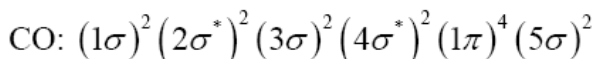
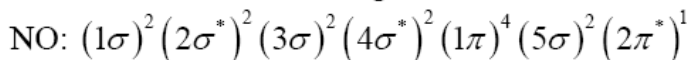


CHEM 1410 HW #9 KEY

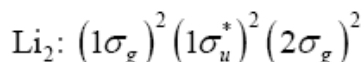
**P13.7)** The ionization energy of CO is greater than that of NO. Explain this difference based on the electron configuration of these two molecules.



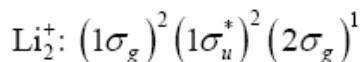
To first order, we assume that the MO energies are the same in each molecule. This is an approximation. Next, we look at the occupied MOs. In CO, the electron is removed from an HOMO that is a bonding orbital. This MO lies lower in energy than the antibonding HOMO in NO from which the electron is removed. Therefore, the ionization energy of CO is greater than that of NO.

**P13.11)** Calculate the bond order in each of the following species. Predict which of the two species in the following pairs has the higher vibrational frequency:

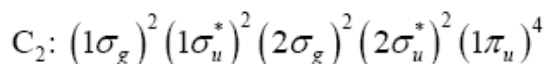
a)  $\text{Li}_2$  or  $\text{Li}_2^+$  b)  $\text{C}_2$  or  $\text{C}_2^+$  c)  $\text{O}_2$  or  $\text{O}_2^+$  d)  $\text{F}_2$  or  $\text{F}_2^-$



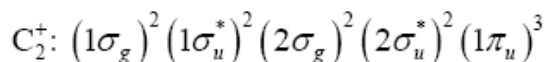
$$\text{Bond Order} = \frac{4-2}{2} = 1$$



$$\text{Bond Order} = \frac{3-2}{2} = 0.5$$



$$\text{Bond Order} = \frac{8-4}{2} = 2$$



$$\text{Bond Order} = \frac{7-4}{2} = 1.5$$

$$\text{O}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-6}{2} = 2$$

$$\text{O}_2^+: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^1$$

$$\text{Bond Order} = \frac{10-5}{2} = 2.5$$

$$\text{F}_2: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^2 (1\pi_g^*)^2$$

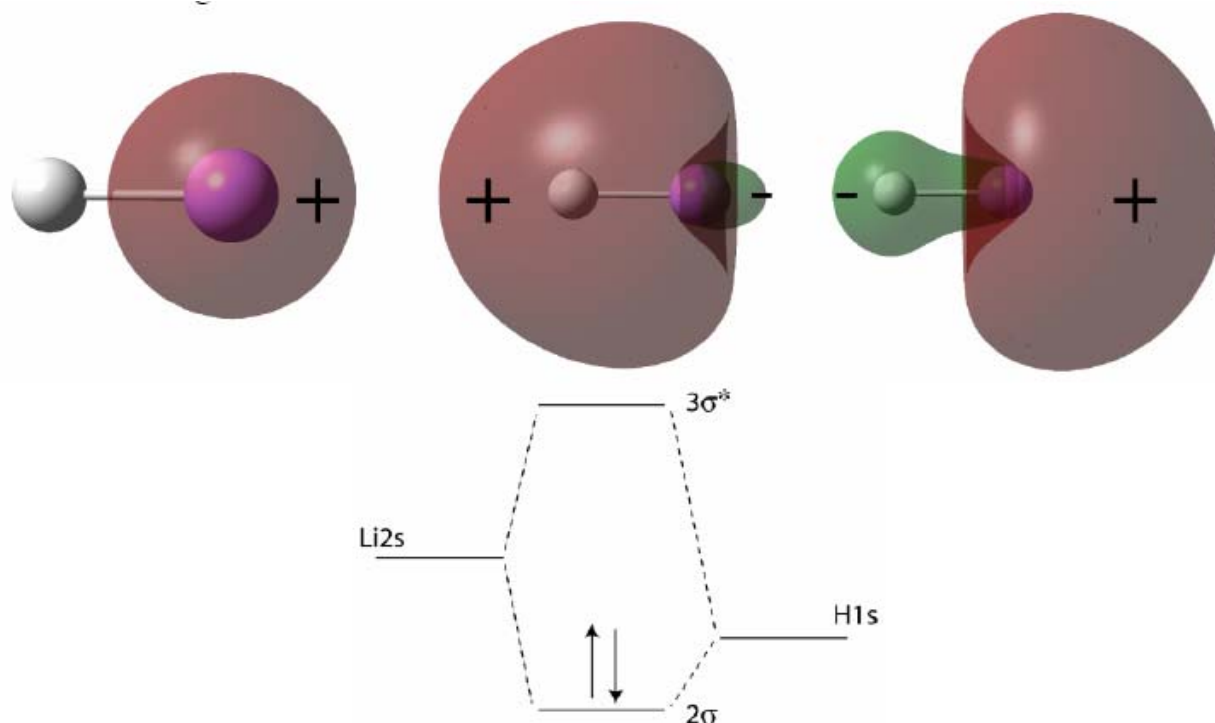
$$\text{Bond Order} = \frac{10-8}{2} = 1$$

$$\text{F}_2^-: (1\sigma_g)^2 (1\sigma_u^*)^2 (2\sigma_g)^2 (2\sigma_u^*)^2 (3\sigma_g)^2 (1\pi_u)^2 (1\pi_u)^2 (1\pi_g^*)^3 (1\pi_g^*)^2$$

$$\text{Bond Order} = \frac{10-9}{2} = 0.5$$

The species with the higher bond order will have the higher vibrational frequency, so the answers are  $\text{Li}_2$ ,  $\text{C}_2$ ,  $\text{O}_2^+$ ,  $\text{F}_2$ .

