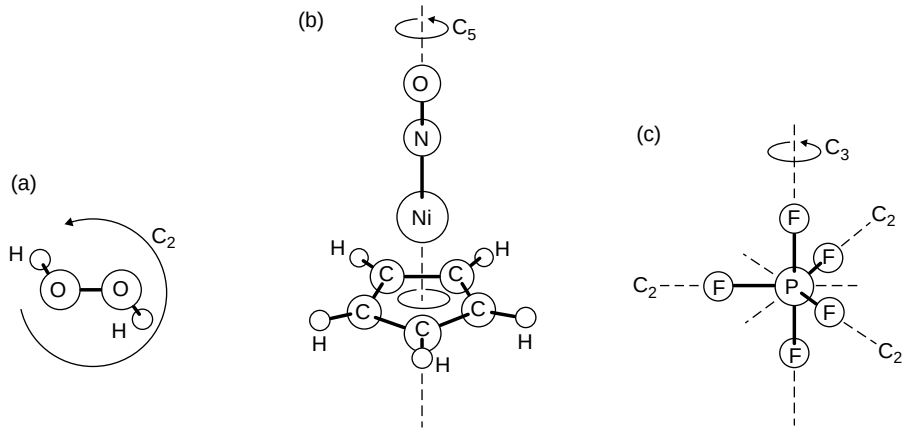

Figure 2.4
Rotation axes relating equivalent atoms in (a) H_2O_2 (C_2), (b) $[Ni(C_5H_5)(NO)]$ (C_5), and (c) PF_5 (C_3 and three C_2).

2.3.1 Symmetry operations and elements

We begin our discussion with the idea of a symmetry operation, which is a process that generates a configuration indistinguishable from the initial one. In total there are five different types of symmetry operation for a single object such as a molecule, namely rotation, inversion, reflection, rotation-reflection, and identity. While the symmetry operation describes the process, the symmetry element describes the property that the molecule must possess in order for that operation to be performed. For example, the symmetry operation 'rotation' requires that the molecule possesses the symmetry element 'an axis of rotation', the operation 'inversion' requires the molecule to possess the element 'inversion center', and so on. There is a proposed convention that the symmetry operation should be written in an italic font and the element in an upright (Roman) font, so, for example, you can perform a C_2 operation around a C_2 axis, and so on.

The rotation operation is defined by 'a rotation about an axis by $2\pi/n$ (i.e. $1/n$th of a revolution), where n is an integer'. This type of operation is given the symbol C_n. Some examples of rotational symmetry in molecules are shown in Figure 2.4. Where only a single rotation axis exists it is conventionally assigned as the z axis, otherwise known as the principal axis; if more than one rotational axis is present then the z axis is assigned to the one with the highest order (that is, the highest value of n).

The second symmetry operation on our list is inversion, which operates through a point, called an inversion center, as shown in Figure 2.5. We give this the symbol i. Next is the reflection operation (denoted

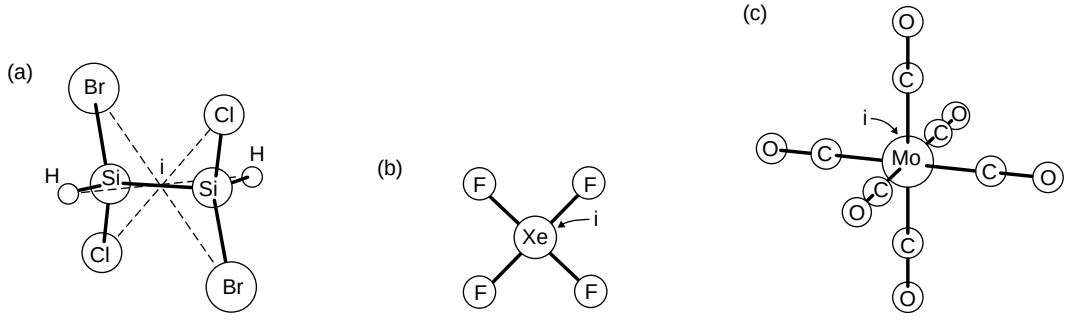

Figure 2.5
Inversion centers relating equivalent atoms in (a) $(SiBrClH)_2$, (b) XeF_4, and (c) $Mo(CO)_6$.

