Chapter 3
Groups

Abstract The concept of a group is introduced using the example of the symmetry group of the ammonia molecule. In spite of its tiny size, this molecule has a structural symmetry that is the same as the symmetry of a macroscopic trigonal pyramid. From the mathematical point of view, a group is an elementary structure that proves to be a powerful tool for describing molecular properties. Three ways of dividing (and conquering) groups are shown: subgroups, cosets, and classes. An overview of molecular symmetry groups is given. The relationship between rotational groups and chirality is explained, and symmetry lowerings due to applied magnetic and electric fields are determined.

Contents

3.1 The Symmetry of Ammonia

The umbrella shape of the ammonia molecule has trigonal symmetry with, in addition, three vertical reflection planes through the hydrogen atoms. Together these symmetry elements form a point group, which, in the Schoenflies notation, is denoted as C_{3v}. It is good practice to start the treatment by making a simple sketch of the molecule and putting it in a right-handed Cartesian frame, as shown in Fig. 3.1. By convention, the z-axis is defined as the principal threefold axis. One of the hydrogens is put in the xz plane as shown in the figure. We attach labels A, B, C to distin-

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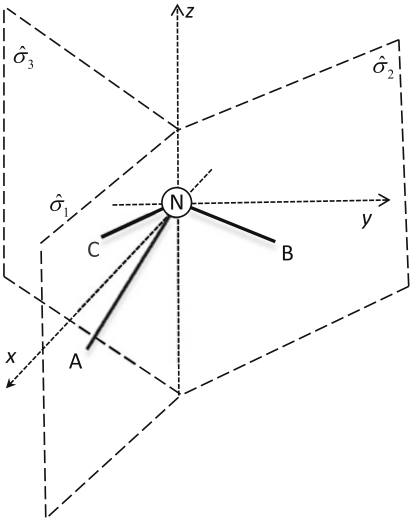
Fig. 3.1 Group theory of the ammonia molecule, with three sets of labels: x, y, z label the Cartesian axes, $\hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3$ label the symmetry planes, and A, B, C label the hydrogen atoms



guish the equivalent hydrogen atoms. In the active view, which we keep throughout, the atoms will be displaced while the symmetry elements remain tied to the immobile Cartesian frame. We shall thus not label the reflection planes by A,B,C, but we shall instead denote them as $\hat{\sigma}_1, \hat{\sigma}_2, \hat{\sigma}_3$. The $\hat{\sigma}_1$ reflection plane coincides with the xz coordinate plane. The action of the symmetry elements will be to permute the atoms. The threefold axis, rotating counterclockwise about z, moves the atom A to the position of B, which itself is displaced to the position originally occupied by C. Finally, C travels to the place previously occupied by atom A. The $\hat{\sigma}_1$ plane will leave A unchanged and will interchange B and C. Now consider the combination $\hat{\sigma}_1 \hat{C}_3$ of these two elements. We place the structure to the right of the right-justified operators and then simply work out the action from right to left; hence, first the $\hat{C}_3$ axis, and then the plane. This is shown in a pictorial way in Fig. 3.2. First, the axis will permute the atoms so that C takes the place of A. Consequently, the $\hat{\sigma}_1$ plane will now conserve C and interchange A and B. The combined action is itself again one of the symmetry elements, viz., $\hat{\sigma}_2$. The reverse product order yields a different result. In summary,

$$\begin{aligned} \hat{\sigma}_1 \hat{C}_3 &= \hat{\sigma}_2 \\ \hat{C}_3 \hat{\sigma}_1 &= \hat{\sigma}_3 \end{aligned} \tag{3.1}$$

In this way we can easily work out the full set of binary products, keeping in mind that applying the threefold rotation three times, or the symmetry planes twice, leaves every atom in place and thus corresponds to the unit element. The results are gathered in the 6 × 6 multiplication Table 3.1. This table should be read from left to right, i.e., the product $\hat{R}_i \hat{R}_j$ is found in the ith row and jth column. We may symbolically denote the matrix elements in the table as

$$M_{ij} = \hat{R}_i \hat{R}_j \tag{3.2}$$

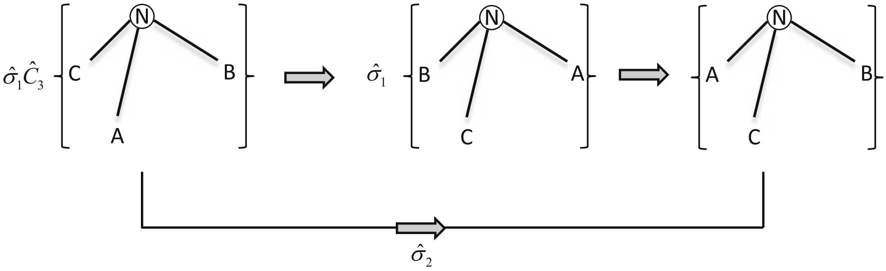


Fig. 3.2 Applying $\hat{\sigma}_1\hat{C}_3$ to the starting structure is equivalent to applying $\hat{\sigma}_2$

Table 3.1 Multiplication table for the point group C_{3v}

C_{3v}	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$\hat{E}$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$
$\hat{C}_3$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$	$\hat{\sigma}_3$	$\hat{\sigma}_1$	$\hat{\sigma}_2$
$\hat{C}_3^2$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$	$\hat{\sigma}_2$	$\hat{\sigma}_3$	$\hat{\sigma}_1$
$\hat{\sigma}_1$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{\sigma}_3$	$\hat{E}$	$\hat{C}_3$	$\hat{C}_3^2$
$\hat{\sigma}_2$	$\hat{\sigma}_2$	$\hat{\sigma}_3$	$\hat{\sigma}_1$	$\hat{C}_3^2$	$\hat{E}$	$\hat{C}_3$
$\hat{\sigma}_3$	$\hat{\sigma}_3$	$\hat{\sigma}_1$	$\hat{\sigma}_2$	$\hat{C}_3$	$\hat{C}_3^2$	$\hat{E}$

As has already been shown, these operations can also be performed directly in function space. Choosing the xy-plane $2p$-orbitals on nitrogen, $\{p_x, p_y\}$, as a suitable basis set, we may represent all the symmetry elements by transformation matrices. The resulting matrices are summarized in Table 3.2. Note that all six matrices are different. The mapping between the symmetry elements and the matrices is therefore one-to-one, and the representation is said to be *faithful*. For the $\hat{C}_3$ axis, the matrix corresponds to the one in Eq. (1.13), with rotation angle $\alpha = 2\pi/3$, and for the $\hat{C}_3^2$ axis, one has $\alpha = 4\pi/3$, which is equivalent to the inverse angle $\alpha = -2\pi/3$. The $\hat{\sigma}_1$ element leaves p_x unchanged and inverts p_y. The other reflection planes are similar to $\hat{\sigma}_1$, which means that they can be obtained by a symmetry transformation of this operator, using the results in Sect. 1.3; hence,

$$\begin{aligned} \hat{\sigma}_2 &= \hat{C}_3\hat{\sigma}_1\hat{C}_3^{-1} \\ \hat{\sigma}_3 &= \hat{C}_3\hat{\sigma}_2\hat{C}_3^{-1} \end{aligned} \tag{3.3}$$

The set of the six matrices in Table 3.2 offers an alternative algebraic way of constructing the multiplication table by direct matrix multiplication. The product $\hat{C}_3\hat{\sigma}_1$ is then replaced by the matrix multiplication $\mathbb{D}(C_3) \times \mathbb{D}(\sigma_1)$:

$$\begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix} \times \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = \begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & +\frac{1}{2} \end{pmatrix} \tag{3.4}$$

which yields the representation matrix for $\hat{\sigma}_3$, in line with Eq. (3.1).

Table 3.2 Representation matrices for the (p_x, p_y) basis in C_{3v}

$\mathbb{D}(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$	$\mathbb{D}(\sigma_1) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$
$\mathbb{D}(C_3) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\mathbb{D}(\sigma_2) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & +\frac{1}{2} \end{pmatrix}$
$\mathbb{D}(C_3^2) = \begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{pmatrix}$	$\mathbb{D}(\sigma_3) = \begin{pmatrix} -\frac{1}{2} & +\frac{\sqrt{3}}{2} \\ +\frac{\sqrt{3}}{2} & +\frac{1}{2} \end{pmatrix}$

3.2 The Group Structure

The set of symmetry operations of ammonia is said to form a *group*, G. This is a fundamental mathematical structure consisting of a set of elements and a multiplication rule with the following characteristics:

- Existence of a unit element, $\hat{E}$, which leaves all elements unchanged:

  $$\hat{E}\hat{R} = \hat{R}\hat{E} = \hat{R} \tag{3.5}$$

  In the list of elements the unit element is placed in front. As a result, the first row and first column of the multiplication table will simply repeat the ordered list of symmetry elements on which the table was based.
- Existence of an inverse element, $\hat{R}^{-1}$, for every element $\hat{R}$:

  $$\hat{R}\hat{R}^{-1} = \hat{R}^{-1}\hat{R} = \hat{E} \tag{3.6}$$

  Hence every action can also be undone. If this were not the case, we would have produced a monster that can only continue to grow. In the multiplication table, a unit element at position ij indicates that $\hat{R}_i$ and $\hat{R}_j$ are mutual inverses. Clearly, for the unit element, as well as for the reflection planes, $\hat{R}$ and $\hat{R}^{-1}$ coincide, while, for the $\hat{C}_3$ axis, the inverse is equal to $\hat{C}_3^2$, which completes a full turn.
- Closure:

  $$\forall \hat{R} \in G \quad \& \quad \hat{S} \in G \Rightarrow \hat{R}\hat{S} \in G \& \hat{S}\hat{R} \in G \tag{3.7}$$

