Multiplication Tables, Rearrangement Theorem

- Each row and each column in the group multiplication table lists each of the group elements once and only once. (Why must this be true?) From this, it follows that no two rows may be identical. Thus each row and each column is a rearranged list of the group elements.

1

1

Subgroups

- A subgroup is a "group within another group"- a subset of group elements. A supergroup is a group obtained by adding new elements to a group (to give a larger group).
- The order of any subgroup g of a group of order h must be a divisor of h:

$$h/g = k \quad \text{where } k \text{ is an integer}$$

2

2

Similarity Transforms, Classes

- $\mathcal{A}$ is said to be **conjugate** with $\mathcal{B}$, if there exists any element of the group, $\mathcal{X}$, such that

$$\mathcal{A} = \mathcal{X}^{-1}\mathcal{B}\mathcal{X}$$

(i) Every element is conjugate with itself.

(ii) If $\mathcal{A}$ is conjugate with $\mathcal{B}$, then $\mathcal{B}$ is conjugate with $\mathcal{A}$.

(iii) If $\mathcal{A}$ is conjugate with $\mathcal{B}$ and $\mathcal{C}$, then $\mathcal{B}$ and $\mathcal{C}$ are conjugate with each other.

3

3

Classes, cont.

- A complete set of elements that are conjugate to one another within a group is called a *class* of the group. The number of elements in a class is called its *order*.
- The orders of all classes must be integral factors of the order of the group.

4

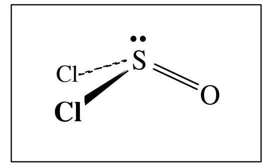
4

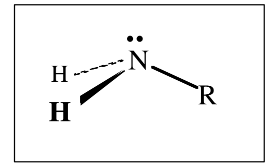
The Symmetry Operations

- ★ Reflection (in a plane) σ
- ★ Inversion (through a point) i
- ★ Rotation (about a proper axis) C_n
- ★ - through an angle 2π/n
- ★ Improper Rotation S_n
- ★ (about an improper axis)
- ★ Identity (do nothing) E

Reflections in a *plane*: σ

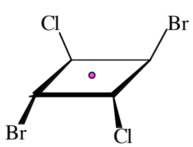
Examples:

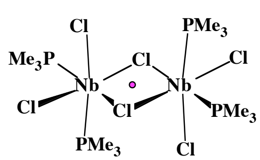




Inversion: *i*

- Examples





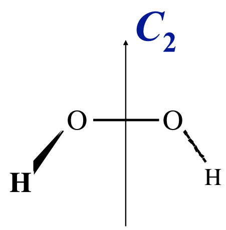
Inversion

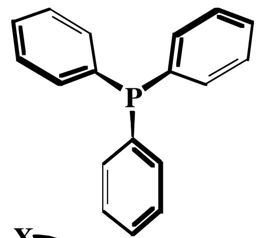
Cat's Eye Nebula

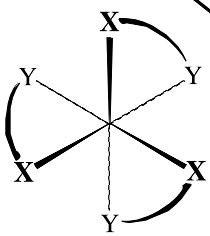
(3000-year old supernova)

Rotations about an *axis*: C_n

Examples



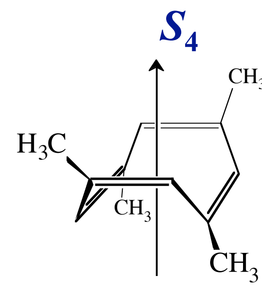




C_3 (coming out of the "paper")

Improper Rotations: S_n

Example



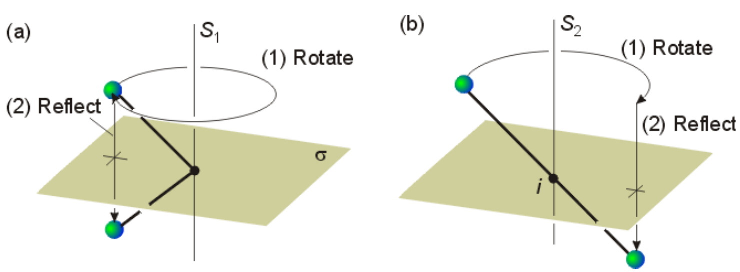
Note:

