Quick Review of Lecture 9 Feb. 4, 2019

- ***Lewis Structures***
- ***Concepts and Vocabulary: Formal Charges, Valences, Oxidation States***
- ***Resonance Structures; Hyper and Hypovalent sites***
- ***VSEPR***

Lewis Structures

- **A bond between two atoms is formed by means of sharing of a pair of electrons**
- **Each atom shares electrons with neighbors to achieve a total of eight valence electrons**
- ***Determine connectivity of the atoms in the molecule***
- ***Sum up the total number of valence electrons in the molecule***
- ***Distribute the electrons so that each atom acquires an octet (duet for H!) in either***

  a) bonding pairs (denoted : or –) shared between a pair of atoms, or

  b) lone pairs (denoted :) that belong to a single atom (i.e., "unused" in making bonds and occupy more space than bonded pairs).

Examples: HF, CF_4, NH_3, $COCl_2$, CO, CO_2, N_2O, H_2CN_2, N_3^-, N_5^+

Vocabulary and Concepts

Valence, Oxidation Number, and Formal Charge: Three Related but Fundamentally Different Concepts

Valence: Number of electrons an atom uses in bonding.

Oxidation State or Number: Charge on atoms according to a set of rules That consider the electronegativity of atoms within the molecule or material.

1) In pure element, Oxidation Number = 0
2) F, the most electronegative element, in a molecule is -1
3) O is typically -2; sometimes (in peroxides), -1
4) Alkali metals, +1; Alkaline Earth metals, +2; Gp 3, generally +3; Transition metals variable + charged.
5) H is +1 when combined with more electroneg. element; -1 when combined with more electropositive element. *Therefore, H in compound with any M is a hydride, H^{-1}.*
6) Summation of Ox. States must equal charge on ion; or zero if neutral molecule.

Formal Charges: Charge on atom according to equation:

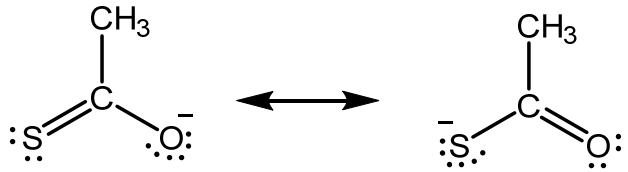
F.C. = # valence electrons - # of electrons in non-bonded pairs – ½ # of electrons in bonds

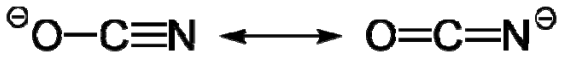
Coordination number: Number of atoms bonded to the atom in question.

Parkin, G. *J. Chem. Educ*. **2006**, *83*, 791
Jensen, W. B. *J. Chem. Educ.* **2006**, *83*, 1751

Resonance Structures: A Way to Delocalize Electrons in Valence Bond Descriptions

- **Resonance structures represent different Lewis structures for the same molecule**
- Resonance structures must have the same connectivity and the same total no. of electrons
- **Resonance structures are *not isomers*, but are various limiting descriptions of the same molecule.**
- If a molecule can be represented by more than one viable resonance structure, its electronic structure should be thought of as a "blend" of the resonance structures. Such "blending" generally lowers the energy of the system.
- **Resonance structure may be of equal or unequal importance ("weight").**
- Guiding principles: **Favor** octets; **minimize** formal charges*; **disfavor** formal positive charge on more electronegative atoms

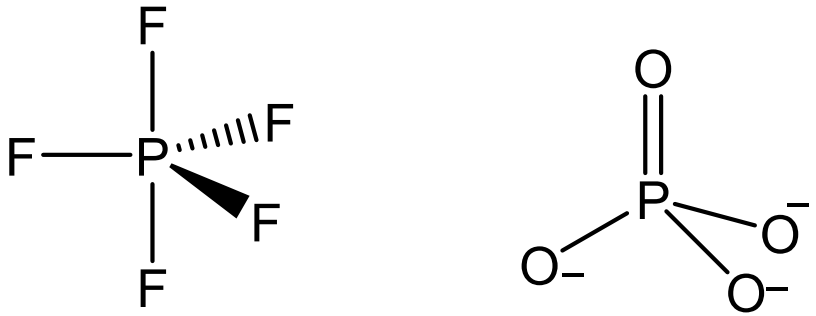




*Pauling's Electroneutrality Principle

Hypervalence

- Hypervalence may be a misnomer by some definitions, but it would probably be the most commonly used misnomer in chemistry
- Aka “octet expansion”
- Can be represented either by an increased number of atoms bound to the “hypervalent” atom or by an increased number of (multiple) bonds to the “hypervalent” atom. Applies to 3rd row and higher non-metals bonds to highly electronegative elements.

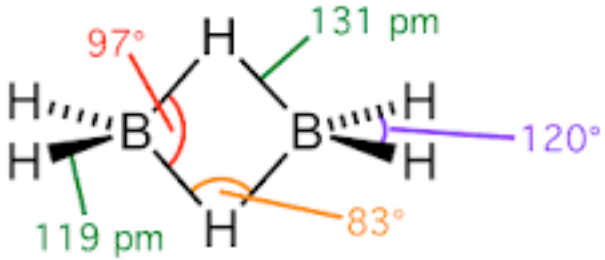


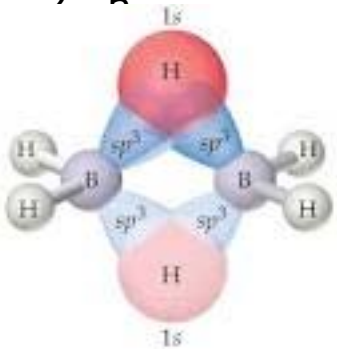
Hypovalence

- Hypovalence occurs in electron deficient molecules such as BH_3
- Can lead to unexpected multiple bonds such as in BF_3
- Can lead to nucleophilic addition processes such as in

