Chapter 1

# Symmetry Elements and Symmetry Operations

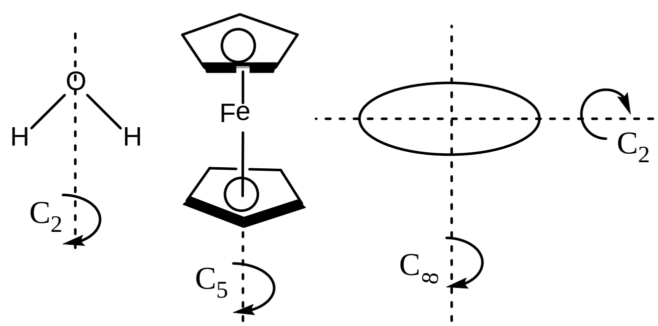
A given system has ***symmetry*** if certain parts of that system can be interchanged without altering its energy or identity. Thus the system has parts that are ***equivalent*** to one another by symmetry.

Equivalent parts of a given system can be interchanged by certain geometrically defined ways so called ***symmetry operations***. The axis, plane or point, through which symmetry operation is performed, is called ***symmetry element***.

There are five types of symmetry operations as following:

***1. Proper rotation ($C_n$) through an axis of symmetry:***

If, on rotation about an axis by (2π/n) radians the system retains its identity, then the system is claimed to have a proper rotation, $\boldsymbol{C_n}$. Examples of molecules that contain $C_2$, $C_5$ and $C_8$ proper rotation operations are structures I, II and III .




I II III

Although rotation could be clockwise or anti-clockwise, the clockwise rotation is normally considered. The effect of a $C_n$ operation on a given arrow, OA, can be represented by a 3(row) × 3(column) matrix. Figure (1.1) shows how a matrix representing the effect of a (1/2 turn) rotation about z-axis, $C_2(z)$, on point A, can be generated:

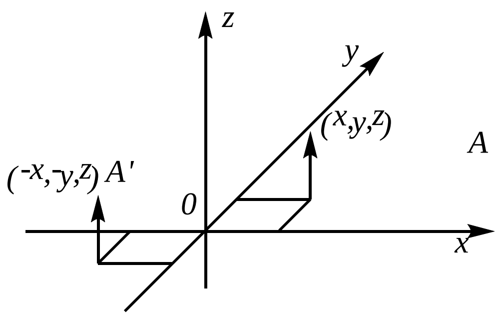



Figure (1.1): A schematic showing effect of $C_2(z)$ rotation on a given point ($x$, $y$, $z$).

The $C_2(z)$ shifts point A to point A', and the new coordinates for point A' will be as shown in equation (1):

$$\begin{aligned} new\,x &= (-1)\,x + (0)\,y + (0)\,z \\ new\,y &= (0)\,x + (-1)\,y + (0)\,z \\ new\,z &= (0)\,x + (0)\,y + (1)\,z \end{aligned} \tag{1}$$

From equation (1), the matrix representing the effect of $C_2(z)$ on point A($x$, $y$, $z$) is:

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

With a character: $\chi = (-1) + (-1) + (1) = 1$

Similarly, the effects of other $C_n(z)$ operations can be studied, and the representing matrices be generated. The general matrix that represents the effect of any $C_n(z)$ operation on a given point is:

$$\begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

It should be noted, however, that a $C_n$ operation can be repeated once or more, to create several $C_n$ operations as exemplified in Figure (1.2).

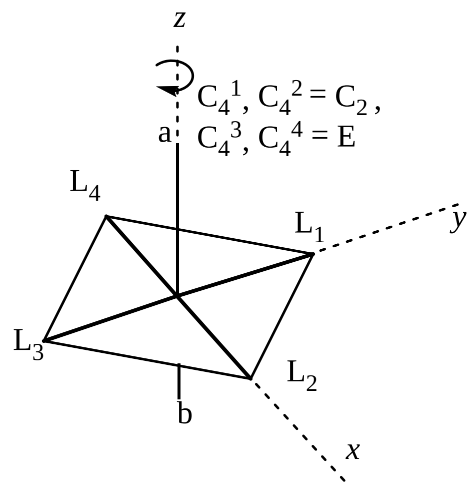



Figure (1.2): Repeated $C_4(z)$ operations on equivalent parts $L_1$, $L_2$, $L_3$ and $L_4$ of a given system.

