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The Great Orthogonality Theorem and Character Table

5.3 The definition of a group

Symmetry operations can be performed consecutively. We shall use the convention that the operation R followed by the operation S is denoted SR. The order of operations is important because *in general* the outcome of the operation SR is not the same as the outcome of the operation RS. When the outcomes of RS and SR are equivalent, the operations are said to **commute**. A general feature of symmetry operations is that the outcome of a joint symmetry operation is *always* equivalent to a single symmetry operation. We have already seen this property when we saw that a two-fold rotation followed by a reflection in a plane perpendicular to the two-fold axis is equivalent to an inversion:

$$\sigma_h C_2 = i$$

In general, it is true that for all symmetry operations R and S of an object, we can write

$$RS = T \tag{5.1}$$

where T is an operation of the group.

A further point about symmetry operations is that there is no difference between the outcomes of the operations $(RS)T$ and $R(ST)$, where (RS) is the outcome of the joint operation S followed by R and (ST) is the outcome of the joint operation T followed by S. In other words, $(RS)T = R(ST)$ and the multiplication of symmetry operations is **associative**.

These observations, together with two others which are true by inspection, can be summarized as follows:

1. The identity is a symmetry operation.
2. Symmetry operations combine in accord with the associative law of multiplication.

3. If R and S are symmetry operations, then RS is also a symmetry operation.
4. The inverse of each symmetry operation is also a symmetry operation.

The third observation implies that R^2 (which is shorthand for RR) is a symmetry operation. In observation 4, the inverse of an operation R, generally denoted R^{-1}, is defined such that

$$RR^{-1} = R^{-1}R = E \tag{5.2}$$

The remarkable point to note is that in mathematics a set of entities called **elements** form a **group** if they satisfy the following conditions:

1. The identity is an element of the set.
2. The elements multiply associatively.
3. If R and S are elements, then RS is also an element of the set.
4. The inverse of each element is a member of the set.

That is, the set of symmetry operations of an object fulfil conditions that ensure they form a group in the mathematical sense. Consequently, the mathematical theory of groups, which is called **group theory**, may be applied to the study of the symmetry of molecules. This is the justification for the title of this chapter.[2]

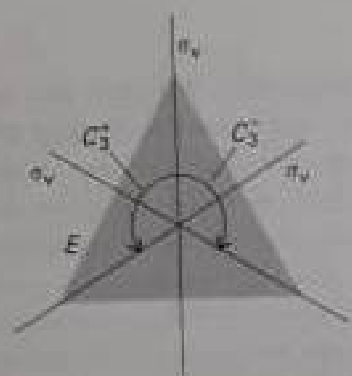

Fig. 5.18 The symmetry elements of the group C_{3v}.

Illustration 5.1 Associative property of multiplication of symmetry operations

Consider a square object and the symmetry operations C_2 (coincident with the principal C_4 axis), i, and σ_h. Then $C_2(i\sigma_h) = C_2C_2 = E$ and $(C_2i)\sigma_h = \sigma_h\sigma_h = E$ and the associative property holds.

the group C_{3v}.

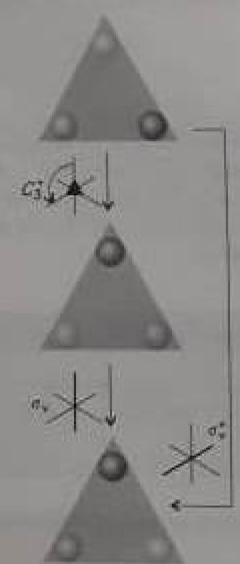

Fig. 5.19 The effect of the operation C_3^+ followed by σ_v is equivalent to the single operation σ_v''.

5.4 Group multiplication tables

A table showing the outcome of forming the products RS for all symmetry operations in a group is called a **group multiplication table**. The procedure used to construct such tables can be illustrated by the group C_{3v}. The symmetry operations for this group are illustrated in Fig. 5.18. We see that there are six members of the group, so it is said to have **order** 6, which we write as $h = 6$.

To determine the outcome of a sequence of symmetry operations, we consider diagrams like those in Fig. 5.19. You should note that the sequence of changes takes place with respect to fixed positions of the symmetry elements, in the sense that if a C_3^+ operation is performed, the line representing the σ_v plane in Fig. 5.18 remains in the same position on the page and is not rotated through 120° by the C_3^+ operation. Thus it follows that

$$C_3^-C_3^+ = E \quad \sigma_vC_3^+ = \sigma_v''\sigma_v'\sigma_v = C_3^+$$

The complete set of 36 (in general, h^2) products is shown in Table 5.2. As can be seen, each product is equivalent to a *single* element of the group. Note that RS is not always the same as SR; that is, not all symmetry operations commute. Similar tables can be constructed for all the point groups.

2. The unfortunate double meaning of the term 'element' should be noted. It is important to distinguish 'element', in the sense of a member of a group, from 'symmetry element', as defined earlier. The symmetry operations are the elements that comprise the group.

Table 5.2 The C_{3v} group multiplication table

First:	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
Second:						
E	E	C_3^+	C_3^-	σ_v	σ_v'	σ_v''
C_3^+	C_3^+	C_3^-	E	σ_v'	σ_v''	σ_v
C_3^-	C_3^-	E	C_3^+	σ_v''	σ_v	σ_v'
σ_v	σ_v	σ_v''	σ_v'	E	C_3^-	C_3^+
σ_v'	σ_v'	σ_v	σ_v''	C_3^+	E	C_3^-
σ_v''	σ_v''	σ_v'	σ_v	C_3^-	C_3^+	E

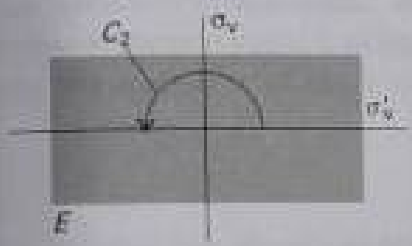

Fig. 5.20 The symmetry elements of the group C_{2v}.

