Chemistry 438/550: Computational Chemistry, Spring 2020

Homework #5, due 23 March

In the last homework, you looked at a study of the strength of CH–O hydrogen bonds, using the dimethyl-formamide dimer as a model system. Here, we are going back to more conventional NH–O hydrogen bonds, using the formamide dimer as our model system. As before, when the two monomers are placed "head–to–tail", two such interactions can be made. You can get the coordinates of a plausible (but very rough – visualize it!) initial structure from `/home/dacase/ccb550/form_dimer.pdb` on Amarel. The file format is what is standard for the Protein Data Bank, and you should be able to extract *xyz* coordinates from this. Use your favorite visualization program to examine the structure.

The idea of this homework is much like what we did in Homework #4: you should optimize the structure of the dimer, then separately optimize the structure of a monomer. But we will add two new computational aspects:

1. *Thermochemistry*: Use this for your route card (for both dimer and monomer):

   ```
   #  B3LYP/6-31G(d) opt freq
   ```

   This will perform a geometry optimization, then compute normal modes and themochemical data. Familiarize yourself with what the frequency calculation puts out. Look especially for lines that start with "sum of electronic and....": these will contain the key numbers you will need to get dimerization thermodynamics.

2. Using the results from step #1, compute the change in electronic energy, in the binding enthalpy, and in the standard free energy, for the reaction $2A \rightarrow A_2$, where "A" is a formamide monomer. Use standard state conditions (which is what Gaussian prints out): 298.15K for temperature, 1 atm for pressure.

3. *Reaction fields:* Repeat steps 1 and 2 using the following route card to add a solvent reaction-field term. (You can find information about this option at gaussian.com/scrf.)

   ```
   #  B3LYP/6-31G(d) scrf opt freq
   ```

   (As you can see at the Gaussian web page, the default for scrf is to assume that the solvent is water.)

4. Create a plain-text file, *lastname.txt*, that has the results requested above (eletronic energies, enthalpies, free energies) for monomer and dimer, and the corresponding energy differences. Briefly(!) discuss the following:

   (a) the general difference in affinity between CH–O and NH–O hydrogen bonds;

   (b) the difference in affinities computed using just electronic energies versus those using enthalpies or free energies;

   (c) the predicted effects of going from gas-phase to aqueous solution.

5. Hand this in via the usual mechanism:

   ```
   cp lastname.txt /home/dacase/ccb550/homework5
   ```

(**Note:** the jobs requested above are not long ones, but they may take several minutes to run. Be sure to use the template in `/home/dacase/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.)