Inorganic Chemistry with Doc M.

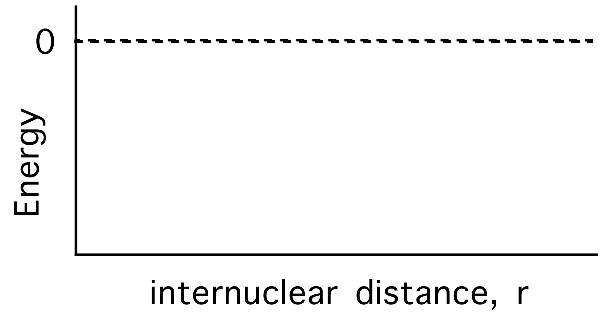
Fall Semester, 2011

Day 6. Molecular Orbitals, Part 1

Name(s):	**Element:**

A. Molecular orbital diagram for two σ-orbitals:

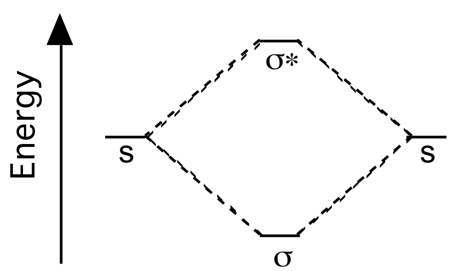
1. From P-Chem, sketch on the plot of total energy (y) vs internuclear distance, r, for two hydrogen atoms. Somewhere on the plot, sketch what you picture what the hydrogen's s-orbitals look like at the energy minimum (overlapping?)



2. The hydrogen bond can be thought of as a linear combination of atomic orbitals, or simply a molecular orbital. Write the equation for the bonding molecular orbital MO for hydrogen, Ψ, from two atomic orbitals, Ψ_A and Ψ_B. Repeat for the antibonding orbitals.

3. The following is a molecular orbital energy diagram for hydrogen, H_2. The "outer" orbitals, labeled "s" are the two 1s atomic orbitals from the two hydrogen atoms. Add the labels "H_A" and "H_B" above the two s orbitals and place one electron ($1s^1$) in each orbital.

MO:

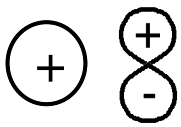


The outer atomic orbitals can be thought of as "the before" and the middle orbitals, the resulting molecular orbitals, can be thought of as "the after." Populate the MOs with the two electrons from the atomic orbitals, AOs.

4. Sketch the bonding and antibonding molecular orbitals using circles to represent the two atomic orbitals .

B. Symmetry.

1. There are three conditions for the formation of a molecular orbital: matching symmetry (constructive overlap must be possible), similar energy and appropriate internuclear distance (not too large). The first condition, matching symmetry, needs a bit more discussion. Sketch a p-orbital and show how it could overlap with an s-orbital, (a) with the s-orbital positioned along the p-orbital's primary axis, that is on the end of one lobe and (b) saddled up along the side. Use the symbols shown below. In one instance, there is no net overlap because the s-orbital overlaps equally with the + and – lobe of the p-orbital. This leads to no gain and is considered symmetry disallowed — we can ignore these sorts of overlaps.

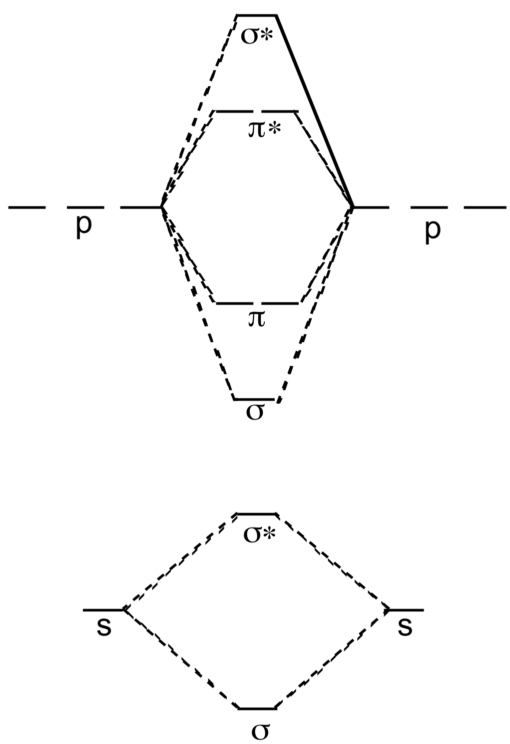


2. Repeat this with two p-orbital. Label the two orbitals you have sketched s (direct overlap) and p (through space overlap).