  In the multiplication table, this is apparent by the fact that no entries are left open.
- Associativity:

  $$\hat{R}(\hat{S}\hat{T}) = (\hat{R}\hat{S})\hat{T} \tag{3.8}$$

It is difficult to imagine that such a simple set of rules can give rise to such a powerful structure on which entire properties of molecules will depend. Note that, compared with a number system, a group is an even more primitive concept since it contains only one operation, multiplication, by means of which two elements of the group may be combined. In contrast, the set of numbers allows for addition and multiplication, which results in two kinds of unit elements, zero for addition and unity for multiplication. A closer look at the multiplication table of the group shows that it has very remarkable properties. Each row and each column represent a permutation of the ordered set of elements, but in such a way that every element occurs only once in each row and column. This is a direct consequence of the group properties. As in many group-theoretical proofs, the simplest way to show this is by a *reductio ad absurdum*. Suppose that a given element, $\hat{T}$, occurred at entries ij and ik, with $\hat{R}_k \neq \hat{R}_j$. Then one would have, by applying the rules:

$$\begin{aligned} \hat{R}_i \hat{R}_j &= \hat{R}_i \hat{R}_k \\ \hat{R}_i^{-1}(\hat{R}_i \hat{R}_j) &= \hat{R}_i^{-1}(\hat{R}_i \hat{R}_k) \\ \big(\hat{R}_i^{-1}\hat{R}_i\big)\hat{R}_j &= \big(\hat{R}_i^{-1}\hat{R}_i\big)\hat{R}_k \\ \hat{E}\hat{R}_j &= \hat{E}\hat{R}_k \\ \hat{R}_j &= \hat{R}_k \end{aligned} \tag{3.9}$$

which would contradict the original supposition. Along the same lines it is easy to prove that the inverse of a product is equal to the product of the inverses in the opposite order:

$$(\hat{R}_i \hat{R}_j)^{-1} = \hat{R}_j^{-1}\hat{R}_i^{-1} \tag{3.10}$$

As a matter of principle, the group multiplication table contains everything there is to know about the group. It is, though, not necessary to store the whole multiplication table. A more compact way uses *generators*. The generators are defined as a minimal set of elements capable of generating the whole group. For the present example, two generators are needed, e.g., $\hat{C}_3$ and $\hat{\sigma}_1$. It is sufficient to make all binary combinations of these two operators in order to generate all remaining elements:

$$\begin{aligned} \hat{C}_3\hat{C}_3 &= \hat{C}_3^2 \\ \hat{\sigma}_1\hat{\sigma}_1 &= \hat{E} \\ \hat{C}_3\hat{\sigma}_1 &= \hat{\sigma}_3 \\ \hat{\sigma}_1\hat{C}_3 &= \hat{\sigma}_2 \end{aligned} \tag{3.11}$$

Alternatively, any pair of reflection planes would suffice as generators, say $\hat{\sigma}_1$ and $\hat{\sigma}_2$, but in this case the remaining symmetry plane can be obtained only by a further multiplication:

$$\begin{aligned} \hat{\sigma}_1\hat{\sigma}_1 &= \hat{E} \\ \hat{\sigma}_2\hat{\sigma}_2 &= \hat{E} \\ \hat{\sigma}_1\hat{\sigma}_2 &= \hat{C}_3 \\ \hat{\sigma}_2\hat{\sigma}_1 &= \hat{C}_3^2 \\ \hat{\sigma}_1\hat{\sigma}_2\hat{\sigma}_1 &= \hat{\sigma}_3 \end{aligned} \tag{3.12}$$

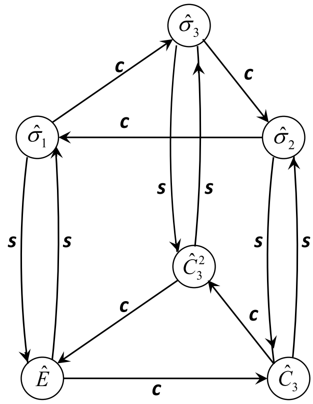


Fig. 3.3 Cayley graph of the C_{3v} point group. The generators are $c = \hat{C}_3$ and $s = \hat{\sigma}_1$

A *presentation* of a group is a set of generators, together with a minimal set of relations that are sufficient to work out any product of two elements. As an example, let us denote the $\hat{C}_3, \hat{\sigma}_1$ generators as c, s. Just three relations among these generators are sufficient to derive the whole multiplication table: $c^3 = s^2 = e, sc = c^2 s$. The generation of the six elements of the group follows from Eq. (3.11):

$$\begin{aligned}\hat{E} &= e \\ \hat{C}_3 &= c \\ \hat{C}_3^2 &= c^2 \\ \hat{\sigma}_1 &= s \\ \hat{\sigma}_2 &= sc \\ \hat{\sigma}_3 &= cs\end{aligned} \tag{3.13}$$

Any product of these elements can be shown to be closed using only the presentation. As an example, the rule $\hat{\sigma}_2\hat{\sigma}_3 = \hat{C}_3$, is expressed in the presentation as follows:

$$sccs = s\left(c^2 s\right) = s(sc) = s^2 c = c \tag{3.14}$$

In this way the whole multiplication table can be derived.

The structure of the group can also be encoded in a graph known as the Cayley graph. A graph is an abstract mathematical object consisting of a set of points, or nodes, and a set of lines connecting pairs of these points. In a *directed graph* these pairs are ordered, which means that directional arrows are added to the connecting lines. In the Cayley graph every element of the group corresponds to a node. The lines correspond to the action of the group generators. The generator $\hat{g}$ connects a given node $\langle \hat{R}_i \rangle$ by a directed line to the resulting node $\langle \hat{g}\hat{R}_i \rangle$. The action of the group on its own Cayley graph will not only map nodes onto nodes, but will also preserve the directed connections. As a result, the symmetry group will map the graph onto itself. Such a mapping is called an *automorphism*. The group G is

Table 3.3 Multiplication table for the point group D_2

D_2	$\hat{E}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$
$\hat{E}$	$\hat{E}$	$\hat{C}_2^x$	$\hat{C}_2^y$	$\hat{C}_2^z$
$\hat{C}_2^x$	$\hat{C}_2^x$	$\hat{E}$	$\hat{C}_2^z$	$\hat{C}_2^y$
$\hat{C}_2^y$	$\hat{C}_2^y$	$\hat{C}_2^z$	$\hat{E}$	$\hat{C}_2^x$
$\hat{C}_2^z$	$\hat{C}_2^z$	$\hat{C}_2^y$	$\hat{C}_2^x$	$\hat{E}$

thus isomorphic to the automorphism group of its Cayley graph. The Cayley graph corresponding to the group C_{3v}, generated by $\hat{C}_3$ and $\hat{\sigma}_1$, is shown in Fig. 3.3. It resembles a trigonal prism, but with opposite directions in the upper and the lower triangle. The $\hat{\sigma}_1$ generator corresponds to the upright edges of the prism. Since this generator is its own inverse, these edges can be traversed in both directions, so they are really undirected.

3.3 Some Special Groups

Abelian groups[1] are groups with a commutative multiplication rule, i.e.,

$$\forall \hat{R} \in G \quad \& \quad \hat{S} \in G \Rightarrow \hat{R}\hat{S} = \hat{S}\hat{R} \tag{3.15}$$

Hence, in an abelian group, the multiplication table is symmetric about the diagonal. Clearly, our group C_{3v} is not abelian.

Cyclic groups are groups with only one generator. They are usually denoted as C_n. The threefold axis gives rise to the cyclic group C_3. Its elements consist of products of the generator. By analogy with number theory, such multiple products are called powers; hence, $C_3 = \{\hat{C}_3, \hat{C}_3^2, \hat{C}_3^3\}$, where the third power is of course the unit element. Similarly, the reflection planes yield a cyclic group of order 2. The standard notation for this group is not C_2 but C_s. Cyclic groups are of course abelian because the products of elements give rise to a sum of powers and summation is commutative:

$$\hat{C}^i \hat{C}^j = \hat{C}^{i+j} = \hat{C}^{j+i} = \hat{C}^j \hat{C}^i \tag{3.16}$$

By contrast, not all abelian groups are cyclic. A simple example is the group[2] D_2 of order 4, which is presented in Table 3.3. It needs two perpendicular twofold axes as generators and thus cannot be cyclic. Nonetheless, it is abelian since its generators commute.

The *symmetric* group, S_n, is the group of all permutations of the elements of a set of cardinality n. The order of S_n is equal to $n!$. As it happens, our C_{3v} group is isomorphic to S_3. The permutations are defined on the ordered set of the three

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[1] Named after the Norwegian mathematician Niels Henrik Abel (1802–1829).

[2] This group is isomorphic to Felix Klein's four-group (*Vierergruppe*).

hydrogen atomic labels ⟨ABC⟩. Interchange of A and B means that, in this row, the element A is replaced by B and vice versa. Another way to express this is that "A becomes B, and B becomes A," and hence (A → B → A). This interchange is a *transposition* or 2-cycle, which will be denoted as (AB). The operation for the entire set is then written as a sequence of two disjunct cycles (C)(AB), where the 1-cycle indicates that the element C remains unchanged. The 3-cycle (ABC) corresponds to a cyclic permutation of all three elements: (A → B → C → A). The successive application of both operations, acting on the letter string, can be worked out as follows:

$$\begin{array}{rc} & \langle \mathrm{ABC} \rangle \\ (\mathrm{C})\,(\mathrm{AB}) & \Downarrow \\ & \langle \mathrm{BAC} \rangle \\ (\mathrm{ABC}) & \Downarrow \\ & \langle \mathrm{CBA} \rangle \end{array} \tag{3.17}$$

The result is to permute A and C, and leave B invariant. This result defines the product of the two operations as

$$(\mathrm{ABC}) \cdot (\mathrm{C})(\mathrm{AB}) = (\mathrm{B})(\mathrm{AC}) \tag{3.18}$$

The multiplication table for the whole group is given in Table 3.4. The group multiplication tables of S_3 and C_{3v} clearly have the same structure, but the isomorphism can be realized in six different ways, as there are six ways to associate the three letters with the three trigonal sites. It is important to keep in mind that the two kinds of groups have a very different meaning. The C_{3v} operations refer to spatial symmetry operations of the ammonia molecule, while the permutational group is a set-theoretic concept and acts on elements in an ordered set. As an example, one might easily identify the $\hat{\sigma}_1$ reflection plane with the (A)(BC) permutation operation since it indeed leaves A invariant and swaps B and C. However, as shown in Fig. 3.2, when this reflection is preceded by a trigonal symmetry axis, the atom C has taken the place of A, and the $\hat{\sigma}_1$ plane now should be described as (C)(AB). For a proper definition of the relationship between nuclear permutations and spatial symmetry operations, we refer to Sect. 5.4, where the molecular symmetry group is introduced.

