Introduction to Modeling and Simulation
Part II : Quantum Modeling

Problem Set #4

The following problem set is to be solved as a group just as in Part I. Each group should hand in only one set of solutions containing the names of all group members.

1. Simulation of a N_2 molecule using nanoHUB

In this problem we will study the molecular binding in a N_2 molecule using the nanoHUB tool: "Berkeley Computational Nanoscience Class Tools". Once the tool is running, select the "Quantum Chemistry (GAMESS)" tool from the top right corner pull-down menu.

Use the default settings for all the parameters to begin with. This means that the run type is "energy", method is "Hartree-Fock", basis set is "3-21G", etc. In the coordinate window in the lower left enter coordinates for the N2 molecule. Do this by selecting "New" and entering the coordinates in xyz format.

(a) Compute the total energy for different values of the separation between the two N atoms. Show how the total energy changes as a function of separation d.

(b) Find the molecular binding distance d_{bind} by finding a minimum in the total energy.

(c) Plot the total energy as a function of d over a reasonable range $d_{min} \leq d \leq d_{max}$ which includes d_{bind}.

(d) Shift your plot such that the total energy for d_{bind} is zero. Fit the resulting plot to a Morse-type potential

$$V(d) = \alpha\left[1 - e^{-\beta(d - d_{bind})}\right]^2$$

Find the parameters α and β and plot the Morse potential together with your shifted total energy curve.

(e) Find the stretching frequency of N_2 by calculating the second derivative of the energy with respect to the interatomic distance, calculated around equilibrium. How does it compare to experiments?

(f) Find d_{bind} for the three different values of the gaussian basis set ("Low", "Medium", and "High"). Discuss your findings.

(g) Now, calculate the total energy of only a single N atom. Be careful to specify the correct spin state in the input. What is the dissociation energy (the energy required to put each N atom in the N_2 molecule infinitely far away from each other) of a N_2 molecule?

(h) All of these properties so far could have been obtained by a classical force field calculation. However, quantum mechanics allows us to compute properties intrinsic to the electronic degrees of freedom. In this vein, look up a plot of the solar flux incident on earth. We care a lot about this in our attempts to harness energy from the sun. Note that there are dips in the terrestrial spectrum. These occur because of absorption by molecules in the atmosphere. But even though N2 makes up a large fraction of the atmosphere it is not responsible for any of these dips. Based on your calculations, please explain why.

(i) Now replace N with O to simulate the O2 molecule. Predict whether this molecule prefers to be in the spin singlet or spin triplet state. Based on a simple molecular orbital diagram for O2, in which you have the energy levels of each oxygen atom drawn on two sides and the energy levels of O2 drawn in the middle, does your result make sense? Be sure to show your orbital picture, with the energies for the levels taken from your calculations.

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