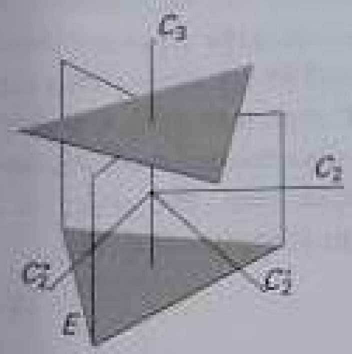

Fig. 5.21 The symmetry elements of the group D_3.

Example 5.2 How to construct a group multiplication table

Construct the group multiplication table for the group C_{2v}, the elements of which are shown in Fig. 5.20.

Method. Consider a single point on the object of the given point group, and the effect on the point of each pair of symmetry operations (RS). Identify the single operation that reproduces the effect of the joint application ($RS = T$), and enter it into the table. Note that $ER = RE = R$ for all R, where E is the identity operation. The orientation on the page of the symmetry elements is unchanged by all the operations.

Answer. The group multiplication table is as follows:

	E	C_2	σ_v	σ'_v
E	E	C_2	σ_v	σ'_v
C_2	C_2	E	σ'_v	σ_v
σ_v	σ_v	σ'_v	E	C_2
σ'_v	σ'_v	σ_v	C_2	E

Comment. Note that in this group $RS = SR$ for all entries in the table. Groups of this kind, in which the elements commute, are called 'Abelian'. The group C_{3v} is an example of a 'non-Abelian group'.

Self-test 5.2. Construct the group multiplication table for the group D_3, with elements shown in Fig. 5.21.

5.5 Matrix representations

Relations such as $RS=T$ are symbolic summaries of the effect of actions carried out on objects. We can enrich this symbolic representation of symmetry operations by representing the operations by entities that can be manipulated just like ordinary algebra. However, because symmetry

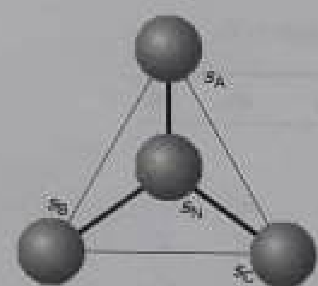

Fig. 5.22 One basis for a discussion of the representation of the group C_{3v}, each sphere can be regarded as an s-orbital centred on an atom.

operations are in general non-commutative (that is, their outcome depends on the order in which they are applied), we should expect to need to use matrices rather than simple numbers, for matrix multiplication is also non-commutative in general. The **matrix representative** of a symmetry operation is a matrix that reproduces the effect of the symmetry operation (in a manner we describe below). A **matrix representation** is a set of representatives, one for each element of the group, which multiply together as summarized by the group multiplication table.

To establish a matrix representative for a particular operation of a group, we need to choose a **basis**, a set of functions on which the operation takes place. To illustrate the procedure, we shall consider the set of s-orbitals s_A, s_B, s_C, and s_N on an NH_3 molecule (Fig. 5.22), which belongs to the group C_{3v}. We have chosen this basis partly because it is simple enough to illustrate a number of points in a straightforward fashion but also because it will be used in the discussion of the electronic structure of an ammonia molecule when we construct molecular orbitals in Chapter 8. The **dimension** of this basis, the number of members, is 4. We can write the basis as a four-component vector (s_N, s_A, s_B, s_C). In general, a basis of dimension d can be written as the row vector f, where

$$f=(f_1,f_2,\ldots,f_d)$$

Under the operation σ_v, the vector changes from (s_N, s_A, s_B, s_C) to $\sigma_v(s_N, s_A, s_B, s_C)=(s_N, s_A, s_C, s_B)$. This transformation can be represented by a matrix multiplication:

$$\sigma_v(s_N,s_A,s_B,s_C)=(s_N,s_A,s_B,s_C)\begin{bmatrix}1&0&0&0\\0&1&0&0\\0&0&0&1\\0&0&1&0\end{bmatrix} \tag{5.3}$$

This portrayal of the effect of the symmetry operation can be verified by carrying out the matrix multiplication. (For information on matrices, see *Further information* 23.) The matrix in this expression is the representative of the operation σ_v for the chosen basis, and is denoted $D(\sigma_v)$. Note that a four-dimensional basis gives rise to a 4×4-dimensional representative, and that in general a d-dimensional basis gives rise to a $d \times d$-dimensional representative. In terms of the explicit rules for matrix multiplication, the effect of an operation R on the general basis f is to convert the component f_i into

$$Rf_i = \sum_j f_j D_{ji}(R) \tag{5.4}$$

where $D_{ji}(R)$ is a matrix element of the representative $D(R)$ of the operation R. For example,

$$\sigma_v s_B = s_N \times 0 + s_A \times 0 + s_B \times 0 + s_C \times 1 = s_C$$

as required.

The representatives of the other operations of the group can be found in the same way. Note that because $Ef = f$, the representative of the identity operation is always the unit matrix.

Example 5.3 How to formulate a matrix representative

Find the matrix representative for the operation C_3^+ in the group C_3, for the *s*-orbital basis used above.