In S_3 the number of transpositions, i.e., pairwise interchanges of atoms, is zero for the unit element, one for the reflection planes, and two for the threefold axes. *Odd permutations* are defined by an odd number of transpositions. The product of two even permutations is an even permutation, and for this reason, the even permutations alone will also form a group, known as the *alternating group*, A_n. In the present example, the alternating group A_3 is isomorphic to the cyclic group C_3. By contrast, the product of two odd permutations is not odd, but even. So odd permutations cannot form a separate group.

Table 3.4 Multiplication table for the symmetric group S_3. The unit element can also be expressed as three 1-cycles: (A)(B)(C)

S_3	$\hat{E}$	(ABC)	(ACB)	(A)(BC)	(B)(AC)	(C)(AB)
$\hat{E}$	$\hat{E}$	(ABC)	(ACB)	(A)(BC)	(B)(AC)	(C)(AB)
(ABC)	(ABC)	(ACB)	$\hat{E}$	(C)(AB)	(A)(BC)	(B)(AC)
(ACB)	(ACB)	$\hat{E}$	(ABC)	(B)(AC)	(C)(AB)	(A)(BC)
(A)(BC)	(A)(BC)	(B)(AC)	(C)(AB)	$\hat{E}$	(ABC)	(ACB)
(B)(AC)	(B)(AC)	(C)(AB)	(A)(BC)	(ACB)	$\hat{E}$	(ABC)
(C)(AB)	(C)(BA)	(A)(BC)	(B)(AC)	(ABC)	(ACB)	$\hat{E}$

The group multiplication table contains all there is to know about a group. It hides a wealth of internal structure that is directly relevant to the physical phenomena to which the group applies. In order to elucidate this structure, three ways of delineating subsets of the group are useful: subgroups, cosets, and classes.

3.4 Subgroups

A subgroup H of G, denoted $H \subset G$, is a subset of elements of G, which itself has the group property. Trivial subgroups are the group containing the identity alone, denoted as $C_1 = \{\hat{E}\}$, and the group G itself. Besides these, in the case of the group of ammonia, C_{3v}, there are four nontrivial subgroups: $C_3 = \{\hat{E}, \hat{C}_3, \hat{C}_3^2\}$, and $C_s = \{\hat{E}, \hat{\sigma}_i\}$ with $i = 1, 2$, or 3. The three C_s groups are equivalent. We can construct a simplified genealogical tree, which shows the subgroup structure (Fig. 3.4). In chemistry and physics, subgroup structures are highly relevant since the distortions of a symmetric system can be described as a descent down the genealogical tree. We shall describe this in Sect. 4.6 as the subduction process. For the moment, we retain Cayley's theorem:

Theorem 1 *Every group of order n is isomorphic with a subgroup of the symmetric group S_n.*

This theorem is immediately clear from the multiplication table. A given row of the table shows how the corresponding element maps the entire set of elements onto itself. This mapping is a permutation of the n elements, and every element gives rise to a different permutation since no two rows are the same. Thus, G must be a subgroup of S_n. The importance of this theorem is especially evident from the mathematical point of view. It tells us that the symmetric groups exhaust all the possible structures of finite groups.

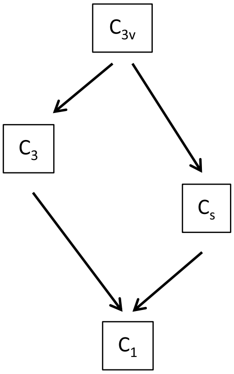

Fig. 3.4 Genealogical tree, representing progressive symmetry breaking of the C_{3v} point group. The C_s box stands for the three equivalent reflections groups

3.5 Cosets

A genuine *partitioning* of a group is achieved when the set of elements is divided into separate subsets that do not exhibit any overlap and, together, constitute the whole group. Subgroups clearly do not form a partitioning since, for instance, they all share the same unit element. On the other hand, cosets do form a partitioning. In molecules, the natural realizations of the cosets are the sets of equivalent sites. These are atoms or groups of atoms that are permuted by the action of the molecular symmetry group. In the example of the ammonia molecule, each of the three hydrogen atoms occupies an equivalent site with C_s symmetry. The nitrogen atom, however, occupies a unique site that has the full C_{3v} symmetry. Now consider the site of one particular hydrogen atom, say A. The C_s subgroup that leaves this site invariant consists of only two symmetry elements: $\hat{E}$ and $\hat{\sigma}_1$. This subgroup is called the *stabilizer* of the site. When we multiply each element of this subgroup (on the left) with an element outside it, say $\hat{C}_3$, we obtain two new elements, $\hat{C}_3$ and $\hat{\sigma}_3$, which both share the property that they map A onto B. They form a (left) coset of the original C_s subgroup, and the element that we used to form this coset is the coset-representative. There is still another coset, which may be generated by one of the remaining elements, say $\hat{C}_3^2$. In this way, one finds the coset, $\{\hat{C}_3^2, \hat{\sigma}_2\}$, of elements which have the property that they both map A onto C. The sum of all the cosets forms the total set, and hence,

$$C_{3v} = \{\hat{E}, \hat{\sigma}_1\} + \{\hat{C}_3, \hat{\sigma}_3\} + \left\{\hat{C}_3^2, \hat{\sigma}_2\right\} \tag{3.19}$$

We can rewrite this in general as

$$G = \sum_n \hat{R}_n H \tag{3.20}$$

where $\hat{R}_n$ denotes a coset representative, and the product $\hat{R}_n H$ denotes the nth coset, obtained by multiplying every element of the subgroup on the left by the generator. The choice of coset representatives is not unique since every element of a given coset may act as representative. In the case of the present group, we can choose all representatives as powers of the threefold axis, which allows introduction of a cyclic summation:

$$C_{3v} = \sum_{n=1}^{3} (\hat{C}_3)^n C_s \tag{3.21}$$

This expression forms a nice illustration of how representatives make different maps of the subgroup. These cosets form an *orbit* inside the group. Note that the way cosets are defined here is based on left multiplication by the generators, giving rise to what are also denoted as *left cosets*. An analogous partitioning of the group can also be based on right cosets. The partitioning of a group in cosets gives rise to the famous Lagrange theorem:

Theorem 2 *The order of a subgroup of a finite group is a divisor of the order of the group.*

Consider a group G and subgroup H with respective orders $|G|$ and $|H|$. The theorem states that $|G|/|H|$ is an integer. The proof is based on two elements. One first has to prove that all elements in a given coset are different and further that different cosets do not manifest any overlap.

Consider a coset $\hat{R}_i H$ with elements $\hat{R}_i \hat{h}_x$. For $\hat{h}_x \neq \hat{h}_y$, $\hat{R}_i \hat{h}_x$ must be different from $\hat{R}_i \hat{h}_y$, simply because two elements in the same row in the multiplication table can never be equal, as was proven in Eq. (3.9). Hence, the size of the coset will be equal to $|H|$. Then we consider an element $\hat{R}_j \notin \hat{R}_i H$. This new element will in turn be the representative of a new coset, $\hat{R}_j H$, and we must prove that this new coset does not overlap with the previous one. This can easily be demonstrated by *reductio ad absurdum*. Suppose that there is an element $\hat{R}_j \hat{h}_x$ in the second coset that also belongs to the first coset, as $\hat{R}_i \hat{h}_y$. We then have:

$$\begin{aligned} \hat{R}_j \hat{h}_x &= \hat{R}_i \hat{h}_y \\ \hat{R}_i^{-1} \hat{R}_j &= \hat{h}_y \hat{h}_x^{-1} \end{aligned} \tag{3.22}$$

Since the subgroup H has the group property, the inverse element $\hat{h}_x^{-1}$ is also an element of H, and so is its product with $\hat{h}_y$. Hence, the product $\hat{R}_i^{-1} \hat{R}_j$ will be an element of H, say $\hat{h}_z = \hat{h}_y \hat{h}_x^{-1}$. The first coset will of course contain the element $\hat{R}_i \hat{h}_z$, which reduces to

$$\hat{R}_i \hat{h}_z = \hat{R}_i \hat{h}_y \hat{h}_x^{-1} = \hat{R}_i \hat{R}_i^{-1} \hat{R}_j = \hat{R}_j \tag{3.23}$$

Hence, $\hat{R}_j \in \hat{R}_i H$, contrary to the assumption. The expansion of the group in cosets thus leads to a complete partitioning in subsets of equal sizes. It starts by the subset formed by the subgroup H. If H is smaller than G, take an element outside H and form with this element a coset, which will have the same dimension as H. If there are still elements outside, use one of these to form a new coset, again containing $|H|$

elements, etc. Each time a coset is formed, a block of size $|H|$ is occupied till the full territory of the group is occupied by subsets of the same size. Their order must thus be a divisor of the group order. In a sense, one could describe this collection of cosets as the quotient, resulting from the "division" of the group by a subgroup. We shall make use of this concept in the induction of representations in Sect. 4.6. In the present example, the point group of ammonia is of order 6, with divisors 1, 2, 3, and 6, and for each of these, there are indeed subgroups. This is rather exceptional, though. It is *not* the case that for every divisor there should be a subgroup. As a further corollary, groups with an order which is a prime number have no nontrivial subgroups.

