

Chem 442: Homework for lecture L23

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

1. Use the link given below

http://www.mathstools.com/section/main/system_equations_solver

a. Numerically diagonalize the matrices

$$\begin{pmatrix} -10 & 4 \\ 4 & -10 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} -5 & 4 \\ 4 & -15 \end{pmatrix}$$

Use the eigenvalues you get for each matrix to find the eigenvectors of said matrix (you will have to do this by hand). Which matrix is more like the H_2^+ problem? Which matrix is more like the HeH^+ problem? How is this reflected in the eigenvectors?

b. Gruebele claimed in class that just truncating (leaving out) high energy basis states from a Hamiltonian matrix when diagonalizing on the computer can give accurate results for the low energy eigenfunctions. Test this proposition by numerically diagonalizing the matrices

$$\begin{pmatrix} 1 & 1.5 & 1.5 \\ 1.5 & 2 & 1.5 \\ 1.5 & 1.5 & 100 \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} 1 & 1.5 \\ 1.5 & 2 \end{pmatrix}$$

Think of the first as the “full problem,” and the second as the truncated problem. Are the two lowest eigenvalues of the first matrix very different from the eigenvalues of the second matrix? Would this truncation be accurate to 1%?

2. Turn in (1-10 guides you through IQmol so you can answer questions a.-d.)

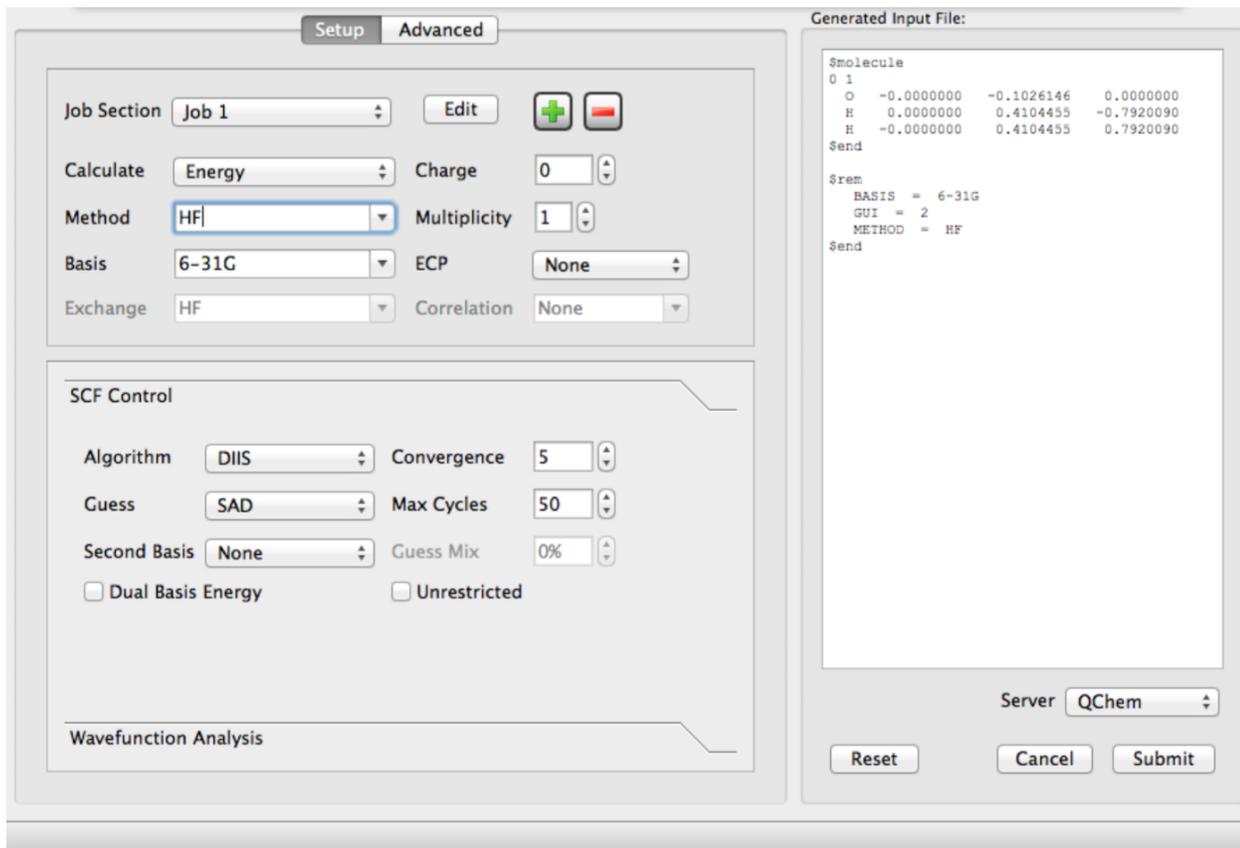
A molecular orbital calculation of H_2 using IQmol to do a bigger basis set and more electrons than the 2 basis functions Gruebele did in lecture for H_2^+ . Make sure you have internet connection. Then start IQmol and go through the following steps:

1. Click the  icon and choose H.
2. Click to put down an H atom, and drag to build a hydrogen molecule with 2 atoms.
3. Click Build → Select Force Field → UFF if not already selected by default.
4. To minimize the energy of the hydrogen molecule, and optimize the bond length you drew by hand to a reasonable value, click the  with the down arrow, which symbolizes energy minimization.