Method. Examine Fig. 5.22 to decide how each member of the basis is transformed under the operation, and write this transformation in the form $Rf = f'$. Then construct a $d \times d$ matrix $D(R)$ which generates f' when $fD(R)$ is formed and multiplied out.

Answer. Inspection of Fig. 5.22 shows that under the operation,

$$C_3^+(s_N, s_A, s_B, s_C) = (s_N, s_B, s_C, s_A)$$

This transformation can be expressed as the matrix product

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

Therefore, the 4×4 matrix above is the representative of the operation C_3^+ in the basis.

Self-test 5.3. Find the matrix representative of the operation C_3^- in the same basis.

[Table 5.3]

The complete set of representatives for this basis are displayed in Table 5.3.

We now arrive at a centrally important point. Consider the effect of the consecutive operations C_3^+ followed by σ_v. From the group multiplication table we know that the effect of the joint operation $\sigma_v C_3^+$ is the same as the effect of the reflection σ_v''. That is,

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

Table 5.3 The matrix representation of C_{3v} in the basis $\{s_N, s_A, s_B, s_C\}$

$D(E)$	$D(C_3^+)$	$D(C_3^-)$
$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \end{bmatrix}$
$\chi(E) = 4$	$\chi(C_3^+) = 1$	$\chi(C_3^-) = 1$
$D(\sigma_v)$	$D(\sigma_v')$	$D(\sigma_v'')$
$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}$
$\chi(\sigma_v) = 2$	$\chi(\sigma_v') = 2$	$\chi(\sigma_v'') = 2$

Now consider this joint operation in terms of the matrix representatives.

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

$$= D(\sigma_v'')$$

That is, the matrix representatives multiply together in exactly the same way as the operations of the group. This is true whichever operations are considered, and so the set of six 4×4 matrices in Table 5.3 form a matrix representation of the group for the selected basis in the sense that

$$\text{if } RS = T, \text{then } D(R)D(S) = D(T) \tag{5.5}$$

for all members of the group.

It follows from the fact that the representatives multiply like the group elements, that the representatives of an operation R and its inverse R^{-1} are related by

$$D(R^{-1}) = D(R)^{-1} \tag{5.6}$$

where D^{-1} denotes the inverse of the matrix D. For instance, because $RR^{-1} = E$, it follows that

$$D(R)D(R^{-1}) = D(R)D(R)^{-1} = \mathbf{1} = D(E)$$

where $\mathbf{1}$ is the unit matrix.

Proof 5.1 The representation of group multiplication

The formal proof that the representatives multiply in the same way as the symmetry operations gives a taste of the kind of manipulation that will be needed later. Once again we consider two elements R and S which multiply together to give the element T. It follows from eqn 5.4 that for the general basis f,

$$RSf_i = R\sum_j f_j D_{ji}(S) = \sum_{j,k} f_k D_{kj}(R) D_{ji}(S)$$

The sum over j of $D_{kj}(R)\, D_{ji}(S)$ is the definition of a matrix product, and so

$$RSf_i = \sum_k f_k \{\mathbf{D}(R)\mathbf{D}(S)\}_{ki}$$

where $\{\mathbf{D}(R)\mathbf{D}(S)\}_{ki}$ refers to the element in row k and column i of the matrix given by the product $\mathbf{D}(R)\mathbf{D}(S)$. However, we also know that $RS = T$, so we can also write

$$RSf_i = Tf_i = \sum_k f_k \{\mathbf{D}(T)\}_{ki}$$

By comparing the two equations we see that

$$\{\mathbf{D}(R)\mathbf{D}(S)\}_{ki} = \{\mathbf{D}(T)\}_{ki}$$

for all elements k and i. Therefore,

$$\mathbf{D}(R)\mathbf{D}(S) = \mathbf{D}(T)$$

That is, the representatives do indeed multiply like the group elements, as we set out to prove.

5.6 The properties of matrix representations

To develop the content of matrix representations, we need to introduce some of their properties. In each case we shall introduce the concept using the s-orbital basis for C_{3v} to fix our ideas, and then generalize the concept to any basis for any group.

To begin, we introduce the concept of 'similarity transformation'. Suppose that instead of the s-orbital basis, we select a linear combination of these orbitals to serve as the basis. One such set might be (s_N, s_1, s_2, s_3), where $s_1 = s_A + s_B + s_C$, $s_2 = 2s_A - s_B - s_C$ and $s_3 = s_B - s_C$ (apart from the requirement that the combinations are linearly independent, the choice is arbitrary, but later we shall see that this set has a special significance). The combinations are illustrated in Fig. 5.23. We should expect the matrix representation in this basis to be similar to that in the original basis. This similarity is given a formal definition by saying that two representations are **similar** if the representatives for the two bases are related by the **similarity transformation**

$$D(R) = cD'(R)c^{-1} \tag{5.7a}$$

where c is the matrix formed by the coefficients relating the two bases (see the proof below for an explicit definition). The inverse relation is obtained by multiplication from the left by c^{-1} and from the right by c:

$$D'(R) = c^{-1}D(R)c \tag{5.7b}$$

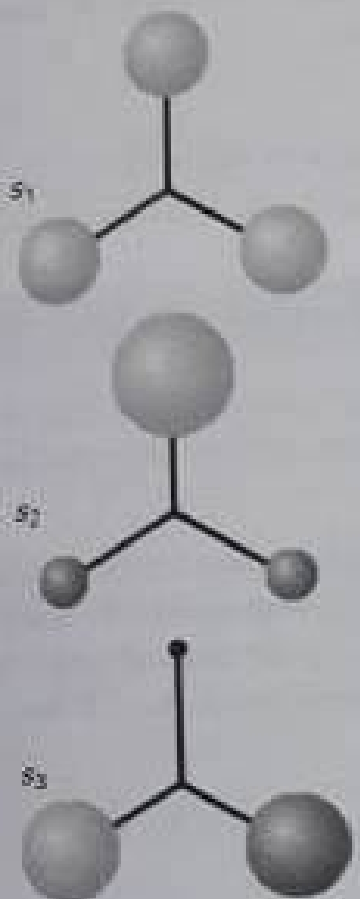

Fig. 5.23 The symmetry-adapted linear combinations of the peripheral atom orbitals in a C_{3v} molecule.

