1.1: Symmetry Elements and Operations

Consider the symmetry properties of an object (e.g. atoms of a molecule, set of orbitals, vibrations). The collection of objects is commonly referred to as a basis set

- *classify* objects of the basis set into symmetry operations
- *symmetry* operations form a group
- *group* mathematically defined and manipulated by group theory

> **Definition: Symmetry Operation**
>
> A **symmetry operation** moves an object into an indistinguishable orientation

> **Definition: Symmetry Element**
>
> A **symmetry element** is a point, line or plane about which a symmetry operation is performed

There are five symmetry elements in 3D space, which will be defined relative to point with coordinate (x_1, y_1, z_1) :

1. **identity, E**

$$E\left(x_1, y_1, z_1\right)=\left(x_1, y_1, z_1\right) \tag{1.1.1}$$

2. **plane of reflection, σ**
3. **inversion, i**

$$\mathrm{i}\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right)=\left(-\mathrm{x}_1,-\mathrm{y}_1,-\mathrm{z}_1\right) \tag{1.1.2}$$

4. **proper rotation axis, $\mathbf{C_n}$** $\left(\text{where } \theta=\frac{2\pi}{n}\right)$

convention is a clockwise rotation of the point

$$\mathrm{C}_2(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right)=\left(-\mathrm{x}_1,-\mathrm{y}_1, \mathrm{z}_1\right) \tag{1.1.3}$$

5. **improper rotation axis, $\mathbf{S_n}$**

two step operation: C_n followed by σ through plane ⊥ to C_n

$$\mathrm{S}_4(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right)=\sigma(\mathrm{xy}) \mathrm{C}_4(\mathrm{z})\left(\mathrm{x}_1, \mathrm{y}_1, \mathrm{z}_1\right)=\sigma(\mathrm{xy})\left(\mathrm{y}_1,-\mathrm{x}_1, \mathrm{z}_1\right)=\left(\mathrm{y}_1,-\mathrm{x}_1-\mathrm{z}_1\right) \tag{1.1.4}$$

Note: rotation of pt is clockwise; Corollary is that axes rotate counterclockwise relative to fixed point

In the example above, we took the **direct product** of two operators:

$\sigma_{\mathrm{h}} \cdot \mathrm{C}_{\mathrm{n}}=\mathrm{S}_{\mathrm{n}}$ ↓ Horizontal mirror plane (normal to C_n)	for n even $: S_n^n=C_n^n \cdot \sigma_h^n=E \cdot E=E$ for n odd: $S_n^n=C_n^n \cdot \sigma_h^n=E \cdot \sigma_h=\sigma_h$ $S_n^{2n}=C_n^{2n} \cdot \sigma_h^{2n}=E \cdot E=\sigma_h$ for m even: $\mathrm{S}_{\mathrm{n}}^{\mathrm{m}}=\mathrm{C}_{\mathrm{n}}^{\mathrm{m}} \cdot \sigma_{\mathrm{h}}^{\mathrm{m}}=\mathrm{C}_{\mathrm{n}}^{\mathrm{m}}$ for m odd: $S_n^m=C_n^m \cdot \sigma_h^m=C_n^m \cdot \sigma_h=S_n^m$

Symmetry operations may be represented as matrices. Consider the vector $\overline{\mathbf{v}}$

1. identity: $E\begin{bmatrix}x_1\\y_1\\z_1\end{bmatrix}=\begin{bmatrix} & ? & \end{bmatrix}\begin{bmatrix}x_1\\y_1\\z_1\end{bmatrix}=\begin{bmatrix}x_1\\y_1\\z_1\end{bmatrix}$

matrix satisfying this condition is:

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

$\therefore \mathrm{E}=\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$ ... E is always the unit matrix

2. reflection: $\sigma(\mathrm{xy})\begin{bmatrix}\mathrm{x}_1\\\mathrm{y}_1\\\mathrm{z}_1\end{bmatrix}=\begin{bmatrix}\mathrm{x}_1\\\mathrm{y}_1\\-\mathrm{z}_1\end{bmatrix} \quad \therefore \sigma(\mathrm{xy})=\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & -1\end{bmatrix}$

similarly similarly $\sigma(\mathrm{xz})=\begin{bmatrix}1 & 0 & 0\\0 & -1 & 0\\0 & 0 & 1\end{bmatrix}$ and $\sigma(\mathrm{yz})=\begin{bmatrix}-1 & 0 & 0\\0 & 1 & 0\\0 & 0 & 1\end{bmatrix}$