In Figure (1.2) a $C_4^{1}(z)$ operation would create the following transformations:

$$\begin{array}{lcl} L_1 & \longrightarrow & L_2 \\ L_2 & \longrightarrow & L_3 \\ L_3 & \longrightarrow & L_4 \\ L_4 & \longrightarrow & L_1 \end{array}$$

Whereas a $C_4^{1}(z)$ rotation followed by another $C_4^{1}(z)$ rotation, $C_4^{2}(z)$, the overall effect becoming $C_2(z)$, creates the following transformations:

$$\begin{array}{lcl} L_1 & \longrightarrow & L_3 \\ L_2 & \longrightarrow & L_4 \\ L_3 & \longrightarrow & L_1 \\ L_4 & \longrightarrow & L_2 \end{array}$$

The sum of four consecutive $C_4^{1}(z)$ operations is a $C_4^{4}(z)$ operation. By looking at its effects, the $C_4^{4}(z)$ operation is clearly equivalent to a no-effect operation, so called ***identity operation***, $E$, as will be seen later.

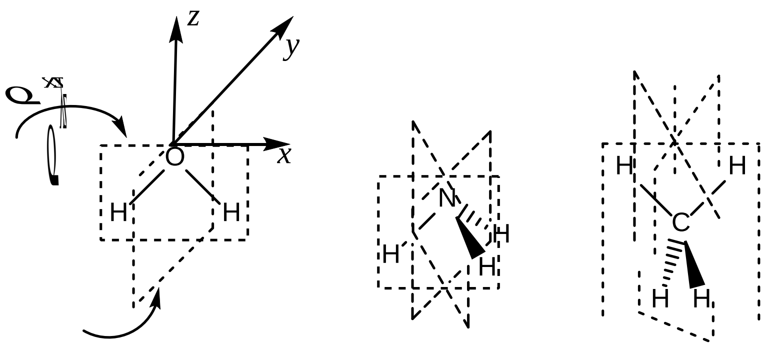
**Example:** Write down the matrix representing the effect of $C_2(x)$ on point $(x, y, z)$.

**Answer:** The matrix is

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

***2. Reflection (σ) through a mirror plane:***

If the system retains its identity on reflection through a plane (that bisects the system) then the system is claimed to have a reflection (σ) operation. Examples of molecules that have one or more reflection planes are shown in structures IV-VI below.




IV V VI

Water molecule, $H_2O$, has two reflection planes as shown in IV. One plane is that of the molecule $\sigma_{xz}$, and the other is perpendicular to it. Ammonia (V) has three planes, and methane (VI) has six ones.

| |
|---|
| Exercise: Draw structures for $NH_2F$, $CH_2Cl_2$ and show all $C_n$ and σ-operations present in each. |

Reflection operations can be represented by matrices. Reflection of point A($x$, $y$, $z$) through $\sigma_{xz}$ would yield point A''($x$, $y$, $z$), thus:

$$\begin{aligned} new\, x &= (1)\ x + (0)\ y + (0)\ z \\ new\, y &= (0)\ x + (-1)\ y + (0)\ z \\ new\, z &= (0)\ x + (0)\ y + (1)\ z \end{aligned} \qquad (2)$$

From equation (2), the matrix representing the effect of $\sigma_{xz}$ reflection on point A is:

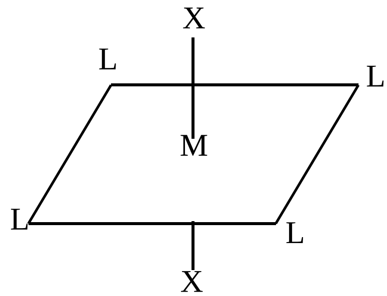
$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

with a character $\chi = 1$. Similarly other reflection operations $\sigma_{yz}$ and $\sigma_{xy}$ can be represented by corresponding matrices, shown below, respectively.

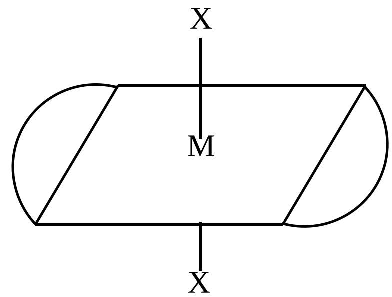
$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \text{ and } \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$$

### ***3. Inversion (i) through a point:***

Each of the structures given below has an inversion operation, where inversion occurs through a point situated at the center of the molecule, as shown in VII and VIII below.




VII




VIII

The inversion operation shifts point A($x$, $y$, $z$) through the origin to point A''($x$, $y$, $z$). Figure (1.3) explains that.