$$BF_3 + F^- \longrightarrow BF_4^-$$

- Can lead to formation of dimers such as B_2H_6





- Both processes “neutralize” the electron deficient Boron

Lecture 10 February 6, 2019

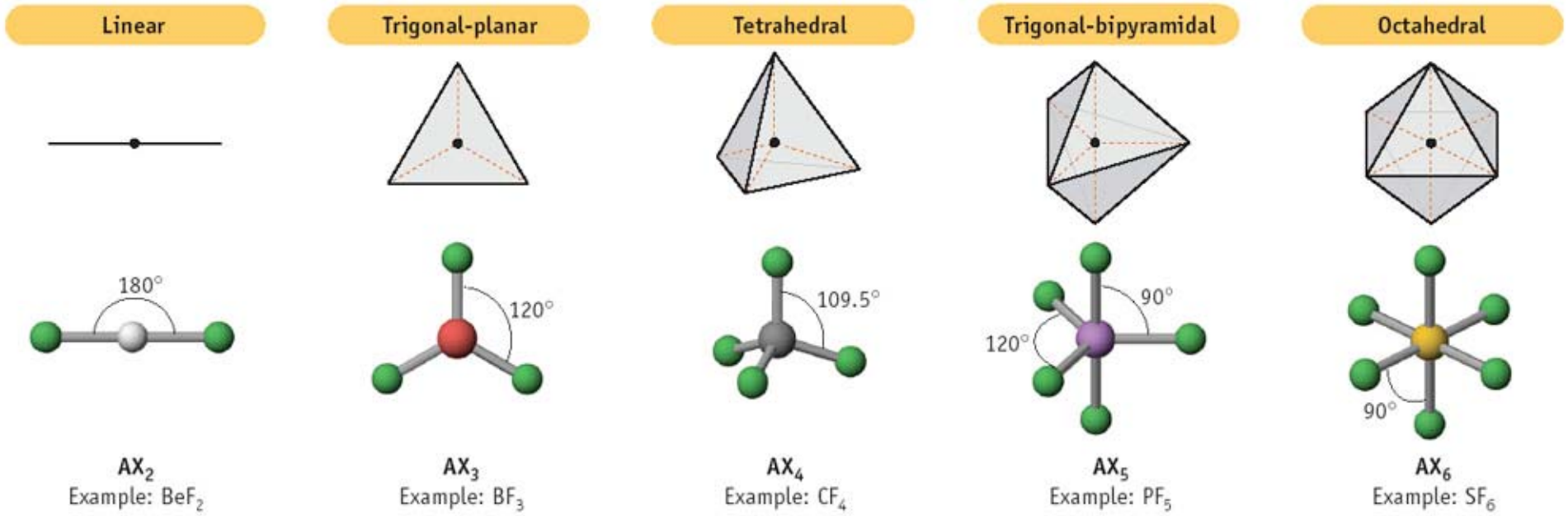
- ***Positions of Electron Pairs in Molecules***
- ***Hybrid Orbitals***
- ***Shapes of Molecules*** ***(Common Stereochemistries in Main Group Compounds)***
- ***VSEPR***
- ***Symmetry Operations and Elements***

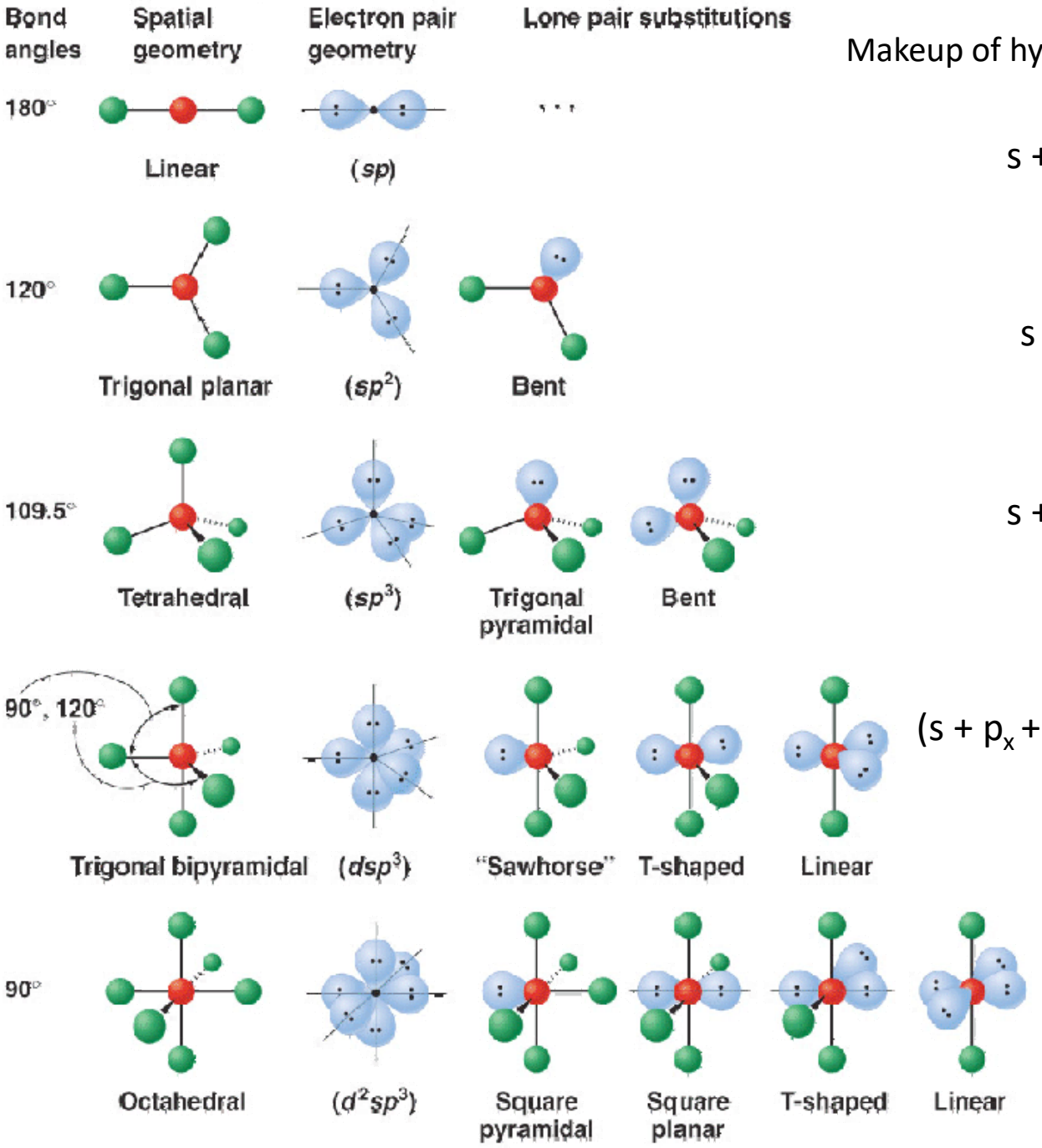
Can Atomic Orbital Overlap Predict Molecular Shapes?

