Chem 102 Spring 2019
Discussion #2
Chapter 10

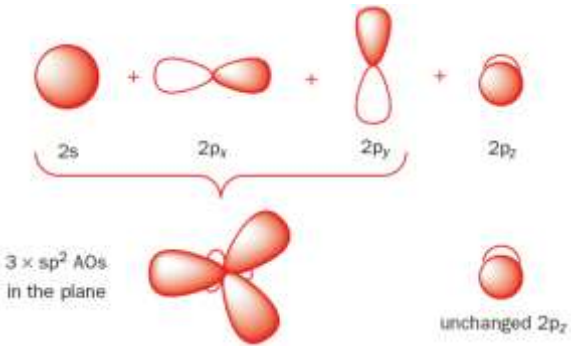
TF's name: _____ Your name: _____ Discussion Section: _____

Things you should know when you leave Discussion today:

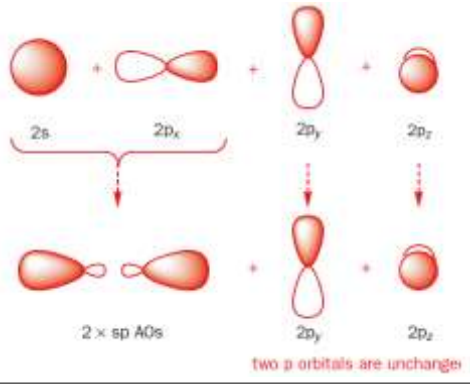
1. Hybridized atomic orbitals (sp^3, sp^2, sp)

a. sp^3 hybridized atomic orbitals:

b. sp^2 hybridized atomic orbitals:



c. sp hybridized atomic orbitals:



2. σ-framework
3. π-framework
4. $\pi_{localized}$ vs. $\pi_{delocalized}$

For help go to :http://goo.gl/6hBD8X and Mahaffy,2e, p386-397, p406-407

<u>Molecular Orbital Instructions--</u>Making correlation diagrams for π-framework of polyatomic molecules:

1. Draw Lewis Structure (LS) and any resonance structures
   a. Count the number of valence electrons
   b. Assign hybridization of all the atoms
      - Determine hybridization of the center atom(s)
      - Terminal atoms will have the same hybridization of the center atom.
2. Identify σ-framework
   a. Identify number of σ bonds in the molecule and the number of e^- involved
   b. Identify number of lone pairs and the number of e^- involved
3. Identify π-framework
   a. Determine the number of electrons involved in the π bonds

   # π electrons = (# valence e^-) – (# σ electrons) – (lone pair electrons in the σ-framework)

   b. Count the p AOs not involved in hybridization
4. Sketch the corresponding π MO.
   a. Rank them in terms of increasing energy (depending on number of loops)
   b. Fill the π MOs with the electrons involving in π bonds
   c. Label the π MOs as bonding, antibonding and/or nonbonding

1. Sketch the MO diagram for HCO_3^-
   a. Draw the Lewis structure and count the number of valence electrons

   b. Assign hybridization of all the atoms
      i. Determine hybridization of the center atom(s)

   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 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. Determine the number of electrons involved in the π bonds
      ii. Count the p AOs not involved in hybridization

   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 MO's with the electrons involving in π bonds
      iii. Label the π MO's as bonding, antibonding and/or nonbonding

2. Sketch the MO diagram for C_4H_6 (1,3-butadiene, $CH_2=CH-CH=CH_2$).
   a. Draw L.S.

   b. Determine and draw σ-framework:

   c. How many pairs of electrons are in the σ-framework

   d. How many pairs of electrons are in the π-framework?

   e. Draw energy diagram for π-framework:

   f. How many pairs of electrons are shared between the middle two carbons in 1,3-butadiene?

   g. How many pairs of electrons are shared between the first two carbons in 1,3-butadiene?

