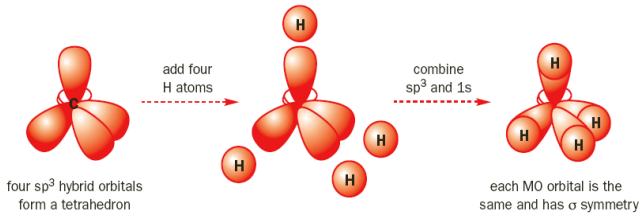
Chem 102 Discussion #2 2018 Chapter 10

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

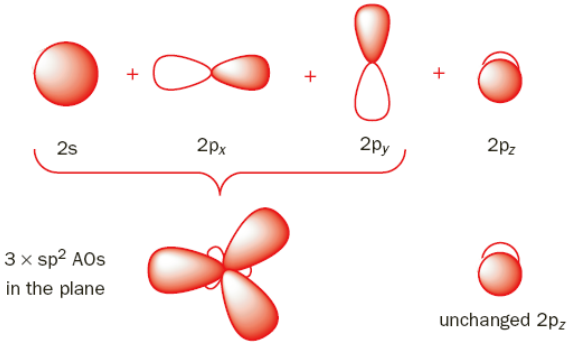
Things you should know when you leave Discussion today.

1. **Hybridized atomic orbital** (sp^3, sp^2, sp…)

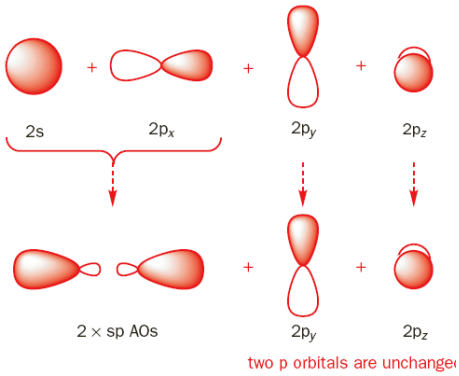
sp^3 hybridized atomic orbitals**:**



sp^2 hybridized atomic orbitals**:**



sp hybridized atomic orbitals**:**



2. Making correlation diagrams for π framework of polyatomic molecules
3. σ framework
4. **π** framework
5. $\pi_{localized}$ verses $\pi_{delocalized}$
6. for help go to :`http://goo.gl/6hBD8X and Mahaffy pp386-397, pp406-407`

Molecular Orbital Instructions:

1. Making correlation diagrams for **π** framework of polyatomic molecules
   - **a.** Draw Lewis Structure and any resonance structures.
     - Count the number of valence electrons
     - Assign hybridization of all the atoms
       a. Determine hybridization of the center atom(s)
       b. Terminal atoms will have the same hybridization of the center atom.
   - **b. Identify σ framework**
- Identify number of **σ** bonds in the molecule and the number of e^- involved
- Identify number of lone pairs and the number of e^- involved
   - **c. Identify π framework**
- Determine the number of electrons involved in the **π** bonds
  a. # **π(electrons)=#Valence e^- - σ(electrons)-** lone pair**(electrons)**
- Count the *p* AO's not involved in hybridization.
- Sketch the corresponding **π** MO.
- Rank them in terms of increasing energy (depending on number of loops)
- Fill the **π** MO's with the electrons involving in **π** bonds
- Label the **π** MO's as bonding, antibonding and /or nonbonding

1. What is a hybridization of the center atoms for the following molecules:
   (Terminal atoms will have the same hybridization of the center atom)

   a. CO_2

   b. H_3COH

   c. HCOOH

2. Are hybridized orbitals atomic orbitals or molecular orbitals?

3. Draw correlation diagram for NH_3, using hybridized AO**s.**

Important Steps

a. Draw the Lewis structure and determine the steric number:

b. How many AO do you start with?

c. Determine the hybridization :

d. How many hybridized atomic orbitals do you have?

e. Draw correlation diagram for NH_3:

4. 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.

a. 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 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.
 # π(electrons) = #Valence e^- - σ electrons - lone pair **electrons**.
ii. Count the *p* AO's not involved in hybridization.

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

5. 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.

b. 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 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.
 # π(electrons) = #Valence e^- - σ electrons - lone pair **electrons**.
ii. Count the *p* AO's not involved in hybridization.

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

6. Sketch the MO diagram for C_4H_6 (1,3-butadiene, $CH_2=CH–CH=CH_2$). (use all the steps)

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 correlation 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

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

a. Carbon 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?

8. What is the hybridization of the oxygen atoms in CO_2?(for help go to :`http://goo.gl/6hBD8`X)

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 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?

9. 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 localized π bonding orbitals?

   d. How many electrons are in localized π antibonding orbitals?

   e. How many electrons are in delocalized π bonding orbitals?

   f. How many electrons are in delocalized π nonbonding orbitals?

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

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

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

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

   k. How many unshared electrons are on N?

Additional Examples: Determine σ framework and corresponding **π** MO correlation diagram for: **H_2CO, $C_3H_5^-$, SO_2, HCO_2^-, $HOCO_2^-$, O_3, O_3, NO_2^-**

Useful information:

$\pi_{localized}$ verses $\pi_{delocalized}$

Properties of π systems

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

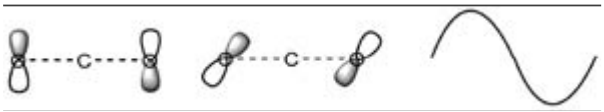
Correlation diagrams for π framework of polyatomic molecules

1. Follow MO recipe above: draw Lewis structure, count electrons, identify hybridization
2. Draw σ framework
3. Draw π framework
   i. Determine the number of p AOs not involved in σ framework
   ii. Count total number of valence electrons that belong to π framework
   iii. Decide if you have $\pi_{localized}$ or $\pi_{delocalized}$
   iv. 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 <u>three</u> atoms have available p AOs next to each other: $\pi_{delocalized}$

1. Lowest-energy (one-loop) **π bonding MO** has all of the p AOs in phase.

10. 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).



11. Highest-energy (three-loops) **π* antibonding** MO has all of the p AOs out-of- phase.

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