

Name: _____

**CHEMISTRY 4021/8021
MIDTERM EXAM — 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.

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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?”

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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.
- (2) A Hartree-Fock (HF) molecular orbital (MO).
- (3) A multiconfiguration self-consistent field (MCSCF) wave function.
- (4) A G3 heat of formation.
- (5) A contracted gaussian atomic orbital basis function.

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 $\langle \mu\nu | \lambda\sigma \rangle$

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