$S_1 = \sigma$

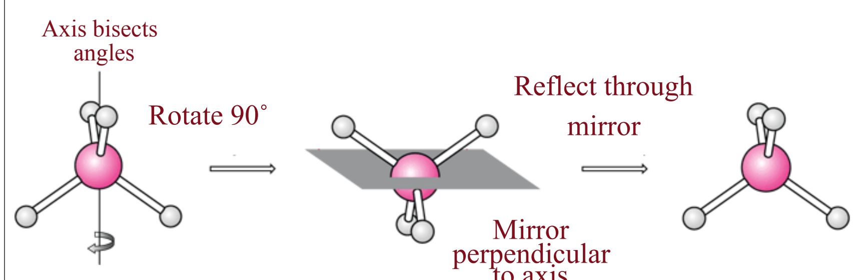
$S_2 = i$

$S^2_{2n} = C_n$

S_1, S_2 are just σ and *i*

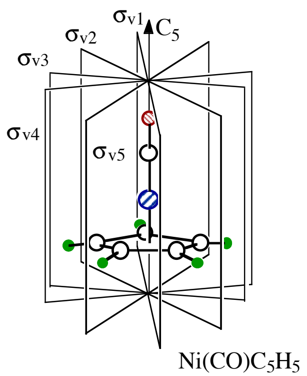


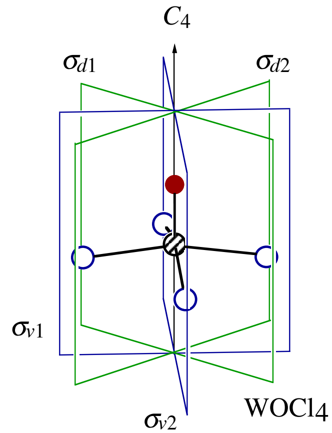
S_4 in action



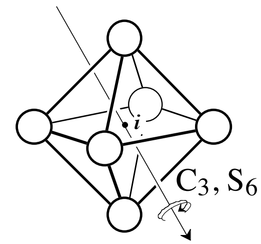
Groups with more Symmetry

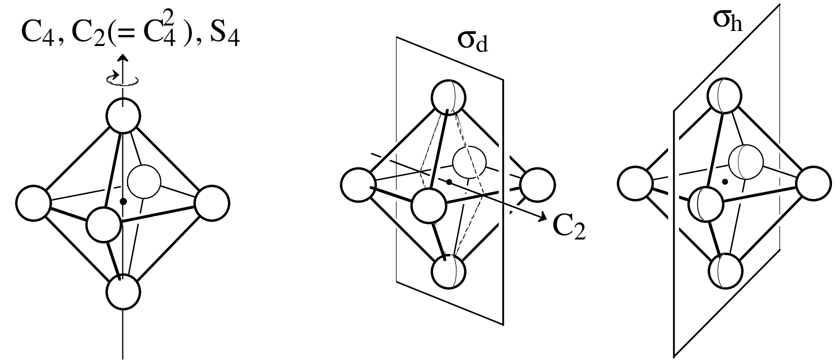
- C_{nv} groups



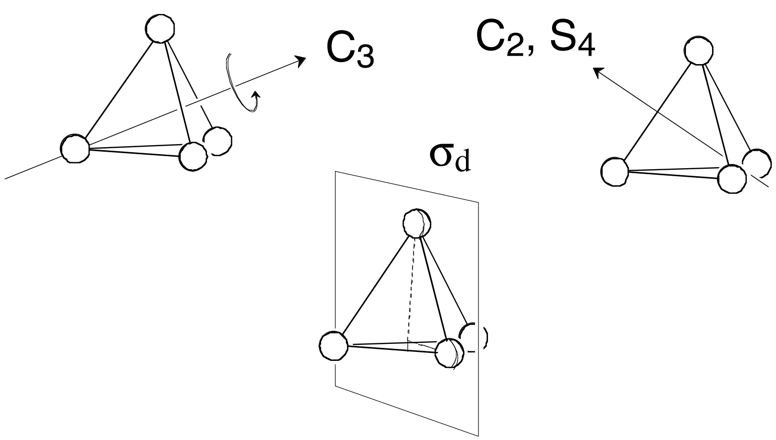


Octahedra

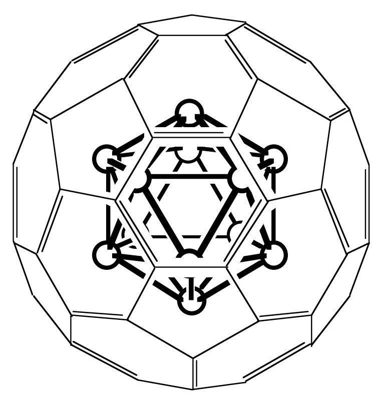




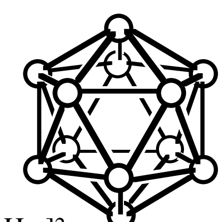
Tetrahedra



Icosahedral Molecules

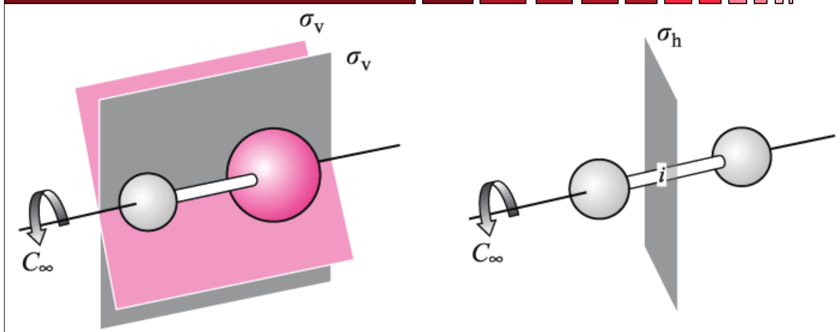


B_{12} inside C_{60}



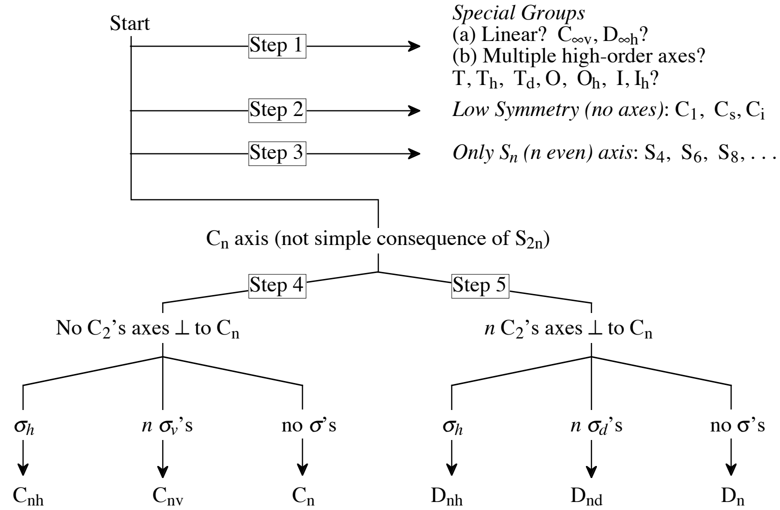
$[B_{12}H_{12}]^{2-}$

