5.04, Principles of Inorganic Chemistry II
MIT Department of Chemistry
Lecture 1: Symmetry Elements and Operations

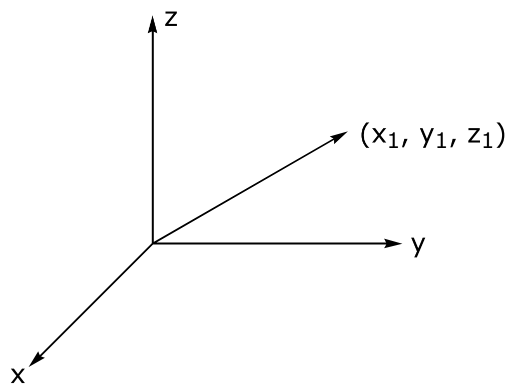
Symmetry properties of an object (e.g. atoms of a molecule, set of orbitals, vibrations)

→ classify into elements
→ elements form a group
→ group mathematically defined and manipulated by group theory

A <u>symmetry operation</u> moves an object into an indistinguishable orientation

A <u>symmetry element</u> is a point, line or plane about which a symmetry operation is performed.

Five symmetry elements defined relative to point with coordinate (x_1, y_1, z_1)

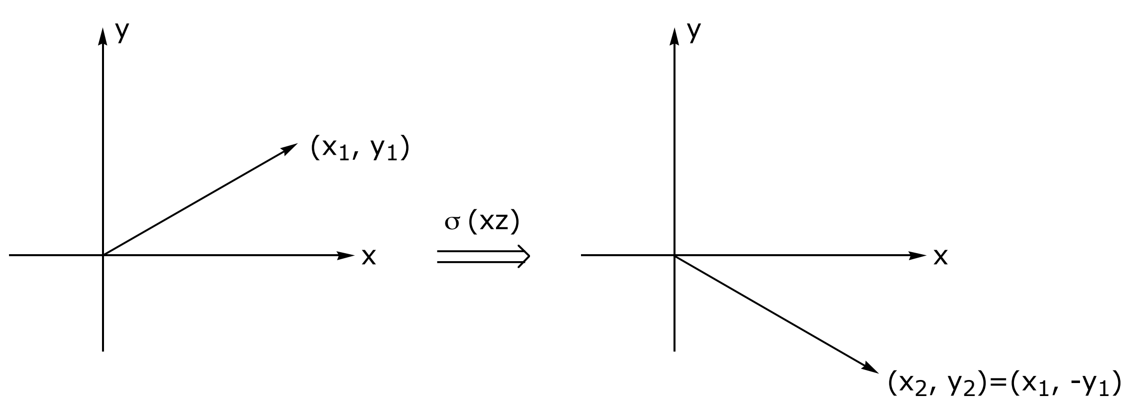


1) identity ≡ E

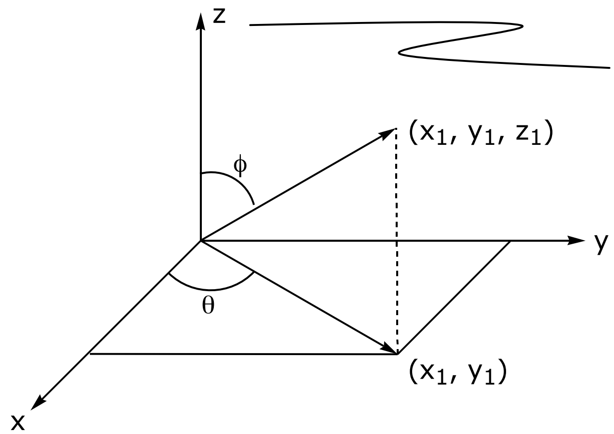
$E(x_1, y_1, z_1) = (x_1, y_1, z_1)$

2) plane of reflection, σ

$\sigma(xz)(x_1, y_1, z_1) = (x_1, -y_1, z_1)$



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



Convention is that the principal axis of rotation (axis with highest n) positioned coincident with z axis

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

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

2) reflection: $\sigma(xy)\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_1 \\ y_1 \\ -z_1 \end{bmatrix} \qquad \therefore \sigma(xy) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

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

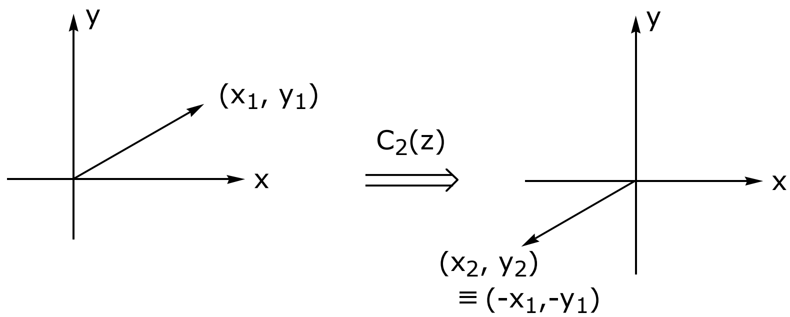
3) inversion: $i\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} -x_1 \\ -y_1 \\ -z_1 \end{bmatrix} \qquad \therefore i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix}$

