

**Chemistry 362 Mini-EXAM 1**  
Chapter 3

**Monday February 18, 2008**

**Professor Kim R. Dunbar**

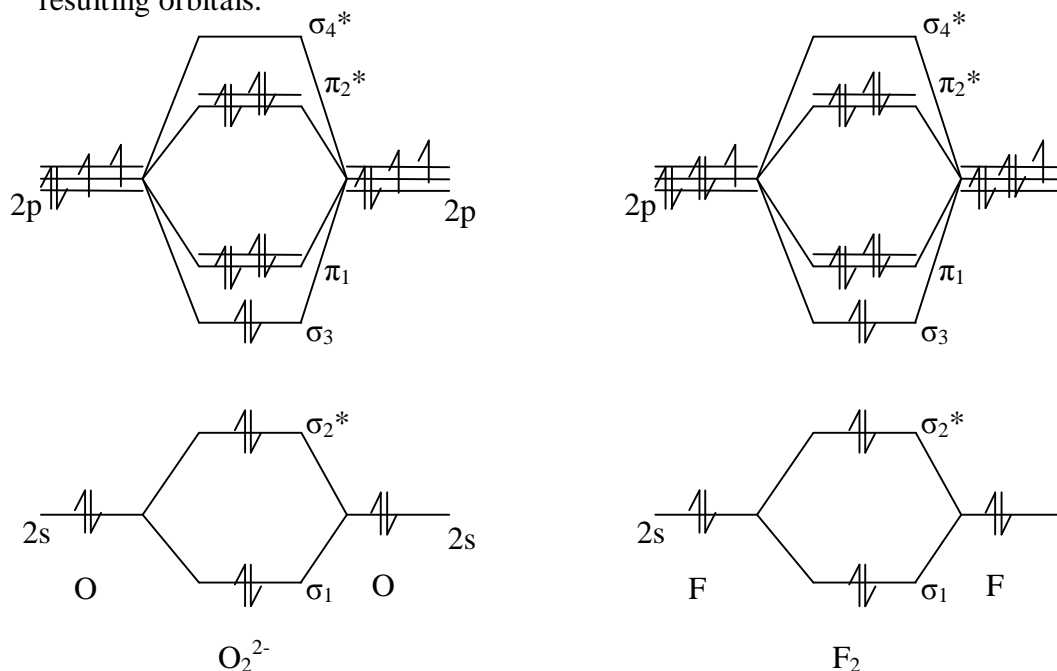
**NAME:** \_\_\_\_\_  
**ID:** \_\_\_\_\_

**You have 30 minutes to work this examination**

**Total Points on Exam is 83 points**

1. (10 pts)

- a. Draw Molecular Orbitals for  $\text{O}_2^{2-}$  and  $\text{F}_2$  molecules and put the electrons in the resulting orbitals.



- b. What are the Bond Orders in each case?

**In both cases the bond order is one.**

- c. Which of the two molecules would you expect to have the longer bond? Why?

**The  $\text{O}_2^{2-}$  molecule has a longer bond than  $\text{F}_2$ . Although these two species are isoelectronic, the oxygen molecule has a smaller effective nuclear charge than fluorine, so the additional two electrons (compared to  $\text{O}_2$ ) are not as strongly attracted to the nuclei resulting in their probability function being more diffuse, lessening the strength of the bond and making it longer.**

2. (10 pts)

Explain how effective nuclear charge determines the relative energies of the valence orbitals in an atom. Use the examples of Li versus F atoms to show the relative differences in the 2s and 2p levels in these atoms.

**The trend of relative energies between  $s$  and  $p$  levels is an increase in the energy difference between them from left to right across the table. This difference is a direct result of the trend of increasing nuclear charge across the table. As the effective nuclear charge ( $Z^*$ ) increases, the energy of the  $s$  orbital decreases due to the increased electrostatic force of the nucleus on the  $s$  electrons. Additional electrons filling  $p$  orbitals are shielded from the nucleus by  $s$  electron density ( $p$  orbitals are less penetrating), so the rate of descent of the  $p$  orbital energies across the table is not as dramatic as the  $s$  orbitals. Li and F illustrate the effect of the relative differences in energies between  $s$  and  $p$  levels nicely. Li, which lies on the far left of the periodic table has  $s$  and  $p$  levels which are closer together in energy**

than the  $s$  and  $p$  levels in F. The effect of this difference is observed in diatomic molecules of both elements.  $\text{Li}_2$  has mixing of the adjacent  $s$  and  $p$  levels when determining molecular orbitals, while the  $s$  and  $p$  levels in  $\text{F}_2$  are energetically different enough to result in no mixing.

