Inorganic Chemistry with Doc M.

Fall Semester, 2011

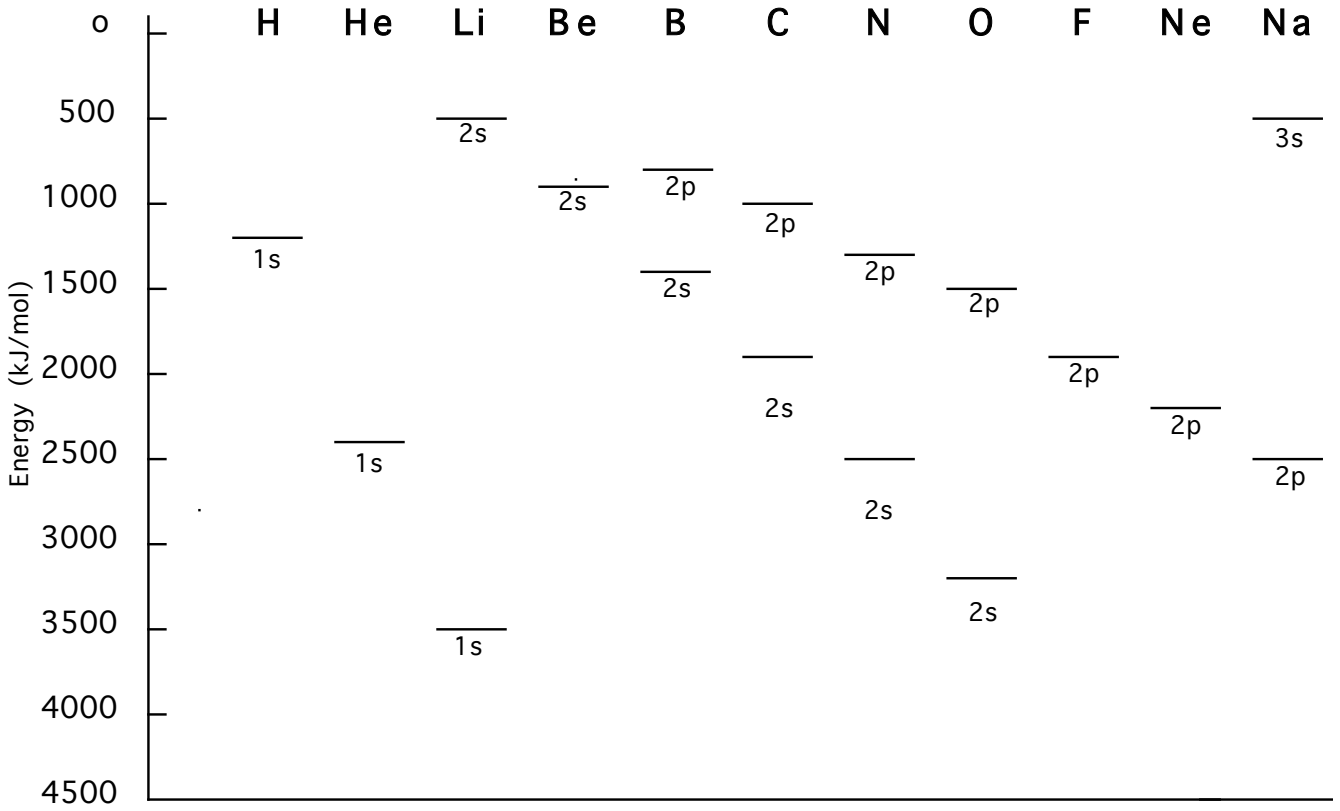
Day 7. Molecular Orbitals, Part 2

Name(s):	Element:

A. **Review.** What are the three criteria for deciding if two or more atomic orbitals can form a molecular orbital?

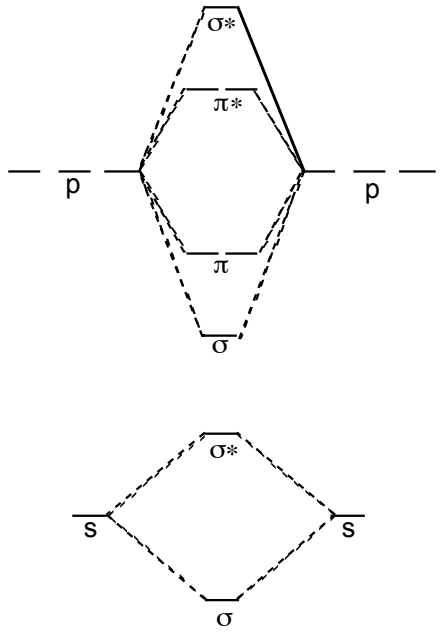
1.
2.
3.