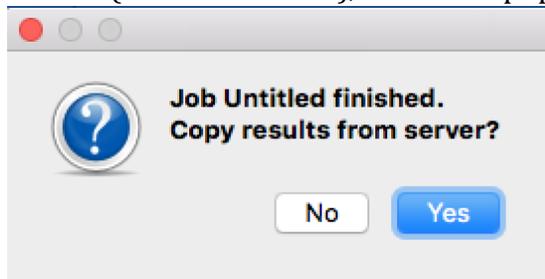
We have now finished building the H_2 molecule, now let's do some calculation. Specifically, let's have IQmol draw the good ol' σ and σ^* molecular orbitals.

0. Make an empty directory or folder called “IQmolResults” on your computer

1. In the menu bar, select Calculation → Q-Chem Setup
2. This menu should appear:



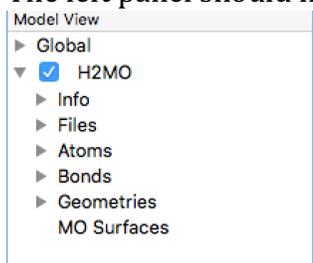
3. Leaving the standard configuration with 6-31G basis, select **Submit**. A menu should pop up asking you to give the job a name. Type the name "H2_lastname", where lastname = your last name lowercase and without spaces, and click **OK**.
4. Now the program will send the built molecule to the Q-Chem Server. After the calculation is finished (a minute or two), a window pops up:



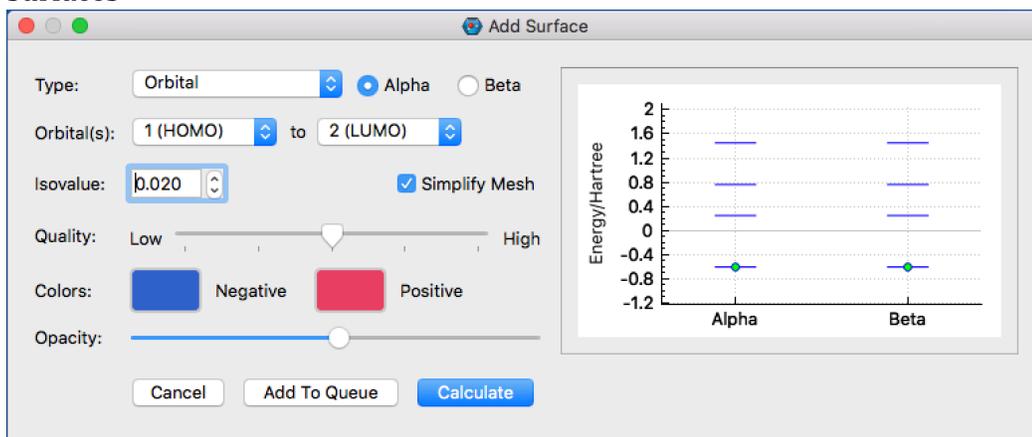
Click **Yes**, and choose the empty directory "IQmolResults" to save the file, or else it will overwrite your files in whatever other directory you pick.

5. Now open up the saved file [filename].FChk by doubling-clicking it, or drag-dropping it onto IQmol, depending on what type of computer you are using.

6. The left panel should have something like:



7. By Double-Clicking the MO Surfaces entry, you will open up a panel to add surfaces



8. On the right is an interactive energy plot of the molecular orbital, on which you can scroll to explore energy levels. Note that two electrons, one alpha spin and one beta spin occupy the lowest MO at -0.6 Hartrees (an energy unit). Initially, the plot will only show the one alpha and beta spin levels. To show the levels as depicted above, place the cursor on the plot and scroll to zoom in/out.

9. Now keep this standard setup and select **Calculate**

10. In the MO Surfaces, entry, there should now be two check boxes named: Alpha 1 (HOMO), and Alpha 2 (LUMO). Clicking the check boxes will present the shape of the molecular orbitals of the hydrogen molecule. You can double click Alpha1 and Alpha2 and a menu pops up that allows you to make the orbitals transparent, so you can see them and the hydrogen nuclei at the same time.

Questions:

- In the interactive energy diagram, zoom (in Mac, by scrolling) to observe the plotted energy levels of the molecular orbitals. What is the energy level, in Hartree units, of the sigma and sigma* orbitals? Now go to this website (<http://www.unitconversion.org/energy/hartree-energy-to-electron-volts-conversion.html>) and convert the energy of the sigma orbital to eV. Compared to the energy of hydrogen atom 1s orbital which is -13.6 eV, is the energy of the sigma orbital greater or lower? How does this explain the natural occurrence of hydrogen gas as a stable molecule?

- b. What is the bond distance of the UFF minimization that you did (click on bonds in menu to left).
- c. What atomic orbitals form the two empty molecular orbitals above the LUMO (the σ^* lowest empty orbital) and HOMO (the σ orbital occupied by 2 electrons)?
- d. Turn in your “.FChk” file to the TA for full credit. This is one of the files downloaded by IQMol after it runs the calculations for you and returns the results.