Proof 5.2 The similarity of representations

Because the new basis $f' = (f'_1, f'_2, \ldots, f'_d)$ is a linear combination of the original basis $f = (f_1, f_2, \ldots, f_d)$, we can express any member as

Proof 5.2 The similarity of representations

Because the new basis $f' = (f'_1, f'_2, \ldots, f'_d)$ is a linear combination of the original basis $f = (f_1, f_2, \ldots, f_d)$, we can express any member as

$$f'_i = \sum_j f_j c_{ji}$$

where the c_{ji} are constant coefficients.[3] This expansion can be expressed as a matrix product by writing

$$f' = fc$$

where c is the matrix formed of the coefficients c_{ji}. Now suppose that in the original basis the representative of the element R is $D(R)$ in the sense that

$$Rf_i = \sum_k f_k D_{ki}(R), \quad \text{or } Rf = fD(R)$$

Likewise, the effect of the same operation on a member of the transformed basis set is

$$Rf'_i = \sum_k f'_k D'_{ki}(R), \quad \text{or} \quad Rf' = f'D'(R)$$

3. For the particular basis $f' = (s_N, s_1 - s_2, s_3)$, the coefficients are specified in Example 5.4.

In general, if two matrices A and B are related by an expression of the form $A = CBC^{-1}$, then the matrices are said to be similar and the expression is a similarity transformation. Such transformations are useful in diagonalizing matrices as encountered in Example 1.10.

The relation between the two 'similar' representatives can be found by substituting $f' = fc$ into the last equation, which then becomes

$$Rfc = fcD'(R)$$

If we then multiply through from the right by c^{-1}, the reciprocal of the matrix c (in the sense that $cc^{-1} = c^{-1}c = 1$), then we obtain

$$Rf = fcD'(R)c^{-1}$$

Comparison of this expression with $Rf = fD(R)$ leads to eqn 5.7a.

Example 5.4 How to construct a similarity transformation

The representative of the operation C_3^+ in C_{3v} for the s-orbital basis is given in Table 5.3. Derive an expression for the representative in the transformed basis given at the start of this subsection.

Method. To implement the recipe in eqn 5.7, we need to construct the matrices c and c^{-1}. Therefore, begin by expressing the relation between the two bases in matrix form (as $f' = fc$), and find the reciprocal of c by the methods described in *Further information* 23. Finally, evaluate the matrix product $c^{-1}D(R)c$.

Answer. The relation between the two bases,

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

can be expressed as the following matrix:

$$(s_N, s_1, s_2, s_3) = (s_N, s_A, s_B, s_C)\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 \end{bmatrix}$$

which lets us identify the matrix c. The reciprocal of this matrix is

$$c^{-1} = \frac{1}{6}\begin{bmatrix} 6 & 0 & 0 & 0 \\ 0 & 2 & 2 & 2 \\ 0 & 2 & -1 & -1 \\ 0 & 0 & 3 & -3 \end{bmatrix}$$

The representative of C_3^+ in the new basis is therefore

$$\begin{aligned} D'(C_3^+) &= c^{-1}D(C_3^+)c \\ &= \frac{1}{6}\begin{bmatrix} 6 & 0 & 0 & 0 \\ 0 & 2 & 2 & 2 \\ 0 & 2 & -1 & -1 \\ 0 & 0 & 3 & -3 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \end{bmatrix}\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 2 & 0 \\ 0 & 1 & -1 & 1 \\ 0 & 1 & -1 & -1 \end{bmatrix} \\ &= \frac{1}{6}\begin{bmatrix} 6 & 0 & 0 & 0 \\ 0 & 6 & 0 & 0 \\ 0 & 0 & -3 & -3 \\ 0 & 0 & 9 & -3 \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & \frac{3}{2} & -\frac{1}{2} \end{bmatrix} \end{aligned}$$

Self-test 5.4. Find the representative for the operation σ_v in the transformed basis.

Table 5.4 The matrix representation of C_{3v} in the basis $\{s_N, s_1, s_2, s_3\}$

$D(E)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}$$

$\chi(E) = 4$

$D(C_3^+)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & \frac{1}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^+) = 1$

$D(C_3^-)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \end{bmatrix}$$

$\chi(C_3^-) = 1$

$D(\sigma_v)$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{bmatrix}$$

$\chi(\sigma_v) = 2$

$D(\sigma_v')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \\ 0 & 0 & \frac{1}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v') = 2$

$D(\sigma_v'')$

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & -\frac{1}{2} & -\frac{1}{2} \\ 0 & 0 & -\frac{1}{2} & \frac{1}{2} \end{bmatrix}$$

$\chi(\sigma_v'') = 2$

The same technique as that illustrated in the example may be applied to the other representatives, and the results are collected in Table 5.4.

