Chemistry 438/550: Computational Chemistry, Spring 2022

Homework #4, due Feb 23.

Starting with this homework assignment, you will be much more "on your own": in place of blow-by-blow instructions, your mission (should you choose to accept it) will be to take more generic instructions, and figure out how to proceed.

A topic of continuing interest involves the strength and prevalence of CH–O hydrogen bonds. One simple model system for this is the dimethyl-formamide dimer. When the two monomers are placed "head–to–tail", two such interactions can be made. You can get the coordinates of a plausible initial structure from `/projects/community/classes/ccb550/dimer_init.xyz` on Amarel. The file format is a simple, *.xyz*, format: the first line contains the number of atoms, the second line is blank, and the remaining lines give the element followed by x,y,z coordinates.

If you transfer this file to your laptop or desk computer, many molecular visualization programs will be able to show you the structure. You can use the WebMO demo program from the last homework: go to File→Import Molecule, choose "xyz format", and browse for the file, asking it to "generate bonds". Click on the "rotate" icon, and get a feeling for the structure. For a more powerful visualization environment, visit www.cgl.ucsf.edu/chimerax/, install it on your laptop, and ask it to open your `dimer_init.xyz` file.

Here are the steps for this homework:

1. Use Gaussian to optimize the geometry, starting from the above initial geometry. Use Hartree-Fock and a 6-31G* basis set. Record the optimized energy, and compute the H–O distances in the two CH–O "hydrogen bonds" between the two monomers.

   (**Note:** the jobs requested above are not long ones, but they may take several minutes to run. Be sure to use the template in `/projects/community/classes/ccb550/g16.pbs.template` as you did in the previous homework: copy this file to your working directory, and edit it according to the instructions in the file.)

2. Create a DMF monomer, say from the first 12 or last 12 atoms. Optimize its geometry, using the same model chemistry. Compute the energy difference between the dimer (from step 1) and two monomers (from this step). How much energy is each CH–O bond worth? (Express you answer in kcal/mol.)

3. Repeat steps 1 and 2 using the B3LYP density functional, adding in empirical dispersion (add `EmpiricalDispersion=GD3` on your route card.) (Density functional theory is an alternative to Hartree-Fock calculations, and we will discuss these in class soon. You can find information about the DFT models available in Gaussian at gaussian.com/dft/.)

4. Create a plain-text file, *lastname.txt*, that has the optimized energies for monomer and dimer, the energy difference (i.e. the binding energy), and the the intermonomer H–O bond lengths, for both the Hartree-Fock and the DFT calculations. Hand this in via the usual mechanism:

   ```
   cp lastname.txt /projects/community/classes/ccb550/homework4
   ```

5. From the Gaussian log file for the Hartree-Fock dimer run, find the optimized geometry, and use it to create a `dimer_final.xyz` file. Practice visualizing it in the same way you looked at the initial coordinates. There is nothing to "hand in" here, but time you spend learning how to visualize your results will be time well-spent.