Molecular Geometry + Symmetry

The VSEPR Model – Valence Shell Electron Pair Repulsion

↳ A Refinement of Lewis Theory that allows us to make predictions about molecular Shape

Basic Assumption: Regions of high e^- density in a molecule will orient as far away from one another as possible

⇓

Driven purely by coulombic repulsion due to the mutual negative charges of e^-s in areas of high e^- density

Regions of Enhanced e^- density

1. Non-bonding lone pairs
2. Bonding e^- pairs
3. Multiple pairs of bonding e^-

Steric Number = # of positions occupied by atoms or non-bonding e^- about a central atom.

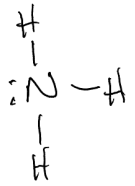
∴ Molecules can be described by AX_mE_n (E: lone pairs of e^-; A: Central Atom; X: groups of atoms around A)

$m + n$ = the total # of occupied positions around A

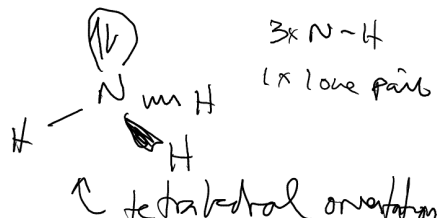
Although both bonding + non-bonding e^- contribute to Shape of the molecule + are used to define the Steric #, the Shape of the molecule is determined by the arrangement of atoms

↑ None

↳ Consider Ammonia (NH_3)



"Shape of NH_3 is trigonal pyramidal"

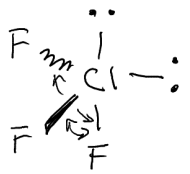


↑ tetrahedral orientation of enhanced e^- density

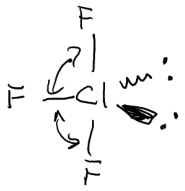
Let's use VSEPR theory to predict molecular shape

Consider ClF_3 ⇒ 28 valence e⁻ ⇒ 3 potential TBP

D_{3h}



C_s



C_{2v}

$E(lp\text{-}lp) > E(lp\text{-}bp) > E(bp\text{-}bp)$

For 90° interactions

	D_{3h}	C_s	C_{2v}
lp-lp	0	1	0
lp-bp	6	3	4
bp-bp	0	2	2

$E(C_{2v}) < E(D_{3h}) < E(C_s)$

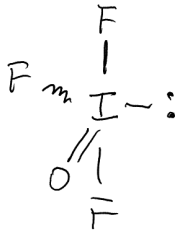
What about when we have multiple bonds (A–X vs A=X)

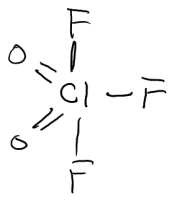
A=X ⇒ greater steric perturbation

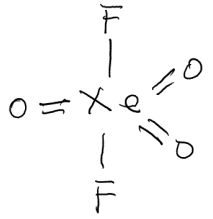
A=X ↑ e⁻ density greater than for A–X

For cases where we have multiple bonds – prefer equatorial position

Consider IOF_3 ClF_3O_2 XeF_2O_3







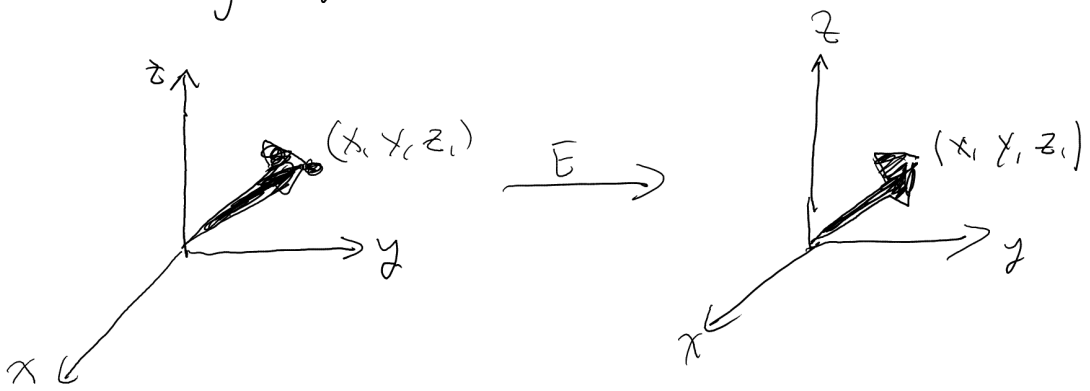
Symmetry + intro to Point Groups

Symmetry operations - moves an object into an indistinguishable representation

Symmetry elements - a point, a line, a plane about which a symmetry operation is performed

5 Symmetry operations, which can be defined wrt to a point $(x_1\ y_1\ z_1)$

① Identity (E)



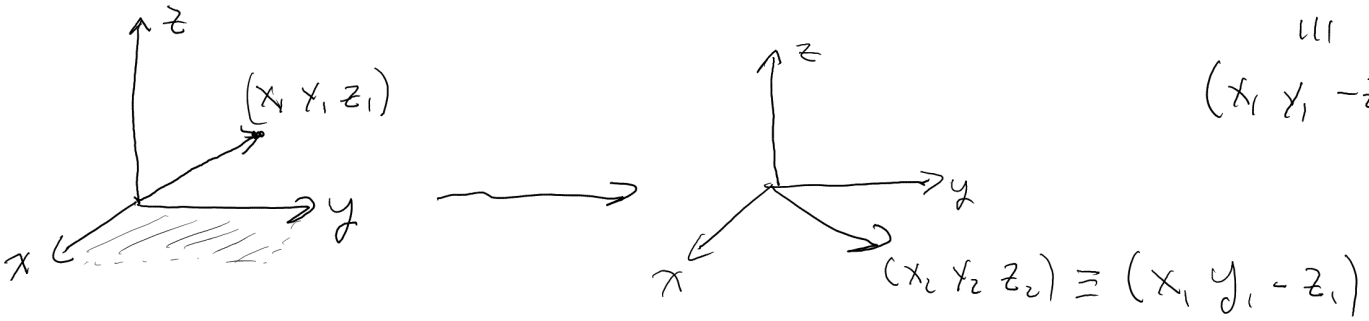
Molecule containing σ cannot be chiral

② Plane of Reflection (σ)

