CHEMISTRY 5021/8021
MIDTERM EXAM KEY — SPRING 2004

1. Molecular Mechanics (50 points)

Write two different functional forms that might be used to describe the potential energy associated with bond stretching. Carefully define all terms in the equations. Now, contrast the two: what are the relative merits of one compared to the other? Why might a given force field adopt one and not the other? Note that there are many possible answers here—I am not looking for any *specific* two forms.

The simplest functional form that has some degree of realism is a harmonic form, i.e.,

$$E(r_{\mathrm{AB}};k_{\mathrm{AB}},r_{\mathrm{AB},eq}) = \frac{1}{2}k_{\mathrm{AB}}\left(r_{\mathrm{AB}} - r_{\mathrm{AB},eq}\right)^2$$

where E is the stretching energy as a function of bond distance r_{AB} (zero at the equilibrium distance parameter $r_{\mathrm{AB},eq}$) and a force constant parameter k_{AB} that controls the width of the parabolic potential (i.e., the stiffness of the bond).

Acceptable other forms that might be offered by contrast include:

$$E(r_{\mathrm{AB}};k_{\mathrm{AB}},k^{(3)}_{\mathrm{AB}},r_{\mathrm{AB},eq}) = \frac{1}{2}k_{\mathrm{AB}}\left(r_{\mathrm{AB}} - r_{\mathrm{AB},eq}\right)^2\left[1 + k^{(3)}_{\mathrm{AB}}\left(r_{\mathrm{AB}} - r_{\mathrm{AB},eq}\right)\right]$$

(adds a cubic term to the quadratic term — generalization to higher order polynomials also an option — the new parameter is the cubic force constant $k^{(3)}_{\mathrm{AB}}$)

$$E(r_{\mathrm{AB}};D_{\mathrm{AB}},\alpha_{\mathrm{AB}},r_{\mathrm{AB},eq}) = D_{\mathrm{AB}}\left[1 - e^{-\alpha_{\mathrm{AB}}\left(r_{\mathrm{AB}} - r_{\mathrm{AB},eq}\right)}\right]^2$$

(the Morse potential — $D_{\mathrm{AB}}$is the dissociation energy and a is a tightness parameter — this function permits bond dissociation where the harmonic potential does not — it has one extra parameter compared to the harmonic potential, and it is somewhat more expensive (from a computational standpoint) to evaluate)

$$E(r_{\mathrm{AB}};\varepsilon_{\mathrm{AB}},\sigma_{\mathrm{AB}}) = 4\varepsilon_{\mathrm{AB}}\left[\left(\frac{\sigma_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^{12} - \left(\frac{\sigma_{\mathrm{AB}}}{r_{\mathrm{AB}}}\right)^{6}\right]$$

(the Lennard-Jones 6-12 potential — this form is more commonly used for weak interactions than for full bonding interactions — it permits dissociation and has a

binding energy of ε_{AB} at an equilibrium bond distance of $2^{1/6}\sigma_{AB}$ — computational evaluation is fairly fast and only two parameters are required)

Other answers are possible. Motivations to choose one form over another will have to do primarily with the availability of experimental data (more is needed to fit more parameters), the desire to permit bonds to break (then only Morse and L-J are viable options), and computational efficiency (quadratic is faster than cubic, etc.)

2. Semiempirical Theory (50 points)

An AM1 calculation on benzene provides a 298 K heat of formation of 23.5 kcal mol^{-1}. Explain in a detailed fashion exactly how this heat of formation value was arrived at. You need *not* explain anything about geometry optimization.

The heat of formation derives from taking the difference between the AM1 electronic energy of the molecule and the sum of the AM1 electronic energies of all of the atoms and adding this quantity to the experimental heats of formation of the atoms. As such, zero-point vibrational energy (in the molecule) and differential thermal contributions (between the molecule and the atoms) are ignored, and it is assumed that by parameterizing against heats of formation, the various AM1 parameters will relax to account for these effects in an average way.

As for computing the electronic energies themselves, they derive from Hartree-Fock calculations where various matrix elements are simplified according to particular approximate conventions. For example, the overlap matrix is assumed to be the unit matrix in the formation of the secular determinant, core electrons are ignored and nuclear charges are reduced to compensate, same-center one-electron integrals are approximated from ionization potential data, two-center one-electron integrals are computed from simple distance-dependent functions, parameters are used for valence 2-electron integrals (ss|ss), (sp|sp), (ss|pp), (pp|pp), and (pp|p´p´) on a single center, 2-electron integrals between multiple centers are ignored unless for a general $(\mu\nu|\lambda\sigma)$ both μ and ν are on a single center and both λ and σ are on a second center, in which case the integral is approximated from an analytical interaction between multipoles defined by the Slater-orbital s and p basis functions.

One could go into endless detail on this answer. Grading will, however, be liberal in recognizing the time constraints of the exam.

3. Ab Initio MO Theory

a) How many basis functions are required for a HF calculation on glycine ($C_2H_5NO_2$) using the 6-31G(d) basis set? (25 points)

Every heavy atom has 15 basis functions (one 1s (core), two 2s (valence), six 2p (valence, 2 ea. of p_x, p_y, and p_z), and six 3d polarization functions (polarization, remember Pople sets are defined to use six cartesian d functions instead of five canonical d functions).

Every H atom has 2 basis functions (two 1s (valence)).

So, total is 5 heavy atoms times 15 basis functions per heavy atom (75 basis functions) plus 5 hydrogen atoms times 2 basis functions per heavy atom (10 basis functions) for a total of **85** basis functions.

b) Select by letter from the list at the bottom of the page the proper answer to the following questions. There is only one correct answer to each question. (5 points each)

(1) This post-Hartree-Fock level employs second-order perturbation theory to estimate the energy associated with electron correlation and formally scales as N^5.

F

(2) This correlated level of theory expresses the complete wavefunction as a linear combination of configuration state functions but fails to be size-consistent.

G

(3) This is a potential problem with unrestricted Hartree-Fock wave functions that is not a problem for restricted open-shell Hartree-Fock wave functions.

B

(4) This is a multilevel model that attempts to correct for incompleteness in basis set size and accounting for electron correlation by additive means.

D

(5) This single level of theory scales less favorably than MP3 but more favorably than MP5.

E

A: MP3	B: spin contamination	C: nondynamical correlation
D: G2	E: CCSD(T)	F: MP2
G: CISD	H: ROHF	I: hyperconjugation