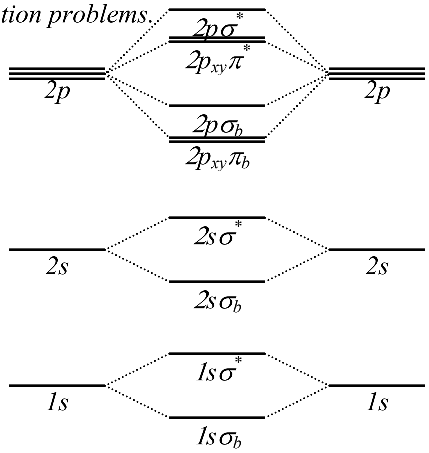
Name
Section
Rec TA

Side 1 of 3

Ch 1a, Problem Set Seven
Due Friday, Nov. 10, 2006
at 4 PM in the Ch1a Box

Problems 3 and 6 are designated ⚐ as no collaboration problems.



1. (50 points) Consider the neutral, anion, and cation species for each of the following homonuclear diatomics. Using the general MO diagram given for homonuclear diatomics, list the orbital configuration (eg: $1s\sigma_b^2\ 1s\sigma^{*2}\ 2p_{x,y}\pi_b^4\ 2p\sigma_b^2\ldots$) and bond order (eg: 0.5, 1.5, 2, etc.) for each of the following molecules and ions. Also label which species are paramagnetic and which are diamagnetic.

    a. Hydrogen (i.e. H_2^+, H_2, H_2^-)
    b. Helium (i.e. He_2^+, He_2, He_2^-)
    c. Lithium (…)
    d. Berillium (…)
    e. Carbon (…)
    f. Nitrogen (…)
    g. Oxygen (…)
    h. Fluorine (…)

For oxygen and Fluorine, remember to put the $2p\sigma_b$ below the $2p_{xy}\pi_b$ MO.

2. (40 points) Hydrazoic acid, HN_3, is a fun compound to work with: not only does it have an irritating odor that is dangerous at concentrations of less than 1 ppm, but in solution it is potentially explosive. Assume the connectivity of atoms in the compounds is the following (*a*, *b*, and *c* are arbitrary indices to label the nitrogens):

    $N_a - N_b - N_c - H$

    a. Draw the three most reasonable resonance structures of HN_3. In each case, give the formal charges on the nitrogen atoms in each resonance form, and estimate the $N_a - N_b - N_c$ and $N_b - N_c - H$ bond angles in each resonance form.
    b. The measured $N_b - N_c - H$ bond angle is 112°. Use VSEPR theory to select the resonance structure(s) that best describe the true structure of this molecule and predict the bond angle. Explain your answer.
    c. The two $N - N$ bond lengths of HN_3 have also been measured. Based on your answer to part b, which of these possibilities would you expect? Why?
        - The $N_b - N_c$ is shorter than the $N_a - N_b$ bond.
        - The $N_b - N_c$ is longer than the $N_a - N_b$ bond.
        - The two $N - N$ bonds have the same length.

⚐ 3. (20 points) Between NO and N_2, which should have the higher ionization energy? Draw populated molecular orbital diagrams for each molecule using proper relative orbital energies. Use the table of valence orbital energies provided on the next page as a guide. The electron configuration of NO is available on page 100 of Gray.

This is a table of valence orbital energies (given in eV). Use this for realtive energies in your MO diagrams, but only as a qualitative guide to the relative energies: you do not need to draw your molecular orbital diagrams to scale. Only parts 4d and 4e require you to quantitatively compare energies. The electron configuration of CO is given in Gray on page 100.

Atom	1s	2s	2p	3d
H	-13.6 (eV)			
He	-24.6			
Li		-5.4		
Be		-9.3		
B		-14	-8.3	
C		-19.4	-10.6	
N		-25.6	-13.2	
O		-32.3	-15.8	
F		-40.2	-18.6	
Ne		-48.5	-21.6	
metals				about -15

4. (40 points) Carbon monoxide forms numerous complexes as a ligand to transition metals. Now that you have learned about molecular orbital (M.O.) theory, we can look at CO from that perspective and compare it to the Lewis structure.

   a. Construct an M.O. diagram of CO and use it to ascertain the bond order. When combining the p orbitals, the π_b molecular orbital has a lower energy than the σ_b molecular orbital.

   b. Draw the Lewis dot structure of CO and assign formal charges based on the bond order from part a. In terms of electronegativity, why is this unusual?

   c. From b, how would CO bond to positive metal ions (be it M^{n+}-CO, or M^{n+}-OC)?

   Although CO has “lone pairs” in the Lewis sense, the more rigorous molecular orbital theory assigns it only bonding and antibonding orbitals. These Lewis “lone pairs” are in fact molecular orbitals formed from the 2s atomic orbitals from carbon and oxygen. Due to their different energies, these 2s atomic orbitals combine poorly. The lowest σ_b retains most of the character of one of the 2s atomic orbitals, while the lowest σ^* retains most of the character of the other 2s atomic orbital. In this sense, these are the molecular orbitals that correspond to the Lewis “lone pairs”.

   d. Using the table of valence orbital energies, predict which atom donates the majority of its character to the σ_b orbital and which atom contributes to the σ^*.

   e. CO donates electrons into empty *d* orbitals of the metal to form a bond. Energetically, would you expect this arrangement to be metal-CO or metal-OC? Explain. Compare this to the bonding (M^{n+}-CO, or M^{n+}-OC) acquired with the Lewis model from part c.

5. (30 points) The hydroxyl radical, OH•, is important not only in atmospheric chemistry but also in cell biology, as it participates in biochemical reactions as a free radical.

   a. Formulate the electronic structure of OH• in terms of M.O. theory. Use only the oxygen *2p* and hydrogen *1s* atomic orbitals.

   b. Which type of M.O. (σ_b, σ^*, π_b, π^*, nonbonding) contains the unpaired electron?

   c. In terms of reactivity and chemistry, why are the other oxygen and hydrogen atomic orbitals not important in OH•?

   d. Is the orbital you specified in part (b.) associated with both constituent atoms or is it localized on a single atom (if so, which one)?

   e. Based on your M.O. diagram what is the bond order of OH•?

   f. Compare your answers in (d.) and (e.) to the Lewis dot structure of OH•.

6. (20 points) Problem five teaches us that when atomic orbitals combine poorly the new molecular orbitals retain much of their original atomic orbital character. That is to say, the molecular orbitals formed, closely resemble Lewis lone pairs.

   a. Consider fluorine as it forms bonds in a Lewis dot structure. Usually fluorine is written having one bond and three lone pairs. Would you expect any of the molecular orbitals in F_2 to behave as lone pairs as written in a Lewis dot structure?

   b. Repeat this treatment for HF. Without knowing the molecular orbital diagram, speculate on the possibility (or not) of any of the molecular orbitals in HF behaving like fluorine lone pairs in a Lewis dot structure.