CHEMISTRY 4021/8021
MIDTERM EXAM — SPRING 2010

1. Molecular Mechanics (50 points)

You are constructing a new molecular mechanics force field for molecules used in the preparation of the Group 13/Group 15 semiconductor indium phosphide; such precursor molecules are composed of H, C, In, and P. Discuss what 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 various parameters.

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2. Two-electron Integrals in Semiempirical and ab Initio Hartree-Fock Theory (50 points)

a. How would the generic two-electron integral ($\mu\nu \mid \lambda\sigma$) be written in standard calculus notation? Define all symbols and variables.

b. What is the physical meaning (in "plain" English) of the two-electron integral ($\mu\mu \mid \lambda\lambda$)?

c. In the complete neglect of differential overlap (CNDO) approximation, one takes ($\mu\nu \mid \lambda\sigma$) = $\delta_{\mu\nu}\delta_{\lambda\sigma}$($\mu\mu \mid \lambda\lambda$). Explain the effect of this approximation in a practical sense. How is the value of ($\mu\mu \mid \lambda\lambda$) itself computed? (A general explanation as opposed to a specific formula or formulas is fine for the last part of the question.)

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d. Various semiempirical levels of theory adopt less severe approximations than CNDO for the two-electron integrals. Discuss any one such difference.

e. What is the motivation for semiempirical levels of theory to adopt approximations for the computation of two-electron integrals?

f. Ignoring symmetry, how many two electron integrals must be evaluated in a calculation of the energy for a fixed geometry of CH_3OH at the HF/3-21G level? (Showing intermediate steps in arriving at a final answer may avoid loss of credit for any simple arithmetic error.)

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3. Ab Initio Wave Function Theory and Molecular Properties

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

(1) The post-HF model with the most favorable scaling, namely, N^5, where N is the number of basis functions.

(2) The single-reference post-HF "gold standard" that scales as N^7, where N is the number of basis functions.

(3) A model is said to have this property if the energy computed for five infinitely separated molecules is equal to five times the energy computed for a single molecule.

(4) To compute the statistical mechanical partition function, these are required.

(5) Something to which correlated methods are more sensitive than the HF model.

(6) Computation of the mixed second derivative of the energy with respect to an external magnetic field **B** and a nuclear spin **I** predicts this.

(7) A useful chemical idea that does *not* have a uniquely defined quantum mechanical operator, so that many different models exist for its prediction.

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(8) A model that permits no spin polarization of doubly-occupied orbitals but guarantees wave functions that are eigenfunctions of S^2.

(9) The proper value of S^2 for a singlet state.

(10) The number of imaginary frequencies associated with a transition-state structure.

A: 1   **B:** UHF   **C:** ROHF

D: Partial atomic charge   **E:** An optimized geometry with associated vibrational frequencies   **F:** 0

G: MP2   **H:** Nuclear chemical shift   **I:** Hyperfine coupling constant

J: Basis-set incompleteness **K:** 2   **L:** CISD

M: Size extensivity   **N:** MNDO   **O:** CCSD(T)

P: $\pi/2$ **Q:** Electric dipole moment   **R:** Spin contamination

S: Acid reflux   **T:** Slater-type orbitals   **U:** MP4SDQ

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