Chem 102 spring 2018, Discussion 2 Answers:

1. Sketch the MO diagram for HCO_3^-

a. Draw the Lewis structure and count the number of valence electrons:

#VE = 24

1(1) + 3(6) + 1(4) = 23e⁻ + 1 = 24e⁻

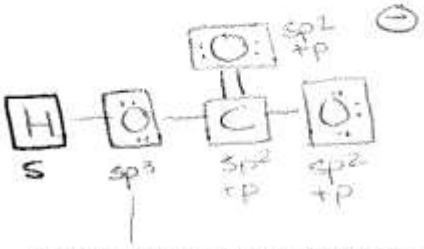
b. Assign hybridization of all the atoms.

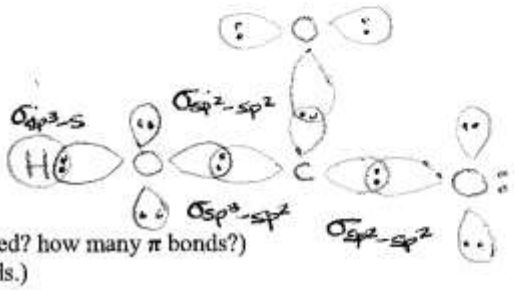
b. Determine hybridization of the center atom(s).
(Terminal atoms will have the same hybridization as the center atom.)

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.

4σ × 2e⁻ = 8e⁻
4σ* × 0 = 0
6σ_{NB} × 2e⁻ = 12e⁻
14MOs 20e⁻





d. Identify π framework (is it localized or delocalized? how many π bonds?)
(Hint: Decide which atoms can participate in π bonds.)

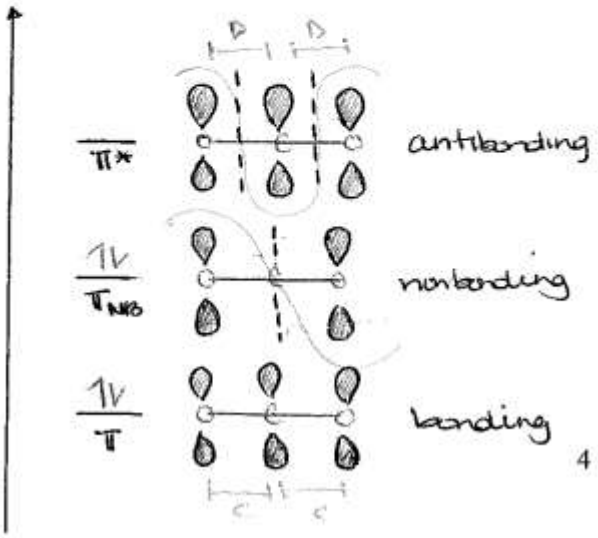
i. Determine the number of electrons involved in the π bonds.
 # π(electrons) = #Valence e⁻ - σ electrons - lone pair **electrons.** 24 − 20 = 4e⁻
ii. Count the *p* AO's not involved in hybridization.

p orbital from O, p orbital from O, p orbital from C

e. Sketch the corresponding π MO and corresponding energy correlation diagram for just π framework.

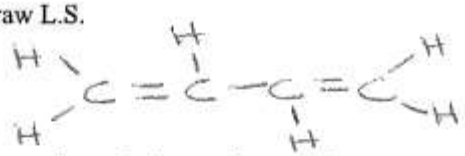
i. Rank them in terms of increasing energy (depending on number of loops).
ii. Fill the π MO's with the electrons involving in π bonds.
iii. Label the π MO's as bonding, antibonding and /or nonbonding.

20e⁻ + 4e⁻ = 24e⁻ ✓



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

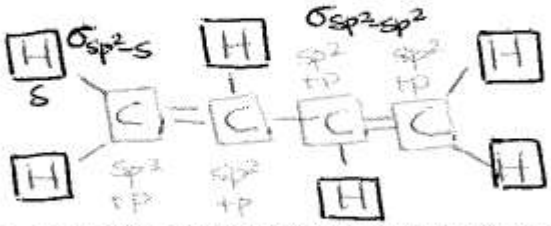
a. Draw L.S.