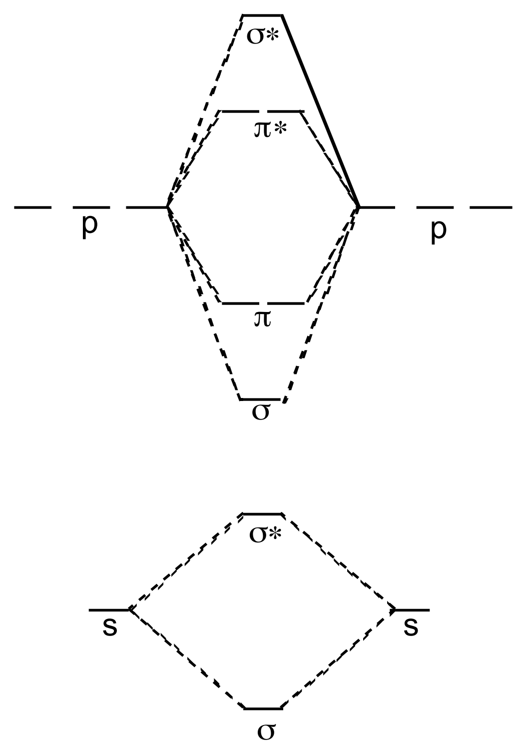
C. Homonuclear Diatomic Molecules

1. For atoms with s and p-orbitals only, such as B, C, N, O, and F, the σ-MOs (from s-orbitals) and the σ- and π-MOs from the p-orbitals, come together as shown here. This is the generic MO diagram for two identical atoms such as F_2 and O_2. Populate the MO diagrams for F_2 and O_2.

F_2



O_2



2. Bond order. Bond order is given by the equation:

Bond order = (number of bonding electrons – number of antibonding electrons)/2

Determine the bond order for both F_2 and O_2.

3. Electron configurations for molecular orbitals. Electron configurations for molecular orbitals can be written as shown for the example for F_2. Complete the electron configurations for O_2:

$$F_2: (\sigma s)^2\ (\sigma s^*)^2\ (\sigma p)^2\ (\pi)^4\ (\pi^*)^4\ (\sigma p^*)^0$$

$$O_2: (\sigma s)\ \ (\sigma s^*)\ \ (\sigma p)\ \ (\pi)\ \ (\pi^*)\ \ (\sigma p^*)$$

Determine the number of unpaired electrons for both F_2 and O_2.

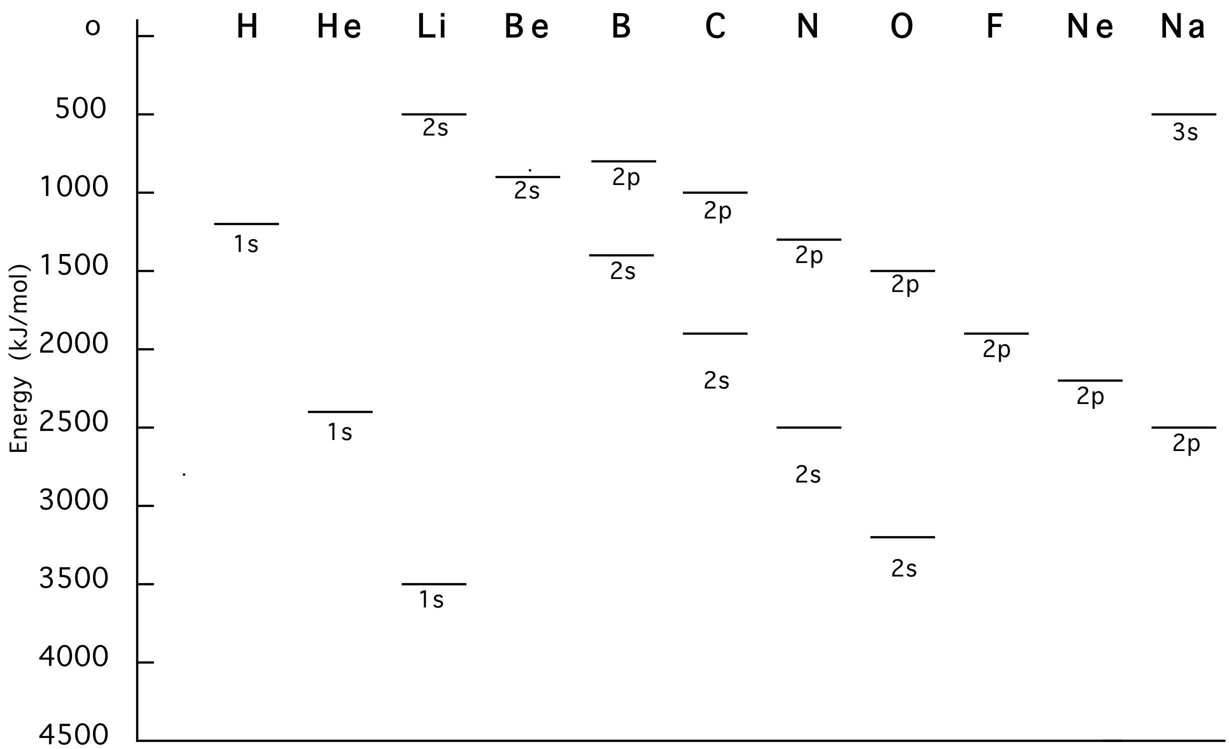
Sketch a MO energy diagram for the superoxide ion, O_2^-.