Consider: HF, H_2S, PH_3 Bonds of all can be ascribed to overlap of 3p valence orbital on F, S, or P with 1s H orbital

But: H_2O, NH_3 , CH_4!!!

Need Hybrid orbitals: sp^3





Makeup of hybrid orbitals

$s + p_z$

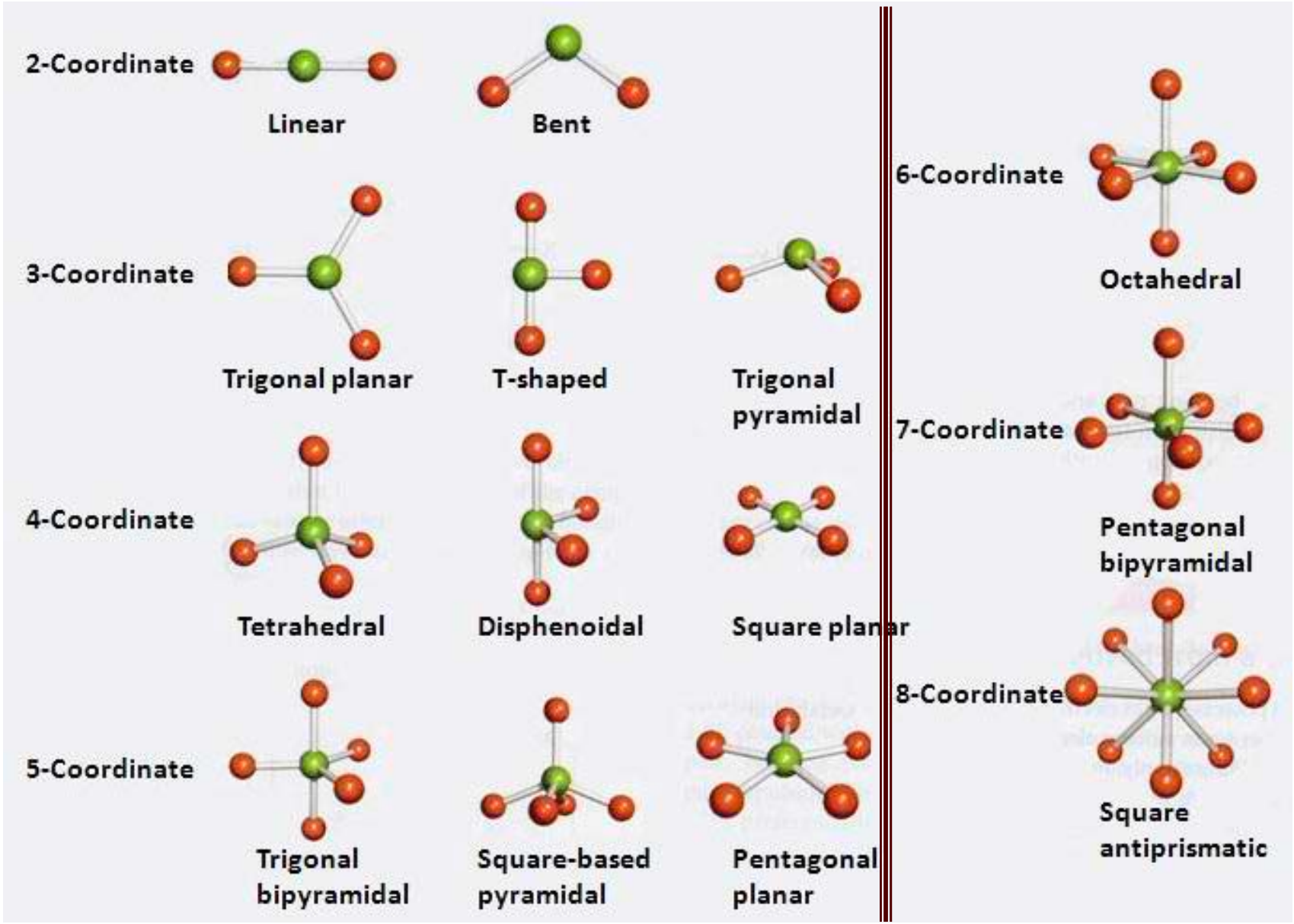
$s + p_x + p_y$

$s + p_x + p_y + p_z$

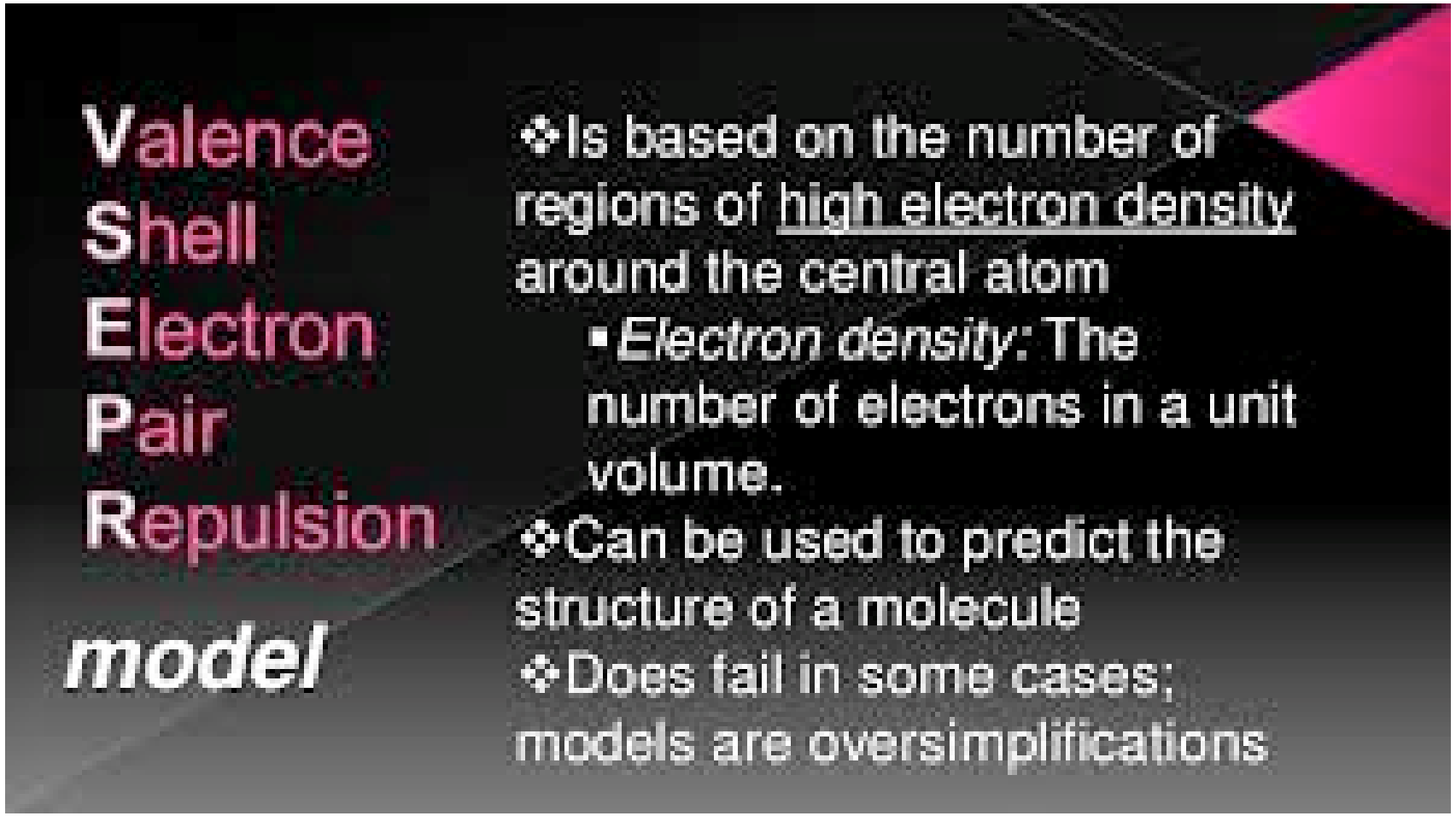
$(s + p_x + p_y) + (p_z + d_{z^2})$

$(s + p_x + p_y + p_z + d_{z^2} + d_{x^2-y^2})$

Descriptions of geometries in mono-centric molecules: It is where The atoms are. . .



A way to predict geometry



Geometries may be predicted via VSEPR:
Valence Shell Electron Pair Repulsion

- **Electron pairs of bonds and lone pairs repel each other**
- **The geometry around any atom is a consequence of minimizing these repulsive interactions**
- Lone pairs are considered to be larger than bonding pairs
- **Multiple bonds are considered to be in the same space as, but larger than, single bonds**
