CH102 Spring 2019
Discussion #1
Chapter 10

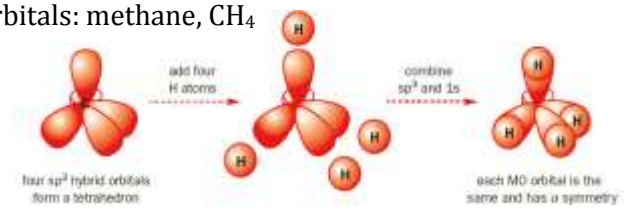
TF's name: _____ LA name: _____ Discussion Day/Time: _____ Student name: _____

Things you should know when you leave discussion today:

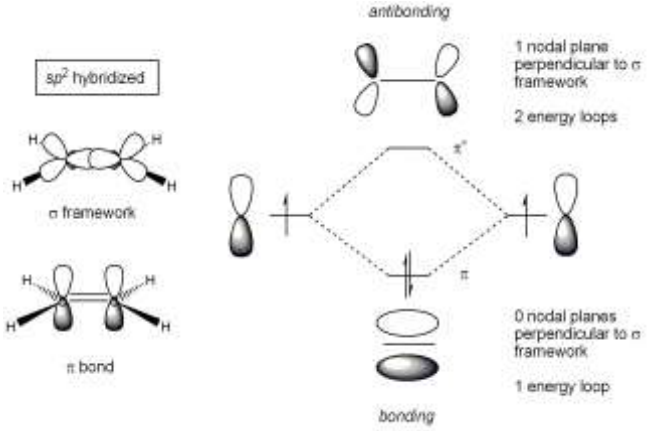
- Polyatomic (more than two) molecular orbitals, http://goo.gl/6hBD8X , Mahaffy, 2e p386-397, p406-407
  - ✓ Review Lewis Structures!!
  - ✓ Steric Number (SN) = number of atoms + number of lone pairs attached to the center atom

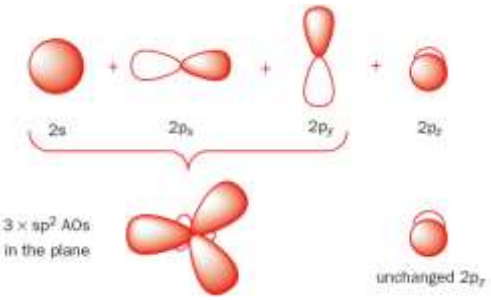
- Hybridized atomic orbitals: sp^3 (SN=4), sp^2 (SN=3), sp (SN=2)
  http://demonstrations.wolfram.com/HybridOrbitalsInOrganicChemistry/

Example 1. A σ-frame with sp^3 hybridized atomic orbitals: methane, CH_4
1s + 3p = 4 sp^3 hybridized AOs
(SN=4, with 109.5° angle)

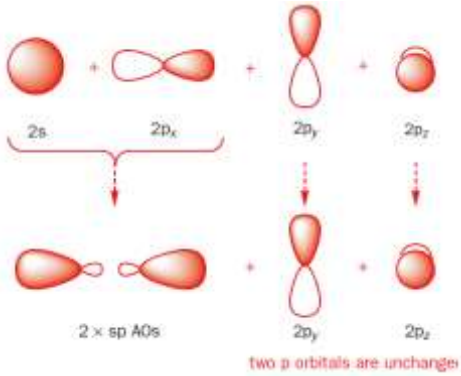


Example 2. A σ-frame (top left), a π-frame (bottom left) and π-energy diagram (in the middle) with sp^2 hybridized orbitals: ethene, H_2CCH_2
1s + 2p = 3 sp^2 hybridized AOs and 1 free p AO perpendicular to the plane of the molecule.
(SN=3, with 120° angle)





Example 3. A σ-frame with sp hybridized atomic orbitals:
1s + 1p = 2 sp hybridized AOs and 2 free p AO perpendicular to the plane of the molecule and perpendicular to each other.
(SN=2, with 180° angle)



1. If you have two atoms that together have 5 atomic orbitals, when those atoms combine to form a molecule, how many molecular orbitals are you going to have?

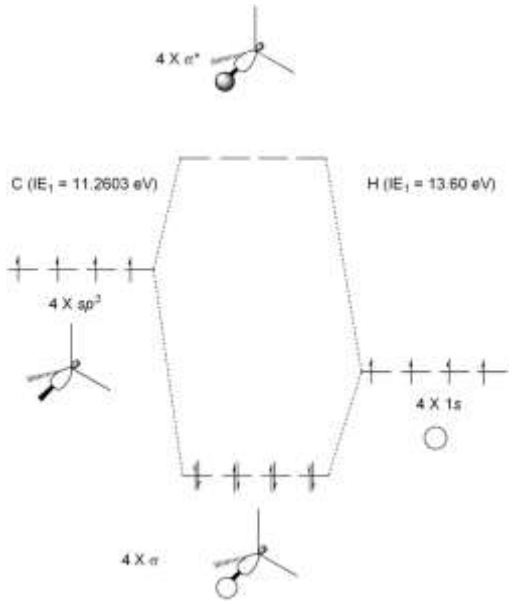
2. Are hybridized orbitals atomic orbitals or molecular orbitals?