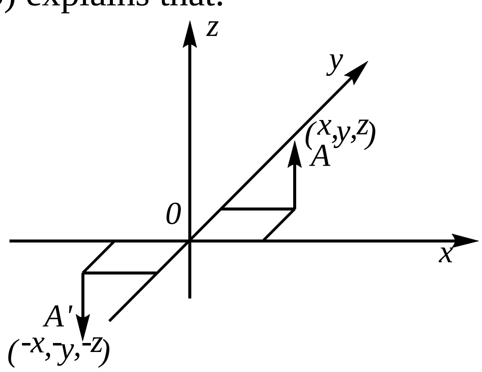



Figure (1.3): A schematic showing effect of $i$ operation on a given point ($x$, $y$, $z$).

thus:

$$\begin{aligned} new\,x &= (-1)\,x + (0)\,y + (0)\,z \\ new\,y &= (0)\,x + (-1)\,y + (0)\,z \\ new\,z &= (0)\,x + (0)\,y + (-1)\,z \end{aligned} \qquad (3)$$

and from equations (3) the matrix representing the $i$ operation is:

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

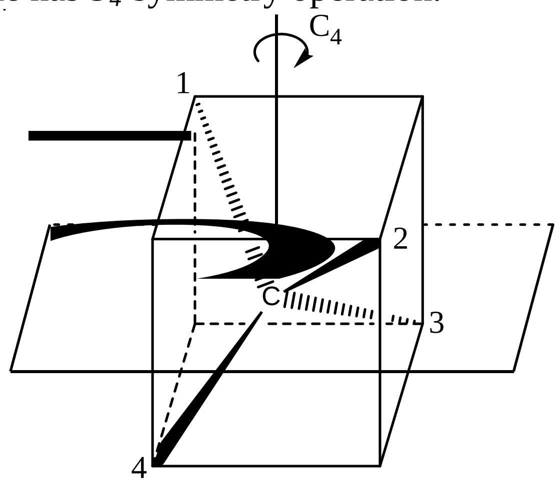
with a character $\chi = -3$.

### 4. *Improper rotation ($S_n$):*

This operation is a combination of two operations performed successively, a ($C_n$) and a perpendicular reflection ($\sigma_{\perp}$) as shown in equation (4).

$$\sigma \times C_n = S_n \tag{4}$$

Methane, $CH_4$, has no $C_4$ or a perpendicular σ independently. A $C_4$ operation, followed by a $\sigma_{\perp}$, would shift $H_{(1)}$ to $H_{(3)}$ as shown in IX below. Therefore, methane has $S_4$ symmetry operation.




IX

The $S_n$ is as a $C_n(z)$ rotation in this case, followed by a reflection through a plane, $\sigma_{xy}$, perpendicular to it. Therefore, the matrix representing $S_n$ operation is deduced by multiplying the matrices representing $\sigma_{xy}$ and $C_n(z)$ operations as shown in equations (5 - 6). Appendix (A) gives a quick reference to matrix multiplication.

$$\sigma_{xy} \quad \times \quad C_{n(z)} \quad = \quad S_{n(z)} \tag{5}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \times \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} \cos(2\pi/n) & \sin(2\pi/n) & 0 \\ -\sin(2\pi/n) & \cos(2\pi/n) & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{6}$$

Exercise: Write down the matrix that represents effect of $S_{4(z)}$ on point ($x$, $y$, $z$).

### 5. *The identity operation (E):*

This is a *no-effect* operation that is equivalent to doing nothing on the system. Therefore, every system should have the *E* operation, which shifts point A($x$, $y$, $z$) to itself. From equation (7):

$$\begin{aligned} new\,x &= (1)\ x + (0)\ y + (0)\ z \\ new\,y &= (0)\ x + (1)\ y + (0)\ z \\ new\,z &= (0)\ x + (0)\ y + (1)\ z \end{aligned} \qquad (7)$$

the operation *E* is represented by the matrix:

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

It should be noted that multiplying two symmetry operations means performing the two operations successively on a given system. The net effect equals a single operation. Thus, equation (8)

$$A \times B = F \qquad (8)$$

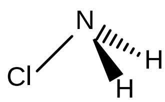
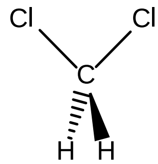
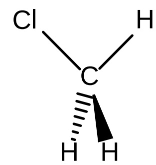
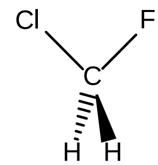
implies that if operation B is performed, followed by performing operation A, the result is equal to the result of operation F. The order of performing operations that are multiplied together is to start with the one on the right. Therefore, in equation (8) we start with B then with A. It should be noted that symmetry operation multiplications are not necessarily commutative, and B × A does not necessarily equal A × B.