- **Several common geometries depending on the number of "occupants" around the atom in question**
- **The "Steric number" of the molecule determines the hybrid orbitals used to account for sigma bonds and lone pairs**

Remember the following things:

1. Multiple bonds behave as a single electron pair bond for the purpose of VSEPR.
2. Order of repulsion between lone pair and lone pair (lp - lp), lone pair and bonding pair (lp- lp), and bonding pair and bonding pair (bp- bp) is lp - lp >> lp- bp >bp -bp .

   when a molecule has lone pairs of electrons , the bonding electron pairs are pushed closer and thus the bond angle is decreased.

https://www.youtube.com/watch?v=1ZlnzyHahvo
https://www.youtube.com/watch?v=xNYiB_2u8J4

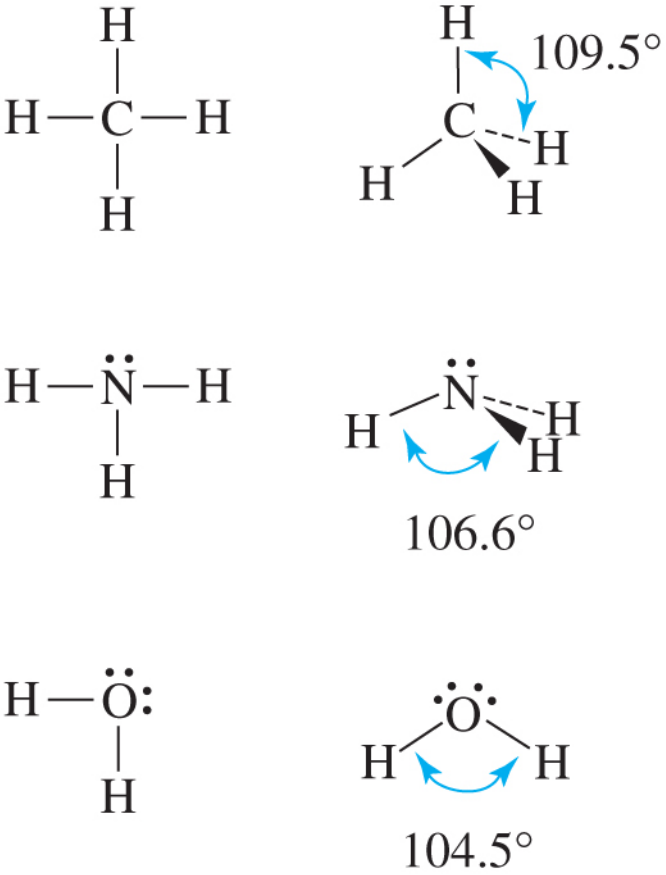
In TBP, lone pairs go in Equatorial positions rather Than axial positions. This minimizes repulsions.

