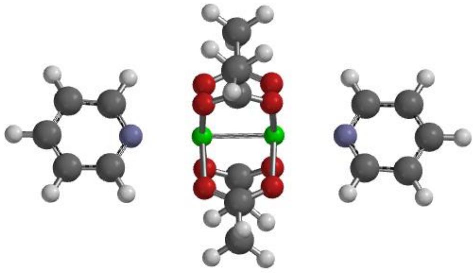
Molecular Modeling Problems

Part C. Molecular Orbitals and Orbital Energies

1. Triplet State of Methylene. Use the STO-3G model to obtain the equilibrium geometry of singlet methylene, and examine the highest-occupied and lowest-unoccupied molecular orbitals (the HOMO and LUMO, respectively). What effect, if any, would promotion of an electron from HOMO and LUMO be expected to have on the geometry, in particular, the HCH bond angle? Is the equilibrium geometry of triplet methylene obtained from the STO-3G model consistent with your expectations? Elaborate.

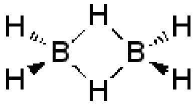
2. Mo_2. Calculate the energy of dimolybdenum assuming a Mo-Mo bond bond distance of 1.94Å, and display the valence molecular orbitals. Use the STO-3G model. Classify each molecular orbital as bonding, non-bonding or antibonding and as σ, π or δ. How many "bonds" connect the two molybdenum atoms?

3. Chromium-Chromium Multiple Bonds. Multiple bonding between transition metals is quite common. Consider, for example, the compound shown below, in which the two chromium atoms are bridged by four acetate ($MeCO_2^-$) groups and each then coordinated to an *axial* pyridine ligand.



Perform an STO-3G energy calculation on the experimental crystal structure of this molecule [the ***.spartan*** file is available in ***chromium-chromium multiple bond***] and, starting from the HOMO, display all the occupied molecular orbitals until you are satisfied that you have located all those that are bonding between the two chromium atoms. How many have such orbitals ("bonds") have you located? Characterize each of as a σ, π or δ orbitals and rationalize the ordering of their energies. How would you describe the metal-metal bond in this molecule?

4. Molecular Orbitals of Diborane. Diborane was originally thought to look like ethane, and only later was assigned the correct structure with two hydrogen atoms positioned above and below the plane formed by the remaining six atoms. In fact, diborane is much more closely related to ethylene than it is to ethane. These two molecules have the same number of valence electrons, that is, they are isoelectronic. Do the molecular orbitals of diborane resemble those of ethylene?



Obtain equilibrium geometries for diborane and ethylene using the STO-3G model. Attempt to associate each of the six valence molecular orbitals in diborane with an orbital in ethylene. Point out differences in both ordering and detailed shape. Describe the molecular orbital in diborane that is associated with the π orbital in ethylene. Is it the HOMO? Locate the unoccupied molecular in diborane that resembles the π^* orbital in ethylene. Is it the LUMO?

5. Lone Pairs in Water and Hydrogen Sulfide. Describe the two highest-occupied molecular orbitals of water as obtained from an STO-3G calculation. Are they primarily bonding, non-bonding or antibonding? Is the highest-occupied orbital a σ orbital or a π orbital?

Repeat your calculations and analysis for hydrogen sulfide. Point out (and attempt to rationalize) any significant differences between the two molecules.

6. Lithium and Sodium Hydroxide. Water is bent (the HOH angle is ~105^o) but both lithium hydroxide and sodium hydroxide are linear. To understand why, compare the highest occupied molecular orbitals for the three molecules. Use the STO-3G model to furnish equilibrium geometries. Characterize the HOMO of water as bonding, antibonding or nonbonding and as σ or π. How (if it all) is it different from the HOMO in lithium hydroxide and sodium hydroxide? How does this relate to the observe change in geometry?

7. Adding and Removing Electrons. Molecular orbitals may show distinct bonding or antibonding character. Loss of an electron from an occupied molecular orbital due to excitation or ionization, or gain of an electron by a previously unoccupied molecular orbital from excitation or electron capture could lead to changes in bonding and accompanying changes in molecular geometry.