## 13.15



The left image corresponds to the  $1\sigma$  MO, because the MO is localized on the Li atom. From the MO diagram, the  $2\sigma$  MO should have a larger coefficient for the H1s AO than for the Li2s AO, following the rules outlined in Section 13.2. Therefore, the middle image is the  $2\sigma$  MO. Following the same reasoning, the  $3\sigma^*$  MO should have a larger coefficient for the Li2s AO. Therefore, the right image is the  $3\sigma^*$  MO. The  $1\sigma$  and  $2\sigma$  MOs are filled, and the  $3\sigma^*$  is empty.

Because the coefficient for the H1s AO is larger than that for the Li2s AO in the  $2\sigma$  MO, the bonding electrons have a higher probability of being on the H than on the Li. Therefore, the negative end of the dipole is on the H atom.

**Q14.1)** On the basis of what you know about the indistinguishability of electrons and the difference between the wave functions for bonding electrons and lone pairs, discuss the validity and usefulness of the Lewis structure for the fluorine molecule,  $:\ddot{\text{F}}-\ddot{\text{F}}:$ .

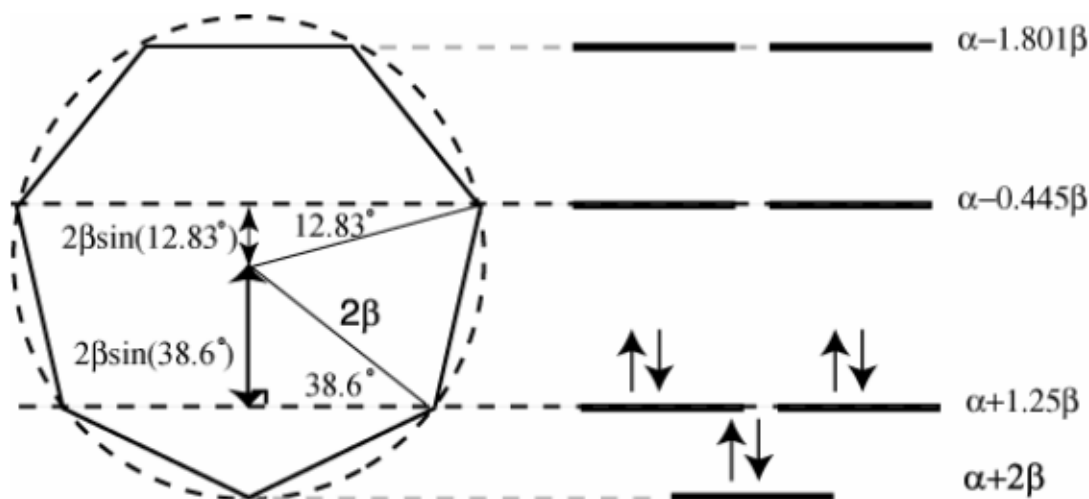
The Lewis structure is based on a localized assumption, specifying that electrons are restricted to specific orbitals, involving bonds and lone pairs. We know that this description is too specific. Electrons can tunnel from one localized orbital to another, and electron indistinguishability keeps us from knowing where a given electron actually is. Therefore, it is not possible to say that a given electron is a bonding electron as opposed to being localized in a lone pair.

**P14.11)** Predict which of the bent molecules, BH<sub>2</sub> or NH<sub>2</sub>, should have the larger bond angle on the basis of the Walsh correlation diagram in Figure 14.10. Explain your answer.

Molecule:	BH <sub>2</sub>	NH <sub>2</sub>
Valence e <sup>-</sup> :	5	7
HOMO:	2a <sub>1</sub>	1b <sub>1</sub>

Both molecules are equivalent through the (2a<sub>1</sub>)<sup>1</sup> orbital. However, by adding the second electron to the 2a<sub>1</sub> orbital and the electron to the 1b<sub>1</sub> orbital, the NH<sub>2</sub> molecule is shifted more to the bent form to lower the energy. Thus, the BH<sub>2</sub> molecule has the larger bond angle.

**P14.17)** Use the geometrical construction shown in Example Problem 14.10 to derive the energy levels of the cycloheptatrienyl cation. What is the total π energy of the molecule? How many unpaired electrons will the molecule have? Would you expect this species, the neutral species, or the anion to be aromatic? Justify your answer.



There are zero unpaired electrons. The π energy is

$$E_{\pi} = 2[\alpha + 2\beta + 2(\alpha + 1.25\beta)]$$

$$E_{\pi} = 6\alpha + 9\beta$$

Using the Hückel rule,  $4 \times 1 + 2 = 6e^{-}$ . The cation is the form that is aromatic.