B. One of your three criteria should have been "orbitals similar in energy." Specifically, with simple diatomics, the relative energies of the s and p-orbitals for each element must be compared. When s- and p- orbitals are relatively close in energy, meaningful MOs can be drawn between the s-orbitals on one atom and the p-orbitals on another atom. From the orbital energy diagram below, one can see that for B and C and to a lesser extent N, the s and p orbitals are close in energy.



C. Sketch an sp-mixing interaction using the orbital shapes.

1. Resketch the energy diagram given below twice. The sketches will account for "sp mixing" as it is called, that occurs in a homonuclear diatomic such as B_2 or C_2. One problem that may occur to you is the extent of sp-mixing and could it be enough to raise the former σ_p to an energy above the π orbitals. Sketch both of these possibilities here.



2. Populate the new diagrams for B_2. How could one determine which one is correct?

3. Now populate the new diagrams for C_2. If it were known that C_2 is paramagnetic, which energy diagram is correct?

D. Molecular orbital diagram for HF, HCl and similar heteronuclear diatomics.

1. Sketch an energy diagram for the valence atomic orbitals for H and F. From the energy chart above, one can conclude that the most important interaction is between hydrogen's 1s and fluorine's 2p. The interaction between hydrogen's 1s and fluorine's 2s can be ignored.

2. What "rule" allows us to ignore he interaction between hydrogen's 1s and fluorine's 2s orbital?

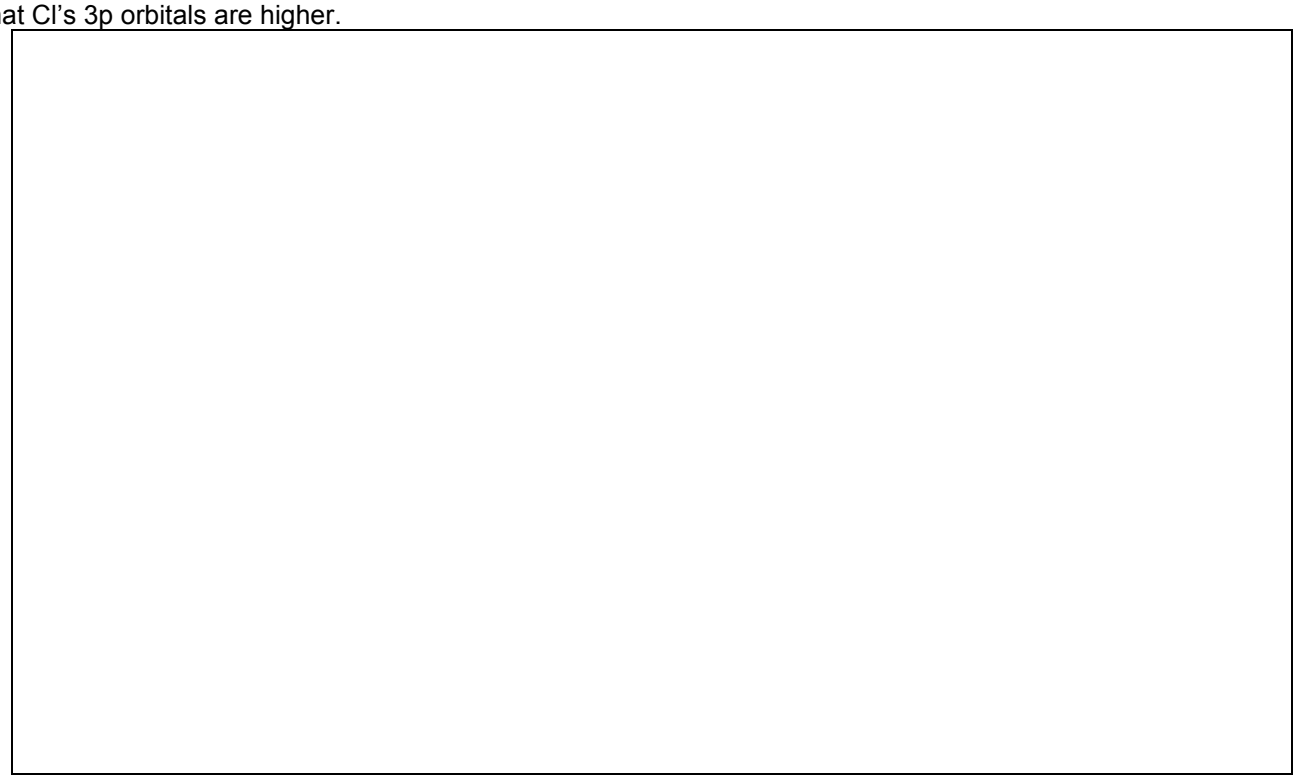
3. Sketch the orbitals and how they overlap near each molecular orbital energy level in the diagram above.

