii) lead to

\[
\psi \propto s_N + s_N + \cdots = 6s_N
\]

The order of the group (the number of elements) is 6, 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

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

The same combination is built from the other two columns, 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 SALCs 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 are found by solving the Schrödinger equation; they do not come directly from the symmetry of the system.

We run into a problem when we try to generate an SALC of symmetry species \(E\), because, for representations of dimension 2 or more, the rules generate sums of SALCs. This problem can be illustrated as follows. In \(C_{3v}\), the \(E\) characters are \(2, -1, -1, 0, 0, 0\), so the column under \(s_N\) gives

\[
\psi = \frac{1}{6}(6s_N - s_N - s_N + 0 + 0 + 0) = 0
\]

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 of these three expressions can be expressed as a sum of the other two (they are not ‘linearly independent’). The difference of the second and third gives \(\frac{1}{2}(s_B - s_C)\), and this combination and the first, \(\frac{1}{6}(2s_A - s_B - s_C)\) are the two (now linearly independent) SALCs we have used in the discussion of \(e\) orbitals.

12.6 Vanishing integrals and selection rules

Integrals of the form

\[
I = \int f_1 f_2 f_3 d\tau
\]

are also common in quantum mechanics for they include matrix elements of operators (Section 8.5d), and it is important to know when they are necessarily zero. For the integral to be nonzero, the product \(f_1 f_2 f_3\) must span \(A_1\) (or its equivalent) or 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 12.6** Deciding if an integral must be zero (2)

Does the integral \( \int (3d_{z^2})x(3d_{x^2}) \, d\tau \) vanish in a \( C_{2v} \) molecule?

**Method** We must refer to the \( C_{2v} \) character table (Table 12.2) and 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).

**Answer** We draw up the following table:

<table>
<thead>
<tr>
<th>( f_3 = d_{xy} )</th>
<th>( f_2 = x )</th>
<th>( f_1 = d_{x^2} )</th>
<th>( f_1f_2f_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E )</td>
<td>( C_2 )</td>
<td>( \sigma_v )</td>
<td>( \sigma'_v )</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
</tbody>
</table>

The characters are those of \( B_2 \). Therefore, the integral is necessarily zero.

**Self-test 12.7** Does the integral \( \int (2p_x)(2p_y)(2p_z) \, d\tau \) necessarily vanish in an octahedral environment? [No]

We saw in Chapters 9 and 10, and will see in more detail in Chapters 13 and 14, 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, \( \mu_{fi} \). The \( z \)-component of this vector is defined through

\[
\mu_{z,fi} = -e \int \psi_i^* z \psi_i \, d\tau \quad [12.9]
\]

where \( -e \) is the charge of the electron. The transition moment has the form of the integral in eqn 12.8, so, once we know the symmetry species of the states, we can use group theory to formulate the selection rules for the transitions.

As an example, we investigate whether an electron in an \( a_1 \) orbital in \( H_2O \) (which belongs to the group \( C_{2v} \)) can make an electric dipole transition to a \( b_1 \) orbital (Fig. 12.29). We must examine all three components of the transition dipole moment, and take \( f_2 \) in eqn 12.8 as \( x \), \( y \), and \( z \) in turn. Reference to the \( C_{2v} \) character table shows that these components transform as \( B_1 \), \( B_2 \), and \( A_1 \), respectively. The three calculations run as follows:

<table>
<thead>
<tr>
<th>( x )-component</th>
<th>( y )-component</th>
<th>( z )-component</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E )</td>
<td>( C_2 )</td>
<td>( \sigma_v )</td>
</tr>
<tr>
<td>( f_3 )</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( f_2 )</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( f_1 )</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( f_1f_2f_3 )</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Only the first product (with \( f_2 = x \)) spans \( A_1 \), so only the \( x \)-component of the transition dipole moment may be nonzero. Therefore, we conclude that the electric dipole
transitions between $a_1$ and $b_1$ are 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 12.7 Deducing a selection rule**

Is $p_x \rightarrow p_y$ an allowed transition in a tetrahedral environment?

**Method** We must decide whether the product $p_y q p_x$, with $q = x, y, z$, spans $A_1$ by using the $T_d$ character table.

**Answer** The procedure works out as follows:

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6\sigma_d$</th>
<th>$6\delta_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$f_3(p_x)$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$f_3(q)$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$f_1(p_x)$</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$f_1 f_2 f_3$</td>
<td>27</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

We can use the decomposition procedure described in Section 12.5a to deduce that $A_1$ occurs (once) in this set of characters, so $p_x \rightarrow p_y$ is allowed.

A more detailed analysis (using the matrix representatives rather than the characters) shows that only $q = z$ gives an integral that may be nonzero, so the transition is $z$-polarized. That is, the electromagnetic radiation involved in the transition has its electric vector aligned in the $z$-direction.

**Self-test 12.8** What are the allowed transitions, and their polarizations, of a $b_1$ electron in a $C_{4v}$ molecule? $[b_1 \rightarrow b_1(z); b_1 \rightarrow e(x,y)]$

The following chapters will show many more examples of the systematic use of symmetry. We shall see that the techniques of group theory greatly simplify the analysis of molecular structure and spectra.

**Checklist of key ideas**

- A symmetry operation is an action that leaves an object looking the same after it has been carried out.
- A symmetry element is a point, line, or plane with respect to which a symmetry operation is performed.
- A point group is a group of symmetry operations that leaves at least one common point unchanged. A space group, a group of symmetry operations that includes translation through space.
- The notation for point groups commonly used for molecules and solids is summarized in Table 12.1.
- To be polar, a molecule must belong to $C_{nv}$, $C_{nv}$, or $C_3$ (and have no higher symmetry).
- A molecule may be chiral only if it does not possess an axis of improper rotation, $S_n$.
- A representative $D(X)$ is a matrix that brings about the transformation of the basis under the operation $X$. The basis is the set of functions on which the representative acts.
- A character, $\chi$, is the sum of the diagonal elements of a matrix representative.
- A character table characterizes the different symmetry types possible in the point group.
- In a reduced representation all the matrices have block-diagonal form. An irreducible representation cannot be reduced further.
- Symmetry species are the labels for the irreducible representations of a group.
- Decomposition of the direct product is the reduction of a product of symmetry species to a sum of symmetry species, $\Gamma \times \Gamma' = \Gamma^{(1)} + \Gamma^{(2)} + \ldots$