3.6 Classes

Probably, the most natural way to partition a group is by putting all elements "of the same kind" into separate classes. Hence, in the group C_{3v} we could put the three planes in one class; the unit element is of course a separate class, but what about the $\hat{C}_3$ and $\hat{C}_3^2$ axes? Are they of the same kind or not? Clearly, we need a rigorous definition of what it means for two symmetry elements to be equivalent. We can use as a criterion the symmetry transformations of an operator, as explained in Sect. 1.3. Hence, two elements $\hat{A}$ and $\hat{B}$ will belong to the same class, $\hat{A} \sim \hat{B}$, if there exists (denoted as $\exists$) a symmetry operation $\hat{U}$ that belongs to the group and transforms $\hat{B}$ into $\hat{A}$:

$$\hat{A} \sim \hat{B} : \exists \hat{U} \in G \rightarrow \hat{A} = \hat{U}\hat{B}\hat{U}^{-1} \tag{3.24}$$

In C_{3v}, the symmetry planes will map $\hat{C}_3$ onto $\hat{C}_3^2$. Hence, we can safely say that the two threefold elements belong to the same class, because of the existence of symmetry planes, which can reverse the direction of rotation. Synonyms for "to belong to the same class" are: "to be (class-)conjugate" or "to be similarity transforms." If the element $\hat{U}$ transforms $\hat{B}$ to $\hat{A}$, then the inverse element, $\hat{U}^{-1}$, which because of the group properties also belongs to G, will do the reverse and will transform $\hat{A}$ into $\hat{B}$. Hence, conjugation is reflexive. It is, furthermore, transitive:

$$(\hat{A} \sim \hat{B})\&(\hat{B} \sim \hat{C}) \rightarrow (\hat{A} \sim \hat{C}) \tag{3.25}$$

The set of all elements that are conjugate with a given element is a *conjugacy class* or simply a class. A class is fully denoted by specifying any one of its elements in the same way as a coset is defined by any one of its representatives. The total group is of course the sum of all its classes. In abelian groups, the similarity transformation will always return the element on which it was acting; hence, in this case, all classes will be singletons (sets of order 1). The unit element is unique, so it is always in its own class.

Theorem 3 *The number of elements in a class is a divisor of the group order.*

The proof makes use of the coset concept. We start by considering all elements that stabilize a given element, say $\hat{A}_0$, of the group. One can prove that these elements constitute a subgroup $H \subset G$. Hence, we write:

$$\hat{h}_x \in H \Leftrightarrow \hat{h}_x \hat{A}_0 \hat{h}_x^{-1} = \hat{A}_0 \tag{3.26}$$

The proof consists of a check of the four group criteria. The closure, for instance, is proven as follows: suppose that both $\hat{h}_x$ and $\hat{h}_y$ stabilize $\hat{A}_0$; then their product will also be a stabilizer:

$$\hat{h}_x \hat{h}_y \hat{A}_0 (\hat{h}_x \hat{h}_y)^{-1} = \hat{h}_x \hat{h}_y \hat{A}_0 \hat{h}_y^{-1} \hat{h}_x^{-1} = \hat{h}_x \hat{A}_0 \hat{h}_x^{-1} = \hat{A}_0 \tag{3.27}$$

where we use the result of Eq. (3.10) that the inverse of a product is equal to the product of the inverses in the reverse order. Next, we expand G in cosets of this newly found subgroup H. All elements of a coset $\hat{R}_i H$, with $\hat{R}_i \notin H$, will transform $\hat{A}_0$ into the same new element $\hat{A}_i$:

$$\hat{R}_i \hat{h}_x \hat{A}_0 (\hat{R}_i \hat{h}_x)^{-1} = \hat{R}_i \hat{h}_x \hat{A}_0 \hat{h}_x^{-1} \hat{R}_i^{-1} = \hat{R}_i \hat{A}_0 \hat{R}_i^{-1} = \hat{A}_i \tag{3.28}$$

The result must be different from $\hat{A}_0$ because, otherwise, $\hat{R}_i$ would be an element of H. In order to prove the theorem, the following remaining questions have to be decided. Do different cosets give rise to different similarity transforms? Does one obtain all elements of a class by finding all transforms of a given starting element? The answers to both questions are affirmative. For the first question, if $\hat{R}_i$ and $\hat{R}_j$ represent different cosets, one should conclude that $\hat{A}_i \neq \hat{A}_j$. Suppose that the opposite is true:

$$\begin{aligned} \hat{R}_i \hat{A}_0 \hat{R}_i^{-1} &= \hat{R}_j \hat{A}_0 \hat{R}_j^{-1} \\ \hat{R}_i^{-1} \hat{R}_j \hat{A}_0 \hat{R}_j^{-1} \hat{R}_i &= \hat{A}_0 \\ \hat{R}_i^{-1} \hat{R}_j \hat{A}_0 \big(\hat{R}_i^{-1} \hat{R}_j\big)^{-1} &= \hat{A}_0 \end{aligned} \tag{3.29}$$

This implies that $\hat{R}_i^{-1} \hat{R}_j$ stabilizes $\hat{A}_0$ and thus must belong to H, where it corresponds to, say, $\hat{h}_z$. But one then again has

$$\hat{R}_i \hat{h}_z = \hat{R}_i \hat{R}_i^{-1} \hat{R}_j = \hat{R}_j \tag{3.30}$$

and thus $\hat{R}_j$ is a representative of the same coset as $\hat{R}_i$, which contradicts the starting assumption. Hence, there will be at least as many equivalent elements in the class as there are cosets of the stabilizing subgroup. Have we then generated the entire class? Yes, because by going through all the cosets, we run through the entire group. In this way, we have found all elements that are conjugate to a given one, but, because of transitivity, this also means that there cannot be other conjugate elements. The one-to-one mapping between conjugate elements and cosets implies that the number in a class is equal to the number of cosets of the stabilizing subgroup and hence—by Lagrange's theorem—must be a divisor of the group order.

The proof illustrates the connection between cosets and conjugacy classes. A special example of this arises in the case of *normal*, or *invariant*, subgroups. A subgroup H is normal if its left and right cosets coincide, i.e., if $\hat{R}_i H = H\hat{R}_i$. This implies that all the elements of the group will map the subgroup onto itself or, for a normal subgroup H,

$$\forall \hat{U} \in G \quad \& \quad \hat{h}_x \in H : \hat{U}\hat{h}_x\hat{U}^{-1} \in H \tag{3.31}$$

Normal subgroups are thus made up of entire conjugacy classes of G. As an example, the group C_3 is a normal subgroup of C_{3v} since it contains the whole conjugacy class of the trigonal elements. A molecular site that is stabilized by a normal subgroup must be unique since it can be mapped only onto itself. Such is the case for the nitrogen atom in ammonia. By contrast, the C_s subgroups stabilizing the hydrogen sites in ammonia are not normal since they are based on only one reflection plane, while there are three symmetry planes in the corresponding conjugacy class. Accordingly, the hydrogen sites are not unrelated.

3.7 Overview of the Point Groups

The highest point group symmetry is that of the spherical symmetry group. The gradual descent in symmetry from the sphere provides a practical tool to determine and classify molecular symmetry groups. Molecules with a symmetry that is closest to the sphere are *isotropic*, in the sense that there is no unique direction to orient them. The corresponding symmetry groups are the cubic and icosahedral groups.

Breaking spherical symmetry gives rise to symmetry groups based on the cylinder. Cylindrical symmetry splits 3D space into an axial 1D component and an equatorial 2D space, which remains isotropic. Molecules with cylindrical shapes have a unique anisotropy axis, along which they may be oriented in space. Conventionally this direction is denoted as the z-direction. Along this direction they have a principal n-fold rotation or rotation–reflection axis, which is responsible for the remaining in-plane isotropy. Finally, further removal of all $\hat{C}_n$ or $\hat{S}_n$ with $n > 2$ leads to molecules that are completely anisotropic and have at most orthorhombic symmetry, D_{2h}. In this section we will provide a concise overview of the point groups, following a path of descent in symmetry. We thereby refer to the list of point groups presented in the character tables in Appendix A.

Spherical Symmetry and the Platonic Solids

Any plane through the center of a sphere is a reflection plane, and any axis through the center is a rotation axis, as well as a rotation–reflection axis. In addition, the sphere also is centrosymmetric, which means that the center is a point of inversion. The resulting infinite-dimensional symmetry group of the sphere is usually denoted

Table 3.5 The Platonic solids and their point groups. The numbers count the triangles, squares, and pentagons, that intersect in a vertex of the solid

	Triangle	Square	Pentagon
3	Tetrahedron (T_d)	Cube (O_h)	Dodecahedron (I_h)
4	Octahedron (O_h)		
5	Icosahedron (I_h)		

as $O(3)$, which refers to the orthogonal group in three dimensions. This assignment is based on the one-to-one correspondence between the symmetry operations of the sphere and the set of 3×3 orthogonal matrices. This will be explained in more detail in Sect. 7.1. Only isolated atoms exhibit spherical symmetry. Molecular shapes that approximate perfect spherical symmetry are based on the *regular polyhedra*, the building blocks of which are *regular polygons*. These polygons are obtained by distributing n points around a circle in such a way that all points are equivalent, i.e., that the distances between any two neighboring points are the same, implying that the angles subtended by adjacent edges are also the same. In this way the circle may circumscribe an equilateral triangle, a square, a regular pentagon, etc.