3. Assume light is absorbed by NO_2^- to create the excited molecule $(NO_2^-)^*$ in which one electron has shifted from the HOMO to the lowest unoccupied molecular orbital (LUMO), the π antibonding MO.
   For an excited state, $(NO_2^-)^*$ answer following questions:

   a. How many electrons are in σ bonding orbitals?

   b. How many electrons are in σ nonbonding orbitals?

   c. How many electrons are in π bonding orbitals?

   d. How many electrons are in π antibonding orbitals?

   e. How many electrons are in π nonbonding orbitals?

   f. How many electrons are shared between O_{left} and N?

   g. How many electrons are shared between O_{right} and N?

   h. How many unshared electrons are on O_{left}?

   i. How many unshared electrons are on O_{right}?

   j. How many unshared electrons are on N?

   k. What is a total number of unshared electrons?

   l. What has happened to the dipole moment of NO_2^-?(assume the σ framework is unaffected.)

4. Sketch the MO diagram for C_4H_2, ($C_AH{\equiv}C_B{-}C_C{\equiv}C_DH$). Diacetylene.

   a. Determine and draw σ-framework:
   b. How many pairs of electrons are in the σ-framework?
   c. How many pairs of electrons are in the π-framework?
   d. Draw energy diagram for π framework:
   e. How many pairs of electrons are shared between the middle two carbons in C_4H_2,
   f. How many pairs of electrons are shared between the first two carbons in C_4H_2

5. What is the hybridization of the oxygen atoms in SO_2?

   a. Sulfur dioxide, SO_2, has a total of 9 pairs of electrons. How many pairs of electrons are in the σ-framework of SO_2?

   b. How many bonding π electrons are there?

   c. How many non-bonding π electrons are there?

   d. How many electrons are there on either terminal atom that are not shared with the central atom?
   e. How many electrons are there on the central atoms that are not shared with the terminal atoms?
   f. How many electrons that are shared with the central and terminal atoms?

6. What is the hybridization of the oxygen atoms in CO_2? (for help go to http://goo.gl/6hBD8X)

   a. Carbon dioxide, CO_2, has a total of 8 pairs of electrons. How many pairs of electrons are in the σ-framework of CO_2?

   b. How many bonding π electrons are there?

   c. How many non-bonding π electrons are there?

   d. How many electrons are there on either terminal atom that not shared with the central atom?

   e. How many electrons are there on the central atoms that not shared with the terminal atoms?

Additional Examples: Determine σ-framework and corresponding π MO energy diagram for: H_2CO, $C_3H_5^-$, HCO_2^-, $HOCO_2^-$, $\mathbf{N_3H}$.

Useful information:

$\pi_{localized}$ vs. $\pi_{delocalized}$

Properties of π systems

- $\pi_{localized}$ electron density localized between two atoms.
- $\pi_{delocalized}$ electron density localized between three or more atoms.
- Stabilizing effect – delocalized π systems are lower in energy than localized

Energy diagrams for π framework of polyatomic molecules

- Follow MO recipe above: draw Lewis structure, count electrons, identify hybridization
- Draw σ-framework
- Draw π-framework
  a. Determine the number of p AOs not involved in σ-framework
  b. Count total number of valence electrons that belong to π-framework
  c. Decide if you have $\pi_{localized}$ or $\pi_{delocalized}$
  d. Sketch the corresponding π MO based on the relative energy levels (depending on number of loops) and identify bonding, nonbonding and antibonding π MO

If three atoms have available p AOs next to each other: $\pi_{delocalized}$	
Highest-energy (three-loops) π^* antibonding MO has all of the p AOs out-of-phase	
Second lowest-energy (two-loops) π nonbonding MO consist of a group of adjacent p AOs with one relative phase, and a group of adjacent AOs with the other relative phase (no overlap)	
Lowest-energy (one-loop) π bonding MO has all of the p AOs in-phase	

Example 1: Here is an example of a delocalized **π** system of the allyl cation, $C_3H_5^+$.