

gements is called "the order" of the rotation axis. Thus one can have 2-, 4- and 6-fold rotation axes, corresponding to invariance under rotations 180°, 120°, 90°, and 60°. For single molecules it is also possible to have 5-fold, 7-fold, etc., axes. Small solid aggregates (clusters) may also display 5-fold rotational symmetry. An example is the particularly stable polyhedron composed of 13 atoms. Icosahedra are formed in the rapid quenching of melts. The solid which is thus formed has a quasi-crystalline structure and produces sharp X-ray diffraction spots that reflect the local 5-fold symmetry [2.1]. For strictly periodic crystals, however, only 2-, 3-, 4- and 6-fold rotation axes are possible. All other orders of rotation are incompatible with the required translational symmetry. The notation describing the possible axes of rotation is given simply by the numbers 2, 3, 4 and 6.

The cyclohexane molecule shown in Fig. 2.4 has a 3-fold rotation axis, a molecule with a 6-fold axis is benzene (C_6H_6), whose carbon skeleton consists of a planar regular hexagon.

Rotation-Inversion Axes

Rotation with simultaneous inversion can be combined to give a new symmetry element — the rotation-inversion axis. It is symbolized by 2, 3, 4, or 6. Figure 2.5 illustrates a 3-fold rotation-inversion axis. From this it is evident that a 3-fold rotation-inversion axis is equivalent to a 3-fold rotation together with inversion. The 6-fold rotation-inversion axis may alternatively be represented as a 3-fold rotation axis plus a mirror plane.

$\bar{3} = 3 + i$

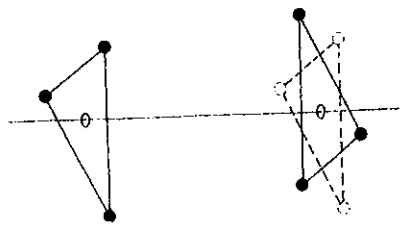


Fig. 2.5. Representation of a 3-fold rotation-inversion axis. The effect can also be described by the combination of other symmetry elements

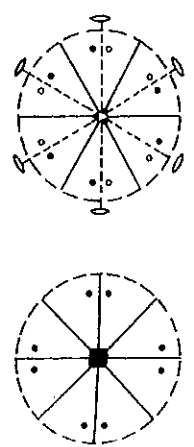
2.3 The 32 Crystal Classes (Point Groups)

The symmetry elements discussed in the previous section may be combined with one another in various ways. Conversely, every crystal may be described by a particular combination of point-symmetry elements. To be complete, the description must satisfy a number of conditions. For example, if two successive symmetry operations are applied, the result must be a further symmetry element: $A \otimes B = C$. Three (or more successive symmetry operations must obey the so-called associativity rule: $(A \otimes B) \otimes C = A \otimes (B \otimes C)$. There is an identity element E , corresponding to no operation or to a rotation about 360°, such that $A \otimes E = A$. Furthermore, every symmetry element A possesses an inverse A^{-1} , which corresponds to the reverse operation, so that $A^{-1} \otimes A = E$. These properties are the mathematical definition of a group. There are 32 distinct crystallographic point groups. If the translational symmetry is also taken into account then one obtains the 230 possible space groups. Although not necessarily true in general, we should note that for translations $A \otimes B = B \otimes A$ (the property of Abelian groups).

The 32 crystallographic point groups are most commonly represented by so-called stereographic projections. These projections were developed by crystallographers in order to obtain a systematic classification of the exposed surfaces of naturally grown crystals. The point at which each surface normal intersects a sphere is marked and then projected onto the plane perpendicular to the highest order symmetry axis. Intersection points above this plane are marked by a full circle, and those on the lower half sphere by an open circle or a cross. Hence, in the systematic representation of the point groups, the highest order axis lies in the center. Stereographic projections of two point groups are shown in Fig. 2.6. A particular point group may be denoted in three different ways:

- 1) by specifying a system of generating symmetry operations;
- 2) by specifying the international point group symbol;
- 3) by the Schönflies symbol.