$\sigma(xy)(x_1\ y_1\ z_1) \longrightarrow (x_2\ y_2\ z_2)$

$\equiv$

$(x_1\ y_1\ -z_1)$



③ point of reflection / Centre of inversion

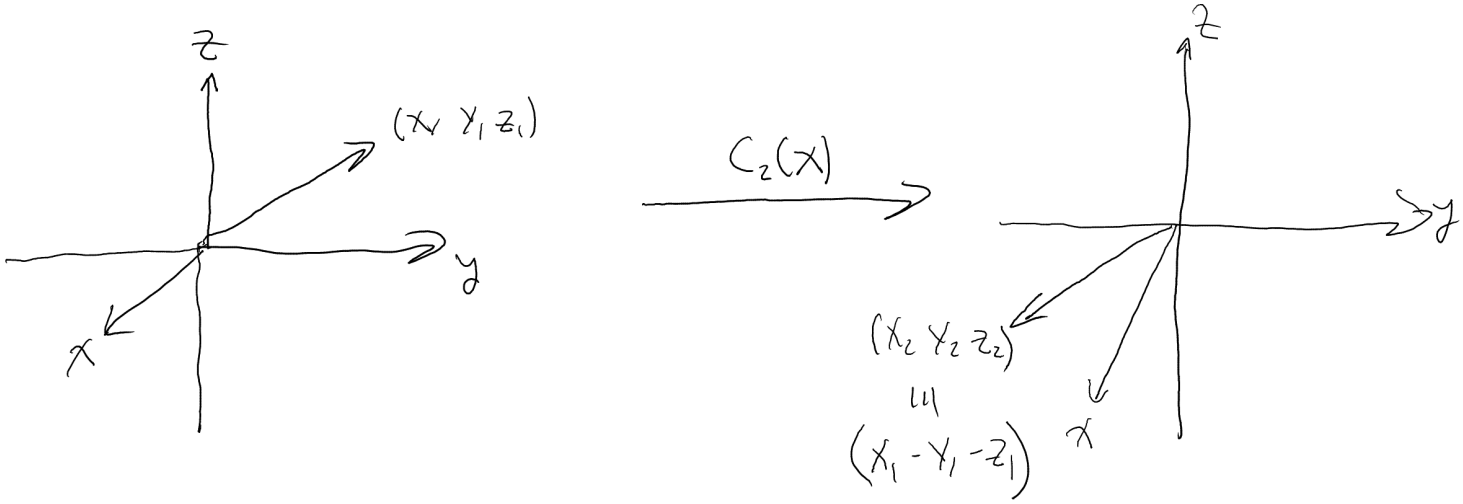
$i(x_1\ y_1\ z_1) \longrightarrow (x_2\ y_2\ z_2)$

$\equiv$

$(-x_1\ -y_1\ -z_1)$

Molecule containing i Cannot be Chiral

④ Proper Axis of Rotation (C_n) $\theta = \frac{2\pi}{n}$ or $360°/n$

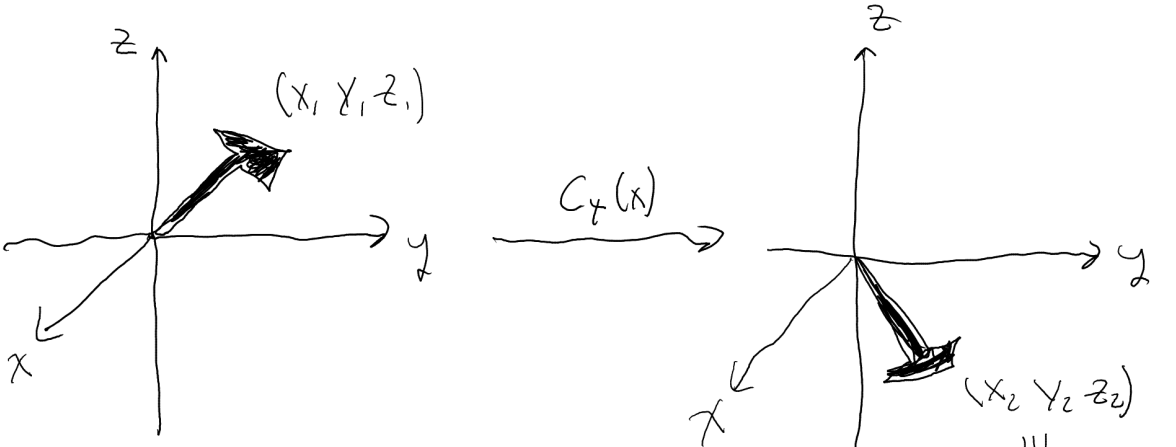


⑤ Improper Axis of Rotation (S_n)

↳ 2 part operation (2 step operation)

C_n followed by reflection through σ that is $\perp$ to C_n

$S_4(X)\ (x_1, y_1, z_1)$



Any molecule containing S_4 cannot be chiral

$\sigma(yz)$