In fact, for any integer n with $3 \leq n \leq \infty$, a regular n-gon can be obtained, though not all of them can be drawn by use of a ruler and compass. In 3D things are quite different. Defining regular polyhedra by distributing n points over a sphere in such a way that all vertices, edges, and faces of the resulting structures are the same cannot be realized in infinitely many ways: quite on the contrary, only five solutions are possible.[3] These are known as the Platonic solids, and they are listed in Table 3.5. They played an important role in Pythagorean tradition, as well as in Eastern philosophy and religion. The fact that in 3D only five solutions exist was considered to reveal a fundamental truth about nature, to the extent that Plato, in his *Timaeus*, based his natural philosophy on these solids. The ancient doctrine of the four elements was placed in correspondence with four of the solids. The tetrahedron (or 4-plane), with symmetry T_d, has the most acute angles and was associated with fire. The cube, or hexahedron (6-plane), with symmetry O_h, is clearly the most stable structure and refers to the earth. The icosahedron (20-plane), with symmetry I_h, contains twenty faces and is therefore closest to a globular surface, which symbolizes the most fluid element, water. Both cube and icosahedron have a dual partner, which is obtained by replacing vertices by faces and vice versa. The dual of the cube is the octahedron (8-plane), which figured for air. In Table 3.5, the octahedron is placed between the tetrahedron and the icosahedron, and this seemed appropriate for air because it is intermediate between fire and water in its mobility, sharpness, and ability to penetrate. The dual of the icosahedron is the regular dodecahedron (12-plane). There being only four elements, the discovery of the fifth solid caused some embarrassment, which found an elegant solution by its being assigned to the substance of the

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[3] The sum of the angles subtended at a vertex of a Platonic solid must be smaller than a full angle of 2π. Hence, no more than five triangles, three squares, or three pentagons can meet in a vertex; regular hexagons are already excluded since the junction of three such hexagons already gives rise to an angle of 2π at the shared vertex.

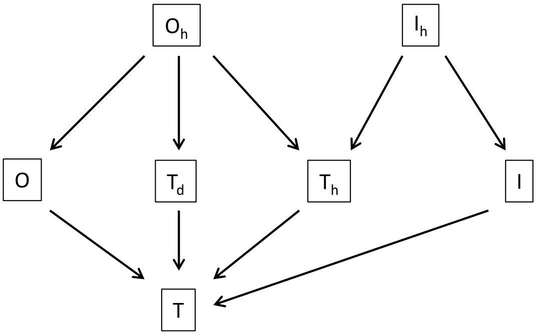

Fig. 3.5 Genealogical tree for the cubic and icosahedral point groups

heavens. The dodecahedron and its intriguing symmetry were considered worthy of the stars, with their perfect cosmic order. Besides the three point groups, T_d, O_h, and I_h, represented by the Platonic solids, there are four more groups that belong to the isotropic family: T_h, T, O, and I. They are subgroups of the octahedral and icosahedral groups, as shown in Fig. 3.5.

The Tetrahedron

T_d symmetry (Fig. 3.6(a)) plays a crucial role in chemistry. It is the symmetry of the valence structure of aliphatic carbon. The attribution of this symmetry to carbon by Van't Hoff[4] as early as 1874, i.e., well before the modern concept of molecular structure and some two and a half millennia after Pythagoras, remains a tribute to the Greek vision that the fundamental structure of matter consists of ideal symmetric shapes. The tetrahedron is the most fundamental of the solids since it is the *simplex* of 3D space. A simplex is a figure consisting of vertices that are all equivalent and are equidistant from each other.[5] In an n-dimensional space the simplex contains $n + 1$ vertices, e.g., in 2D Euclidean space exactly three points can be distributed in such a way that they are equidistant, viz., by occupying the vertices of an equilateral triangle. In 3D space only four points can be distributed in such a way that they have this property, the solution being the tetrahedron. The perfect permutational symmetry of the vertices of the n-simplex implies that the corresponding symmetry group is isomorphic to the symmetric group S_n. We have already seen that the triangular symmetry of the hydrogens in ammonia could be described by S_3; in the same way the tetrahedral symmetry group is isomorphic to S_4. The rotational subgroup of T_d is the group T, which, in turn, is isomorphic to the alternating group A_4. An extraordinary member of the tetrahedral family is the group T_h, which has the same

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[4] Van't Hoff published his findings in 1874 in Utrecht. In the same year, Le Bel came to the same conclusion, based on the investigation of optical rotatory power. An English translation of the original papers of both chemists can be found in: [1].

[5] In graph theory the graph of a simplex with n vertices is the complete n-graph, K_n. In such a graph, each of the n vertices is connected to all the other $(n - 1)$ vertices. There is only one simplex for each dimension.

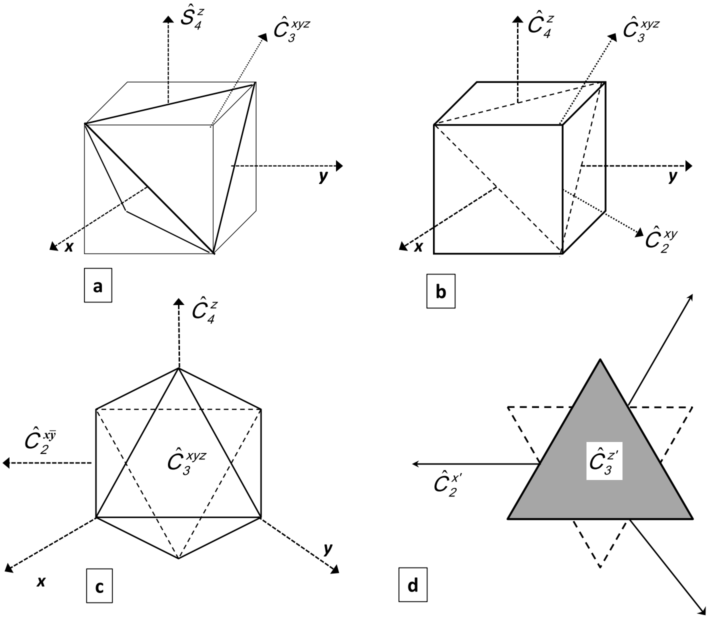

Fig. 3.6 The tetrahedral and octahedral symmetry groups: (**a**) tetrahedron, inscribed in a cube by connecting four alternating corners; (**b**) orientation of the cube based on fourfold axes along the Cartesian directions; $\hat{C}_2^{xy}$ lies along the acute bisector of the x and y directions; the dashed triangle is one face of the inscribed tetrahedron; (**c**) construction drawing of the octahedron in the same fourfold setting; the $\hat{C}_2$ axis shown is the bisector of the positive x and negative y direction; and (**d**) same drawing of the octahedron with a trigonal coordinate orientation: the z' direction is along the $\hat{C}_3$ axis, and the x'-direction is along the bisector of the positive x- and negative y-directions

order as T_d and also contains T as its rotational subgroup. Molecular examples of this group are quite rare and will mostly be encountered as symmetry lowering of cubic or icosahedral molecules (see later, Fig. 3.8).

The Cube and Octahedron

The group O_h contains 48 elements and is the symmetry group of the octahedron and the cube (see Fig. 3.6(b)). The system of Cartesian axes itself has octahedral symmetry, and, as such, this symmetry group is the natural representative of 3D space. It is ubiquitous in ionic crystals, where it corresponds to coordination numbers 6 (as in rock salt, NaCl) or 8 (as in caesium chloride, CsCl). It is also the dominant symmetry group of coordination compounds. The rotational subgroup is the group O with 24 elements. The octahedron provides us with an insight into the basic architecture of polyhedra. There are three structural elements: vertices, edges, and faces. Through each of these runs a rotational symmetry axis: a $\hat{C}_4$ axis through the vertices, a $\hat{C}_2$ axis through the edge, and a $\hat{C}_3$ axis through the face center. In

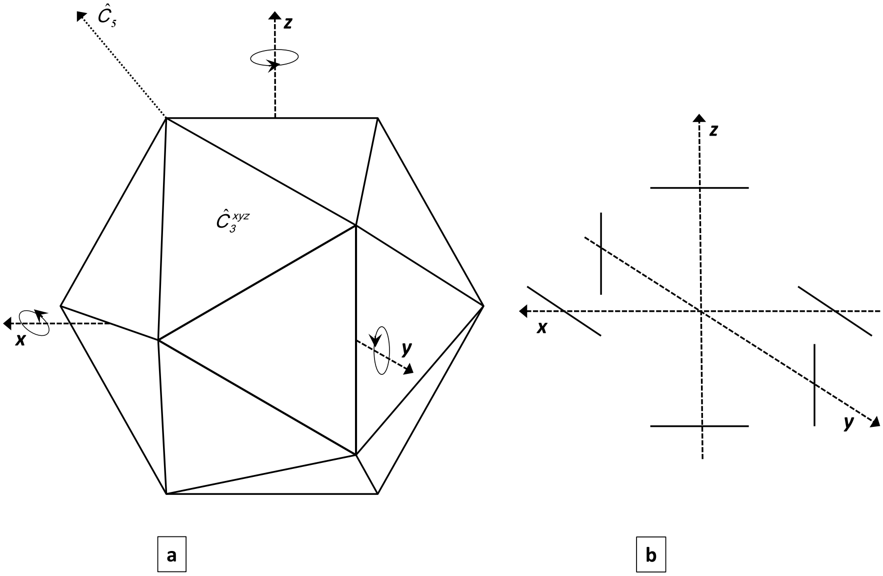

Fig. 3.7 (**a**) Icosahedron in a D_{2h} setting, (**b**) T_h structure based on the icosahedral edges through the Cartesian coordinate axes

a triangular face, the product of the three rotations equals the unit element. For the triangle that is turned toward the viewer in Fig. 3.6(c), this is

$$\hat{C}_2^{xz}\hat{C}_3^{xyz}\hat{C}_4^{z} = \hat{E} \tag{3.32}$$

The symmetry elements are labeled by the indices x, y, and z, which refer to their orientation in the Cartesian coordinate system, e.g., $\hat{C}_3^{xyz}$ indicates the $\hat{C}_3$ axis, which is the diagonal of the positive Cartesian directions. This notation emphasizes that symmetry elements are tied to the coordinate system and stay fixed in space.