3. What is the hybridization of the center atoms for the following molecules? *Hint: Draw the Lewis structures. Terminal atoms will have the same hybridization of the center atom.*
   a. CO_2

   b. H_3COH

   c. HCOOH

4. Draw correlation diagram for NH_3 using hybridized AOs**.** *Hint: use a correlation diagram of CH_4 below for guidance.*
   a. Draw the Lewis structure for NH_3 and determine the steric number.
   b. How many AOs do you start with?
   c. Determine the hybridization.
   d. How many hybridized atomic orbitals do you have?
   e. Draw correlation diagram for NH_3.



5. Using hybridized atomic orbitals, sketch the σ-frame for the MO structure for C_2H_6. *Hint: first draw a Lewis structure, and determine steric number (SN) of the center atoms.*

6. Using the sp^2 hybrid orbitals, sketch σ-frame and π-frame structure for H_2CCH_2

7. Using the sp hybrid orbitals, sketch MO structure for HCCH. (Sketch σ-frame and π-frame, draw π-energy diagram)

Challenge problem in preparation for next week:

8. Sketch the MO structure of H_2CO_3.
   a. Draw the Lewis structure and count the number of valence electrons:

   b. Assign hybridization of all the atoms (use your Lewis structure).
      i. Determine hybridization of the center atom(s).Terminal atoms will have the same hybridization as the center atom.

c. Identify and sketch σ-framework.
   i. Identify number of σ bonds in the molecule and the number of e^- involved.
   ii. Identify number of lone pairs in the **σ** framework and the number of e^- involved.
d. Identify π-framework, is it localized or delocalized? How many π bonds? *Hint: Decide which atoms can participate in π bonds.*
   i. Count the p AOs not involved in hybridization.

   ii. Determine the number of electrons involved in the π bonds.
   # π electrons = (# valence e^-) – (# σ electrons) – (lone pair electrons in the σ-framework)

e. Sketch the corresponding π MO and corresponding energy diagram for just π-framework.
   i. Rank them in terms of increasing energy (depending on number of loops).
   ii. Fill the π MOs with the electrons involving in π bonds.
   iii. Label the π MOs as bonding, antibonding and/or nonbonding.

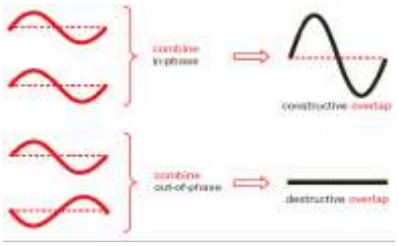
Instructions to make correlation diagrams for π-framework of polyatomic molecules:

1. Draw the Lewis structure and count the number of valence electrons.
2. Assign hybridization of all the atoms.
3. Determine hybridization of the central atom(s).
   Note: Terminal atoms will have the same hybridization as the central atom.
4. Identify and sketch σ-framework.
5. Identify number of σ bonds in the molecule and the number of e^- involved.
6. Identify number of lone pairs and the number of e^- involved.
7. Identify π-framework (Is it localized or delocalized? How many π bonds?) *Hint: Decide which atoms can participate in π bonds.*
8. Determine the number of electrons involved in the π bonds.
   # π electrons = (# valence e^-) – (# σ electrons) – (lone pair electrons in the σ-framework)
9. Count the p AOs not involved in hybridization.
10. Sketch the corresponding π MO and corresponding energy correlation diagram for just π-framework.
    i. Rank them in terms of increasing energy (depending on number of loops).
    ii. Fill the π MOs with the electrons involving in π bonds.
    iii. Label the π MO's as bonding, antibonding and/or nonbonding.

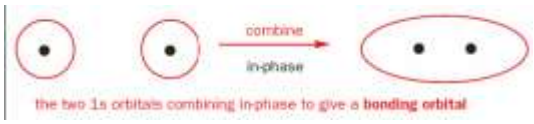
Handout Answers:

1. 5
2. Atomic orbital
3.
   a. sp
   b. sp^3, sp^3
   c. sp^3 ; sp^2; sp^2

Review from last semester:

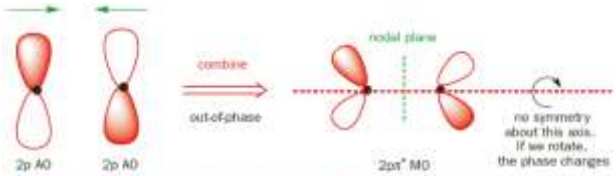


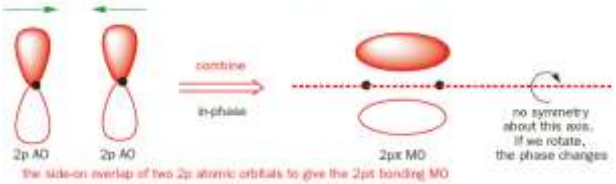
1. Atomic Orbital (s, p, d, f) vs. Molecular Orbital (σ, σ*, NB, π, π*, π_{nb})
2. Total Number of AO = Total Number of MO
3. Constructive and destructive interference (in phase and out-of-phase interaction)