5.7 The characters of representations

There is one striking feature of the two representations in Tables 5.3 and 5.4. Although the matrices differ for the two bases, for a given operation the sum of the diagonal elements of the representative is the same in the two bases. The diagonal sum of matrix elements is called the **character** of the matrix, and is denoted by the symbol $\chi(R)$ where χ is chi:

$$\chi(R) = \sum_i D_{ii}(R) \tag{5.8}$$

In matrix algebra, the sum of diagonal elements is called the **trace** of the matrix, and denoted tr. So, a succinct definition of the character of the operation R is

$$\chi(R) = \mathrm{tr}\, D(R) \tag{5.9}$$

We now demonstrate that *the character of an operation is invariant under a similarity transformation of the basis*. The proof makes use of the fact (which we shall use several times in the following discussion) that the trace of a product of matrices is invariant under cyclic permutation of the matrices:

$$\mathrm{tr}\, ABC = \mathrm{tr}\, CAB = \mathrm{tr}\, BCA \tag{5.10}$$

Proof 5.3 The invariance of the trace of a matrix and the character of a representative

First, we express the trace as a diagonal sum:

$$\operatorname{tr} ABC = \sum_i (ABC)_{ii}$$

Then we expand the matrix product by the rules of matrix multiplication:

$$\operatorname{tr} ABC = \sum_{ijk} A_{ij}B_{jk}C_{ki}$$

Matrix elements are simple numbers that may be multiplied in any order. If they are permuted cyclically in this expression, neighbouring subscripts continue to match, and so the matrix product may be reformulated with the matrices in a permuted order:

$$\operatorname{tr} ABC = \sum_{ijk} B_{jk}C_{ki}A_{ij} = \sum_j (BCA)_{jj} = \operatorname{tr} BCA$$

as required.

Now we apply this general result to establish the invariance of the character under a similarity transformation brought about by the matrix $\boldsymbol{c}$:

$$\chi(R) = \operatorname{tr} \boldsymbol{D}(R) = \operatorname{tr} \boldsymbol{c}\boldsymbol{D}'(R)\boldsymbol{c}^{-1} = \operatorname{tr} \boldsymbol{D}'(R)\boldsymbol{c}^{-1}\boldsymbol{c} = \operatorname{tr} \boldsymbol{D}'(R) = \chi'(R)$$

That is, the characters of R in the two representations, $\chi(R)$ and $\chi'(R)$, are equal, as we wanted to prove.

5.8 Characters and classes

One feature of the characters shown in Tables 5.3 and 5.4 is that the characters of the two rotations are the same, as are the characters of the three reflections. These equalities suggest that the operations fall into various classes that can be distinguished by their characters.

The formal definition of the **class** of a symmetry operation is that two operations R and R' belong to the same class if there is some symmetry operation S of the group such that

$$R' = S^{-1}RS \tag{5.11}$$

The elements R and R' are said to be **conjugate**. Conjugate members belong to the same class. The physical interpretation of conjugacy and membership within a class is that R and R' are the same kind of operation (such as a rotation) but performed with respect to symmetry elements that are related by a symmetry operation.

Example 5.5 How to show that two symmetry operations are conjugate

Show that the symmetry operations C_3^+ and C_3^- are conjugate in the group C_{3v}.

Method. We need to show that there is a symmetry transformation of the group that transforms C_3^+ into C_3^-. Intuitively, we know that the reflection of a rotation in a vertical plane reverses the sense of the rotation, so we can suspect that a reflection is the necessary operation. To work out the effect of a succession of operations, we use the information in the group multiplication table (Table 5.2); to find the reciprocal of an operation, we look for the element that produces the identity E in the group multiplication table.

Answer. We consider the joint operation $\sigma_v^{-1}C_3^+\sigma_v$. According to Table 5.2, the inverse of σ_v is σ_v itself. Therefore, from the group multiplication table we can write

$$\sigma_v^{-1}C_3^+\sigma_v = \sigma_v(C_3^+\sigma_v) = \sigma_v\sigma_v' = C_3^-$$

Hence, the two rotations belong to the same class.

Self-test 5.5. Show that σ_v and σ_v' are members of the same class in C_{3v}.

With the concept of conjugacy established, it is now straightforward to demonstrate that symmetry operations in the same class have the same character in a given representation.

Proof 5.4 The invariance of character

We use the cyclic invariance of the trace of the product of representatives (eqn 5.10). We also use the fact (as a result of eqn 5.11) that $D(R')$ and $D(R)$ are related by a similarity transformation:

$$\begin{aligned}\chi(R') &= \mathrm{tr}\,D(R') = \mathrm{tr}\,D^{-1}(S)D(R)D(S) = \mathrm{tr}\,D(R)D(S)D^{-1}(S) = \mathrm{tr}\,D(R)\\ &= \chi(R)\end{aligned}$$

A word of warning: although it is true that all members of the same class have the same character in a given representation, the characters of different classes may be the same as one another. For example, as we shall see, one matrix representation of a group consists of 1×1 matrices each with the single element 1. Such a representation certainly reproduces the group multiplication table, but does so in a trivial way, and hence is called the **unfaithful representation** of the group. We shall see later that this representation is in fact one of the most important of all possible representations. The characters of all the operations of the group are 1 in the unfaithful representation, and although it is true that members of the same class have the same character (1 in each case), different classes also share that character.

