

**CHEMISTRY 4021/8021
MIDTERM EXAM KEY — SPRING 2009**

1. Molecular Mechanics Functional Forms (50 points)

The first paper that we read in class, by Nicholas et al., described the development of a force field for zeolites composed exclusively of Si and O atoms. You ambitiously decide to extend this force field to faujasite, which is composed of Si, O, and Al. Discuss what new parameters you will need to include in your force field definition and how you might go about determining optimal values. You need not define a full potential energy function (although you are welcome to do so if you want to) but you should be reasonably specific about the nature of the parameters.

Any generic force field will likely have bond stretching, angle bending, torsional, and electrostatic and non-electrostatic non-bonded interaction terms. The new Al atom will be able to make up to 3 new kinds of bonds (Al-X, where X is Si, O, or Al, although Al-Al bonds don't actually occur in faujasite), roughly 15 new kinds of angles (a complete list is not necessary—again, knowledge of faujasite structure might narrow this down, but credit on this problem does not depend on that), some 39 or so new torsions, and 3 each new non-bonded and electrostatic pairwise interactions. For bond stretches and angle bends, if the force field is harmonic, at least a force constant and an equilibrium value will be needed for each new combination. For torsions, amplitudes and phase angles will be needed for each Fourier term. Non-bonded and electrostatic interactions will require either pairwise terms or individual terms if combining rules are used (thus, e.g., σ and ϵ for a Lennard-Jones potential and a partial charge q if electrostatics derive from q - q interactions).

Optimal parameters will derive either from fitting to experiment using a necessarily arbitrary penalty function for data (that will need to be chosen), or from fitting to high-level (i.e., trustworthy) theoretical data if experimental data are not available. Relaxing the prior parameters at the same time as the new ones are optimized may deliver a more robust model but one might choose not to do this for practical reasons.

Other answers are certainly possible if one envisions force field functions for particular terms different from those that I have chosen above.

2. Semiempirical Foundations (50 points)

What motivates the development and application of semiempirical Hartree-Fock theories (like, say, the AM1 method)? That is, why might one choose to make approximations relative to ab initio HF theory, which is mathematically consistent and well described? To answer this question, you don't necessarily need to be detailed about the specifics of all of the approximations in any one or more semiempirical theories (although you may do so if it illuminates your answer)—the question is more “why?” than it is “what?” A discussion of advantages and disadvantages is likely appropriate.

Hartree-Fock theory is an approximation to the Schrödinger equation that fails to account for electron correlation, so even an exact (i.e., with an infinite basis set) solution at the ab initio level will not include the electron correlation energy and thus agreement with experiment may be quite poor. One motivation for introducing semiempirical approximations, then, may be to introduce electron correlation by using parameters fitted to experimental data. The parameterization may range from quite general (e.g., designed to be applicable to the whole periodic table) to very specific (e.g., designed exclusively to study Diels-Alder reactions involving cyclopentadiene moieties). INDO/S is a good example of a very general parameterization, but one that is designed only to give good energies for electronic excited states.

Semiempirical approximations are primarily motivated by a desire to increase computational efficiency. Thus, for example, various integrals whose evaluation is costly (either because they are intrinsically difficult or because there are a very large number) may be approximated by simpler functions or look-up values. As one can always imagine wanting to study a molecule larger than is currently accessible with ab initio HF theory, or very large datasets of different molecules, this extends the range of systems that may be studied by this quantum mechanical technique. (Other simplifications that could be mentioned include using effective nuclear charges that account for the core electrons, use of a minimal basis set for overlap integrals, etc.)

The above advantages are balanced by the disadvantages of potentially poor generality (e.g., in application to molecules quite different from those used in parameterization), limited opportunities for systematic improvement (you get what you get), and the observed poor performance of semiempirical HF models for non-bonded interactions.

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3. Ab Initio HF Theory and Post-HF Models

Select by letter from the list at the bottom of the page the proper answer to the following questions (the same list appears on both pages for your convenience). There is only one best answer to each question. (5 points each)

- (1) The constituents from which a contracted gaussian atomic basis function is constructed.

D

- (2) A one-electron integral that might appear in a Fock matrix element for a calculation on the water molecule.

M

- (3) A two-electron integral that might appear in a Fock matrix element for a calculation on the water molecule.

E

- (4) An exact solution to the one-electron Schrödinger equation for an atom.

G

- (5) To what the roots of the secular equation correspond.

N

A: G3B3

B: CCSD(T)

C: $\langle \Psi_i^a | H | \Psi \rangle$

D: Primitive gaussian type orbitals

E: $\langle 1s_O 1s_O | 2p_{xO} 1s_{H_b} \rangle$

F: Expectation values of the $\langle S^2 \rangle$ operator

G: Slater-type orbitals

H: spin polarization

I: $2\alpha_O + 2\sqrt{2}\beta_H$

J: MP3

K: spin contamination

L: nondynamical correlation

M: $8 \int \frac{1s_{H_a}(\mathbf{r}) 2s_O(\mathbf{r})}{|\mathbf{r} - \mathbf{r}_O|} d\mathbf{r}$

N: Molecular orbital energies

O: MP2

P: CISDT

Q: ROHF

R: hyperconjugation

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- (6) A correlated level of theory that expresses the complete wavefunction as a linear combination of configuration state functions but fails to be size-consistent for more than three electrons.

P

- (7) A single level of theory scales less favorably than MP3, more favorably than MP5, and has been referred to as the ab initio “gold standard” for single level calculations.

B

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

O

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

K

- (10) A multilevel model that attempts to correct for incompleteness in basis set size and accounting for electron correlation by additive means.

A

A: G3B3

B: CCSD(T)

C: $\langle \Psi_i^a | H | \Psi \rangle$

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