www.youtube.com/watch?v=nxebQZUVvTg

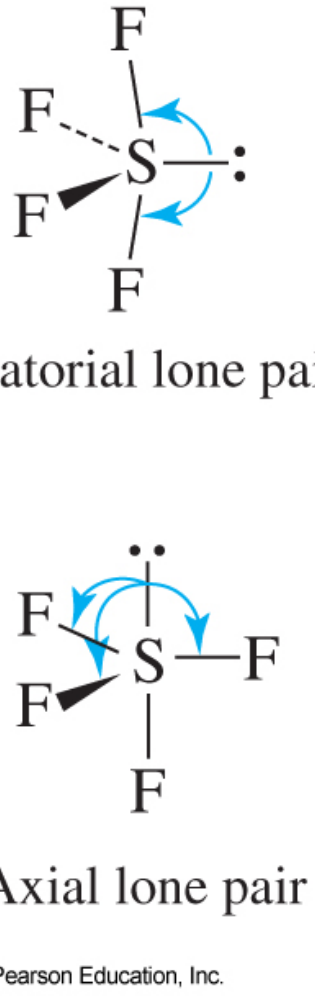
http://ocw.mit.edu/courses/chemistry/5-111-principles-of-chemical-science-fall-2008/video-lectures/lecture-13/

https://www.youtube.com/watch?v=1ZlnzyHahvo
https://www.youtube.com/watch?v=xNYiB_2u8J4

VSEPR rationalizes bond angles and geometry of molecules

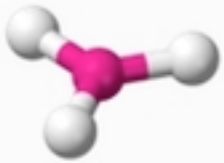
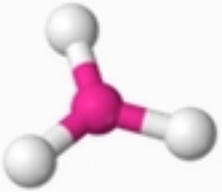
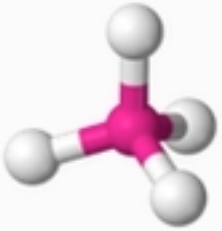
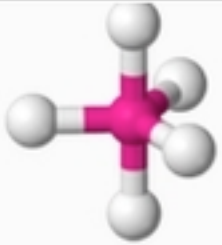
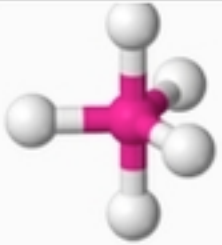


For H_2O and NH_3, lone pairs are in sp^3 hybrid orbitals; for H_2S and PH_3 No hybrid orbitals needed.

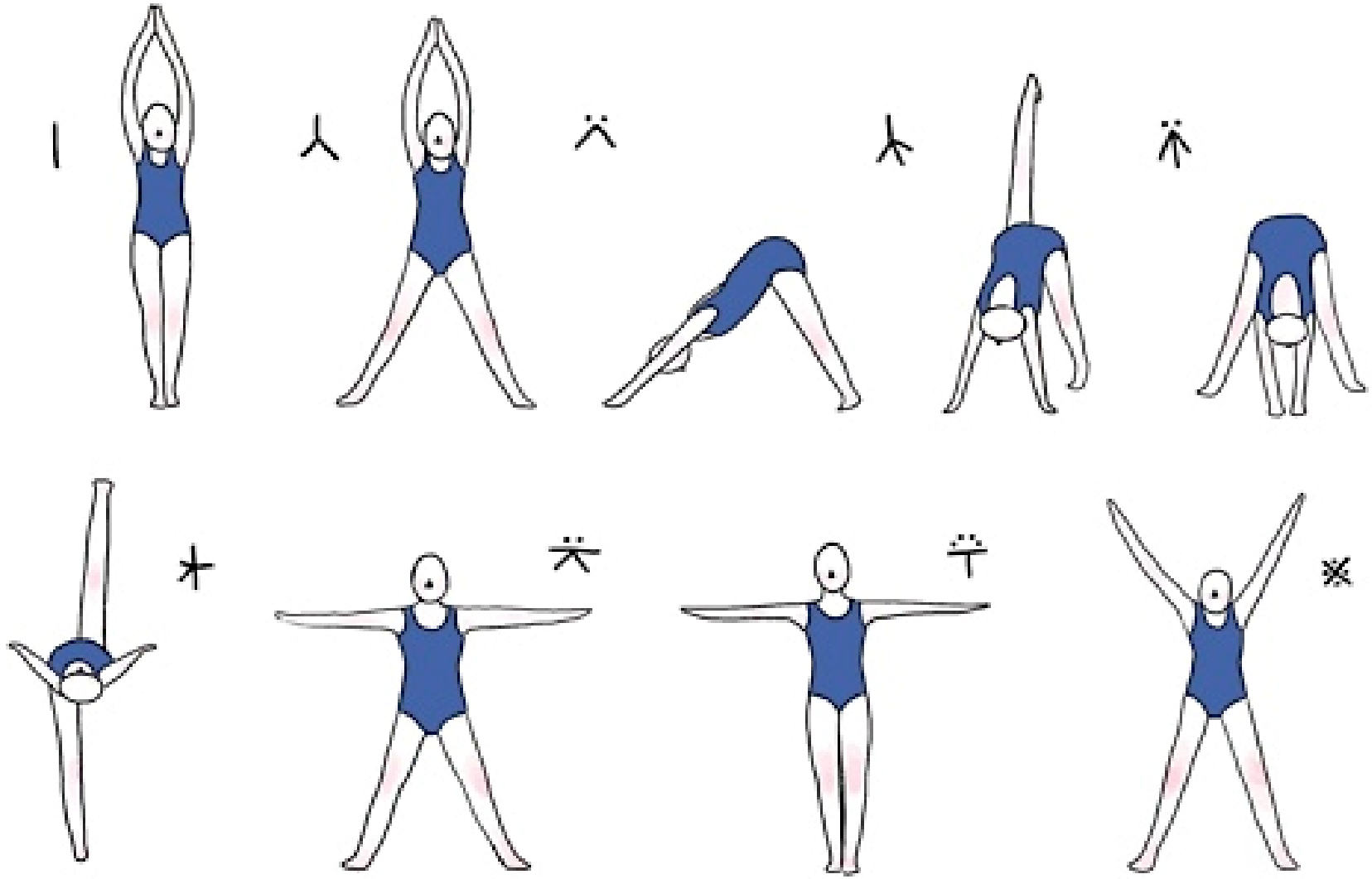


For SF_4 the lone pair is more stable in the sp^2 subset of the sp^3d hybrid orbitals