3) inversion, i

$$i\left(x_1, y_1, z_1\right) = \left(-x_1, -y_1, -z_1\right)$$

4) proper rotation axis, C_n (where $\theta = \frac{2\pi}{n}$)

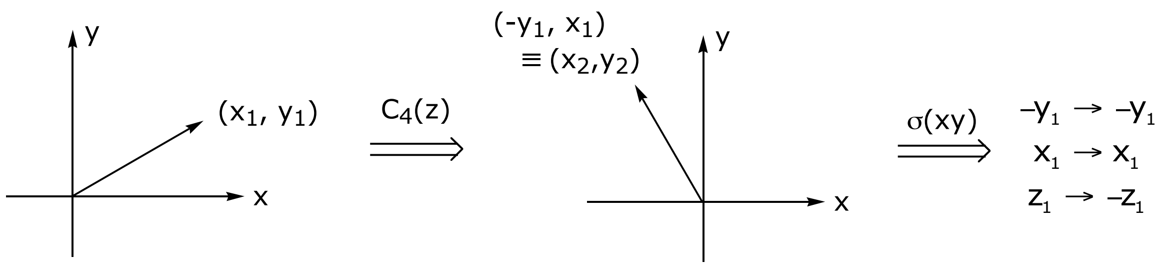
$$C_2(z)\left(x_1, y_1, z_1\right) = \left(-x_1, -y_1, z_1\right)$$



5) improper rotation axis, S_n

a two step operation: C_n followed by σ through plane $\perp$ to C_n

$$S_4(z)\left(x_1, y_1, z_1\right) = \sigma(xy)C_4(z)\left(x_1, y_1, z_1\right) = \sigma(xy)\left(-y_1, x_1, z_1\right) = \left(-y_1, x_1, -z_1\right)$$



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

In the example above, we took the <u>direct product</u> of two operators:

$\sigma_h \cdot C_n = S_n$

↓

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: $S_n^{\,n} = C_n^{\,n} \cdot \sigma_h^{\,n} = E \cdot \sigma_h = \sigma_h$

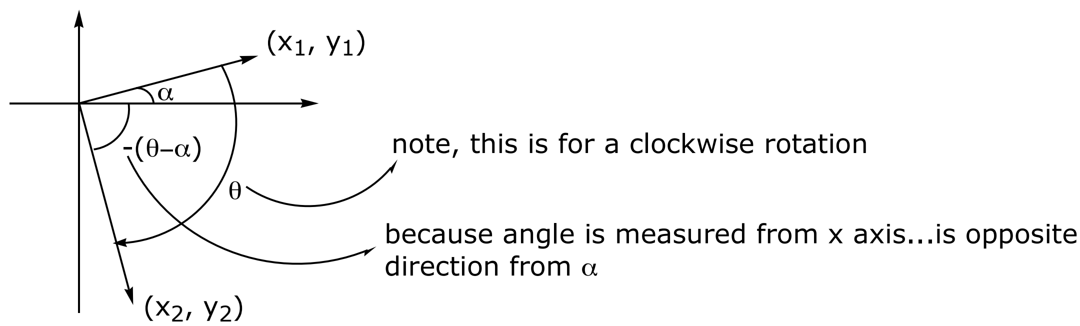
$S_n^{\,2n} = C_n^{\,2n} \cdot \sigma_h^{\,2n} = E \cdot E = \sigma_h$

for m even: $S_n^{\,m} = C_n^{\,m} \cdot \sigma_h^{\,m} = C_n^{\,m}$

for m odd: $S_n^{\,m} = C_n^{\,m} \cdot \sigma_h^{\,m} = C_n^{\,m} \cdot \sigma_h = S_n^{\,m}$

4) proper rotation axis:

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



$$x_1 = \bar{v}\cos\alpha \qquad \xrightarrow{C_n(\theta)} \qquad x_2 = \bar{v}\cos\left[-\left(\theta-\alpha\right)\right] = \bar{v}\cos\left(\theta-\alpha\right)$$
$$y_1 = \bar{v}\sin\alpha \qquad\qquad\qquad y_2 = \bar{v}\sin\left[-\left(\theta-\alpha\right)\right] = \bar{v}\sin\left(\theta-\alpha\right)$$

using identitity relations:

$$x_2 = \bar{v}\cos\left(\theta-\alpha\right) = \bar{v}\cos\theta\cos\alpha + \bar{v}\sin\theta\sin\alpha = x_1\cos\theta + y_1\sin\theta$$
$$y_2 = \bar{v}\sin\left(\theta-\alpha\right) = -\left[\bar{v}\sin\theta\cos\alpha - \bar{v}\cos\theta\sin\alpha\right] = -x_1\sin\theta + y_1\cos\theta$$

Reformulating in terms of matrix representation:

$$C_n(\theta)\begin{bmatrix} x_1 \\ y_1 \\ z_1 \end{bmatrix} = \begin{bmatrix} x_1\cos\theta + y_1\sin\theta \\ -x_1\sin\theta + y_1\cos\theta \\ z_1 \end{bmatrix}$$

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

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

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

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

5) improper rotation axis :

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

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

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

Another example:

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

$$C_2(z) \quad \cdot \quad \sigma_h \quad = \quad i$$