Other additional useful relations in symmetry operation multiplications are shown below.

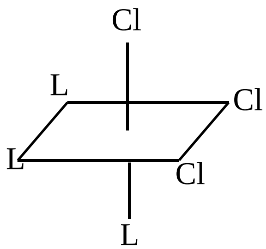
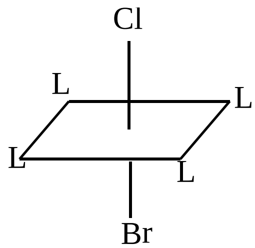
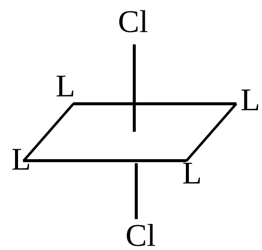
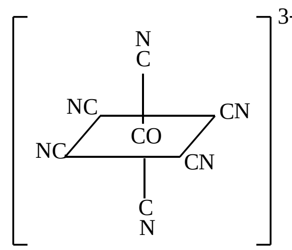
| | | | | |
|---|---|---|---|---|
| $C_n$ | $C_4^2 = C_2$ | $C_6^2 = C^3$ | | $C_2^2$ , $C_3^3$, $C_6^6$ $C_n^n = E$ |
| $S_2$ | $S_2 = i$ | $S_2^2 = E$ | | |
| $S_3$ | $S_3^2 = C_3^2$ | $S_3^3 = \sigma_h$ | $S_3^4 = C_3$ | $S_3^6 = E$ |
| $S_4$ | $S_4^2 = C_2$ | $S_4^4 = E$ | | |
| $S_6$ | $S_6^2 = C_3$ | $S_6^3 = i$ | $S_6^4 = C_3^2$ | $S_6^6 = E$ |

**Exercises**:

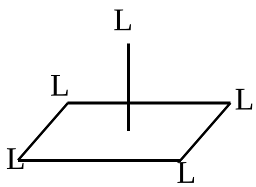
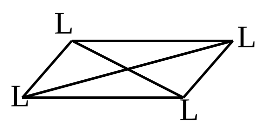
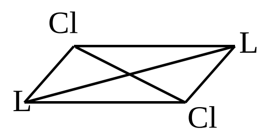
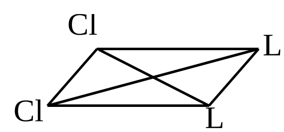
1) For each of the following species, find out all existing symmetry operations:

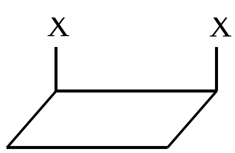
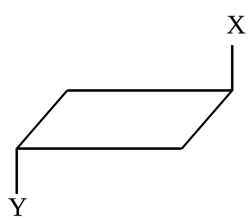
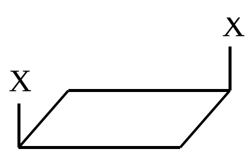
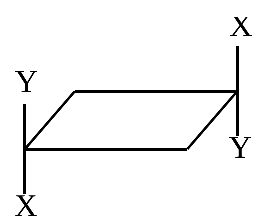
*i* *ii* *iii* *iv*

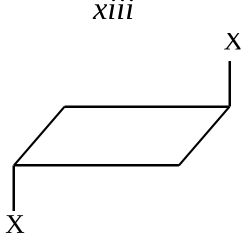
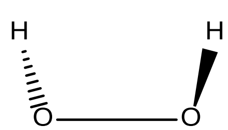
*v* *vi* *vii* *viii*

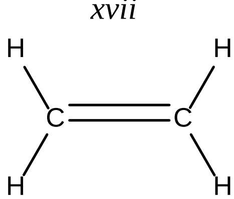
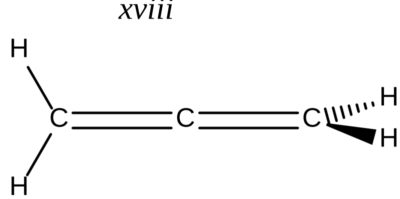
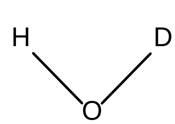
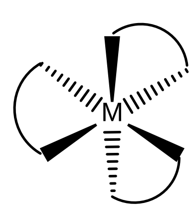
*ix* *x* *xi* *xii*

