HW 2 (7,9,11-13)
CHEM 362

Available: Jan. 25, 2008 Due: Feb. 1, 2008

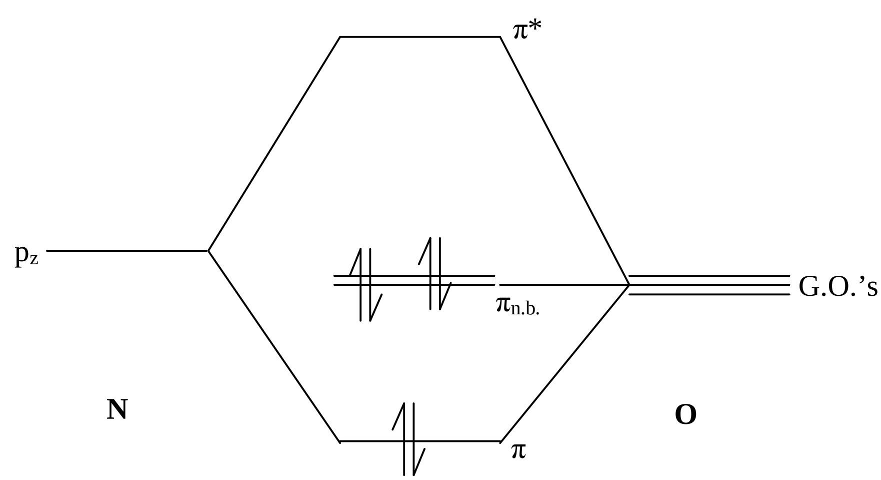
7. Are the 2*s* and 2*p* orbitals in a N atom *higher* or *lower* than those of O? Explain your answer.

The 2*s* and 2*p* orbitals on the N atom are higher than those of O. An O atom has 1 more proton than a N atom and thus has a higher effective nuclear charge. This lowers the energy of the 2*s* and 2*p* orbitals by holding them closer to the nucleus (consider the trend for atomic radii to decrease as you go from left to right across the periodic table).

9. Explain by M.O. theory why the NO bonds in NO_3^- have a bond order of 1 1/3.

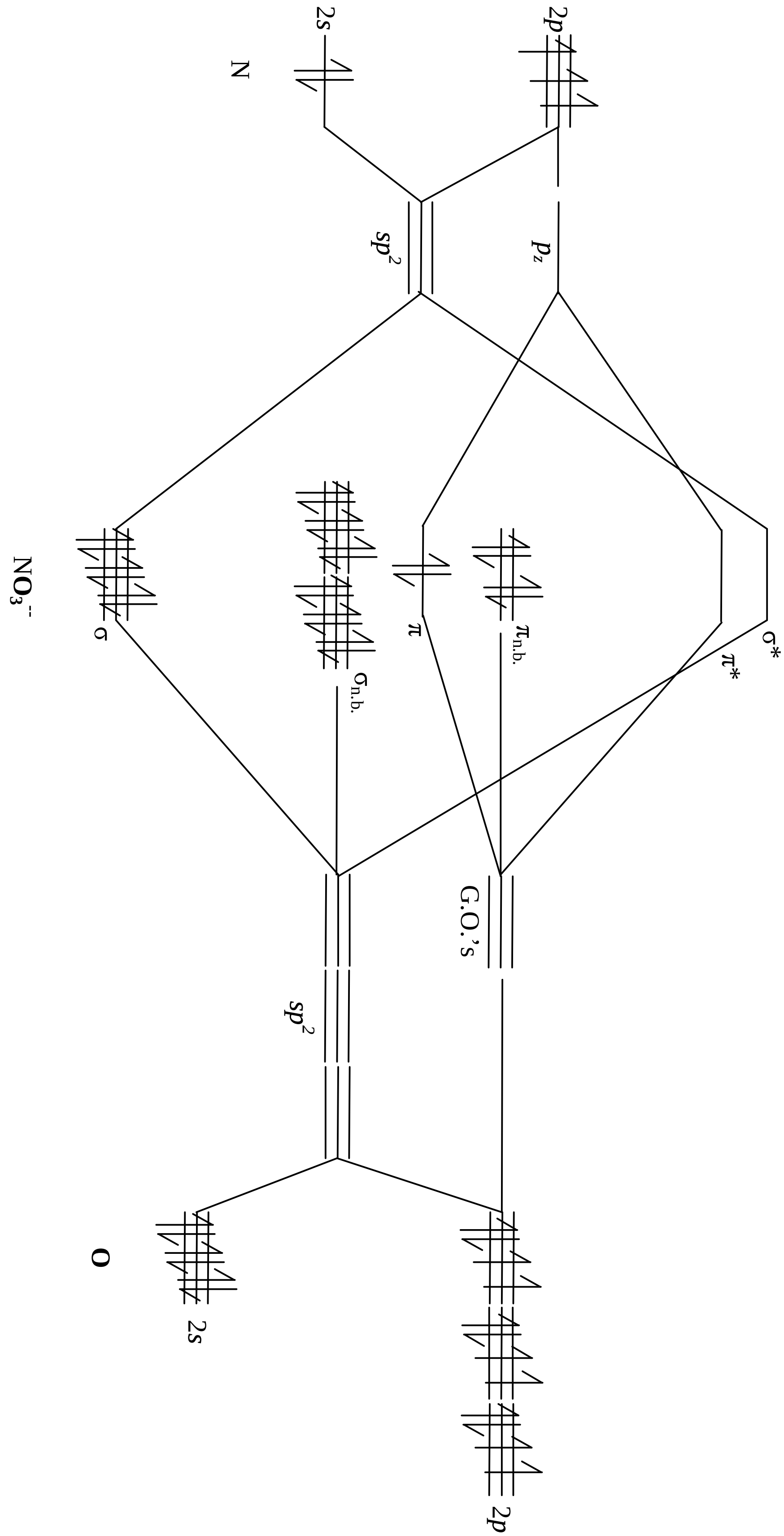
NO_3^- is a trigonal planar molecule and in molecules of this type the all the atoms can be treated as sp^2 hybridized atoms. NO_3^- has 24e$^-$, each sp^2 hybrid contains 2e$^-$. This accounts for the 3 σ bonds between the N atom and the O atoms (6e$^-$) and 2 lone pairs for each O (12e$^-$). This leaves 6 of the 24e$^-$ unaccounted for. These electrons go into the unhybridized p_z orbitals that we can use to form 3 G.O's (group orbitals) on the oxygen atoms. One of these orbitals forms a π bond with the unhybridized p_z orbital on N, while the other two form nonbonding orbitals. The sum of σ and π bonding electrons in NO_3^- is 8e$^-$ (and there are no antibonding electrons) giving 4 bonds over 3 atoms with a B.O. of 1 1/3 for each