5.9 Irreducible representations

Inspection of the representation of the group C_{3v} in Table 5.3 for the original *s*-orbital basis shows that all the matrices have a **block-diagonal form:**

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & & & \\ 0 & & & \\ 0 & & & \end{bmatrix}$$

As a consequence, we see that the original four-dimensional basis may be broken into two, one consisting of s_N alone and the other of the three-dimensional basis (s_A, s_B, s_C):

$$\begin{array}{ccc} E & C_3^+ & C_3^- \\ 1 & 1 & 1 \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 1 \\ 1 & 0 & 0 \\ 0 & 1 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{bmatrix} \\ \sigma_v & \sigma_v' & \sigma_v'' \\ 1 & 1 & 1 \\ \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} & \begin{bmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{bmatrix} & \begin{bmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{bmatrix} \end{array}$$

The first row in each case is the one-dimensional representation spanned by s_N and the 3×3 matrices form the three-dimensional representation spanned by the three-dimensional basis (s_A, s_B, s_C).

The separation of the representation into sets of matrices of lower dimension is called the **reduction** of the representation. In this case, we write

$$D^{(4)} = D^{(3)} \oplus D^{(1)} \qquad (5.12)$$

and say that the four-dimensional representation has been reduced to a **direct sum** (the significance of the $\oplus$ sign) of a three-dimensional and a one-dimensional representation. The term 'direct sum' is used because we are not simply adding together matrices in the normal way but creating a matrix of high dimension from matrices of lower dimension.

larger dimension from matrices of lower dimension.

There are several points that should be noted about the reduction. First, we see that one of the representations obtained is the unfaithful representation mentioned earlier, in which all the representatives are 1×1 matrices with the same single element, 1, in each case. Another point is that the characters of the representatives of symmetry operations of the same class are the same, as we proved earlier. That is true of $D^{(4)}$, $D^{(3)}$, and $D^{(1)}$ (although the characters do have different values for each representation).

The question that we now confront is whether $D^{(3)}$ is itself reducible. A glance at the representation in Table 5.4 shows that the similarity transformation we discussed earlier converts $D^{(4)}$ to a block-diagonal form of structure

$$\begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & & \\ 0 & 0 & & \end{bmatrix}$$

which corresponds to the reduction

$$D^{(4)} = D^{(1)} \oplus D^{(1)} \oplus D^{(2)}$$

The two one-dimensional representations in this expression are the same as the single one-dimensional (and unfaithful) representation introduced above, so in effect the new feature we have achieved is the reduction of the three-dimensional representation:

$$D^{(3)} = D^{(1)} \oplus D^{(2)}$$

In this case, the linear combination s_1 is a basis for $D^{(1)}$ whereas before the single orbital s_N was a basis for $D^{(1)}$. A glance at Fig. 5.23 shows the physical reason for this analogy: the orbital s_N has the 'same symmetry' as s_1. However, we are now moving to a position where we can say what we mean by the colloquial term 'same symmetry': we mean *act as a basis of the same matrix representation.*

The question that immediately arises is whether the two-dimensional representation can be reduced to the direct sum of two one-dimensional representations by another choice of similarity transformation. As we shall see shortly, group theory can be used to confirm that $D^{(2)}$ is an **irreducible representation** ('irrep') of the molecular point group in the sense that no similarity transformation (that is, linear combination of basis functions) can be found that *simultaneously* converts the representatives to block-diagonal form. The unfaithful representation $D^{(1)}$ is another example of an irreducible representation.

Each irreducible representation of a group has a label called a **symmetry species**. The symmetry species is ascribed on the basis of the list of characters of the representation. Thus, the unfaithful representation of the group C_{3v} has the list of characters (1, 1, 1, 1, 1, 1) and belongs to the symmetry species named A_1.[4] The two-dimensional irreducible representation has characters (2, −1, −1, 0, 0, 0), and its label is E. The letters A and B are used for the symmetry species of one-dimensional irreducible representations, E is used for two-dimensional irreducible representations, and T is used for three-dimensional irreducible representations. The irreducible representations labelled A_1 and E are also labelled $\Gamma^{(1)}$ and $\Gamma^{(3)}$, respectively (we meet $\Gamma^{(2)}$ shortly: the numbers on Γ do not refer to the dimension of the irreducible representation, they are just labels). We shall use the Γ notation for general expressions and the A, B, ... labels in particular cases. If a particular set of functions is a basis for an irreducible representation Γ, then we say that the basis **spans** that irreducible representation. The complete list of characters of all possible irreducible representations of a group is called a **character table**. As we shall shortly show, there are only a finite number of irreducible representations for groups of finite order, and we shall see that these tables are of enormous importance and usefulness.

We are now left with three tasks. One is to determine which symmetry species of irreducible representation may occur in a group and establish their characters. The second is to determine to what direct sum of irreducible representations an arbitrary matrix representation can be reduced—that is equivalent to deciding which irreducible representations an arbitrary basis spans. The third is to construct the linear combinations of members of an arbitrary basis that span a particular irreducible representation. This work requires some powerful machinery, which the next subsection provides.

4. For any point group, the unfaithful representation will be labelled with the letter A.

5.10 The great and little orthogonality theorems

The quantitative development of group theory is based on the **great orthogonality theorem** (GOT), which states the following. Consider a group of order h, and let $D^{(l)}(R)$ be the representative of the operation R in a d_l-dimensional irreducible representation of symmetry species $\Gamma^{(l)}$ of the group. Then

$$\sum_R D^{(l)}_{ij}(R)^* D^{(l')}_{i'j'}(R) = \frac{h}{d_l}\delta_{ll'}\delta_{ii'}\delta_{jj'} \tag{5.13}$$

Note that this form of the theorem allows for the possibility that the representatives have complex elements; in the applications in this chapter, however, they will in fact be real and complex conjugation has no effect. Although this expression may look fearsome, it is simple to apply. In words, it states that if you select any location in a matrix of one irreducible representation, and any location in a matrix of the same or different irreducible representation of the group, multiply together the numbers found in those two locations, and then sum the products over all the operations of the group, then the answer is zero unless the locations of the elements are the same in both sets of matrices, and indeed the same set of matrices (the same irreducible representations) are chosen. If the locations are the same, and the two irreducible representations are the same, then the result of the calculation is h/d_l.