VSEPR and the AXE Description of Electron Arrangements

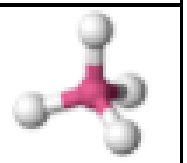
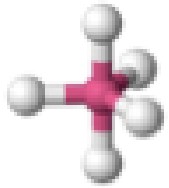
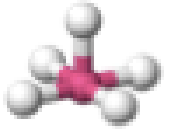
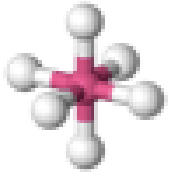
Molecule Type	Shape	Electron arrangement†	Geometry‡	Examples
AX_2E_0	Linear			$BeCl_2$, $HgCl_2$, CO_2
AX_3E_0	Trigonal planar			BF_3, CO_3^{2-}, NO_3^-, SO_3
AX_4E_0	Tetrahedral			CH_4, PO_4^{3-}, SO_4^{2-}, ClO_4^-, $TiCl_4$, XeO_4
AX_5E_0	Trigonal bipyramidal			PCl_5
AX_6E_0	Octahedral			SF_6, WCl_6

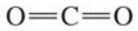
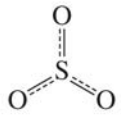
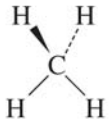
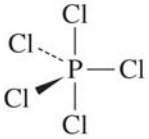
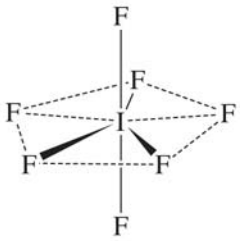
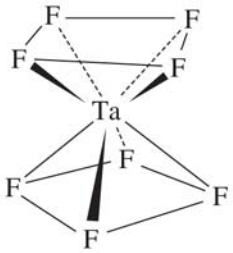
VSEPR YOGA



VSEPR Theory

# of Atoms	# of electron pairs	Formula Type	Geometry	Bond Angle	Examples	Hybridization	Structure
3	0	AB_2	Linear	180	CO_2, CS_2, BeH_2		
3	1	AB_2	Bent	117.5	$GeCl_2$, SO_2, NO^-_2	sp^2	
3	2	AB_2	Bent	105	H_2O, H_2S	sp^3	
4	0	AB_3	Trigonal planar	120	BCl_3, $AlBr_3$,	sp^2	
4	1	AB_3	Pyramidal	107	NH_3, PCl_3, $AsBr_3$	sp^3	
4	2	AB_3 (Inter halogen)	T-shaped	90, 180	ICl_3, BrF_3,	sp^3d	

5	0	AB_4	Tetrahedron	109.5	CCl_4, CH_4, $SiBr_4$	sp^3	
5	1	AB_4	Distorted tetrahedron (Seesaw)		SF_4, SBr_4, $SeCl_4$	sp^3d	
5	2	AB_4	Square planar	90, 180	XeF_4,	sp^3d^2	
6	0	AB_5	Trigonal bipyramidal	90, 180, 120	PCl_5,	sp^3d	
6	1	AB_5 (Inter halogen)	Square pyramid		ClF_5, ICl_5, IBr_5	sp^3d^2	
7	0	AB_6	Octahedron	90, 180	SF_6	sp^3d^2	

Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	TaF_8^{3-}	70.5°, 99.6°, 109.5°	

Hybrid orbitals

$sp = s + p_z$

$sp^2 = s + p_x + p_y$

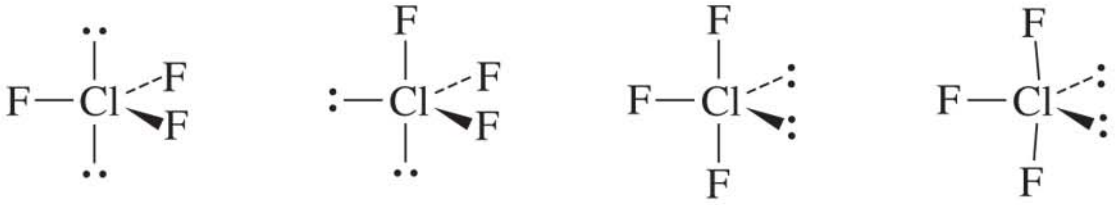
$sp^3 = s + p_x + p_y + p_z$

$sp^3d = (s + p_x + p_y) + (p_z + d_{z^2})$

$sp^3d^2 = s + p_x + p_y + p_z + d_{x^2 - y^2} + d_{z^2}$

How about the 5 pairs of electrons about Cl in ClF_3?

