Introduction to Hartree-Fock calculations in Spartan

In this exercise, you will get to use state of the art software for carrying out calculations of wavefunctions for molecues, the Spartan program. The program is installed on one of the Macintosh computers in the chemistry computer lab. Follow the instructions in this file and provide answers to the questions raised in a word processor file that you then e-mail to the instructor, hj-at-hi.is.

The program 'Spartan' by Wavefunction Inc. (in Irvine, California, USA) can be used to calculate wavefunctions for electrons in molecules by solving the time-independent Schroedinger equation in an approximate way. At the basic level, these are so-called 'self-consistent-field' (SCF) calculations, or, in the limit of an infinite basis set for the atomic orbitals, Hartree-Fock (HF) calculations. Other levels of approximation are also available in this software. Spartan is research level software which, nevertheless, makes it easy to set up the calculations and visualize the results.

The newest versions of the Spartan program on the Macintoshes is called Spartan06. The instructions given here are tailored to an older version but the commands are quite similar in the various versions of the program. Use the 'help' menu to quide you to the right commands.

Once you start the program, it will open a window for displaying the molecules and menu bar with various pull-down menus appears at the top of the screen. The help facility contains information about the various aspects of the program as well as a tutorial with various exercises. You will learn about the basic functionality of the program by working through the examples below, but you should consult the user's guide for further information.

A.   Molecular orbitals of H_2:

In the first part of this exercise, you will calculate the electron wavefunction of the H_2 molecule. You should review the disucssion of diatomic molecules and molecular orbitals in your first year chemistry textbook before doing this exercise.

To set up a calculation of a molecule in Spartan, select **File** and then **New**. A menu opens which allows you to assemble molecules from a panel. In this first part of the Spartan exercise, you will carry out calculations on teh H_2 molecule. To create the molecule in Spartan, click on the box with a H atom. Then move the cursor to the main window to the left and click on the mouse button to add the atom. The single bond which at this point is left 'dangling' will automatically be terminated by a H atom when you exit the molecule builder. Alternatively, you can click on the dangling bond and another H-atom will appear. Select **Save** under the **File** menu. You will be prompted for a name of the folder that will contain all input and output from the program relating to this molecule.

The H_2 molecule should now be displayed on the screen. You can rotate the molecule

by pressing the mouse button and sliding the mouse. Rotation in a different plane is obtained if you also hold down the Apple key while sliding the mouse. You can move the molecule by pressing the Alt key and sliding the mouse. You can make the molecule larger or smaller by holding down the Alt and Apple key on the keyboard and sliding the mouse. Check the *Help* menu (top right) for other options. You can change the way the molecule is displayed by selecting from various options under the **Model** menu. Try them all. Finally, select **Ball and Wire** representation and turn labels on by selecting 'Labels' under the **Model** menu.

To set up a Hartree-Fock calculation, select **Calculations** under the **Setup** menu. By default the program calculates the wavefunction using the Hartree-Fock approximation and the 3-21G Gaussian basis set to represent the atomic orbitals (the meaning of this notation is explained below). The button in the upper left corner reads 'Equilibrium Geometry' which means that the calculation will be repeated for different locations of the nuclei until no force acts on the atoms, that is the optimal, minimum energy configuration of the atoms is found. After each calculation, the nuclei are moved according to the forces acting on them. Such an optimization needs to be carried out to determine the optimal bond lengths (and angles in larger molecules).

Click on the button that by default reads 'Hartree-Fock'. A list of the various computational methods that are available in Spartan appears. 'Molecular Mechanics' stands for a calculation using empirical potentials (such as Morse functions, and other functional forms). Empirical means that experimental data on chemical bonding has been used to parametrize the functions. No wavefunction is calculated for the electrons in this case. This is the cheapest but least reliable method. In the 'Semi-Empirical' methods a wavefunction of the Hartree form is calculated but the most difficult integrals in the calculation are skipped and functions fitted to experimental data are used instead. These are fast methods, but they only work if the type of molecule being studied and its geometry are similar to the ones used to to fit the empirical functions. If 'Semi-Empirical' is selected, then the button to the right specifies which of the available semi-empirical schemes is used, such as 'AM1', 'PM3' or 'MNDO'.