Based on your energy diagram for superoxide,

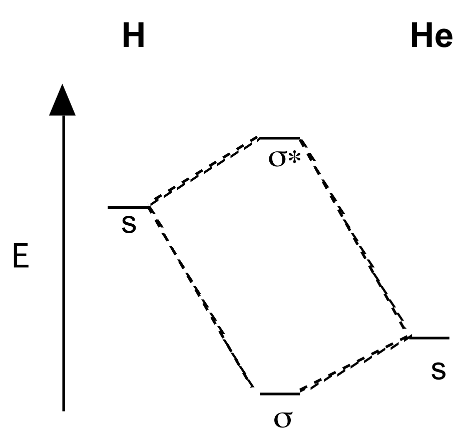
(a) What is the bond order?
(b) Write the electron configuration for superoxide.
(c) Is the superoxide ion diamagnetic or paramagnetic?
(d) Which would have a stronger oxygen-oxygen bond, molecular oxygen or the superoxide ion?
(e) Which would have a shorter oxygen-oxygen bond, molecular oxygen or the superoxide ion?

4. Some vocabulary: The highest occupied molecular orbital (including partially occupied) is abbreviated H.O.M.O. or simply "HOMO." The lowest unoccupied (empty) molecular orbital is abbreviated LUMO. Identify the HOMO and LUMO for F_2. (Answer should be in the format s_s, etc.)

5. **Heteroatom diatomic molecular orbitals.** Relative orbital energy and orbital overlap. The relative energies of s and p orbitals for the first eleven elements are given here.



Thus, if one were to sketch the MO diagram for the hypothetical molecule HHe, it would look like:



6. Molecular orbitals tend to have characteristics that reflect the atomic orbitals closest in energy. As a result, the σ MO is more similar in energy to helium's 1s orbital and therefore is a little more "helium-like" than hydrogen-like. Conversely, the antibonding molecular orbital is more hydrogen-like. Because the s MO is also the HOMO for HHe^+, more of the electron density is on helium, simply because the s MO is helium-like. Sketch the bonding σ MO and label the He end δ^- and the H end δ^+.

7. Sketch a MO energy diagram for nitrogen monoxide and related NO diatomics compounds. Also, prepare line sketches of each bonding and antibonding orbital.

Use the diagram to determine the bond order for:

NO
NO^+
NO^-

Refer again to the MO diagram you drew for NO. Is the unpaired electron in an orbital that is more nitrogen-like or oxygen-like?

Review for ACS Final Exam in Inorganic Chemistry

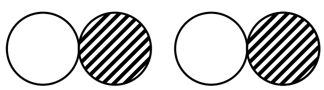
Molecular Orbital Theory

1. Molecular orbital theory predicts that all of these are diamagnetic except:
   (a) N_2
   (b) NO^+
   (c) NO^-
   (d) O_2^{-2}
   (e) O_2^{+2}

2. Which of these has a bond order of 2?
   (a) N_2
   (b) NO^+
   (c) NO^-
   (d) O_2^{-2}
   (e) O_2^{+2}

Answers: C, C, B, D

3. For N_2, the following molecular orbital is described as:



   (a) s_p
   (b) $s_p{}^*$
   (c) p
   (d) p*
   (e) $s_s{}^*$

4. Which of the following is ***not*** expected to exist according to molecular orbital theory?
   (a) H_2^-
   (b) He_2^+
   (c) H_2^+
   (d) He_2
   (e) Be_2^+