$C_{\infty v}$ and $D_{\infty h}$



Is the molecule linear?
If so, does it have inversion symmetry?

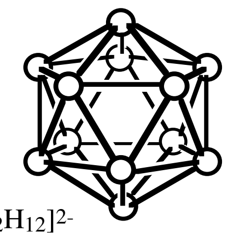
Point Group Flow Chart



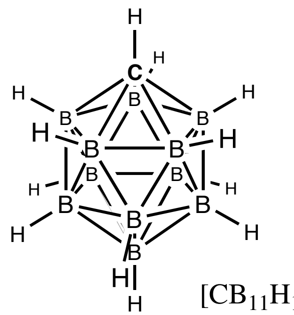
Examples

- A unopened can of soup, unlabeled; A opened, empty soup can?
- $[N_5]^+$ (isolated by Christie)
- Ethane, staggered
- SF_4, PF_5, BrF_5
- Enneper's minimal surface: $\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} u - \frac{u^3}{3} + uv^2 \\ v - \frac{v^3}{3} + vu^2 \\ u^2 - v^2 \end{bmatrix}$
- $[Co(en)_3]^{3+}$, $[Co(en)_2Cl_2\ ]^+$
  ignore ring conformations, H-atoms
- $[B_{12}H_{12}]^{2-}$, $[CB_{11}H_{12}]^-$, 1,12-$C_2B_{10}H_{12}$