When the Hartree-Fock approximation is selected, the button to the right specifies the basis set used, i.e. how many Gaussians are used to represent the atomic basis functions. The default basis set is 3-21G which means that three Gaussians are used to represent the atomic orbitals (but two coefficients can be varied for the valence electrons, one multiplies a fixed combination of two of the Gaussians and the other multiplies the third Gaussian - for core electrons all three Gaussians have a fixed linear combination). More flexibility is needed for the valence electrons because they participate in chemical bonding. Choose the 3-21G basis set for now. The charge of the molecule is by default set to zero ('Neutral'), as is appropriate here. Also, the multiplicity is appropriately set to 'Singlet' by default. (The multiplicity is the number $2S + 1$ where S is the net spin of all the electrons in the molecule. A singlet corresponds to S=0 and is designated by multiplicity of 1). Then, click on **OK** to store this setup.

Spartan can give various information about the calculated results. To get visualization of 3-dimensional isosurfaces illustrating the electron density or molecular orbitals, select **Surfaces** under the **Setup** menu. A pop-up menu allows you to select various options, and several different isosurfaces. You can choose which quantity the isosurface will represent and you can have it colored according to a second property. Click on **Add** to add a new isosurface to the list of surfaces that will be calculated. By default you get the option of a density surface with no property color coded on the density. Click on **OK** to include this surface. Then click on **Add** again and select **HOMO** from the **Surface** button. HOMO

stands for 'highest occupied molecular orbital'. Finally, add also the 'lowest unoccupied molecular orbital', **LUMO**. You should then have a list of three isosurfaces on order.

Go back to the **Setup** menu and select **Submit**. A menu will pop up to inform you that the calculation is being carried out. Another pop-up menu will tell you the job has finished. Click on the **OK**. The results from the calculations are obtained from the **Display** menu. Select **Surfaces** and then click on the box by the surface you want to display. You may need to adjust the size of the display (Alt-Apple and mouse). Notice that the density is almost spherical, just slightly elongated along the molecular axis. You can turn off the density surface by clicking again on the small box. That removes the check mark. After turning off the display of the electron density, turn on the display of the HOMO surface. Then, display the LUMO surface (just one surface at a time). The red and blue colors represent positive and negative value of the wavefunction.

*Q1: Copy the image of the HOMO and the LUMO (one at a time) into your word processor window. Before copying the image, increase its size to fill the window. To copy a figure from Spartan to a word processor, select **Copy** under **Edit** on the Spartan menu bar, then select the word processor window and select **Paste**. (You can reduce the excess white area around the figure by selecting the figure and using the 'crop' button.). Arrange the images of the HOMO and LUMO side by side. Write text underneath to label each molecular orbital as bonding or antibonding. Also, specify whether the molecular orbitals are sigma or pi orbitals.*

To get the optimal bond distance in the H_2 molecule predicted by the calculation, select **Measure Distance** under the **Geometry** menu. Click on the atoms in the molecule, one after the other, using the left mouse button. The value of the distance appears near the lower right corner of the Spartan window.

Q2: What is the optimal bond length in a H_2 molecule predicted by the Hartree-Fock calculations? Compare with the experimental value for the bond lenght, $0.74Å$.

To get the energy of the molecule in this configuration, click on **Display** and then **Output**. The window that opens contains various information about the calcualtion, for example what energy is obtained in each iteration to self-consistency as the Hartree-Fock equations are solved. The energy is given in atomic units (au) which means the unit of energy is $Hartree = 27.2\ eV$, twice the ground state energy of a H-atom. The final value of the energy is given in the line 'E(HF)= ....'.