4. What is the bond order for HF?

5. Is the HOMO more H-like or F-like? Is the LUMO more H-like or F-like?

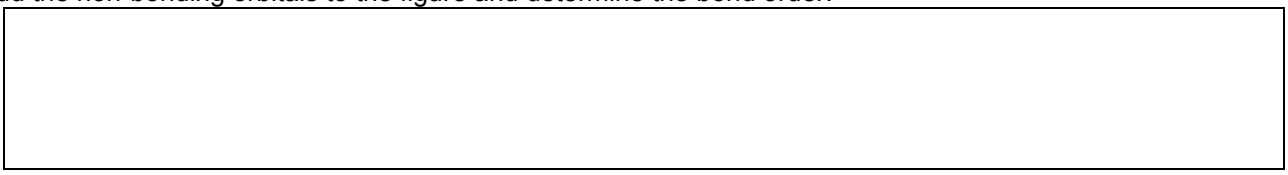
6. Orbitals that are not involved in MOs are called non-bonding orbitals. In HF, they are the 2s, the $2p_x$ and $2p_y$, all from fluorine. They need to be sketched into the MO diagram to complete the diagram (conservation of orbitals). Complete the MO portion of the diagram above. Add all labels.

7. Sketch an energy diagram for the valence atomic orbitals for H (1s) and Cl (2s, $2p_x$, $2p_y$,$2p_z$). The chart doesn't go as high as Cl, but Cl's 3s orbital is lower than H's 1s orbital in energy by about the same amount that Cl's 3p orbitals are higher.



8. We need to consider two important interactions: the interaction between hydrogen's 1s and chlorine's 2s and the interaction between hydrogen's 1s and chlorine's $2p_z$. That is, we have three interested atomic orbitals. Follow the procedure discussed in lecture to prepare three molecular orbitals from three atomic orbitals. Sketch these into the diagram above.

9. Add the non-bonding orbitals to the figure and determine the bond order.



E. Carbon monoxide.

1. Sketch a MO energy diagram for carbon monoxide. Mixing between carbon's s and oxygen's p-orbitals is important, while mixing between oxygen's s and carbon's p-orbitals can be ignored. Your diagram will require you to use what you've learned in the HCl example (3 AOs → 3 MOs).

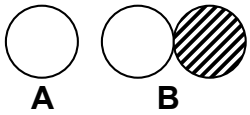
2. Prepare line sketches of each bonding and antibonding orbital.

3. Determine the bond order for CO.

Review for ACS Final Exam in Inorganic Chemistry

Molecular Orbital Theory

1. The following molecular orbital is



(a) symmetry forbidden.
(b) called a d-bond.
(c) is important if the energy of orbital A is similar to the energy of orbital B.
(d) occurs only when atoms A and B are different.
(e) occurs only when atoms A and B are the same.

Answer: C