3. inversion: $\mathrm{i}\begin{bmatrix}\mathrm{x}_1\\\mathrm{y}_1\\\mathrm{z}_1\end{bmatrix}=\begin{bmatrix}-\mathrm{x}_1\\-\mathrm{y}_1\\-\mathrm{z}_1\end{bmatrix} \quad \therefore \quad \mathrm{i}=\begin{bmatrix}-1 & 0 & 0\\0 & -1 & 0\\0 & 0 & -1\end{bmatrix}$

4. proper rotation axis:

because of convention, φ, and hence z_i, is not transformed under $C_n(\theta)$ ∴ projection into xy plane need only be considered… i.e., rotation of vector $v(x_i,y_i)$ through θ

$x_1=\vec{v}\cos\alpha$ $y_1=\vec{v}\sin\alpha$	$C_n(\theta)$	$\mathrm{x}_2=\bar{\mathrm{v}}\cos[-(\theta-\alpha)]=\bar{\mathrm{v}}\cos(\theta-\alpha)$ $y_2=\vec{v}\sin[-(\theta-\alpha)]=-\bar{v}\sin(\theta-\alpha)$

using identity relations:

$x_2=\vec{v}\cos(\theta-\alpha)=\vec{v}\cos\theta\cos\alpha+\vec{v}\sin\theta\sin\alpha=x_1\cos\theta+y_1\sin\theta$

$y_2=-\bar{v}\sin(\theta-\alpha)=-[\bar{v}\sin\theta\cos\alpha-\bar{v}\cos\theta\sin\alpha]=-x_1\sin\theta+y_1\cos\theta$

Reformulating in terms of matrix representation:

$$\mathrm{C_n}(\theta)\begin{bmatrix}\mathrm{x}_1\\\mathrm{y}_1\\\mathrm{z}_1\end{bmatrix}=\begin{bmatrix}\mathrm{x}_1\cos\theta+\mathrm{y}_1\sin\theta\\-\mathrm{x}_1\sin\theta+\mathrm{y}_1\cos\theta\\\mathrm{z}_1\end{bmatrix}$$

$$\therefore \mathrm{C_n}(\theta)=\begin{bmatrix}\cos\theta & \sin\theta & 0\\-\sin\theta & \cos\theta & 0\\0 & 0 & 1\end{bmatrix} \quad \text{where } \theta=\frac{2\pi}{\mathrm{n}}$$

Note… the rotation above is clockwise, as discussed by HB (pg 39). Cotton on pg. 73 solves for the counterclockwise rotation… and presents the clockwise result derived above. To be consistent with HB (and math classes) we will rotate *clockwise* as the convention.

The above matrix representation is completely general for any rotation θ…

Example: $C_3, \theta=\frac{2\pi}{n}$

$$C_3=\begin{bmatrix}\cos\frac{2\pi}{3} & \sin\frac{2\pi}{3} & 0\\-\sin\frac{2\pi}{3} & \cos\frac{2\pi}{3} & 0\\0 & 0 & 1\end{bmatrix}=\begin{bmatrix}-\frac{1}{2} & \frac{\sqrt{3}}{2} & 0\\-\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0\\0 & 0 & 1\end{bmatrix} \tag{1.1.5}$$

5. improper rotation axis :

$\sigma_h \cdot C_n(\theta)=S_n(\theta)$

$$\begin{bmatrix}1 & 0 & 0\\0 & 1 & 0\\0 & 0 & -1\end{bmatrix}\cdot\begin{bmatrix}\cos\theta & \sin\theta & 0\\-\sin\theta & \cos\theta & 0\\0 & 0 & 1\end{bmatrix}=\begin{bmatrix}\cos\theta & \sin\theta & 0\\-\sin\theta & \cos\theta & 0\\0 & 0 & -1\end{bmatrix} \tag{1.1.6}$$

Like operators themselves, matrix operations may be manipulated with simple matrix algebra…above direct product yields matrix representation for S_n.

Another example:

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \cdot \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{1.1.7}$$

σ_{xy} ($\equiv \sigma_h$) $\cdot$ C_2 (z) = i