Chemistry 324, 2008
HW #4, Due M, Feb 25

"*Complicated orbitals are always regarded as combinations of simpler orbitals.*"

I don't know if anyone ever said that, but it is true, so someone should lay claim to it. As you know, my plan is to break transition state molecular orbitals down into combinations of reactant molecular orbitals (mostly frontier orbitals). Molecular orbitals can, likewise, be broken down into combinations of single atom orbitals, and if these are messy (e.g. hybrid orbitals), we can try to break them down some more.

The following assignment asks you to keep this idea of *combination* in your head while you closely scrutinize a set of molecular orbitals. Questions that you might be able to answer after you complete this assignment: What happens to MO energy when atomic orbitals combine? What happens to MO shape when atomic orbitals combine? Are these changes related to things I already know from resonance theory? Will I be able to look at molecular formulas in the future and guess (at least a little bit) how an alkene's π bonding, or antibonding, orbital will be affected by substituents?

A word of warning, this assignment may verge on the tedious. You are going to gather data on several molecules, look at the properties of each orbital, and then look for patterns between molecules and orbitals. All of this looking-looking-looking and comparing-comparing-comparing may tire you out. Unfortunately, it is the only way to demonstrate that a pattern exists. My advice: <u>*don't* try to do all of this in one sitting – you will just get exhausted and bored. *Do* work on this in groups.</u>

1. I have listed 3 sets of molecules: electron-rich alkenes, electron-poor alkenes, dienes below (some molecules appear in more than one set).
    a. Build these molecules
    b. Retrieve their 3-21G structures from the *Spartan* database
    c. Calculate **Energy** of ground state using **Hartree-Fock 3-21G** (neutral charge, singlet multiplicity, symmetry doesn't matter) and **Print: Orbitals & Energies**
    d. Calculate HOMO and LUMO surfaces for each
    e. Collect orbital data
        i. E(HOMO) in eV
        ii. E(LUMO) in eV
        iii. HOMO shape[1]
        iv. LUMO shape[1]

    Set #1: electron-rich CH_2=CHX where X = H, Me, OMe, SMe, CH=CH_2.
    Set #2: electron-poor CH_2=CHX where X = H, CN, CHO, NO_2, CF_3
    Set #3: mono-substituted dienes where substituent = 1-OMe, 2-OMe

2. Basic questions:
    a. Does the alkene HOMO always have same basic nodal structure, i.e., is this always a π bonding orbital in the vinyl group? (combine sets #1 & #2)

[1] Remember that shape info can be gathered in two ways. Basic shape properties (s v. p, node positions, etc.) are obtained most easily using HOMO/LUMO surfaces. Subtle shape properties (mixing coefficients) must be gathered from the output (use **Model:Labels** to help identify carbons).

   b. Does the alkene LUMO always have the same basic nodal structure, i.e., is this always a π antibonding orbital in the vinyl group? (combine sets #1 & #2)
   c. Repeat 2a. and 2b. for the diene frontier MO (instead of thinking about vinyl group, think about 4 carbons in the diene).

3. More advanced questions:
   a. HOMO energies indicate a molecule's electron donor ability. Rank the substituents by their effect on E(HOMO).
      i. Have I correctly identified electron-rich/poor alkenes or are some molecules listed in the wrong group? (use X = H as a molecule that is neither electron-rich nor poor)
      ii. Which parts of the ranking make sense according to resonance theory?
      iii. Which parts of the ranking can be explained by looking at the nodal structure of the HOMO? (focus on whether a substituent creates a π bonding or antibonding interaction with the adjacent vinyl carbon)
   b. LUMO energies indicate a molecule's electron acceptor ability. Rank the substituents by their effect on E(LUMO). Repeat 3.a.i-iii for these alkenes.
   c. Set #1 only: How do substituents affect the shape of the HOMO that lies *inside* the vinyl group? Is there a correlation between distortions of this part of the HOMO and E(HOMO)?
   d. Set #2 only: How do substituents affect the shape of the LUMO that lies *inside* the vinyl group? Is there a correlation between distortions of tthis part of the LUMO and E(LUMO)?
   e. Set #3 only: How do substituents affect the shape of the HOMO that lies *inside* the diene group? Is there a correlation between substituent position and HOMO distortion?

4. Bottom-line: All of the patterns that I want you to discover can be predicted using some simple mathematics and quantum mechanical principles (two lectures required). However, because this class does not assume a background in quantum mechanics, I am trying to take a detour. My detour will work, i.e., bring you to the desired destination, only if the questions that I have asked above bring you nose-to-nose with <u>general</u> and <u>clear</u> ideas about molecular structure vs. MO properties. If you can, summarize VERY BRIEFLY the effect of an electron-donating substituent on the HOMO (energy, shape) of an alkene. Summarize an electron-withdrawing substituent's effect on the LUMO of an alkene. And, summarize an electron-donating substituent's effect on the HOMO of a diene.

If, after you do all of this, you feel that your understanding would be even more secure if it were based on some quantum mechanics, COME SEE ME. *It won't take nearly 2 hours to explain things* after *you have attempted this assignment.*