

CHEMISTRY 4021/8021
MIDTERM EXAM KEY – SPRING 2007

1. Molecular Mechanics (50 points)

You are constructing a new molecular mechanics force field for molecules used in the preparation of Group 13/Group 15 semiconductors. You currently have a fully parameterized force field for H, B, and N, and you are now ready to add the atom Ga to the list that your force field can handle. 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.

A generic force field is likely to have bond stretch, angle bend, torsion, electrostatic, and non-bonded interaction terms. The new Ga atom will be able to make 4 new kinds of bonds (Ga-X, where X is H, B, N, or Ga), roughly 16 new kinds of angles (a complete list is not necessary), some 64 or so new torsions, and 4 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 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 vs. ab Initio Hartree-Fock Theory (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?”

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).

Semiempirical approximations may also be used to increase efficiency. Thus, for example, certain 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, 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.)

3. The Basis Set Concept

a) Select by letter from the list at the bottom of the page the proper answer to the following questions. There is only one best answer to each question. Each line below specifies an item that is constructed as a linear combination of other items (which last define the basis). Choose the letter for the basis set that is used in the construction. (10 points each)

(1) A configuration interaction (CI) wave function.

C

(2) A Hartree-Fock (HF) molecular orbital (MO).

H

(3) A multiconfiguration self-consistent field (MCSCF) wave function.

A

(4) A G3 heat of formation.

E

(5) A contracted gaussian atomic orbital basis function.

D

A: A collection of determinants differing in their occupation of orbitals that, in most cases, were optimized at the same time as the coefficients in the linear combination

B: Molecular orbital energies computed after extrapolation to an infinite basis set

C: The HF determinant and all other determinants that can be generated by alternative occupations of the HF molecular orbitals

D: Primitive gaussian type orbitals

E: Energy components computed at various levels of theory designed to maximize physicality and efficiency

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

G: Slater-type orbitals

H: Atomic orbital basis functions

I: Electron repulsion integrals $\langle \mu\nu | \lambda\sigma \rangle$