

Chem 442: Homework for lecture L25

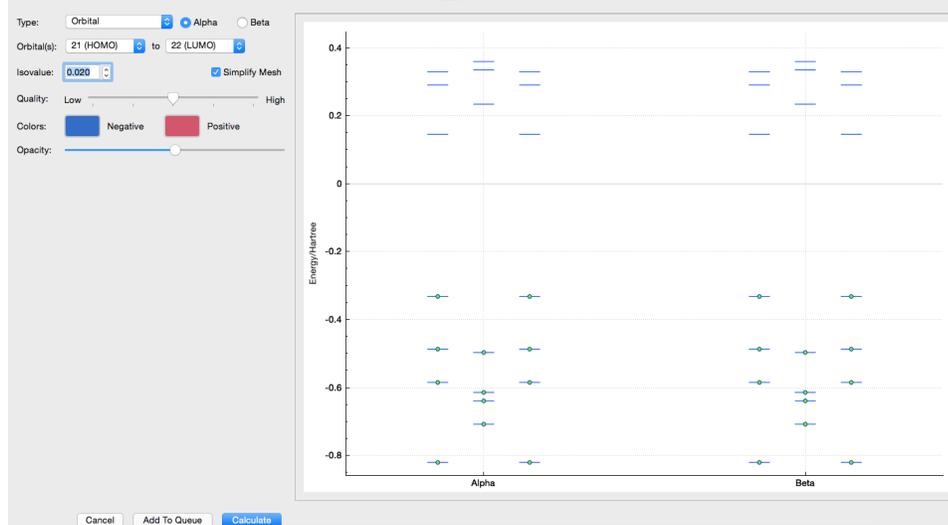
(only turn in **BOLD** assignment first lecture next week of classes; do all assignments)

1. Problem 8.8 in the book.

2. **Turn in:** benzene in IQMol

You will do a molecular orbital calculation for benzene like you did for H_2 a couple of lectures back, using a bigger basis set than the Hückel model.

1. Select C atom from the periodic table like you did H. Click it to the screen.
2. Keep click-dragging bonds to add 5 more C atoms connected by a single bond, and arrange them in a hexagonal fashion like you know benzene looks like. Make sure to draw a bond between the last and first C-atom, so you have a closed ring.
3. Once the hexagon is formed, you need to ensure you add the alternate double bonds. You can do this by click-dragging the cursor from C to C between already formed single bonds.
4. Click the 'Add Hydrogens' icon to add H atoms. You should see one H atom attached to each carbon. Use the energy minimization icon (red "E" with green arrow point down) to roughly minimize the structure. When you click on C-C bonds you should get a 1.399 Å UFF force field bond length.
5. Now go to the Q-Chem setup, and submit a job using the default 6-31G basis set, and save the result as "benzene" when the calculation is done. This diagonalizes the big matrix using a gaussian basis set.
6. Either open the benzene.FChk file, or click on the arrow next to "benzene" in the "Model View" panel on the left of the IQmol window. Double click the "MO surfaces" tab. You get the panel below, showing orbital energies as lines, electrons as dots. Scroll or zoom (the lowest energy orbitals are at -11.25 hartrees!):



7. Keep this setup (orbitals 21=HOMO to 22=LUMO), set 'Opacity' to 50% and hit 'Calculate'
8. Click on "Bonds" in the "Model View" panel next to the molecule display to get bond lengths. Use click-drag in the display window to rotate benzene if you want. Select or unselect the HOMO or LUMO in "MO Surfaces" to view the different orbitals individually.

Questions:

1. What are the energies in eV of the HOMO and the LUMO? Note that both the HOMO and LUMO are doubly degenerate, just like the simple Hückel calculation showed. Look up the conversion from hartree to eV if you need to.
 2. What are the bond distances C_2-C_3 and C_3-C_4 ? Is there any difference $>0.01 \text{ \AA}$? The energy minimization took care of the fact that benzene is more stable than cyclo-hexatriene owing to delocalization/conjugation.
 3. Check the boxes Alpha 21 and Alpha 22 separately. Draw the shapes of the HOMO and LUMO of benzene. You may capture the screenshots and paste them into your homework.
 4. Click on "MO Surfaces" again and select orbital #1 this time. What atomic orbitals is benzene orbital #1 really made up from? Do you think it shows any significant bonding overlap?
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3. Problem 8.10 in the book.