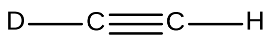
*xiii* *xiv* *xv* *xvi*

*xvii* *xviii* *xix* *xx*

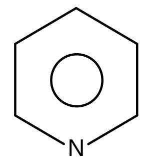
   

*xxi* *xxii* *xxiii* *xxiv*

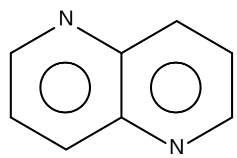



$Ni(CO)_4$

$[Pt(CN)_4]^{2-}$

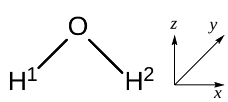



*xxv* *xxvi* *xxvii* *xxviii*

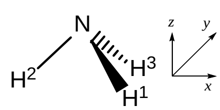



*xxix*

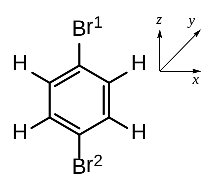
2) In each of the following species, show the operation resulting from multiplying the stated symmetry operations:



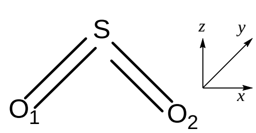

1. $\sigma_{xz} \times \sigma_{yz} =$
2. $C_{2(z)} \times \sigma_{xz} =$
3. $\sigma_{yz} \times \sigma_{yz} =$



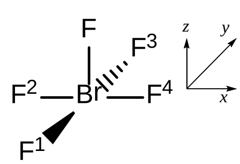

1. $\sigma_{(1)} \times C_3^1 =$
2. $C_3^2 \times \sigma_{(2)} =$
3. $\sigma_{(3)} \times \sigma_{(1)} =$



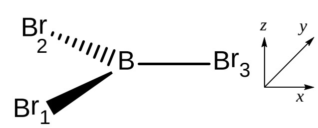

1. $\sigma_{yz} \times C_{2(z)} =$
2. $C_{2(x)} \times \sigma_{xy} =$
3. $i \times C_{2(y)} =$



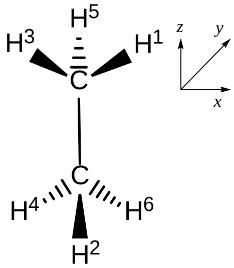

1. $\sigma_{yz} \times \sigma_{xz} =$
2. $C_2 \times \sigma_{yz} =$
3. $\sigma_{xz} \times C_2 =$

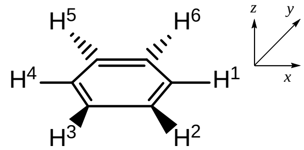


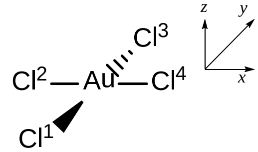

1. $\sigma_{(1)} \times C_4^3 =$
2. $C_2^1 \times \sigma_{(1-2)} =$
3. $\sigma_{(2)} \times \sigma_{(2-3)} =$




1. $S_3^2 \times \sigma_{xy} =$
2. $C_3^2 \times C_2^1 =$
3. $S_3 \times \sigma_{(2)} =$







| | | |
|---|---|---|
| 1. $i \times S_6 =$ | 1. $\sigma_{xy} \times C'_{2(1)} =$ | 1. $C_2 \times C''_{2(1-2)} =$ |
| 2. $\sigma_{(6)} \times C_2^3 =$ | 2. $S_3^2 \times C''_{2(1-2)} =$ | 2. $S_4 \times C'_{2(1)} =$ |
| 3. $\sigma_{(3)} \times C_2^1 =$ | 3. $C_6^5 \times S_3 =$ | 3. $C_4^3 \times i =$ |
| 4. $C_3 \times \sigma_{(2)} =$ | 4. $i \times \sigma_{(3)} =$ | 4. $\sigma_{(1-2)} \times C_4 =$ |
| 5. $C_3^2 \times S_6^5 =$ | 5. $\sigma_{(3-4)} \times C_6 =$ | 5. $S_4^3 \times \sigma_1 =$ |

Please note that:

1) $\sigma_{(i)}$ is a reflection plane that bisects atom (i).

2) $\sigma_{(i\text{-}j)}$ is a reflection plane between atoms (i) and (j).