Chem 260 Laboratory 9

This lab demonstrates bond formation. HyperChem is used to display molecular orbitals, but the Extended Hückel program available in the Lite version is not able to model the energy minimum at the equilibrium bond length. A different package, Molecular Modeling Basic, includes other semi-empirical quantum chemistry programs which are more suitable for the exploration of the energetics of bond formation.

BOND FORMATION – H_2 ORBITAL SHAPES

1. Start HyperChem and draw the H_2 molecule.
2. Select the bond and use Edit/Set Bond Length to separate the H atoms by a large amount (e.g. 20 Å) to represent the unbonded situation. Use Display/Scale to Fit.
3. Perform a single point EHT calculation and display the Orbitals window. There are two orbitals of the same energy (provided the H atoms are well separated). Click on Labels to see where the electrons are. If they are in the same orbital you have H^-…..H^+. Go back to Setup/Options and specify a spin multiplicity of 3. Repeat the EHT calculation and return to Orbitals. Each H now has its own electron.
4. Compute and display orbitals. A 2D contour plot is more useful than the 3D option. Now change the bond length successively to 2 Å, 1 Å, and 0.5 Å. In each case do an EHT calculation and look at the orbital display. Notice how the circular contours of the H atoms are distorted by the nodal plane between the atoms. Clearly triplet hydrogen is non-bonding.
5. Set the spin multiplicity to 1 and look at the orbital again. The nodal plane has disappeared. Some electron density has been "sucked in" between the H atoms. Note, however, that the electron density peaks at the nuclei *not* between them. Try a few different bond lengths to appreciate the way in which the atomic orbitals combine to form the molecular bond.
6. Use Model Build to set the standard bond length, and paste orbital contour plots of both singlet and triplet H_2 in your lab report.

BOND FORMATION – H_2 ORBITAL ENERGIES

7. Set the molecule back to the singlet state and open a log file (EHT print level 1). Step through a series of bond lengths (e.g. 0.3, 0.5, 0.7, 1.0, 2.0, 10.0 Å), doing an EHT calculation at each step.
8. Inspect the log file and record Sum of One-Electron Energies (a.u.) and the two orbital Eigenvalues (in eV; label them E_1 and E_2) in an Excel file. Convert the Sum of One-Electron Energies to eV and add 27.2 eV (so that E = 0 for separated atoms). Similarly, add 13.6 eV to each Eigenvalue. Plot all three (E_1, E_2 and Singlet) on a single graph.
9. Do a single calculation for triplet H_2, e.g. at 1.0 Å. Notice that Sum of One-Electron Energies = $E_1 + E_2$ (because there is one electron in each orbital). Use your tabulated values of $E_1 + E_2$ to calculate the Sum for triplet H_2, and add these points as a new plot on the graph.

10. It is obvious from the plot that singlet H_2 has less energy than triplet H_2 but can you tell the optimum bond length? Why not? The energy calculated by EHT drops as the H atoms get closer. What is to stop the two H atoms fusing? Now you know why we don't use the EHT method to optimize geometry – it doesn't work well except at standard bond lengths, which are used by the program's Model Build feature.
11. Close HyperChem.

H_2 Orbital Energies Calculated by CNDO

12. Start Molecular Modeling Basic. Draw H_2.
13. Use Geometry/Reference…/Change Bond Length to set the H atom separation.
14. MM Basic does not have HyperChem's orbital plotting capability but it does have some semi-empirical methods for calculating molecular energies. For this lab use Tools/CNDO/open shell. Try it. The results are displayed in a text file (CNDO.txt). This file is overwritten every time a new calculation is done, so be sure to copy any needed results to your Excel file as you go along. [HyperChem Lite is limited to single-point Extended Hückel energy calculations, but the full version of HyperChem includes all the methods available in MM Basic … at a price!].
15. Step through the series of bond lengths (e.g. 0.3, 0.5, 0.7, 1.0, 2.0, 3.0, 4.0 Å) and for each one do a CNDO calculation for the molecule in the singlet state and also in the triplet state (i.e. multiplicity = 1 and 3, respectively). Tabulate the Total Energy for each case. assume that a bond length of 4.0 Å is equivalent to separated atoms, and shift the energy scales so that they give zero energy at this separation. [A larger separation can give misleading results for the singlet state, as the program tends to put both electrons on one atom, i.e. it calculates the ionic $H+H^-$ state. If you want to see this try 10 Å or more, and look at the Partial Charges and Dipole Moment in the output file.]
16. Plot the results as a function of bond length. Use the same graph for singlet and triplet H_2.. Paste it into your lab report.