As in class, the sigma orbitals in this case will be ignored and only the pi system will be considered.



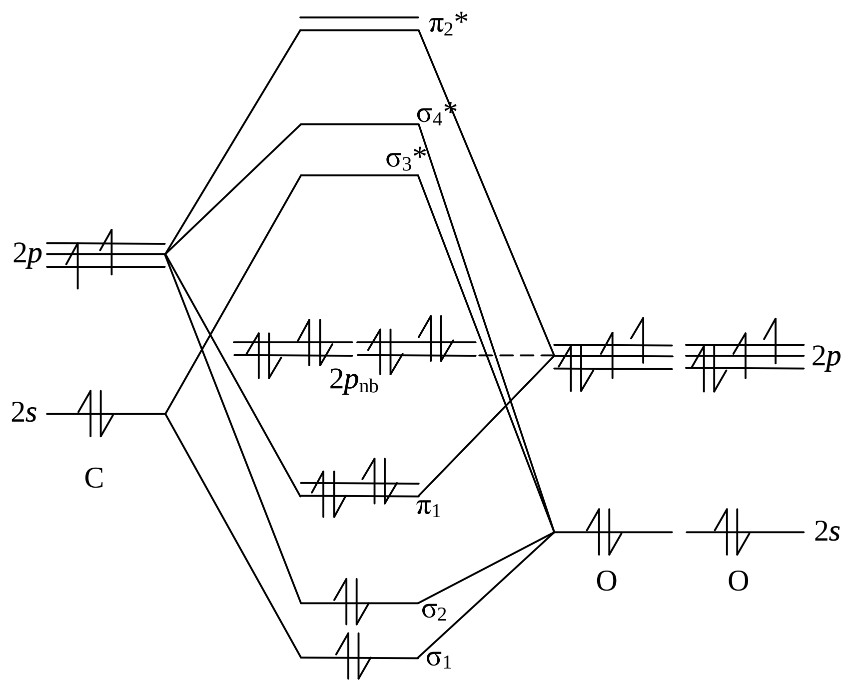
On the next page there is a M.O. diagram containing the sigma and pi orbitals. YOU WERE NOT EXPECTED OR ASKED TO DRAW THIS DIAGRAM. I INCLUDED IT IN CASE YOU WERE CURIOUS WHAT IT WOULD LOOK LIKE. YOU ARE ONLY RESPONSIBLE FOR THE PI SYSTEM DRAWN ABOVE. Please note that the pi bonding orbital could have been above or below the sigma non-bonding, without theoretical data it is impossible to know where the orbital actually is.