The Icosahedron and Dodecahedron

Icosahedral symmetry is less obvious and thus more intriguing than cubic symmetry. Whilst tetrahedral and octahedral molecules were already known before the turn of the nineteenth/twentieth century, the first structural study of an icosahedral molecule was the closo-dodecaborane, $B_{12}H_{12}^{2-}$, in 1960. More examples would follow: in 1984, dodecahedrane, $C_{20}H_{20}$, and then the supermolecule Buckminsterfullerene, C_{60}, which has the shape of a truncated icosahedron [2–4]. Icosahedral structures can be drawn inside a regular hexagon, as shown in Fig. 3.7(a). The coordinate axes in this figure are chosen in such a way that each of the Cartesian directions coincides with a twofold axis. These axes together form a D_{2h} subgroup. This orientation thus corresponds to a D_{2h} setting. Figure 3.7(b) shows the orientation of the edges through the Cartesian directions. When going from one axis to a

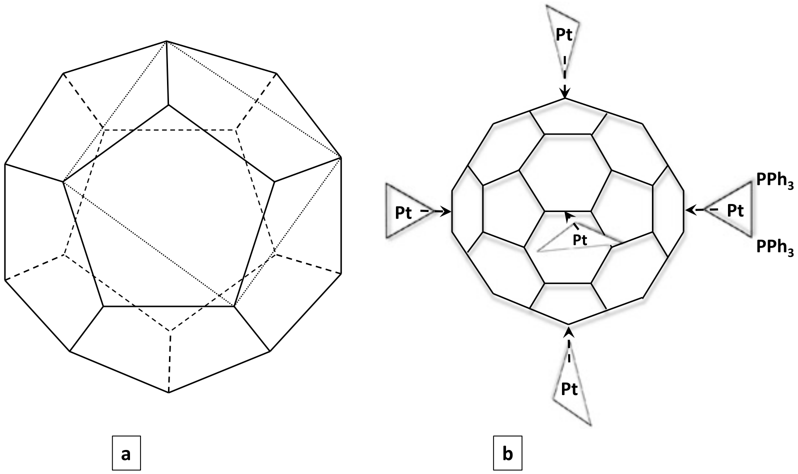

Fig. 3.8 (**a**) Dodecahedron, the square is the top face of an inscribed cube; (**b**) supramolecular complex of C_{60} Buckminsterfullerene with six η^2-platina-bis(triphenyl)phosphine adducts on double bonds adjacent to two hexagons; the adducts adopt a D_{2h} setting and reduce the icosahedral symmetry of the buckyball to T_h

neighboring axis, one always rotates the edges by 90°. In fact, there are two ways to realize this D_{2h} setting either with the top edge in the xz plane, as in Fig. 3.7(b), or in the yz plane [5]. The reason is that the O_h symmetry of the Cartesian frame is not a subgroup of I_h since $|O_h|$ is not a divisor of $|I_h|$. Their highest common subgroup is the 24-element group T_h, as indicated in Fig. 3.5. The structure of the six edges in Fig. 3.7(b) does indeed have T_h symmetry. Note that T_h is a normal subgroup of O_h, but not of I_h. The dual of the icosahedron is the dodecahedron, shown in Fig. 3.8(a). In a dodecahedron, one can select a set of eight vertices that form the corners of a cube. The dashed square in the figure is the top face of such an inscribed cube. Euclid already demonstrated that a cube could be drawn inside a dodecahedron in such a way that its twelve edges each lie in one of the twelve faces of the dodecahedron. In turn, in the center of each of the faces of this cube there lies a dodecahedral edge, which breaks the fourfold symmetry axes of the cube. The stabilizer of the cube inside I_h is the subgroup T_h. The icosahedral group can be partitioned into five cosets of T_h, which can be generated in a cyclic orbit by a pentagonal generator:

$$I_h = \sum_{n=1}^{5} (\hat{C}_5)^n T_h \tag{3.33}$$

Each of the cosets refers to an inscribed cube, exactly as the three C_s cosets in C_{3v} ammonia refer to the three equivalent hydrogen sites. Hence, in a dodecahedron there will be five inscribed cubes. Since the order of the I_h group is 120, which equals 5!, it is tempting to think of this group as isomorphic to S_5, permuting the five inscribed cubes. This, however, is not the case since I_h contains 10-fold rotation-reflection axes, which are not present in S_5. On the other hand, the rotational subgroup I is indeed isomorphic to the alternating group A_5. The icosahedral rotations act transitively on the set of five cubes. The icosahedron also contains six-fold rotation–reflection axes, $\hat{S}_6$. These symmetry elements act transitively on the set of the six pentagonal directions. C_{60} (Buckminsterfullerene) has perfect I_h symmetry and corresponds to a truncated icosahedron. Bonds that are adjacent to two hexagons have pronounced double-bonding character. Metal fragments can coordinate [6] to these bonds, as shown in Fig. 3.8(b). A hexa-adduct is formed with near T_h symmetry.

Cylindrical Symmetries

Cylinders, Prisms, Antiprisms

The full symmetry group of an ideal cylinder is denoted by $D_{\infty h}$. The D stands for *dihedral*[6] and h for *horizontal*. Like the spherical group, the cylindrical symmetry group is a continuous symmetry group, which has an infinite number of elements. It contains any rotation or rotation–reflection about the z-axis, any $\hat{C}_2$ axis in the equator and any vertical symmetry plane, $\hat{\sigma}_v$. In addition there are four singleton classes, viz. the identity, the $\hat{C}_2^z$ rotation, the unique horizontal symmetry plane, and spatial inversion. Cylindrical symmetry is met only in linear molecules such as homonuclear diatomics. Obviously, in nonlinear molecules the rotational symmetry of the cylinder is replaced by a finite cyclic symmetry. Two shapes are realizations of maximal finite subgroups of the cylinder: prisms and antiprisms with respective symmetries D_{nh} and D_{nd}. In both structures the principal axis is a $\hat{C}_n$ axis, perpendicular to which there are n twofold axes. The horizontal symmetry plane is conserved only in prisms, and not in antiprisms. In Fig. 3.9(a), the staggered configuration in ferrocene exemplifies a pentagonal antiprism, while the eclipsed configuration in ruthenocene is a pentagonal prism. The presence of inversion symmetry depends on the parity of n. It is present only in D_{2nh} prisms and $D_{(2n+1)d}$ antiprisms. The cylindrical symmetries reach their lower limit when the principal rotation axis is twofold. In the D_{2h} case, the equatorial directions are no longer equivalent, and we have a rectangular parallelepiped that is an *orthorhombic* structure with three different and mutually perpendicular directions. By contrast, in the twofold antiprism, with symmetry D_{2d}, we have a scalenohedron that has two directions perpendicular to the z-axis, which are equivalent. In fact, the highest symmetry element in this case is an $\hat{S}_4$ rotation–reflection axis, which is responsible for the equivalence of the

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[6] Dihedral means literally "having two planes." The dihedral angle is an important molecular descriptor. The dihedral angle of the central B$-$C bond in an A$-$B$-$C$-$D chain is the angle between the ABC and BCD faces. In the present context, the term dihedral originates from crystallography, such as when two plane faces meet in an apex of a crystal.

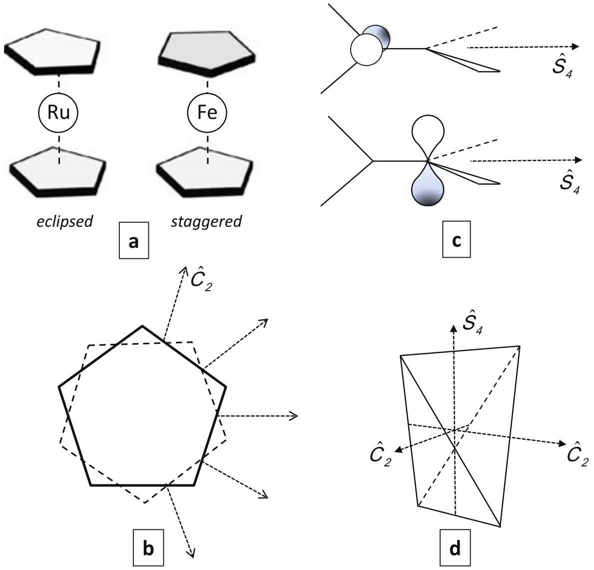


Fig. 3.9 Molecular realizations of cylindrical symmetry: (**a**) D_{5h} ruthenocene in an eclipsed pentagonal prismatic conformation and D_{5d} ferrocene in a staggered pentagonal antiprismatic conformation; (**b**) top view of the pentagonal antiprism with the position of the five twofold axes perpendicular to the pentagonal direction; (**c**) staggered conformation of triplet ethylene with D_{2d} symmetry and horizontal $\hat{S}_4$ axis (in the triplet the two carbon $2p$-orbitals shown are singly occupied); (**d**) alternative view of the D_{2d} symmetry of a bisphenoid, with vertical $\hat{S}_4$ axis

in-plane $\hat{C}_2$ axes. The triplet excited state of ethylene adopts a staggered conformation, which has D_{2d} symmetry (Fig. 3.9(c)). Benzene has prismatic D_{6h} symmetry. In this case, there are two classes of perpendicular twofold axes, which are distinguished in the tables by the labels $\hat{C}_2'$ and $\hat{C}_2''$, and, likewise, two classes of vertical symmetry planes, $\hat{\sigma}_v$ and $\hat{\sigma}_d$. The standard choice for orienting these elements in the hexagonal molecular frame is shown in Fig. 3.10. This choice is conventional and may be changed, but note that the two symmetries are coupled in that the $\hat{\sigma}_v$ planes contain the $\hat{C}_2'$ axes and, similarly, the $\hat{\sigma}_d$ planes contain the $\hat{C}_2''$ axes.