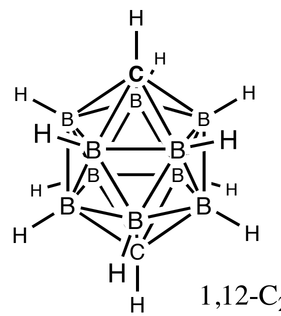
Enneper's minimal surface



$[B_{12}H_{12}]^{2-}$

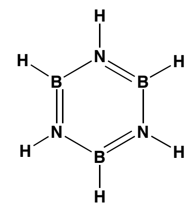


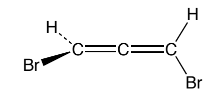
$[CB_{11}H_{12}]^{-}$

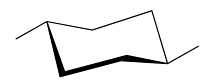


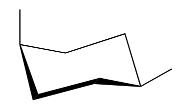
$1{,}12\text{-}C_2B_{10}H_{12}$

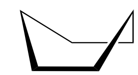
More Examples











Building up Groups from *Generators*

The philosophy of the Hermann-Mauguin (international) notation is to supply the minimal number of group operations in the group symbol (and those operations *generate* the rest…).

- Point group examples:

  $C_{2v} = mm$; $D_{2h} = mmm$; $C_{4v} = 4mm$;

  $4/mmm = ?$; $422 = ?$; $\bar{4}2m = ?$; $\bar{3}m = ?$

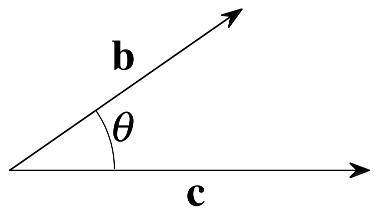
32 Crystallographic Point Groups

Schoenflies	Hermann-Mauguin
$C_1, C_i, C_2, C_s, C_{2h}, C_{2v}, D_2,$	$1, \bar{1}, 2, m, 2/m, mm, 222,$
$D_{2h}, C_4, S_4, C_{4h}, C_{4v}, D_{2d},$	$mmm, 4, \bar{4}, 4/m, 4mm, \bar{4}2m,$
$D_4, D_{4h}, C_3, S_6, C_{3v}, D_3, D_{3d},$	$422, 4/mmm, 3, \bar{3}, 3m, 32, \bar{3}m,$
$C_6, C_{3h}, C_{6h}, D_{3h}, C_{6v}, D_6,$	$6, \bar{6}, 6/m, 6m2, 6mm, 622,$
$D_{6h}, T, T_h, T_d, O, O_h$	$6/mmm, 23, m3, \bar{4}3m, 432, m3m$

- These are all the point symmetries compatible with translational symmetry of crystals.

Vectors… quickie review

★ Dot (Scalar) product



$\mathbf{b} \cdot \mathbf{c} = bc\cos\theta$ where $b = |\mathbf{b}|$ and $c = |\mathbf{c}|$

In any set of orthogonal coordinates,

$$\mathbf{b} \cdot \mathbf{c} = \sum_i b_i c_i = \begin{bmatrix} b_1 & b_2 & \cdots & b_{n-1} & b_n \end{bmatrix} \begin{bmatrix} c_1 \\ c_2 \\ \vdots \\ c_{n-1} \\ c_n \end{bmatrix}$$

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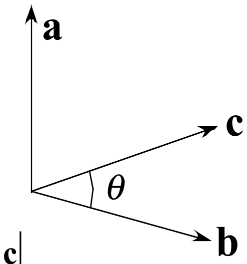
Vectors… quickie review

★ Cross product (3-D only)



$|\mathbf{b} \times \mathbf{c}| = bc\sin\theta$ where $b = |\mathbf{b}|$ and $c = |\mathbf{c}|$