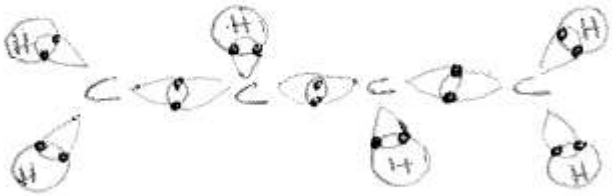


H-VE = 22

$6e(1)+H(4) = 22e^-$

b. Determine and draw σ framework:





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

$9\sigma \times 2e^- = 18e^-$

$9\sigma^* \times 0 = 0$

$0\sigma_{NB} \times 0 = 0$

$18e^-$

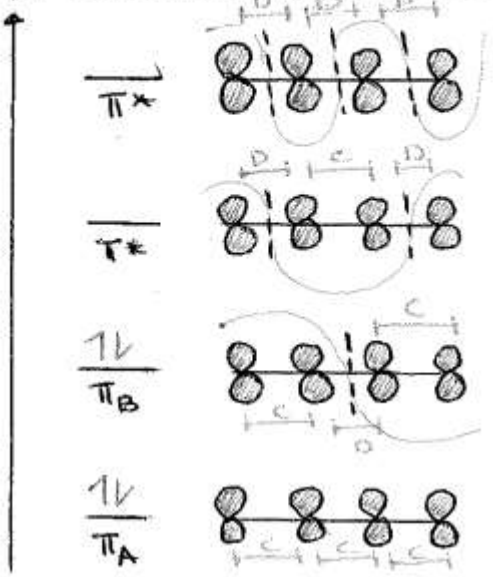
18MOs

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

$22e^- - 18e^- = 4e^-$

4MOs p from C x 4

e. Draw correlation diagram for π framework:



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

$C_A-C_B-C_C-C_D$

1 pair σ

1/3 π_A

0 π_B

1 1/3 pair

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

$C_A-C_B-C_C-C_D$

1 pair σ

1/3 π_A

1/2 π_B

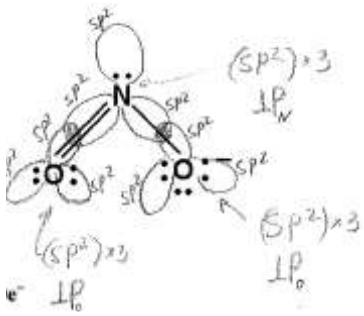
11/6 pairs

$11/6 + 11/6 + 4/3 = 5$ bonds between carbons

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:

$(NO_2^-)^*$: 12MO and 18valence electrons

σ_{FRAME}	2σ	4v.e⁻
	$2\sigma^*$	0 v e⁻
	$5\sigma_{NB}$	10v.e⁻
π_{FRAME}	3 MO ;	4v.e⁻



a. How many electrons are in σ bonding orbitals? **$4e^-$**

b. How many electrons are in σ nonbonding orbitals? **$10e^-$**

c. How many electrons are in π bonding orbitals? **$2e^-$**

d. How many electrons are in π antibonding orbitals? **$1e^-$**

e. How many electrons are in π nonbonding orbitals? **$1e^-$**

f. How many electrons are shared between O_{left} and N? **$3e^-$**

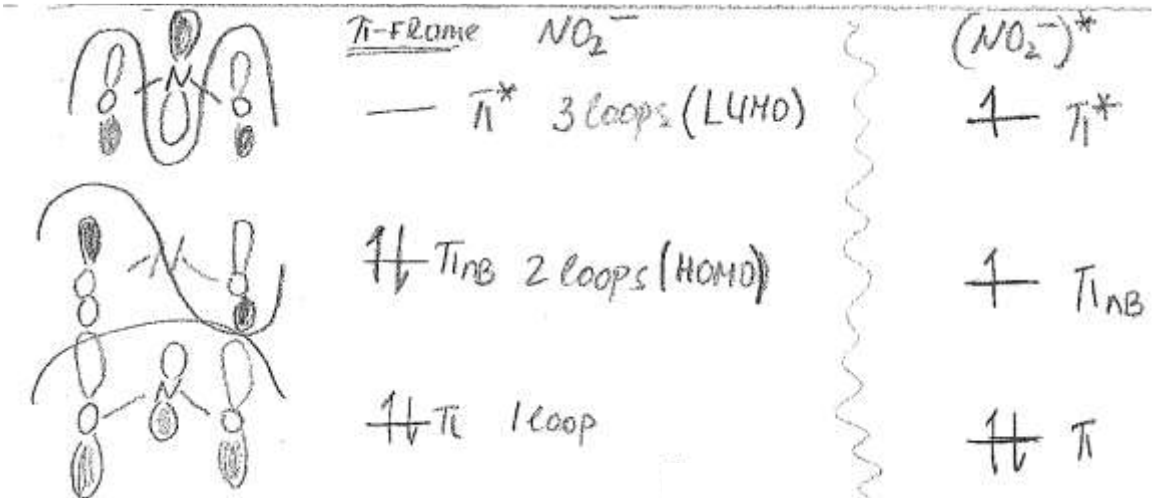
g. How many electrons are shared between O_{right} and N? **$3e^-$**