- Sigma bond is achieved by head–on–overlap
- Bonding MO (σ, π): constructive interference in-phase interaction

- Antibonding MO (σ*, π*): destructive interference out-of-phase interaction
- π formed from side-by-side overlap of available p AO
- π* is out-of-phase overlap of available p AO



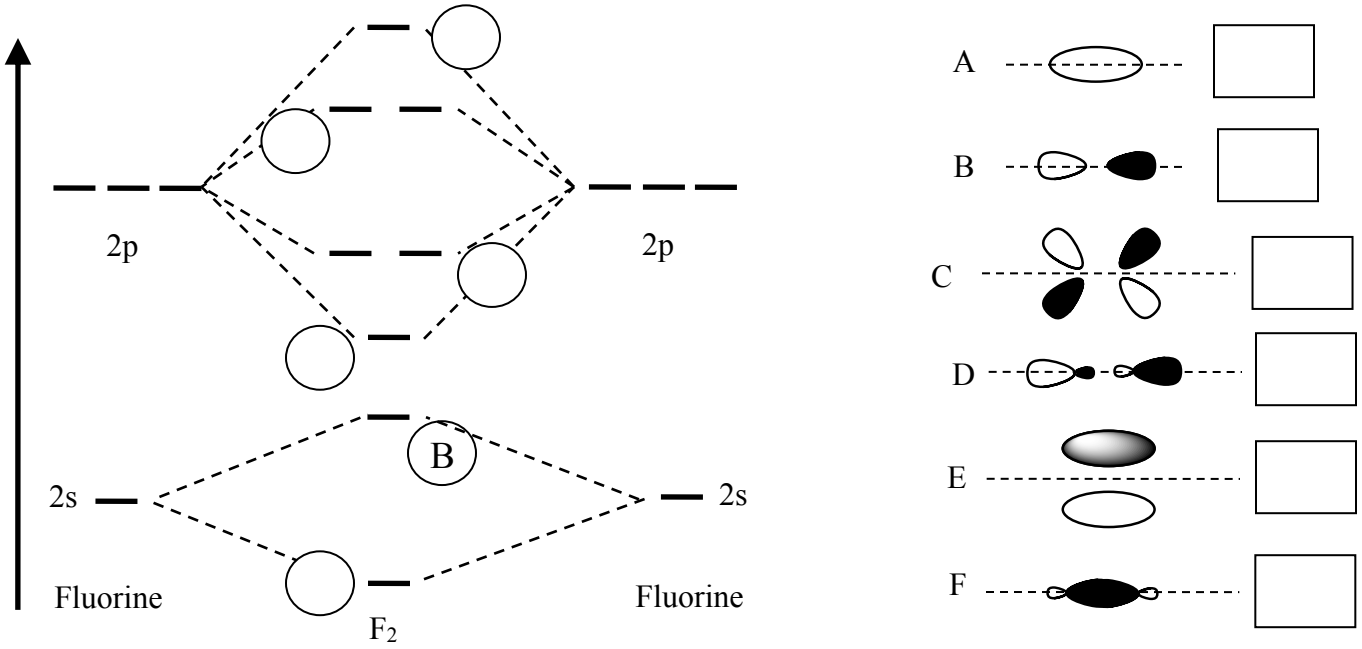


1. Below on the left is an empty molecular orbital diagram of F_2. Below to the right are various molecular orbitals, with the inter-nuclear axes shown with a dotted line. You will fill in the boxes next to the molecular orbitals in part (a). You will fill in the circles on the molecular orbital diagram in part (b). <u>Carefully follow the instructions below</u>.

   a. In the box to the <u>right</u> of the molecular orbitals formed in F_2 above, provide the proper name of each molecular orbital (e.g. σ_{2s}, π^*, etc).

   b. Match each molecular orbital on the right to the molecular orbital diagram on the left. Show your answer by placing the <u>letter</u> in the circle beside the molecular orbital. Letter "B" is filled in for you.

   c. In the molecular orbital diagram above, populate both the atomic and molecular orbitals with electrons by putting arrows on the horizontal lines for F_2 and the fluorine atoms. All three systems are in the ground state.



d. Using the diagram above to guide you, calculate the bond orders for the following species.

F_2^+ : _____ F_2^{2-} : _____

e. Naturally Fluorine is a diamagnetic molecule. Let say in the planet far, far away we found a fluorine that is paramagnetic: propose and draw the molecular orbitals that Fluorine must have to be paramagnetic.