CHEM2100J Chapter 04 RC

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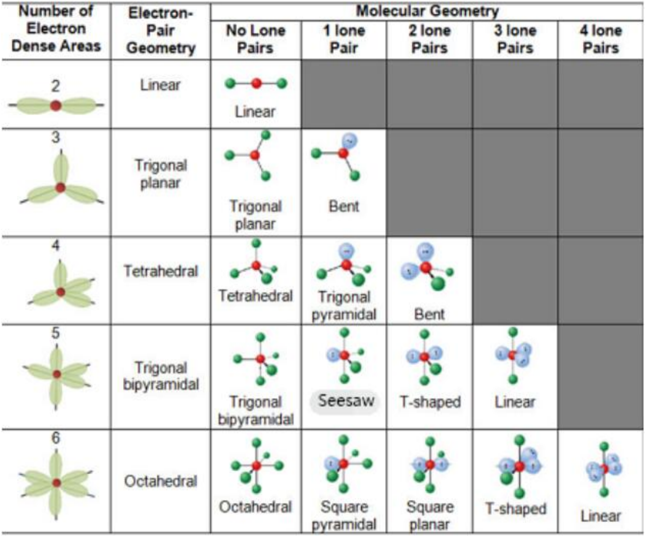
Basic VSEPR Model

- Basic Rules
  - 1. Regions of high electron density are either bonding or lone pairs which repel one another to minimize repulsion.
  - 2. Electron pairs in multiple bonds are treated as the same as single bonds.
  - 3. The electronic arrangement only considers positions of atoms when reporting the shape of a molecule.
  - 4. Lone pair repulsion energies order: lone pair-lone pair>lone pair-atom>atom-atom.
- Generic Formula: AX_nE_m
  - A - central atom; X - attached atom; E - lone pair

Basic VSEPR Model



Number of Electron Dense Areas	Electron-Pair Geometry	Molecular Geometry				
		No Lone Pairs	1 lone Pair	2 lone Pairs	3 lone Pairs	4 lone Pairs
2	Linear	Linear				
3	Trigonal planar	Trigonal planar	Bent			
4	Tetrahedral	Tetrahedral	Trigonal pyramidal	Bent		
5	Trigonal bipyramidal	Trigonal bipyramidal	Seesaw	T-shaped	Linear	
6	Octahedral	Octahedral	Square pyramidal	Square planar	T-shaped	Linear

How to Determine the Generic Formula?

- Method 1
  - Draw the Lewis structure and directly count the number of bonding and lone pairs
- Method 2
  - $m = \frac{1}{2}(a - nb)$
  - a - number of valence electrons of the central atom
  - b - number of the electrons the terminal atom needs

Exercise

Determine the VSEPR model and molecule shape of:

$$NO_2,\ NO_2^+,\ NO_2^-,\ SF_4,\ XeF_2$$

Consequences of Molecular Shape

- Repulsion
  - lp-lp$\gg$lp-bp$>$bp-bp
  - Result - different in bond angle and bond length
- Polarity
  - A nonpolar molecule has no total electric dipole moment
  - Asymmetric $=$ Polar
  - Symmetric Dipole $=$ Non-polar

Exercise

(1) Explain why in H_2O_2, N_2H_4 and C_2H_6 the bond length

$$\text{O-O} > \text{N-N} > \text{C-C}$$

(2) Which of the following molecules are polar?

$$NH_3,\ C_2H_2Cl_2,\ CCl_4,\ ClF_3,\ SF_4,\ XeF_4$$

Valence-Bond Theory

- σ and π Bonds
  - σ bond - End to end
  - π bond - Side by side
  - σ bond is usually stronger than π bond because of greater overlap of electron cloud
  - ONLY single bonds can spin
- Covalent Bond Types
  - A single bond is a σ bond
  - A double bond is a σ bond plus one π bond
  - A triple bond is a σ bond plus two π bonds

Hybridization

- Electron Promotion
  - The promotion of electrons will occur if it leads to a lowering of energy by permitting the formation of more bonds
- Hybridization of Orbitals
  - The hybrid orbitals are formed from the linear combination of the original atomic orbitals
  - Number of hybrid orbitals $=$ Number of atomic orbitals
  - The hybrid orbitals contain electrons in σ bonds and lone pairs
  - The hybrid orbitals can form stronger covalent bonds
- Summary of Bonds for C
  - Four σ bonds $\rightarrow$ sp^3
  - Three σ bonds $\rightarrow$ sp^2
  - Two σ bonds $\rightarrow$ sp

Hybridization & VSEPR Model

Class of hybridization	sp	sp^2		sp^3		
Class of molecule	AB_2	AB_3	AB_2E	AB_4	AB_3E	AB_2E_2
Geometry of molecule	Linear	Trigonal plane	Bent	Tetrahedron	Trigonal pyamidal	Bent
Examples	CO_2 CS_2	BF_3 $NPCl_2$	SO_2 ONCl	XeO_4 CCl_4	NCl_3 AsH_3	H_2O OF_2