To compute cross products:

$$\mathbf{b} \times \mathbf{c} = \begin{vmatrix} \hat{\mathbf{x}} & \hat{\mathbf{y}} & \hat{\mathbf{z}} \\ b_x & b_y & b_z \\ c_x & c_y & c_z \end{vmatrix} = (b_y c_z - b_z c_y)\hat{\mathbf{x}} - (b_x c_z - b_z c_x)\hat{\mathbf{y}} + (b_x c_y - b_y c_x)\hat{\mathbf{z}}$$

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Cartesian Vectors

All vectors in normal 3-D space are built up with Cartesian unit vectors: $\hat{\mathbf{x}}, \hat{\mathbf{y}}, \hat{\mathbf{z}}$
(calculus books use $\hat{\mathbf{i}}, \hat{\mathbf{j}}, \hat{\mathbf{k}}$)

$$\hat{\mathbf{x}} = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad \hat{\mathbf{y}} = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad \hat{\mathbf{z}} = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

Any general vector, **r**, is written as:

$$\mathbf{r} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x \\ 0 \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ y \\ 0 \end{bmatrix} + \begin{bmatrix} 0 \\ 0 \\ z \end{bmatrix} = x\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} + y\begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} + z\begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = x\hat{\mathbf{x}} + y\hat{\mathbf{y}} + z\hat{\mathbf{z}}$$

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Scalar × Vector = Vector

$$\alpha\mathbf{b} = \mathbf{c}$$

$$\alpha \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \end{bmatrix} = \begin{bmatrix} \alpha b_1 \\ \alpha b_2 \\ \alpha b_3 \\ \alpha b_4 \\ \alpha b_5 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \\ c_5 \end{bmatrix}$$

$\alpha b_1 = c_1$, $\alpha b_2 = c_2$, etc.

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Scalar × Matrix = Matrix

$\alpha B = C$

$$\alpha \begin{bmatrix} b_{11} & b_{12} & b_{13} & b_{14} & b_{15} \\ b_{21} & b_{22} & b_{23} & b_{24} & b_{25} \\ b_{31} & b_{32} & b_{33} & b_{34} & b_{35} \\ b_{41} & b_{42} & b_{43} & b_{44} & b_{45} \\ b_{51} & b_{52} & b_{53} & b_{54} & b_{55} \end{bmatrix} = \begin{bmatrix} \alpha b_{11} & \alpha b_{12} & \alpha b_{13} & \alpha b_{14} & \alpha b_{15} \\ \alpha b_{21} & \alpha b_{22} & \alpha b_{23} & \alpha b_{24} & \alpha b_{25} \\ \alpha b_{31} & \alpha b_{32} & \alpha b_{33} & \alpha b_{34} & \alpha b_{35} \\ \alpha b_{41} & \alpha b_{42} & \alpha b_{43} & \alpha b_{44} & \alpha b_{45} \\ \alpha b_{51} & \alpha b_{52} & \alpha b_{53} & \alpha b_{54} & \alpha b_{55} \end{bmatrix}$$

$$= \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} \\ c_{41} & c_{42} & c_{43} & c_{44} & c_{45} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} \end{bmatrix}$$

$\alpha b_{11} = \mathbf{c_{11}}$, $\alpha b_{21} = \mathbf{c_{21}}$, etc.

Matrix × Vector = Vector

$\mathbf{Ab} = \mathbf{c}$

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} \end{bmatrix} \begin{bmatrix} b_1 \\ b_2 \\ b_3 \\ b_4 \\ b_5 \end{bmatrix} = \begin{bmatrix} c_1 \\ c_2 \\ c_3 \\ \mathbf{c_4} \\ c_5 \end{bmatrix}$$

$$a_{41} \times b_1 + a_{42} \times b_2 + a_{43} \times b_3 + a_{44} \times b_4 + a_{45} \times b_5 = \mathbf{c_4}$$