h. How many unshared electrons are on O_{left}? **$(4e^-)_{\sigma\text{-frame}}+(1/2\ e^-)_{\pi\ nonbonding}+(1/3\ e^-)_{\pi^*}=4*(5/6)e^-$**

i. How many unshared electrons are on O_{right}? **$4*(5/6)e^-$**

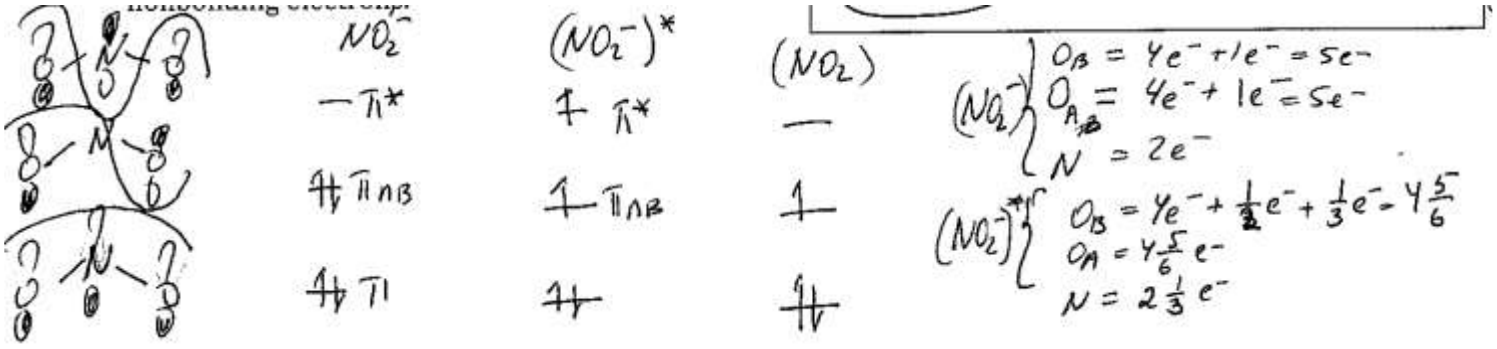
j. How many unshared electrons are on N? **$(2e^-)_{\sigma frame} + (1/3\ e^-)_{\pi^*}=2*(1/3)\ e^-$**

k. What is a total number of unshared electrons =**$2*(1/3)\ e^- + 4*(5/6)e^- + 4*(5/6)e^-$** =12 **$e^-$**



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

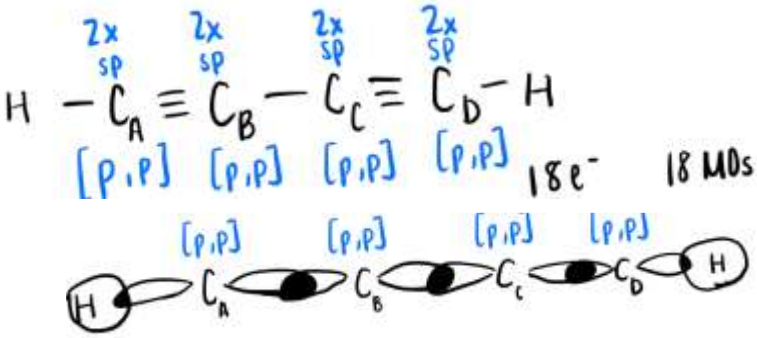
Dipole moment will decrease less separation of the charge.