Use the STO-3G model to obtain equilibrium geometries for ethylene ($H_2C{=}CH_2$), formaldimine ($H_2C{=}NH$) and formaldehyde ($H_2C{=}O$), and examine the HOMO for each. What would you expect to happen to the geometry around carbon (remain planar vs. pyramidalize), to the C=X bond length (lengthen, shorten or remain the same) and (for formaldimine) to the C=NH bond angle (increase, decrease or remain the same) were an electron to be removed from this orbital?

Obtain equilibrium geometries for the ethylene, formaldimine and formaldehyde radical cations using the STO-3G model, and compare with those of the corresponding neutral molecules. Are the changes in geometry in line with what you expect?

Examine the LUMO for each of the three molecules. Guess what would happen to the geometry around carbon, C=X bond length and (for formaldimine) the C=NH bond angle were an electron to be added to this orbital.

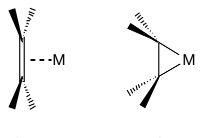
Obtain equilibrium geometries for the ethylene, formaldimine and formaldehyde radical anions using the STO-3G model, and compare with those of the corresponding neutral molecules. Are the changes in geometry in line with what you expect?

8. Carbon Monoxide as a Ligand. Carbon monoxide is certainly the most common ligand in transition-metal organometallic compounds. It acts by donating electrons from the σ lone pair on carbon into an empty orbital on the metal and accepting electrons from the metal atom into low-lying π* orbital.

Use the B3LYP/6-31G* model to obtain the geometry for carbon monoxide and examine the HOMO. Is it bonding, antibonding or essentially non-bonding between carbon and oxygen? What, if anything, would you expect to happen to the CO bond as electrons are donated from the HOMO to the metal atom? Display the LUMO. (There are actually two equivalent orbitals, designated LUMO and LUMO+1, and you can base arguments on either one.) Is it bonding, antibonding or essentially non-bonding between carbon and oxygen? What if anything would you expect to happen to the CO bond if electrons were donated from the metal atom into this orbital? Taken together, will donor-acceptor interactions involving carbon monoxide and a metal affect the ligand?

Obtain the geometry the iron pentacarbonyl, $Fe(CO)_5$, using the B3LYP/6-31G* model. It has a trigonal bipyramidal structure with three *equatorial* and two *axial* CO ligands. Delete one of the *equatorial* ligands to make iron tetracarbonyl, $Fe(CO)_4$. Calculate the energy of this fragment but ***do not optimize the geometry***. Display the HOMO. Does it have significant amplitude in the location where the carbon monoxide ligand will attach? If so, does it have the proper symmetry to interact with the LUMO in CO?

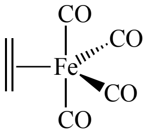
9. Binding Ethylene to a Metal. Two limiting structures can be drawn to represent ethylene bonded to a transition metal. The first may be thought of as a weak complex in that it maintains the carbon-carbon double bond, while the second destroys the double bond in order to form two new metal-carbon σ bonds, leading to a three-membered ring (a metallacycle). The bonding is "real" metal-alkene complexes presumably falls in between these two extremes.



Optimize the geometry of ethylene using the B3LYP/6-31G* model, and examine both the HOMO and LUMO. Is the HOMO bonding, antibonding or non-bonding between the two carbons? What if anything should happen to the carbon-carbon bond as electrons are donated from the HOMO to the metal? Do you expect the carbon-carbon bond length to decrease, increase or remain about the same? Elaborate.

The LUMO is where the next (pair of) electrons will go. Is this orbital bonding, antibonding or non-bonding between the two carbons? What, if anything, should happen to the carbon-carbon bond as electrons are donated (from the metal) into the LUMO? Is the expected change in the carbon-carbon bond due to this interaction in the same direction or in the opposite direction as any change due to interaction of the HOMO with the metal? Elaborate.

Optimize the geometry of ethylene iron tetracarbonyl using the B3LYP/6-31G* model. Compare the length of the carbon-carbon bond in the complex to that in ethylene and, based on this comparison, describe the bonding between the ethylene and the metal.



