Chem 860. Homework 7 Due: Apr. 20 2009

Electrostatics

April 10, 2009

1 Pencil exercises

1. Show that the "self-interaction" in Ewald summation (interaction between the point charge and its own "correcting (compensating) Gaussian charge" is given by $-\frac{q_i^2}{\sqrt{\pi}}2\beta$. *Hint: use the short-range expansion of the electrostatic potential due to a Gaussian charge.*

2. Use the Born solvation model to consider a toy "ligand optimization" problem. Model ligand binding as the merging of a small sphere (radius r) into a large sphere (radius R). The charge for the "protein" is Q, that for the ligand is q. What is the binding energy (take ϵ to be ∞ to simplify algebra)? Can one optimize q to obtain the most favorable binding? Show explicitly that the solution indeed gives the most favorable binding rather than a local stationary result. *Hint:An interesting related reference is: Tidor et al., J. Chem. Phys. 109, 7522, 1998*

2 Computational exercises

Scripts are in hw7_09.

2.1 Ewald simulation of water

File: tip3_ewald.inp. This is essentially the same water simulation as before, except that we now use the Ewald summation to treat electrostatics. Compare the RDF and diffusion constant from those simulations to your previous results. Which are closer to experimental values? Does the result surprise you? I also encourage you to explore the speed and convergence of energy/force with different Ewald parameters (e.g., κ - the width of Gaussian, and the number of $\mathbf{k}$ vector summations); also compare the efficiency of standard Ewald and the Particle-Mesh-Ewald (PME).

2.2 Implicit solvation: a GBSW simulation

File: gbsw.inp. This is a standard test script for a popular GB model in CHARMM (GBSW). Refer to gbsw.doc (http://www.charmm.org/html/documentation/c35b1/gbsw.html) for some relevant references and key words. The sample script gives you the template for carrying out such calculations using a number of standard options, especially concerning the definition of the dielectric interface. (1) Modify the input to carry out MD simulation using one of your favorite set of keywords till RMSD plateaus; explain your choice of simulation parameters. (2) Also run a simulation for the same system in vacuum for the same length, is the system stable? What is the speed difference? (3) Can you somehow estimate the speed difference from an explicit solvent simulation?