The notation based on the generating symmetry operators is common in crystallography, whereas the Schönflies symbols have largely been adopted in group theory and spectroscopy. The Schönflies notation consists of a



$4m\bar{m} = C_{4v}$ $\bar{3}m = D_{3d}$

Fig. 2.6. Representation in stereographic projection of the symmetry elements of two point groups. The symbols (○), (▲) and (■) denote 2-, 3-, and 4-fold rotation axes. The full lines are mirror planes. When the outer circle is also drawn as a full line, this indicates that the plane of the drawing is also a mirror plane

Table 2.2. The Schönflies point group symbols

Classification according to rotation axes and principal mirror planes	Symbol	Meaning
C_j	$(j=2, 3, 4, 6)$ j -fold rotation axis	
S_j	j -fold rotation-inversion axis	
D_j	j two-fold rotation axes \perp to a $(j$ -fold) principal rotation axis	
T	4 three- and 3 two-fold rotation axes as in a tetrahedron	
O	4 three- and 3 four-fold rotation axes as in an octahedron	
C_i	a center of inversion	
C_h	a mirror plane	
h	horizontal = perpendicular to the rotation axis	
v	vertical = parallel to the main rotation axis	
d	diagonal = parallel to the main rotation axis in the plane bisecting the 2-fold rotation axes	

main symbol that characterizes the axes of rotation (if any) of the system, and a subsidiary symbol that gives the positions of the symmetry planes. The symbols and their meanings are summarized in Table 2.2. As an example, we consider the water molecule, for which the highest order rotation axis is a 2-fold axis. The symmetry planes are vertical, i.e. they lie parallel to the main axis of rotation. The corresponding Schönflies symbol is C_{2v} . A cube has three 4-fold rotation axes, four 3-fold rotation axes and symmetry planes perpendicular to the 4-fold axes. Its Schönflies symbol is O_h .

2.4 The Significance of Symmetry

To the uninitiated, the correct assignment and symbolization of symmetry often seems complicated and confusing. It will thus be useful to give a brief overview of the importance of symmetry in the description of a solid. For this purpose, we must base our discussion on quantum mechanics. As we have seen, the water molecule, for example, has two mirror planes. The presence of these two mirror planes must somehow be reflected in all the physical properties of the molecule. When the electronic or vibrational properties of the molecule are described by a Hamiltonian, then this has 2-fold mirror symmetry, i.e., it remains invariant under the corresponding coordinate transformation. This invariance can also be expressed in other ways. An operator σ is assigned to the reflection. When σ operates on the Hamiltonian \mathcal{H} , on an eigenstate ψ or on \mathbf{R} , the result should describe \mathcal{H} , ψ or \mathbf{R} in the transformed (mirror image) coordinates.

Such operators are represented as matrices. Thus the reflection of coordinates in the yz -plane is represented by the matrix operation

$$\begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = \begin{pmatrix} -x \\ y \\ z \end{pmatrix}$$

This is a three-dimensional representation. The same operation can also be expressed in terms of three one-dimensional matrices,

$$[(-1)x; (1)y; (1)z] = (-x; y; z),$$

each of which acts on only one coordinate component. In this case three-dimensional representation is known as "reducible", whereas the corresponding one-dimensional representation is called "irreducible" since cannot be further simplified. It is easy to see that the irreducible representation of a rotation through 180° (a 2-fold rotation axis) is also one-dimensional: for a suitable choice of coordinates, it can be expressed simply by sign reversal. However, for 3-, 4- and 6-fold rotation axes, except for case of a 360° rotation, the operations always involve two coordinate changes. The irreducible representation is therefore two-dimensional.

If the Hamiltonian operator possesses a particular symmetry, for example mirror symmetry, then it makes no difference whether the reflection operation appears before or after the Hamiltonian operator, i.e., the two operators commute. As is well known from quantum mechanics, such operators have a common set of eigenstates. Thus the possible eigenstates of can be classified according to their eigenvalues with respect to the symmetry operators. In the case of mirror symmetry and that of a 2-fold rotation axis C_2 , one has $\sigma^2=1$ and $C_2^2=1$ and thus the eigenvalues can only be

$$\begin{aligned} \sigma \psi_+ &= +\psi_+, & C_2 \psi_+ &= +\psi_+, \\ \sigma \psi_- &= -\psi_-, & C_2 \psi_- &= -\psi_-. \end{aligned}$$

The eigenstates of \mathcal{H} may therefore be either symmetric or antisymmetric with respect to these operators. This is often expressed by saying that eigenstates have even or odd "parity". We have already met an example of even and odd parity in our discussion of the chemical bonding between diatomic atoms (Sect. 1.2). The bonding state was a symmetric combination of atomic wavefunctions and therefore a state of even parity. As see in this example, the eigenstates ψ_+ and ψ_- belong to distinct eigenvalues. The corresponding energy levels are thus nondegenerate. From this we may conclude, for example, that the water molecule can possess only one degenerate energy states (we ignore here any accidental degeneracy of energy levels or normal mode vibrations).

To illustrate the above discussion we will apply these ideas to the normal mode vibrations of the water molecule. Accordingly, the atoms move symmetrically or antisymmetrically with respect to the two mirror planes of the molecule. For atoms that lie in a mirror plane, antisymmetric motion with respect to the plane implies motion perpendicular to the plane since only then can reflection reverse the motion. The corresponding