

Name: _____

**CHEMISTRY 4021/8021
MIDTERM EXAM – 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.

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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.

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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.
- (2) A one-electron integral that might appear in a Fock matrix element for a calculation on the water molecule.
- (3) A two-electron integral that might appear in a Fock matrix element for a calculation on the water molecule.
- (4) An exact solution to the one-electron Schrödinger equation for an atom.
- (5) To what the roots of the secular equation correspond.

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.
- (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.
- (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 .
- (9) A potential problem with unrestricted Hartree-Fock wave functions that is *not* a problem for restricted open-shell Hartree-Fock wave functions.
- (10) A multilevel model that attempts to correct for incompleteness in basis set size and accounting for electron correlation by additive means.

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: CISD	Q: ROHF	R: hyperconjugation

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