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? 10 e−

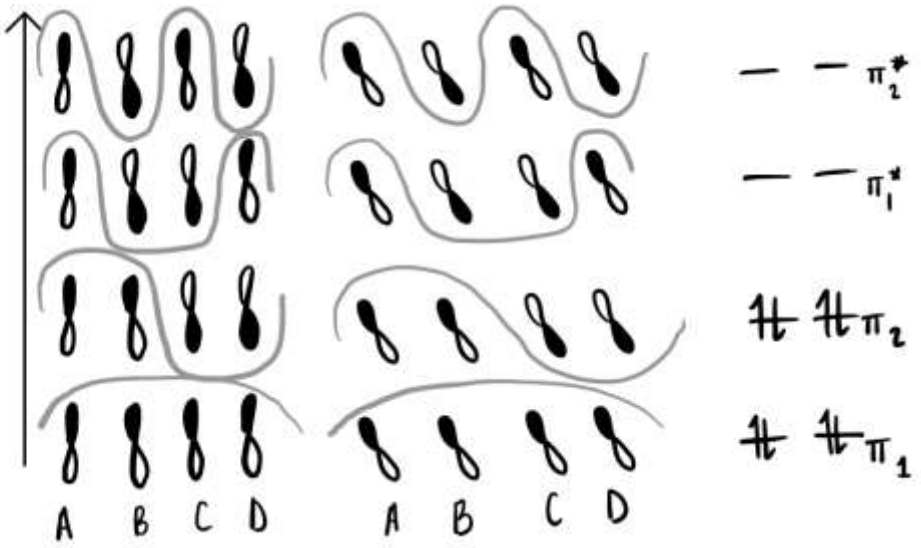


5.

   a. How many pairs of electrons are in the π framework? 8 e−

   b. Draw energy diagram for π framework:

c.



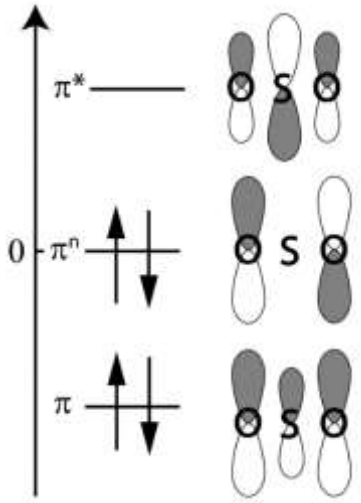
   d. How many pairs of electrons are shared between the middle two carbons in C_4H_2 **1(2/3) pairs or 3(1/3)e−**

   e. How many pairs of electrons are shared between the first two carbons in C_4H_2, **2(2/3) pairs or 5(1/3) e−**

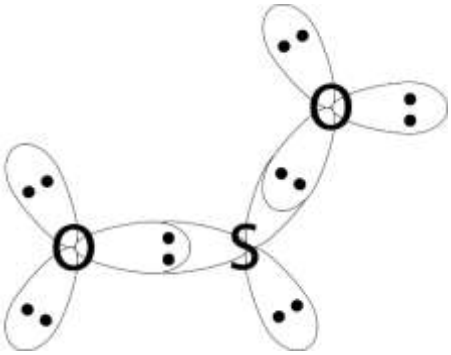
6. What is the hybridization of the oxygen atoms in SO_2?

   a. Carbon dioxide, SO_2, has a total of 9 pairs of electrons.
   b. How many pairs of electrons are **in the σ framework** of SO_2?
   c. How many bonding π electrons are there? $2e^-$
   d. How many non-bonding π electrons are there? $2\ e^-$
   e. How many electrons are there on either terminal atom that are **not shared** with the central atom? $5e^-$
   f. How many electrons are there on the central atoms that are **not shared** with the terminal atoms?$2e^-$
   g. How many electrons that are **shared** with the central and terminal atoms? $6e^-$

π framework diagram

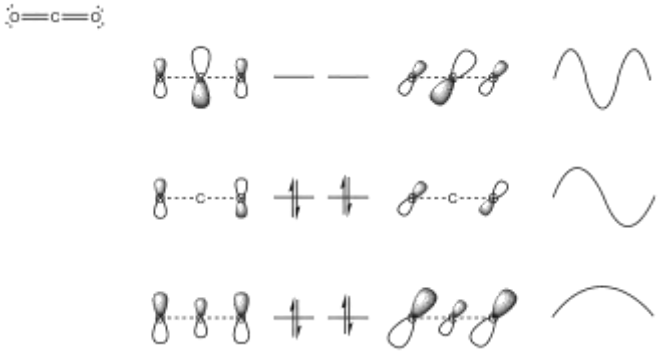


σ framework



7. 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? 4 pairs
   b. How many bonding π electrons are there? $4e^-$
   c. How many non-bonding π electrons are there?$4e^-$
   d. How many electrons are there on either terminal atom that are **not shared** with the central atom? $4e^-$
   e. How many electrons are there on the central atoms that are **not shared** with the terminal atoms? 0



Additional Examples: Determine σ-framework and corresponding π MO correlation diagram for: H_2CO, $C_3H_5^-$, HCO_2^-, $HOCO_2^-$, N_3H