The Rotating Cylinder

Other than geometrical distortions, symmetry breaking of a cylinder may also be realized by a dynamic effect, as in a *rotating cylinder*. In this case, only symmetry elements that will not change the direction of rotation are allowed. As a result, the twofold rotation axes have to be removed, and the cylindrical symmetry is reduced to that of the point group, $C_{\infty h}$. This is the symmetry of an *axial* vector or pseudovector. It corresponds to the spatial symmetry of a magnetic field. Note that this group is abelian, and so are its molecular subgroups, with symmetry C_{nh}. Again, the parity of n is important here. $C_{(2n+1)h}$ groups are cyclic. They have one generator,

Fig. 3.10 Hexagonal D_{6h} symmetry of benzene: Orientation of twofold symmetry elements. $\hat{C}_2'$ and $\hat{\sigma}_v$ pass through opposite atoms; $\hat{C}_2''$ and $\hat{\sigma}_d$ bisect opposite bonds

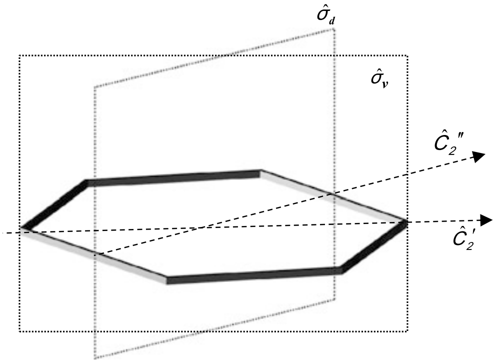
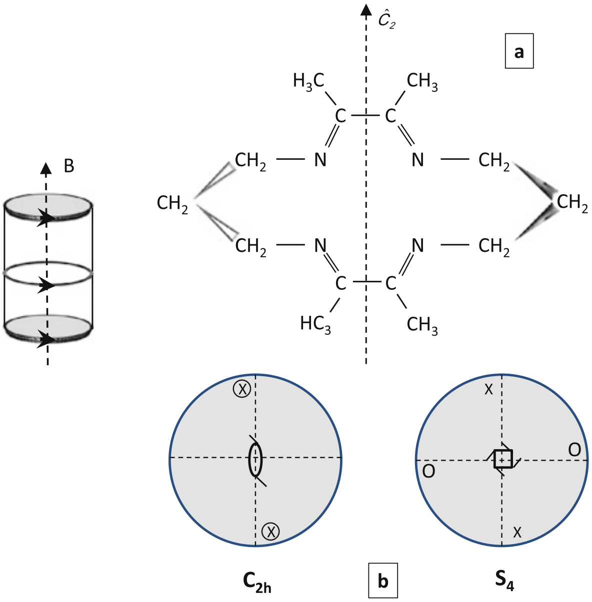


Fig. 3.11 The rotating cylinder has the symmetry of a magnetic field, B, along the cylinder axis. (**a**) shows a tetra-imine macrocycle, with the bridging CH_2 groups below and above the molecular plane; the resulting symmetry group is C_{2h}; (**b**) shows stereographic projections of C_{2h} and S_4



which is a reflection axis, $\hat{S}_{2n+1}$, of order $4n + 2$. For rotations of even order, two kinds of subgroups arise: the C_{2nh} groups and the S_{2n} groups. The latter are not to be confused with the symmetric groups but designate cyclic groups, generated by a $2n$-fold rotation–reflection axis. Figure 3.11 shows the stereographic projections for C_{2h} and S_4, and a molecular realization of C_{2h}. Note that the latter symmetry group is a combination of the three different kinds of binary symmetry elements of the point groups: a twofold rotation, the reflection plane, and the spatial inversion. It reminds us of the famous Euler identity $e^{i\pi} = -1$, which brings together three special numbers: the base of natural logarithms (e), the square-root of -1 (i), and the ratio of the circumference to the diameter of a circle (π).

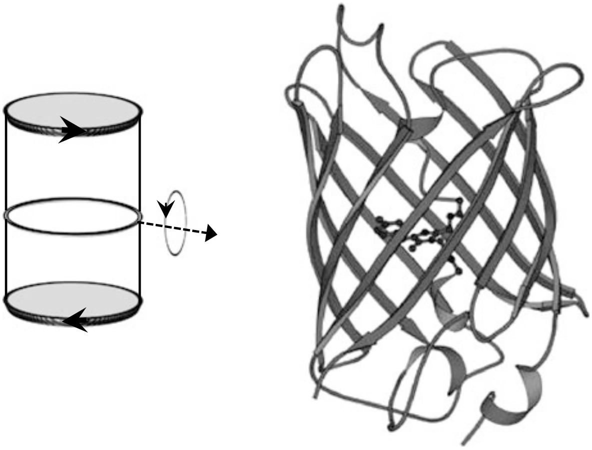


Fig. 3.12 The twisted cylinder. On the right is a cartoon of the green fluorescent protein (GFP). It adopts a β-barrel structure. Eleven β-sheet strands are wound in a helix around the central fluorophore. The approximate symmetry is D_{11}. In the barrel a cleft is opened to provide interactions with the surrounding solvent

The Twisted Cylinder

An alternative symmetry lowering of the cylinder is attained in the twisted cylinder. Here, all improper symmetry elements are broken, the remaining group being the rotational subgroup, D_∞ (see Fig. 3.12). The twist itself can be in two opposite directions, which are mirror images of each other. Molecules of this type may be formed by applying a twist to prisms or antiprisms. A simple example is ethane. In the eclipsed high-energy conformation this is a prism with D_{3h} symmetry, while in the staggered conformation it is an antiprism, D_{3d}. By rotating the two methyl groups with respect to each other in opposite senses about the threefold axis, we may interconvert these two conformations. In between the two extremal conformations the frame adopts the largest common subgroup, which is D_3.

Cones

A cone can be considered as a deformation of a cylinder, in which the poles of the uniaxial direction are no longer equivalent. The symmetry group is reduced accordingly to $C_{\infty v}$, where only the vertical symmetry planes remain. Conical symmetry is exemplified by hetero-nuclear diatomic molecules, but it is also the symmetry of a *polar* vector, such as a translation in a given direction, or a polarized medium or an electric field, etc. Conical molecules have C_{nv} symmetries, as was the case for the ammonia model. Again, the smallest trivial member of this series is C_{2v}, which is fully anisotropic. This is the point group of the water molecule.

The Rotating Cone

Adding a rotation to the cone will destroy the vertical symmetry planes, since reflection in these planes would alter the sense of the rotation. As a result, only rotations

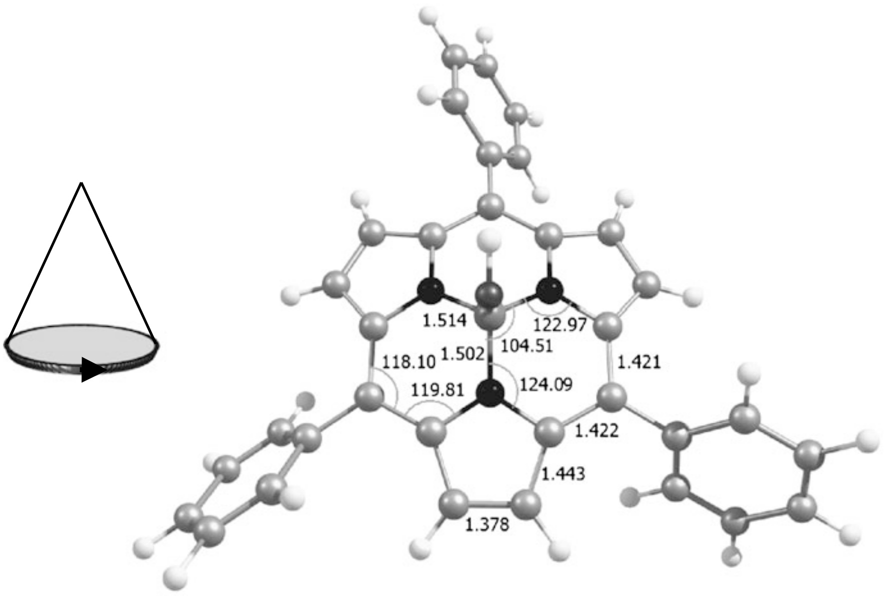


Fig. 3.13 The rotating cone. The molecule is a subporphyrin and consists of a central boron in a tri-pyrrole macrocycle. The subporphyrin itself has the shape of a trigonal dome and exhibits C_{3v} symmetry. Three phenyl substituents at the meso-positions are arranged like a propeller and reduce the symmetry to C_3. A further symmetry lowering to C_1 is caused by an apical hydroxyl substituent at the boron position, with its hydrogen pointing in the direction of the upper phenyl group

around the axis of the cone are retained, limiting the symmetry group to C_∞. Its molecular point groups are the cyclic groups, C_n. These symmetries are encountered in propeller-like molecules. An example of a subporphyrin [7] is shown in Fig. 3.13. The smallest nontrivial C_n group is found for $n = 2$. This is the symmetry of the Möbius strip, which may also be attained in Möbius-type annulenes.