3. (25 pts)

Draw Lewis Dot Structures for the following molecules (be sure to include all lone pairs of electrons). Now apply the VSEPR methods to predict the shapes of the molecules. Tell in each case if the molecule is saturated, unsaturated or electron deficient.

- $\text{NHF}_2$
- $\text{As}(\text{CH}_3)_4^+$
- $\text{GeCl}_4$
- $\text{PCl}_5$
- $\text{OICl}_5$

4. (10 pts)

In the case of  $\text{AB}_3$  molecules, we used a specific approach in class to account for the  $\sigma$  and the  $\pi$ -bonding. In very brief terms, describe the approach that was used for the  $\text{BF}_3$  molecule. THERE IS NO NEED TO DRAW ANY M.O.'s.

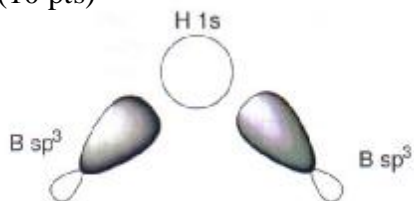
**The atoms in this trigonal planar system are  $\text{sp}^2$  hybridized. Each major  $\text{sp}^2$  lobe on every atom contains 2 electrons, for a total of 18 electrons. 6 of these electrons comprise the  $\sigma$  bonding system of the molecule, which consist of 3 bonds one between each B and each F. The remaining 6 electrons ( $24\text{ e}^- - 18\text{ e}^-$ ) are in the unhybridized  $p_z$  orbitals on F, which can be used to make the three group orbitals. One of these group orbitals makes bonding and antibonding overlaps with the B  $p_z$  orbital, while the other two make non-bonding overlap with the B  $p_z$  orbital.**

5. (12 pts)

Sketch all the possible overlap patterns that result from combining the orbitals on atoms A and B. In each case, identify the symmetry ( $\sigma$ ,  $\pi$ ,  $\delta$ ) and type of molecular orbital (bonding, non-bonding, antibonding) that your drawing corresponds to. (Label the axes  $x$ ,  $y$ ,  $z$  in each case)

- a  $d_{xz}$  on atom A and a  $d_{xz}$  on atom B
- an  $s$  orbital on atom A and a  $p_x$  orbital on atom B

6. (10 pts)



Draw the Molecular Orbitals that result from the possible in-phase and out-of-phase combinations of the two B  $\text{sp}^3$  orbitals and the H  $1s$  orbital in the  $\text{B}_2\text{H}_6$  bridge shown to the left. Use both shading and signs to show the positive and negative signs of the lobes.

7. (10 pts)

The two fundamentally different Bonding Theories for Molecules presented in class are Localized and Delocalized. **Briefly** describe the two approaches and how they differ. Cite an example for which the Delocalized Theory is clearly superior in describing the reactivity of a particular molecule and explain why it works better.

Localized theory uses the Lewis scheme to describe structure and bonding and the Delocalized theory which describes the formation of molecular orbitals for atomic orbitals based on atomic orbital wavefunctions. Although the localized theory is quite powerful in its descriptive ability, the delocalized approach more thoroughly accounts for more bonding phenomenon and physical properties. One molecule that illustrates the superiority of the delocalized approach versus localized in terms of reactivity is carbon monoxide. Carbonyl complexes of metals contain CO bonded through the carbon end, which is contrary to what one might assume based on electronegativity and a traditional Lewis model. The molecular orbital approach however illustrates the energy and reactivity of the lone pair of electrons on carbon and correctly predicts the binding of CO through carbon.