Full M.O. diagram for NO_3^-. YOU ARE NOT RESPONSIBLE FOR THIS.



N
2s
2p
sp^2
p_z
NO_3^-
σ
$\sigma_{n.b.}$
π
$\pi_{n.b.}$
π*
σ*
G.O.'s
sp^2
O
2s
2p

11. Draw a qualitatively correct energy-level diagram for the CO_2 molecule. Show that it accounts correctly for the presence of double bonds.

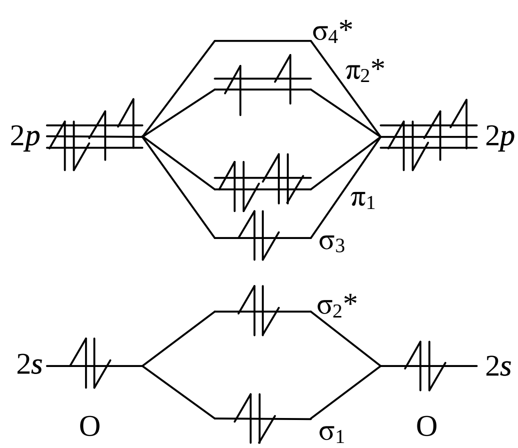


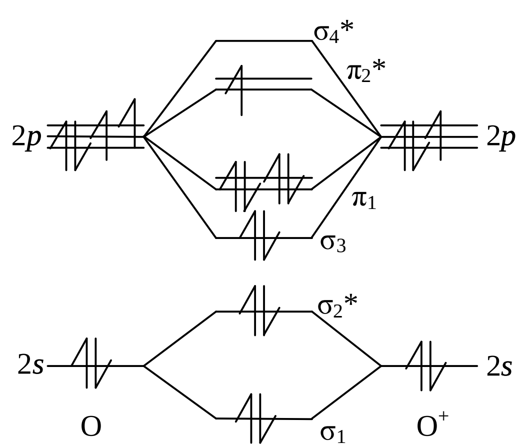
The diagram predicts that there will be two sigma bonds and two pi bonds between the carbon atom and the oxygen atoms and four lone pairs on the oxygen atoms.

12. Explain why there is 2*s*-2*p* mixing in the M.O. energy-level diagram of Li_2, but none for F_2.

As you move from left to right across the periodic table the energy gap between the 2*s* and 2*p* increases. At Li, the 2*s* and 2*p* are close enough in energy to allow for some *s-p* mixing. But by the time you reach F, the 2*p* orbital is so much higher in energy than the 2*s*.

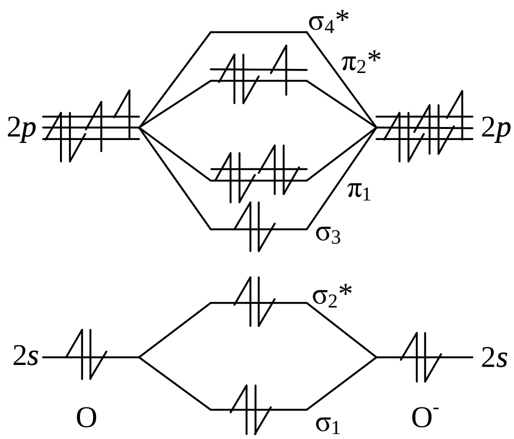
13. For the series of diatomics: O_2^+, O_2, O_2^-, O_2^{2-}, determine from an M.O. diagram how the bond lengths will vary and how many unpaired electrons each will have.



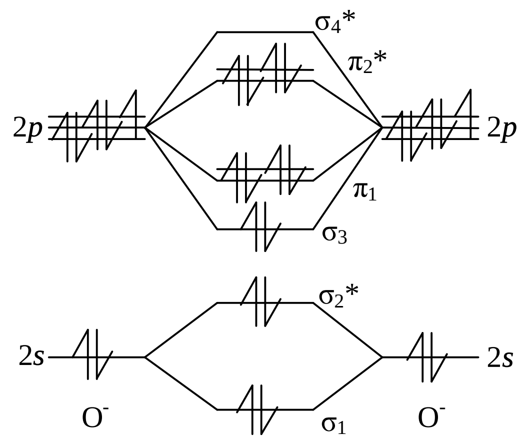


O_2 will have 2 unpaired electrons (B.O. = 2) O_2^+ will have 1 unpaired electron (B.O. = 2.5)

O_2^-



O_2^{2-}



O_2^- will have 1 unpaired electron (B.O. = 1.5) O_2^{2-} will have 0 unpaired electrons (B.O. = 1)

From shortest bond to longest bond: $O_2^+ < O_2 < O_2^- < O_2^{2-}$