CHE 332: Molecular Orbital Modeling Exercise

We will use Spartan to calculate the energies of the MOs of several species and draw the shapes of the orbitals.

1. In each case, build and minimize the structure. Your initial drawing should have the molecule in a horizontal orientation, with the less electronegative atom on the left. I suggest that you use the ball and wire model rather than the ball and spoke model.

2. On the Setup, Calculations menu select the choices to calculate equilibrium geometry using the semi-empirical method (AM1 model unless you are told differently). Start from the initial geometry, subject to symmetry. Indicate the total charge of the species. The multiplicity will be singlet in all cases, meaning that all electrons are paired (spin multiplicity = n+1, where n is the number of unpaired electrons). Compute electrical charges and print orbitals and energies, plus atomic charges. Submit the molecule for calculations.

3. When the calculations are finished, display the output. Note the number of basis functions, which is the number of valence-shell atomic orbitals that you began with. Spartan also gives you the point group of the molecule. This is not terribly interesting for the linear molecules that we are examining, but you might find it interesting to try some polyatomic molecules and examine the structure and the point group to identify all of the symmetry operations.

4. Information on the molecular orbitals is printed out in a large table. The MOs will be numbered from 1 to the maximum number of orbitals (note that this number should be equal to the basis set). The energy of each MO in electron volts is given. Below these two lines, the contribution of each basis-set orbital to the particular MO is given. Thus, you can see, e.g., that a certain MO has contributions primarily from the 2p_z orbitals of the two atoms, or if there is a mixture of 2s and 2p_z character in the MO. The atomic charges enable you to make conclusions about the direction of polarity of the molecule. The information that is to be reported is the heat of formation, number of basis functions, point group, table of "Closed-Shell Molecular Orbital Coefficients," and atomic charges for each species. Rather than print out the entire display, use cut and paste to put the required information into a word-processor document and print it out (properly labeled as to which species it is for).

5. Access the Display, Surfaces menu. Click on Add, and choose the HOMO (highest occupied MO) and the LUMO (lowest unoccupied MO). Also, use the HOMO- and LUMO+ choices, changing the numbers as appropriate (HOMO-1, HOMO-2, etc.), to calculate the shapes of all of the MOs. Submit the calculation again. When the calculations are complete, minimize the output table pane and check one of the boxes for the MO surfaces that you designated. You will see the shape of the MO with color coding to show the phase of the wave function. It is instructive to view these in order from lowest energy (lowest MO below the HOMO) to highest energy (highest above the LUMO). When you click on the picture, a style box appears at the bottom of the screen. You may experiment with different styles of plotting to see which has the best clarity (I like the transparent style).

6. Next, we want to print out a diagram showing the shapes of the MOs from lowest energy at the bottom of the page to highest energy at the top. When you have a given MO displayed, use the Edit, Copy command to copy it to the clipboard. Open the Windows Paint program (under Accessories on the All Programs choice on the main Windows Start menu). Paste the picture of the MO into Paint. Use the selection tool to draw an outline that just encloses the MO. Use the Copy command and paste the picture of the MO into a word processor document. Continue to follow this same procedure for all of the MOs of the molecule. After they are all on the page, you may move them around so that they are in order of energy, lowest energy at the bottom of the page (note that some may be degenerate and should be at the same level). Label each MO with an appropriate designation, e.g., $\sigma^*$, and the energy.

7. Use the information from the table to sketch a MO energy-level diagram for the species and fill in the electrons and determine the bond order. You should examine the phases of the MOs carefully to determine whether each is bonding, antibonding, or nonbonding.

Species to examine:
1. N₂
2. CN⁻ (Draw with the C atom on the left and don’t forget the charge.) Compare the features of these first two.
3. HF (Be careful about identifying nonbonding MOs on this and the next species).
4. HF₂⁻ (don’t forget the charge)
5. BeH₂ (use the PM3 model)