Matrix Multiplication

$\mathbf{AB} = \mathbf{C}$

$$\begin{bmatrix} a_{11} & a_{12} & a_{13} & a_{14} & a_{15} \\ a_{21} & a_{22} & a_{23} & a_{24} & a_{25} \\ a_{31} & a_{32} & a_{33} & a_{34} & a_{35} \\ a_{41} & a_{42} & a_{43} & a_{44} & a_{45} \\ a_{51} & a_{52} & a_{53} & a_{54} & a_{55} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & b_{13} & b_{14} & b_{15} \\ b_{21} & b_{22} & b_{23} & b_{24} & b_{25} \\ b_{31} & b_{32} & b_{33} & b_{34} & b_{35} \\ b_{41} & b_{42} & b_{43} & b_{44} & b_{45} \\ b_{51} & b_{52} & b_{53} & b_{54} & b_{55} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & c_{13} & c_{14} & c_{15} \\ c_{21} & c_{22} & c_{23} & c_{24} & c_{25} \\ c_{31} & c_{32} & c_{33} & c_{34} & c_{35} \\ c_{41} & \mathbf{c_{42}} & c_{43} & c_{44} & c_{45} \\ c_{51} & c_{52} & c_{53} & c_{54} & c_{55} \end{bmatrix}$$

$$a_{41} \times b_{12} + a_{42} \times b_{22} + a_{43} \times b_{32} + a_{44} \times b_{42} + a_{45} \times b_{52} = \mathbf{c_{42}}$$

Summation Notation

$\mathbf{AB} = \mathbf{C}$

$$\sum_k a_{ik} b_{kj} = c_{ij}$$

row index   column index

Block Factored Matrices

$$\begin{bmatrix} a_{11} & a_{12} & 0 & 0 & 0 \\ a_{21} & a_{22} & 0 & 0 & 0 \\ 0 & 0 & a_{33} & a_{34} & a_{35} \\ 0 & 0 & a_{43} & a_{44} & a_{45} \\ 0 & 0 & a_{53} & a_{54} & a_{55} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} & 0 & 0 & 0 \\ b_{21} & b_{22} & 0 & 0 & 0 \\ 0 & 0 & b_{33} & b_{34} & b_{35} \\ 0 & 0 & b_{43} & b_{44} & b_{45} \\ 0 & 0 & b_{53} & b_{54} & b_{55} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} & 0 & 0 & 0 \\ c_{21} & c_{22} & 0 & 0 & 0 \\ 0 & 0 & c_{33} & c_{34} & c_{35} \\ 0 & 0 & c_{43} & c_{44} & c_{45} \\ 0 & 0 & c_{53} & c_{54} & c_{55} \end{bmatrix}$$

$$\begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} c_{11} & c_{12} \\ c_{21} & c_{22} \end{bmatrix} \qquad \begin{bmatrix} a_{33} & a_{34} & a_{35} \\ a_{43} & a_{44} & a_{45} \\ a_{53} & a_{54} & a_{55} \end{bmatrix} \begin{bmatrix} b_{33} & b_{34} & b_{35} \\ b_{43} & b_{44} & b_{45} \\ b_{53} & b_{54} & b_{55} \end{bmatrix} = \begin{bmatrix} c_{33} & c_{34} & c_{35} \\ c_{43} & c_{44} & c_{45} \\ c_{53} & c_{54} & c_{55} \end{bmatrix}$$

Matrices… Definitions, Properties

- ★Character, χ (often called the *Trace*) of a Matrix
  - ✦ if **C** = **AB** and **D** = **BA**, then $\chi_{\mathbf{C}} = \chi_{\mathbf{D}}$.
  - ✦ Conjugate matrices have equal characters
- ★Transpose ($\mathbf{A}^{\mathrm{T}}$): $(\mathbf{A}^{\mathrm{T}})_{ij} = (\mathbf{A})_{ji}$
  - ✦ just transpose the rows and columns
- ★Matrices and Geometrical Transformations
- ★Orthogonal Matrices
  - ✦ inverse matrix is just the transpose

Why are the matrices of symmetry operations always orthogonal matrices?