Q3: Record the energy of the H_2 molecule in your report. What is the zero of energy in this case? Using the exact value of the energy of an H-atom, calculate the bond energy. (This is, actually, not a good procedure since the two numbers subtracted are not calculated at the same level of theory. Generally, one relies on cancellation of errors in ab initio calculations and should, therefore, consistently use the same level of approximation for all numbers subtracted or added).

Q4: Repeat the calculation using the lowest level, $STO-3G$ basis set. Here, all atomic orbitals are represented by a fixed linear combination of three Gaussians. What is the predicted bond length and what is the energy of the molecule? Is the energy higher or lower than for the $3-21G$ basis set? Explain why the energy is different and why the energy must necessarily change in the direction it did (become lower or higher). Recall, SCF calculations are variational calculations. Is there any such rule for how the bond energy

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changes as the basis set is changed (why/why not)?.

B.   Electron density of HF and LiH molecules:

Do Hartree-Fock calculations for a HF molecule. Again, click on **New** under the **File** menu and select a F atom. When you save, the dangling bond will be saturated with a H atom. Display the electron density and compare the results with the electron density of the H_2 molecule. (Note: when two or more molecules are displayed simultaneously in the Spartan window, one can choose which one is 'active' by clicking on the molecule with the mouse).

Q5: Does the electron density near the H atom increase or decrease when it binds to an F atom? (Make the electron density in both molecules transparent and overlay the H-atoms to compare the diameter of the lobes enclosed by the electron density surfaces). How does this correlate with the electronegativity of the atoms?

Q6: Do Hartree-Fock calculations for a LiH molecule. In order to get a Li atom, select **Expert** *in the upper part of the menu. Click on* **Element** *and you will see the whole periodic table. Also, there are more bonding options in expert mode. The* **-X** *specifies that the atom only forms one bond. Compare the results for LiF with those for the H_2 and HF molecules. Comment on how the electron density at the H-atom in LiH compares with those in H_2 and HF.* Explain the trend.

C.   Molecular orbitals of N_2 and O_2: and O_2

Do Hartree-Fock calculations of a N_2 molecule using the $6 - 31G^*$ basis set. Use the 'Entry' mode of the molecule builder when you assemble the molecule and select a N-atom that forms a triple bond. After one N-atom has been added to the window, click on the yellow line (the dangling bond) to add another N-atom thereby forming a diatomic molecule. Select HOMO and LUMO densities in the same way you did for the H_2 molecule in part A. To see the molecular orbital that is next lower in energy than the HOMO, select **HOMO-** when you set up the surfaces and dial one to the right of the Surface button. You can get the **HOMO-2** molecular orbital by changing the number 1 to 2, etc. Calculate and display the various molecular orbitals, ranging from HOMO-6 to LUMO+2. Select **Orbitals & Energies** in the **Print** field of the **Setup/Calculations** menu. This makes Spartan write out information about the molecular orbitals in the output file at the end of the SCF calculation. Information about the progress of the SCF calculation and the calculated results can also be found in the output file, which is opened by clicking on **Output** under the **Display** menu. The energy of the various molecular orbitals is given in the output file as well as the coefficients in the expansion of the MOs in terms of atomic basis functions (not the atomic orbitals but rather atom centered basis functions with angular part corresponding to S, P_x, P_y, etc.). The line labeled **Eigenvalues** gives the energy of the MOs in Hartrees and the line below that gives the energy in eV. The column of numbers under each energy value gives the linear expansion coefficients of the molecular orbital in terms of the atomic basis functions. By looking at the magnitude of the expansion coefficients, you can see roughly which atomic orbitals are the primary components in the MOs. You can figure out which orbital is the HOMO and which is the

LUMO by counting the electrons. Remember that two electrons go into each MO, starting at the lowest orbital, then the next higher, etc.

Q7: Display all the MOs in your report and classify each one of them as bonding, anti-bonding or non-bonding, and say whether the symmetry of the orbital is sigma or pi. Sketch a molecular orbital diagram using the values of the energy of the MOs from the output file and compare your diagram with the one in your freshman chemistry textbook. It can be useful to inspect the coefficients of the molecular orbitals.