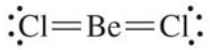
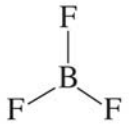
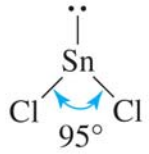
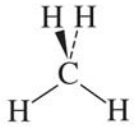
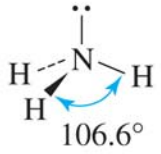
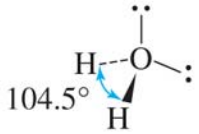
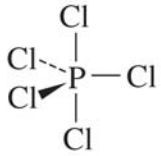
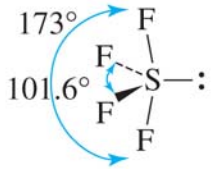
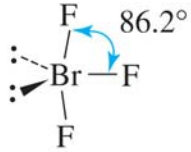
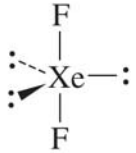
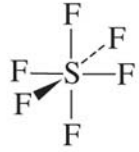
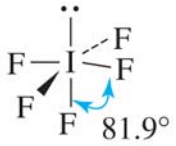
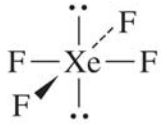
Analysis of lone pair/lone pair vs. lone pair/bonded pair vs. bonded pair/bonded pair repulsions



A B C Experimental

Interaction	Calculated			Experimental
	A	B	C	
lp-lp	180°	90°	120°	Cannot be determined
lp-bp	6 at 90°	3 at 90°	4 at 90°	Cannot be determined
		2 at 120°	2 at 120°	
bp-bp	3 at 120°	2 at 90°	2 at 90°	2 at 87.5°
		1 at 120°		Axial Cl—F 169.8 pm
				Equatorial Cl—F 159.8 pm

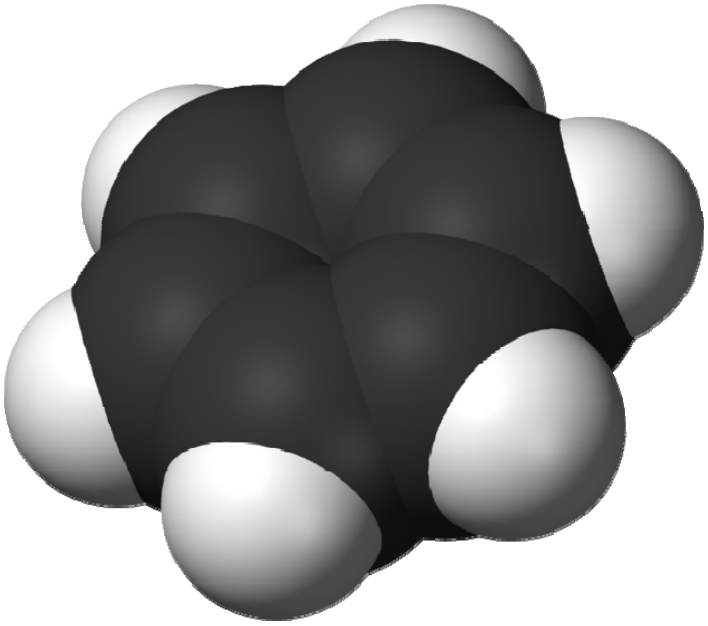
Conclusion: larger pairs of electrons adopt equatorial plane positions, i.e., sp^2 subset

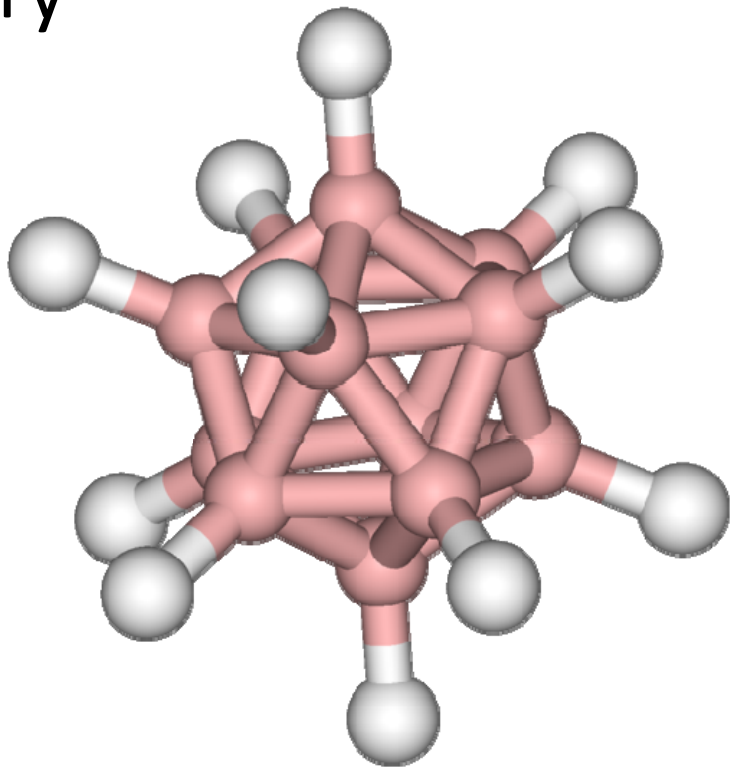
Steric Number	*Number of Lone Pairs on Central Atom*			
	None	*1*	*2*	*3*
2				
3				
4				
5				
6				

Lecture 11 February 8, 2019

- ***Using the shapes of Molecules to define:***
- ***Symmetry Operations***
- ***Symmetry Elements***
- ***Point Groups and Assignments***