Assume an orthogonal set of unit column vectors,

$$\hat{\mathbf{x}}_1 = \begin{bmatrix} 1 \\ 0 \\ 0 \\ \vdots \\ 0 \end{bmatrix};\ \hat{\mathbf{x}}_2 = \begin{bmatrix} 0 \\ 1 \\ 0 \\ \vdots \\ 0 \end{bmatrix};\ \hat{\mathbf{x}}_3 = \begin{bmatrix} 0 \\ 0 \\ 1 \\ \vdots \\ 0 \end{bmatrix};\ \cdots\ \hat{\mathbf{x}}_n = \begin{bmatrix} 0 \\ 0 \\ 0 \\ \vdots \\ 1 \end{bmatrix}, \text{ note that } \hat{\mathbf{x}}_i^T \bullet \hat{\mathbf{x}}_j = \delta_{ij}$$

The action of symmetry operation **R** on these unit vectors will map them on to a new set of vectors, $\{\hat{\mathbf{x}}_i, i = 1, \cdots, n\} \xrightarrow{\mathbf{R}} \{\hat{\mathbf{y}}_i, i = 1, \cdots, n\}$. But by the rules of matrix multiplication, the columns of must just be the $\hat{\mathbf{y}}_i$ vectors:

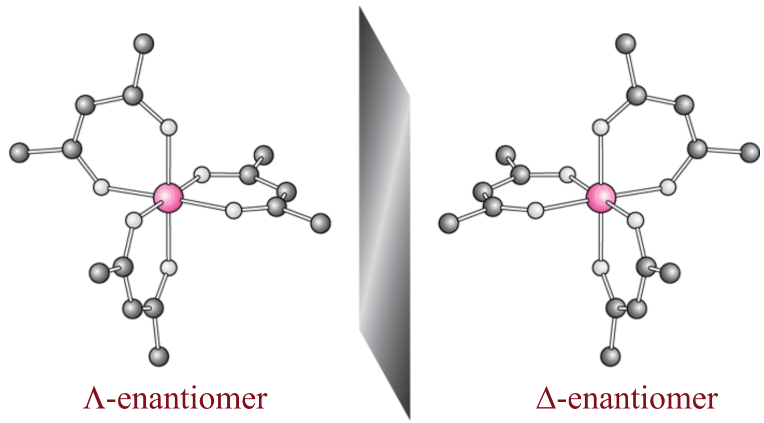
$$\mathbf{R} = \begin{bmatrix} \hat{\mathbf{y}}_1 & \hat{\mathbf{y}}_2 & \hat{\mathbf{y}}_3 & \cdots & \hat{\mathbf{y}}_n \end{bmatrix}.$$

Since symmetry operations are just rotations or reflections, the set of vectors, $\{\hat{\mathbf{y}}_i, i = 1, \cdots, n\}$, are mutually orthogonal. Therefore, the columns of **R** are orthogonal.

Symmetry and Physical Properties

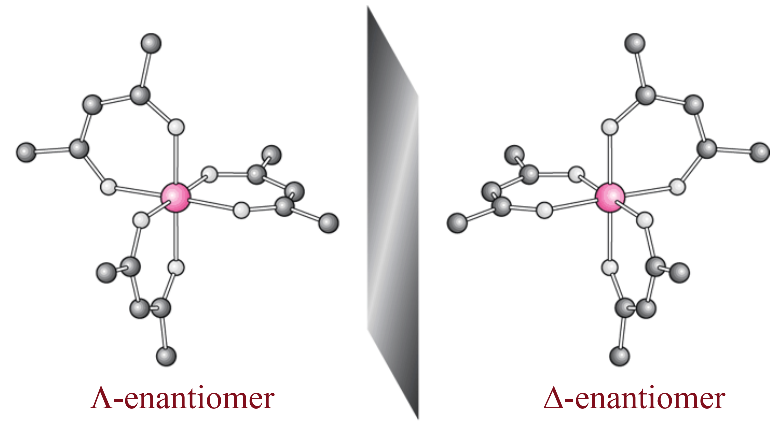
- Dipole moments
  - ✦ moment must be invariant under all symmetry operations
- Chirality
- 2nd-rank tensors (e.g., polarizability tensor, hyperfine and *g*-tensors in EPR; in the solid state: conductivity, susceptibility, & stress tensors) - skip this.

Chirality - Symmetry requirement



If a molecule is not superimposable on its mirror image, it said to be *chiral*.

If no S_n axis - molecule is Chiral



The act of "superimposing" molecules after reflecting is equivalent to executing a rotation.