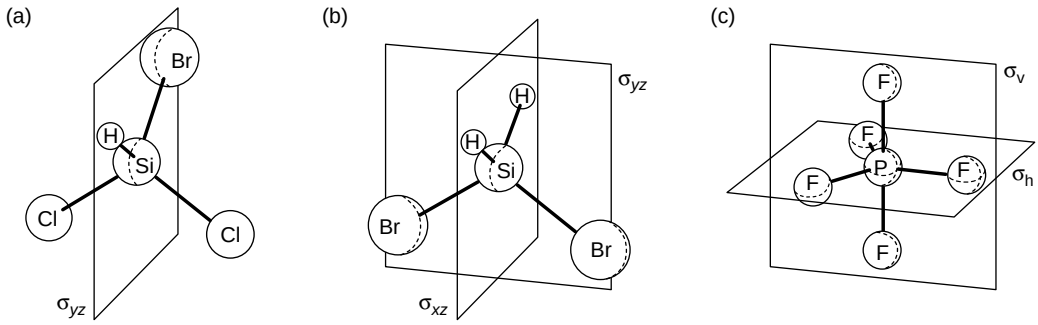

Figure 2.6
Mirror planes relating equivalent atoms in (a) $SiBrCl_2H$, (b) SiH_2Br_2 (two vertical planes, σ_v), and (c) PF_5 (one of three vertical mirror planes, σ_v, and one horizontal plane, σ_h).

by the symbol σ, which can bear the subscripts 'v' or 'h' indicating vertical or horizontal with respect to the principal axis (which is always presumed to be vertical), or 'd' (dihedral, defined in the next section), or two labels of the Cartesian axis system that define the mirror plane directly. Examples of this symmetry operation are illustrated for several molecules in Figure 2.6.

We can also describe the symmetry of a molecule using the compound rotation-reflection operation, i.e. 'rotate about an axis by $2\pi/n$ and then reflect in the plane perpendicular to that axis'. This type of operation is given the symbol S_n. The symmetry element consists of an axis and a plane. Examples of rotation-reflection operations are shown in Figure 2.7. It is crucial to note that the reflection plane must be perpendicular to the rotation axis. Also, a rotation-reflection axis of order $2n$ will be associated with a pure-rotation axis of order n.

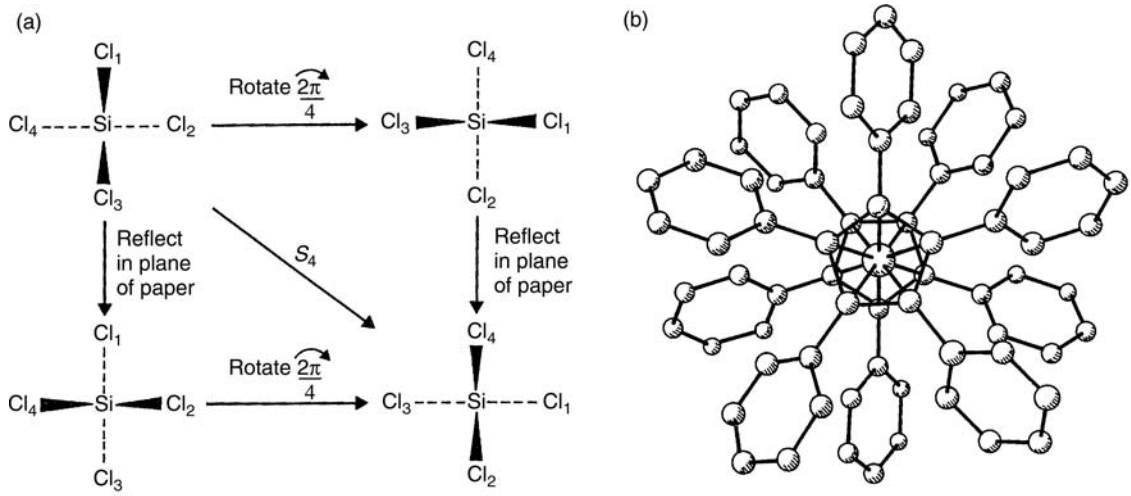

Figure 2.7
Rotation-reflection operations in (a) $SiCl_4$, drawn looking down the S_4 axis; note that in this example neither the rotation by $2\pi/4$ by itself nor the reflection in a plane perpendicular to this axis generate a configuration equivalent to the initial one, but the combined operation does; (b) $Sn(\eta^5\text{-}C_5Ph_5)_2$, showing an almost perfect S_{10} operation, looking down the axis. Reprinted with permission from [2]. Copyright 1984 American Chemical Society.