## Matrices and Symmetry

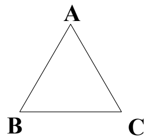
The algebra of matrices is ideal for describing the symmetry elements of molecules.

Matrices can be used with varying degrees of sophistication – the simplest is to use them to operate on atomic labels.

## A Simple Example

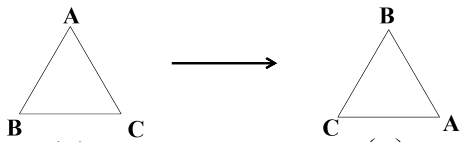
The configuration of this triangular molecule can be represented by a column matrix

$$\begin{pmatrix} A \\ B \\ C \end{pmatrix}$$




Any symmetry operation can be characterised by its effect on the column matrix – and thus can be represented as a (3x3) matrix

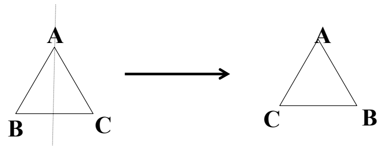
## Rotation Clockwise by 120º




$$\begin{pmatrix} A \\ B \\ C \end{pmatrix} \longrightarrow \begin{pmatrix} B \\ C \\ A \end{pmatrix}$$

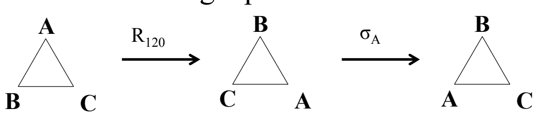
$$\begin{pmatrix} B \\ C \\ A \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = R_{120}\begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

## Reflections / Mirror Planes




$$\begin{pmatrix} A \\ C \\ B \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \sigma_A\begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

## Combining Operations – R then σ

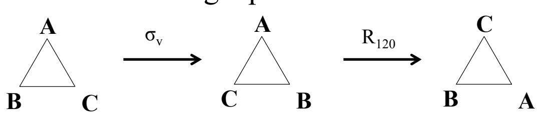



Apply $R_{120}$ then $\sigma_v$

$$\sigma_A R_{120}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 1 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} B \\ A \\ C \end{pmatrix} = \sigma_C$$

## Combining Operations - σ then R




Apply $\sigma_v$ then $R_{120}$

$$R_{120}\sigma_A\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} 0 & 1 & 0 \\ 0 & 0 & 1 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix}$$

$$= \begin{pmatrix} 0 & 0 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 0 \end{pmatrix}\begin{pmatrix} A \\ B \\ C \end{pmatrix} = \begin{pmatrix} C \\ B \\ A \end{pmatrix} = \sigma_B$$

## Summary

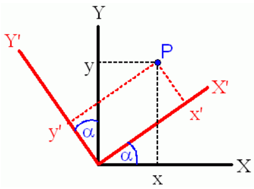
The column vector conveniently represents the essentials of the molecular topology.

Symmetry operations can be represented by matrices.

The normal rules of matrix multiplication reproduce application of multiple symmops

A non-commutative algebra.

## General Rotations




- In the normal X,Y system P is (x,y).
- In the rotated X′, Y′ system P is (x′,y′)

$$x' = x\cos(\alpha) + y\sin(\alpha)$$
$$y' = -x\sin(\alpha) + y\cos(\alpha)$$

## Rotation Matrices – 2D

Rewriting as a matrix equation

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} \cos(\alpha) & \sin(\alpha) \\ -\sin(\alpha) & \cos(\alpha) \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = R_\alpha \begin{pmatrix} x \\ y \end{pmatrix}$$

The operation "rotate the coordinate system anti-clockwise by α", is identical to "rotate objects clockwise by α"

The operation is implemented by multiplying the matrix onto the coordinates of any object.

## Rotation Matrices – 3D

Rotation about the z-axis

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos(\alpha) & \sin(\alpha) & 0 \\ -\sin(\alpha) & \cos(\alpha) & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = R_z(\alpha) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

Or the x axis…

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos(\alpha) & \sin(\alpha) \\ 0 & -\sin(\alpha) & \cos(\alpha) \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} = R_x(\alpha) \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$