Symmetry

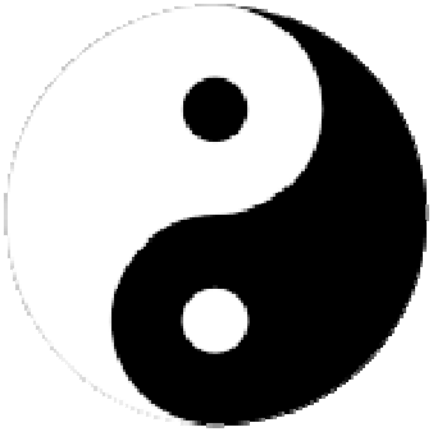




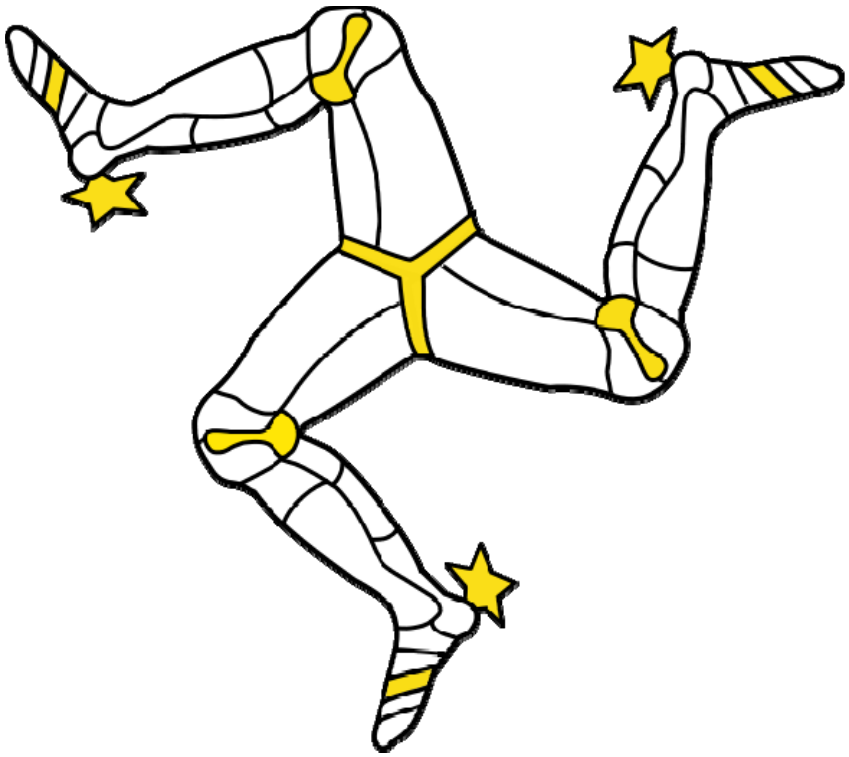
Intuitively, we know symmetry when we see it.

But how do we put in quantitative terms that allows us to compare, assign, classify?

Symmetry: mirror planes

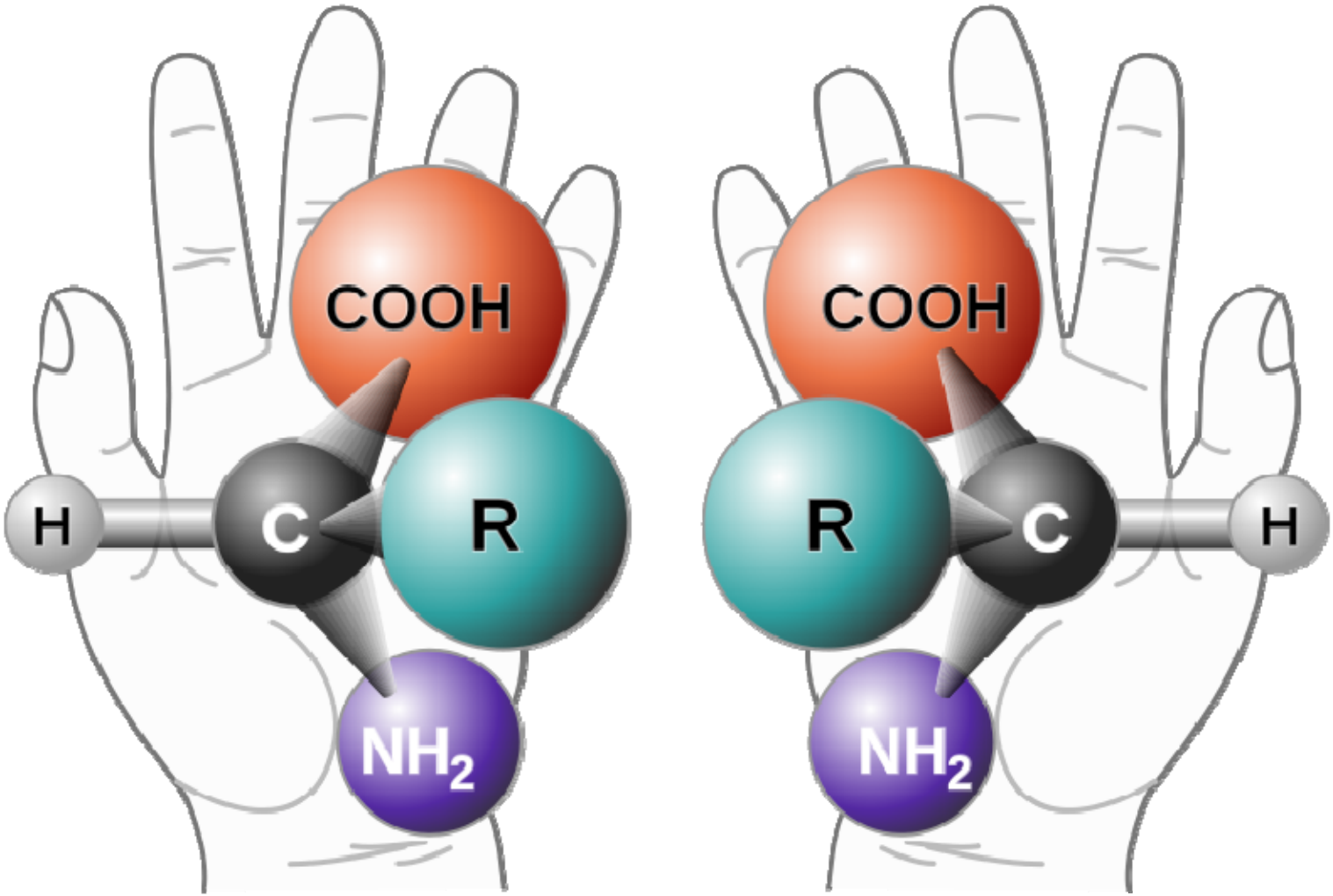


Symmetry



C_3 Rotation Axis

Chirality: Non-superimposable mirror images (aka optical isomers or enantiomers)



Specifically, a chiral compound can contain no improper axis of rotation (S_n), which includes planes of symmetry and inversion center. Asymmetric molecules are always chiral.