Example 5.6 How to use the great orthogonality theorem

Illustrate the validity of the GOT by choosing two examples from Table 5.3, one that gives a non-zero value and one that gives a zero value according to the theorem.

Method. For a non-zero outcome, we must choose the same location in the same matrix representation: a simple example would be to use the one-dimensional unfaithful representation A_1. For the zero outcome, we can choose either different locations in a single irreducible representation or arbitrary locations in two different irreducible representations. Refer to Table 5.3 for the specific values of the matrix elements.

Answer. (a) For C_{3v}, for which $h = 6$, take the irreducible representation A_1 (which has $d = 1$), in which the matrices are 1, 1, 1, 1, 1, 1. The sum on the left of the GOT with each matrix element multiplied by itself is

$$\sum_R D_{11}^{(A_1)}(R)^* D_{11}^{(A_1)}(R) = 1 \times 1 + 1 \times 1 + 1 \times 1 + 1 \times 1 + 1 \times 1 + 1 \times 1 = 6$$

which is equal to $6/1 = 6$, as required by the theorem. (b) Consider two different locations in the two-dimensional irreducible representation E. For example, take the 34 and 33 elements of the matrices in Table 5.3:

$$\begin{aligned}\sum_R D_{34}^{(E)}(R)^* D_{33}^{(E)}(R) &= D_{34}^{(E)}(E)^* D_{33}^{(E)}(E) + D_{34}^{(E)}(C_3^+)^* D_{33}^{(E)}(C_3^+) + \cdots \\ &= 0 \times 1 + 0 \times 0 + 1 \times 0 + 1 \times 0 + 0 \times 0 + 0 \times 1 = 0\end{aligned}$$

which is also in accord with the theorem.

Example 5.7 How to construct a character table

Use the restrictions derived above and the LOT to complete the C_{3v} character table.

Method. We have identified two of the irreducible representations of the six-dimensional group, namely A_1 and E. The restriction given above will tell us the number of symmetry species to look for, and we can use eqn 5.19 to determine their dimensions. The characters themselves can be found from the LOT by ensuring that they are orthogonal to the two irreducible representations we have already found.

Answer. The order of the group is $h=6$ and there are three classes of operation; therefore, we expect there to be three symmetry species of irreducible representation. The dimensionality, d, of the unidentified irreducible representation must satisfy

$$1^2+2^2+d^2=6$$

Hence, $d=1$, and the missing irreducible representation is one-dimensional. We shall call it A_2. At this stage we can use the LOT to construct three equations for the three unknown characters. With $l=l'=A_2$, eqn 5.16 is

$$\{\chi^{(A_2)}(E)\}^2+2\{\chi^{(A_2)}(C_3)\}^2+3\{\chi^{(A_2)}(\sigma_v)\}^2=6$$

With $l=A_2$ and $l'=A_1$ we obtain

$$\chi^{(A_2)}(E)\chi^{(A_1)}(E)+2\chi^{(A_2)}(C_3)\chi^{(A_1)}(C_3)+3\chi^{(A_2)}(\sigma_v)\chi^{(A_1)}(\sigma_v)=0$$

and with $l=A_2$ and $l'=E$

$$\chi^{(A_2)}(E)\chi^{(E)}(E)+2\chi^{(A_2)}(C_3)\chi^{(E)}(C_3)+3\chi^{(A_2)}(\sigma_v)\chi^{(E)}(\sigma_v)=0$$

When the known values of the characters of A_1 and E are substituted, these two equations become

$$\chi^{(A_2)}(E)+2\chi^{(A_2)}(C_3)+3\chi^{(A_2)}(\sigma_v)=0$$

and

$$2\chi^{(A_2)}(E)-2\chi^{(A_2)}(C_3)=0$$

The three equations are enough to determine the three unknown characters, and we find $\chi^{(A_2)}(E)=1$, $\chi^{(A_2)}(C_3)=1$, and $\chi^{(A_2)}(\sigma_v)=-1$. The complete set of characters is displayed in Table 5.5.

Comment. The character of the identity in a one-dimensional irreducible representation is 1, so that value could have been obtained without any calculation.

Self-test 5.7. Construct the character table for the group C_{2v}.

[See Table 5.6]

Table 5.5 The C_{3v} character table

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Table 5.6 The C_{2v} character table

C_{2v}	E	C_2	σ_v	σ_v'
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

The character table for any symmetry group can be constructed as we have illustrated, and a selection of character tables is given in Appendix 1.

Reduced representations

A great deal depends on being able to establish what irreducible representations are spanned by a given basis. This problem leads us into the applications of group theory that we shall use throughout the text.

5.11 The reduction of representations

The question we now tackle is, given a general set of basis functions, how do we find the symmetry species of the irreducible representations they span? Often, as we shall see, we are interested more in the symmetry species and the characters than in the actual irreducible representation (the set of matrices). We have seen that a representation may be expressed as a direct sum of irreducible representations

$$D(R) = D^{(\Gamma^{(1)})}(R) \oplus D^{(\Gamma^{(2)})}(R) \oplus \cdots \tag{5.20}$$

by finding a similarity transformation that *simultaneously* converts the matrix representatives to block-diagonal form. It is notationally simpler to express this reduction in terms of the symmetry species of the irreducible representations that occur in the reduction:

$$\Gamma = \sum_l a_l \Gamma^{(l)} \tag{5.21}$$

where a_l is the number of times the irreducible representation of symmetry species $\Gamma^{(l)}$ appears in the direct sum. For example, the reduction of the s-orbital basis we have been considering would be written $\Gamma = 2A_1 + E$.