Class of hybridization	sp^3d				sp^3d^2		
Class of molecule	AB_5	AB_4E	AB_3E_2	AB_2E_3	AB_6	AB_5E	AB_4E_2
Geometry of molecule	Trigonal bipyramid	Distorted tetrahedron (or see saw)	T-shaped	Linear	Octahedron	Square pyramid	Square plane
Examples	PCl_5 $AsCl_5$	$TeCl_4$ SCl_4	ClF_3 $XeOF_2$	I_3^- XeF_2	SF_6 PCl_6^-	$XeOF_4$ IF_5	XeF_4 IF_4^-

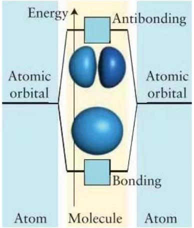
Molecular Orbital Theory

- Basic Concept
  - Molecular orbitals are built from linear combinations of atomic orbitals
  - Bonding orbital - AOs interfere constructively, energy $\downarrow$
  - Antibonding orbital - AOs interfere destructively, energy $\uparrow$
- Electron Configurations of Diatomic Molecules
  - MOs are built from the available valence-shell AOs and every AO produces an MO
  - Analogous to the electron configuration of atoms, we need to obey the building-up principle
  - σ-orbital - end to end; π-orbital - side by side
  - Allow single electron bonds

Bonding in Diatomic Molecules

- Homonuclear
  - Equal sharing of bonding electrons
  - Equal contribution to bonding orbitals and antibonding orbitals
- Heteronuclear
  - Unequal sharing of bonding electrons
  - More electronegative elements has AO lower in energy and contributes more to the bonding orbitals
  - Less electronegative elements has AO higher in energy and contributes more to the antibonding orbitals

MO Energy-level Diagrams



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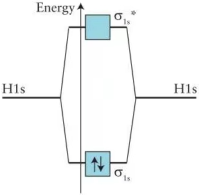
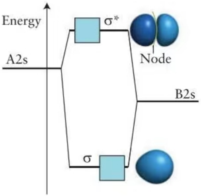


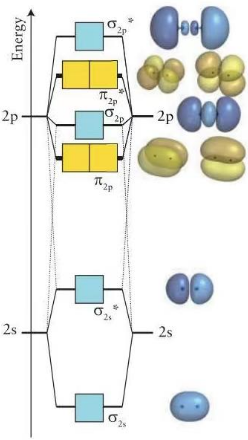
Homonuclear



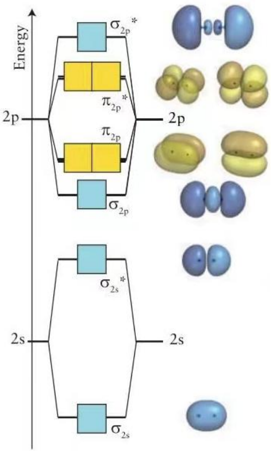
Heteronuclear

MO Energy-level Diagrams

- For Homonuclear Diatomic Molecules of Period 2 Elements



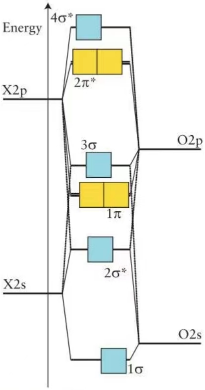
Li_2 to N_2



O_2 and F_2

MO Energy-level Diagrams

- For Heteronuclear Diatomic Molecules of Period 2 Elements



XO(X=C or X=N)

- Tip: The energy-level can not be determined qualitatively.

Bond Order

- Formula
  - BO=$\frac{1}{2}$(N-N*)
  - N - number of electrons in bonding orbitals
  - N* - number of electrons in antibonding orbitals
- BO$\uparrow$ $\Rightarrow$ stronger covalent bond $\Rightarrow$ more stable molecule
- BO=0 $\Rightarrow$ no covalent bonds formed

Magnetic Properties of Molecules

- Diamagnetic
  - Tend to move out of a magnetic field
  - All electrons are paired
- Paramagnetic
  - Tend to move into a magnetic field
  - Exist unpaired electrons

Steps to Solve MO Problems

1. Identify all AOs in the valence shell
2. Construct the MO energy-level diagram
3. Count the total number of valence electrons
4. Construct the electron configuration using the building-up principle
5. Determine the bond order
6. Determine whether the molecule is paramagnetic or diamagnetic

Exercise

(1) According to MO theory, how many σ bonds and π bonds are there in an O_2 molecule?
(2) Write the ground-state electron configurations of CO and NO and determine which molecule is more stable.

Reference

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Thanks!