3.8 Rotational Groups and Chiral Molecules

The symmetry operations that we have encountered are either *proper* or *improper*. Proper symmetry elements are rotations, also including the unit element. The improper rotations comprise planes of symmetry, rotation–reflection axes, and spatial inversion. All improper elements can be written as the product of spatial inversion and a proper rotation (see, e.g., Fig. 1.1). The difference between the two kinds of symmetry elements is that proper rotations can be carried out in real space, while improper elements require the inversion of space and thus a mapping of every point onto its antipode. This can only be done in a virtual way by looking at the structure via a mirror. From a mathematical point of view, this difference is manifested in the sign of the determinant of the corresponding representation matrices in the (x, y, z) basis. For proper rotations, the determinant is equal to $+1$. For improper rotations, it is equal to -1. This minus sign comes from the representation matrix for the inversion centre, which corresponds to minus the unit matrix:

$$\hat{\imath}\begin{pmatrix} x & y & z \end{pmatrix} = \begin{pmatrix} x & y & z \end{pmatrix}\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{pmatrix} \tag{3.34}$$

Since the determinant of a matrix product is the product of the determinants of the individual matrices, multiplication of proper rotations will yield again a proper rotation, and for this reason, the proper rotations form a rotational group. In contrast, the product of improper rotations will square out the action of the spatial inversion and thus yield a proper rotation. For this reason, improper rotations cannot form a subgroup, only a coset. Since the inversion matrix is proportional to the unit matrix, the result also implies that spatial inversion will commute with all symmetry elements.

In all the point groups with improper rotations, we shall thus always also have a rotational subgroup, like D_n in D_{nd} or D_{nh}, or T in T_d and T_h, etc. Moreover, this rotational subgroup is always a halving subgroup, i.e., its order is half the order of the full group. This can easily be demonstrated. Let H_{rot} be the rotational subgroup of G, and consider an improper symmetry element, $\hat{S}_i$, as coset generator. The coset $\hat{S}_i H_{\text{rot}}$ will contain only improper symmetry elements, and its order will be equal to $|H_{\text{rot}}|$. Now is it possible that the group contains additional improper elements, outside this coset? Suppose that we find such an element, say $\hat{S}_j$. Of course, the product $\hat{S}_i^{-1}\hat{S}_j$ is the combination of two improper elements and thus must be a proper rotation, included in the rotational subgroup. Let us denote this element as $\hat{R}_z$. Hence, it follows that

$$\hat{S}_i \hat{R}_z = \hat{S}_i \hat{S}_i^{-1} \hat{S}_j = \hat{S}_j \tag{3.35}$$

This result confirms that S_j is included in the coset of $\hat{S}_i$ and thus implies that there is only one coset of improper rotations, covering half of the set of symmetry elements.

A group is a *direct product* of two subgroups, H_1 and H_2, if the operations of H_1 commute with the operations of H_2 and every operation of the group can be written uniquely as a product of an operation of H_1 and an operation of H_2. This may be denoted in general as

$$G = H_1 \times H_2 \tag{3.36}$$

This is certainly the case when a group is *centrosymmetric*, i.e., when it contains an inversion centre. Since the inversion operation commutes with all operations, a centrosymmetric group can be written as the direct product $C_i \times H_{\text{rot}}$, where $C_i = \{\hat{E}, \hat{\imath}\}$. However, direct product groups are not limited to centrosymmetry. In the group D_{3h}, for example, the horizontal symmetry plane forms a separate conjugacy class, which means that it commutes with all the operations of the group. It thus

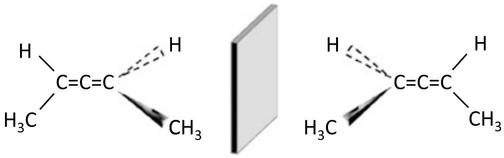


Fig. 3.14 Dimethyl substituted allene occurs in two chiral forms, which are the mirror image of each other, and cannot be superimposed; the point group of each form is C_2

generates a normal C_s subgroup. The full group D_{3h} can then be written as a direct product of this normal subgroup and the rotational subgroup:

$$D_{3h} = C_s \times D_3 \tag{3.37}$$

When the symmetry of a molecule is a purely rotational group, then the molecule does not coincide with its mirror image, and there will be two copies of it, which relate to each other as do right and left hands. This is illustrated in Fig. 3.14. Molecules with only rotational symmetry are *chiral*, meaning that the molecule and its reflection form optical antipodes. A synonym is *enantiomeric*, which literally means: on both sides of the mirror. By contrast, when a molecular point group contains any improper symmetry element, the molecule will be congruent to its mirror image and is *achiral*. Why does the absence of an improper symmetry element prevent the molecule's coinciding with its mirror image? Congruence operations are whole rotations and/or translations that are performed in order to superimpose the image on the object. As we have shown, when reflecting a molecule through a mirror, spatial inversion is implied, and this cannot be undone by rotations or translations, but only by another improper symmetry element that restores the inversion. Such symmetry elements are absent in molecules with only rotational point group symmetries, and, hence, they cannot be made to coincide with their mirror image. Molecular chirality thus derives from an obvious and basic symmetry characteristic; nonetheless, it has far reaching physical and chemical consequences. Chiral molecules are optically active, which means that the plane of polarization of linearly polarized light is rotated when passing through a medium with chiral molecules. The absorption coefficients of chiral molecules for left- and right-circularly polarized light are also different, giving rise to natural circular dichroism (CD) spectra. This will be illustrated in Sect. 6.8. The chemical consequences of chirality are of vital importance: living organisms are based on biochemical molecules with strict chirality.

3.9 Applications: Magnetic and Electric Fields

In many spectroscopic applications external magnetic or electric fields are applied to a molecular sample. For magnetic fields, the perturbing influence of the field is known as the Zeeman effect. Electric fields give rise to the Stark effect. As we have seen, uniform magnetic and electric fields have symmetries $C_{\infty h}$ and $C_{\infty v}$, respectively. In this case, the symmetry group of the experiment will be constrained to these operations, which leave the $\{\text{molecule} + \text{field}\}$ combination invariant. It

Table 3.6 Symmetries of a tetrahedral molecule in a uniform magnetic (B) or electric (E) field

	$\hat{E}$	$8\hat{C}_3$	$3\hat{C}_2$	$6\hat{S}_4$	$6\hat{\sigma}_d$	$T_d \cap C_{\infty h}$
$B \parallel \hat{S}_4$	$\hat{E}$		$\hat{C}_2$	$2\hat{S}_4$		S_4
$B \parallel \hat{C}_3$	$\hat{E}$	$2\hat{C}_3$				C_3
$B \perp \hat{\sigma}_d$	$\hat{E}$				$\hat{\sigma}_d$	C_s
						$T_d \cap C_{\infty v}$
$E \parallel \hat{S}_4$	$\hat{E}$		$\hat{C}_2$		$2\hat{\sigma}_d$	C_{2v}
$E \parallel \hat{C}_3$	$\hat{E}$	$2\hat{C}_3$			$3\hat{\sigma}_d$	C_{3v}
$E \in \hat{\sigma}_d$	$\hat{E}$				$\hat{\sigma}_d$	C_s

will thus consist only of symmetry elements that are common to both parts. These elements form the *intersection* of both symmetry groups. The elements of an intersection themselves form a group, which is the largest common subgroup of both symmetry groups. This can be written as follows:

$$\begin{aligned} \text{magnetic field}: H &= G \cap C_{\infty h} \\ \text{electric field}: H &= G \cap C_{\infty v} \end{aligned} \tag{3.38}$$

This intersection group will depend on the orientation of the field in the molecular frame. In Table 3.6 we work out an example of a tetrahedral molecule. The top row lists the symmetry elements of T_d. The fields can be oriented along several directions. The highest symmetry positions are along the fourfold or threefold axes. A lower symmetry position is within or perpendicular to a symmetry plane, or finally along an arbitrary direction with no symmetry at all. In Appendix B we list representative intersection groups for several point groups and orientations. Note that in the case of a magnetic field, the resulting intersection group is always abelian. This is of course a consequence of $C_{\infty h}$ being abelian.

3.10 Problems

3.1 The multiplication table of a set of elements is given below. Does this set form a group?

	A	B	C	D
A	C	D	A	B
B	D	C	B	A
C	A	B	C	D
D	B	A	D	C

3.2 Use molecular ball and stick models to construct examples of molecules that have a reflection plane as the only symmetry element. Similarly, for a center of inversion and for a twofold axis. In each case find the solution with the smallest number of atoms! Explain your reasoning. What is the smallest molecule with no symmetry at all?

3.3 The 2D analogue of a polyhedron is a polygon. In a regular polygon all vertices, edges, and angles between adjacent edges are identical. A 2D plane can be tessellated in identical regular polygons, which then form a covering of the plane. In how many ways can this be performed?

3.4 Why is the order of a rotational axis of a polyhedral object always an integer?

3.5 Prove that a halving subgroup is always a normal subgroup.

3.6 Determine the point group of a soccer ball, a tennis ball, a basketball, and a trefoil knot.

3.7 The parameter equations defining a helix in Cartesian space are given by

$$x(t) = a\cos\left(\frac{nt}{a}\right)$$

$$y(t) = a\sin\left(\frac{nt}{a}\right)$$

$$z(t) = t$$

Here a is the radius. Is this helix left- or right-handed? Write down the parameterization of its enantiomer. The symmetry of a helix is based on a screw axis, which corresponds to a translation in t. It is composed of a translation along the z-direction with a concomitant rotation in the xy-plane. Now decorate the helix with atoms at points $t_k/a = 2\pi k/m$, where k and m are integers. Determine the screw symmetry of this molecular helix. If n/m is irrational, the helix is *noncommensurate*. Will it still have a symmetry in this case?

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