Our task is to find the coefficients a_l. To do so, we make use of the fact that because the character of an operation is invariant under a similarity transformation, the character of the original representative is the sum of the characters of the irreducible representations into which it is reduced (Fig. 5.24). Therefore,

$$\chi(R) = \sum_l a_l \chi^{(l)}(R) \tag{5.22}$$

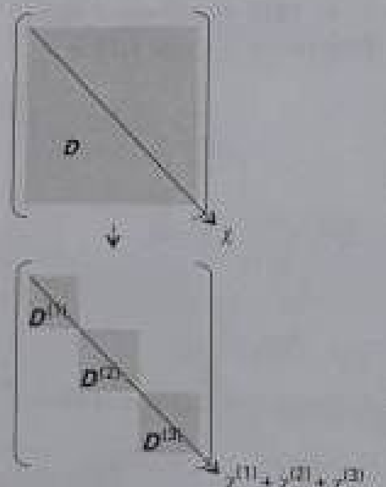

Fig. 5.24 A diagrammatic representation of the reduction of a matrix to block-diagonal form. The sum of the diagonal elements remains unchanged by the reduction.

Now we use the LOT to determine the coefficients. To do so, we multiply both sides of this equation by $\chi^{(l')}(R)^*$ and sum over all the elements of the group:

$$\sum_R \chi^{(l')}(R)^*\chi(R) = \sum_R \sum_l a_l \chi^{(l')}(R)^*\chi^{(l)}(R)$$
$$= h\sum_l a_l \delta_{ll'} = h a_{l'}$$

That is, the coefficients are given by the rule

$$a_l = \frac{1}{h}\sum_R \chi^{(l)}(R)^*\chi(R) \tag{5.23}$$

Because the characters of members of the same class of operation are the same, we can express this equation in terms of the characters of the classes:

$$a_l = \frac{1}{h}\sum_c g(c)\chi^{(l)}(c)^*\chi(c) \tag{5.24}$$

Although the last two expressions provide a formal procedure for finding the reduction coefficients, in many cases it is possible to find them by inspection. For example, in the s-orbital basis for C_{3v}, the characters are (4, 1, 2) for the classes (E, $2C_3$, $3\sigma_v$). By inspection of the character table (Table 5.5), it is immediately clear that the reduction is $2A_1 + E$. However, in more complicated cases, the formal procedure is almost essential.

Example 5.8 How to determine the reduction of a representation

What symmetry species do the four H1*s*-orbitals of methane span?

Method. Methane belongs to the point group T_d; the character table can be found in Appendix 1. The character of each operation in the four-dimensional basis (H_a, H_b, H_c, H_d) can be determined by noting the number (N) of members left in their original location after the application of each operation: a 1 occurs in the diagonal of the representative in each case, and so the character is the sum of 1 taken N times. (If the member of the basis moves, a zero appears along the diagonal which makes no contribution to the character.) Only one operation from each class need be considered because the characters are the same for all members of a class. With the characters $\chi(c)$ established, apply eqn 5.24 to determine the reduction.

Answer. Refer to Fig. 5.25. The numbers of unchanged basis members under the operations E, C_3, C_2, S_4, σ_d are 4, 1, 0, 0, 2, respectively. The order of the group is $h = 24$. It follows from eqn 5.24 that

$$a(A_1) = \tfrac{1}{24}\{(4\times1)+8(1\times1)+3(0\times1)+6(0\times1)+6(2\times1)\} = 1$$
$$a(A_2) = \tfrac{1}{24}\{(4\times1)+8(1\times1)+3(0\times1)-6(0\times1)-6(2\times1)\} = 0$$
$$a(E) = \tfrac{1}{24}\{(4\times2)-8(1\times1)+3(0\times2)+6(0\times0)+6(2\times0)\} = 0$$
$$a(T_1) = \tfrac{1}{24}\{(4\times3)+8(1\times0)-3(0\times1)+6(0\times1)-6(2\times1)\} = 0$$
$$a(T_2) = \tfrac{1}{24}\{(4\times3)+8(1\times0)-3(0\times1)-6(0\times1)+6(2\times1)\} = 1$$

Hence, the four orbitals span $A_1 + T_2$.

Comment. In some cases, an operation changes the sign of a member of the basis without moving its location (an example is the O2p_x-orbital in H_2O under the operation C_2). This sign reversal results in -1 appearing on the diagonal. In other cases, such as for the basis (p_x, p_y) on the central atom in a molecule belonging to the group C_{3v}, a fractional value appears on the diagonal: see Section 5.13.

Self-test 5.8. What symmetry species do the five Cl3*s*-orbitals of PCl_5, a trigonal bipyramidal molecule in the gas phase, span?

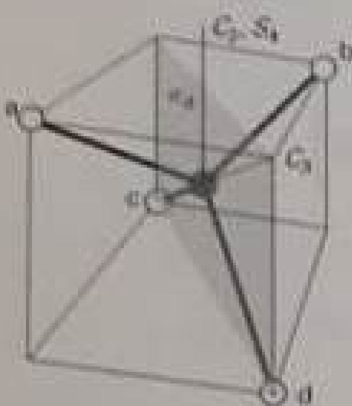

Fig. 5.25 The symmetry elements of the group T_d used in Example 5.8.