Delete the ethylene ligand (and the ligand attachment point), and calculate the energy of the resulting (iron tetracarbonyl) fragment (***do not optimize the geometry***). Examine both the HOMO and LUMO of this fragment. Is the LUMO likely to interact with the HOMO of ethylene? Elaborate. Would you expect electron donation from ethylene to the metal to occur? Is the HOMO likely to interact with the LUMO of ethylene? Elaborate. Would you expect electron donation from the metal to ethylene to occur?

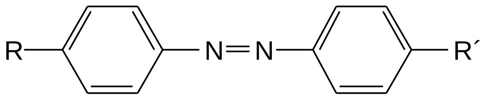
10. Anticipating Excited-State Geometries. Excited states may be thought of as arising from electron promotion from filled to empty molecular orbitals. In this view, the lowest-energy excited state should arise from promotion of an electron from the HOMO to the LUMO. Any influence that the bonding or antibonding character of the HOMO may have on geometry is weakened and in return the consequences of any bonding or antibonding interactions present in the LUMO are felt. Therefore, examination of the HOMO and LUMO for a molecule in its ground state should provide insight into the geometry of the excited state.

Obtain the equilibrium geometry for nitrogen using the STO-3G model. Examine the HOMO and LUMO. Would you characterize the lowest-energy electronic transition as *n* --> π* or π --> π*? Elaborate. Would you expect the NN bond length in the ground state to shorten, lengthen or remain unchanged upon excitation? Elaborate

Obtain the equilibrium geometry for acetone and examine the HOMO and LUMO. Would you characterize the lowest-energy electronic transition *n* --> π* or π --> π*? Elaborate. Would you expect the CO bond in the ground state to shorten, lengthen or remain unchanged upon excitation? Would you anticipate any other changes in geometry? Elaborate.

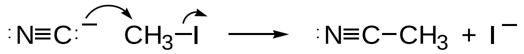
11. Anticipating Color Changes. The color of a molecule may reasonably be assumed to be related to λ_{max}, the difference in energy the ground and first excited states. This in turn should be reflected by the difference in energies between the highest-occupied and lowest-unoccupied molecular orbitals, the so-called, HOMO-LUMO gap. The smaller the gap, the lower the energy of the spectral transition and the more the color will tend toward the "red". The energies of molecular orbitals depend on structure, and it is reasonable to expect that the changes in the HOMO/LUMO gap with changes in molecular structure will anticipate the changes in color.

Use the STO-3G model to obtain equilibrium geometries for azobenzene (R=R′=H), 4-hydroxyazobenzene (R=OH, R′=H) and 4-amino-4′-nitroazobenzene (R=NH_2, R′=NO_2).



Azobenzene is orange. Use the change in HOMO/LUMO gap to predict whether the color of each of the other molecules will be shifted toward the red or blue end of the spectrum.

12. S_N2 Reaction of Methyl Iodide. Attack of cyanide anion, onto the backside of methyl iodide leads to acetonitrile and iodide anion.



$$:N{\equiv}C:^{-}\quad CH_3{-}I \longrightarrow :N{\equiv}C{-}CH_3 + I^{-}$$

A simple picture is that the HOMO of cyanide interacts with the LUMO of methyl iodide, leading to formation of a carbon-carbon bond and loss of a carbon-iodine bond. Use the STO-3G model to obtain the geometry of methyl iodide. Examine the LUMO. Is it bonding, antibonding or non-bonding between carbon and iodine? What would you expect to happen to the CI bond were a pair of electrons to be added to this orbital?

13. Ionization Potentials of Amines: Experimental ionization potentials for a series of amines and amides follow: NH_3, 10.1; $MeNH_2$, 8.9; Me_2NH, 8.2, Me_3N, 7.9; $PhNH_2$, 7.7; NH_2CHO, 10.2; NF_3, 12.9; NCl_3, 10.1. Use the 6-31G* model to obtain equilibrium geometries for these compounds, and plot HOMO energy vs. ionization potential. Point out (and try to rationalize) any significant deviations from linear correlation.