Uva Wellassa University, Sri Lanka
End Semester Examination – April 2011
SCT 333 – 2 Computational Chemistry (Repeat)

Time: Two (02) hours

Total **five (05)** questions
Answer **all** questions
All symbols carry standard meanings

01. a. State the Hamiltonian operator of CH_4 molecule within the Born-Oppenheimer approximation? Express the operators in atomic units.

(20 marks)

b. Write down the Slater determinant for the wave function of electrons in C atom (Z = 6).

(20 marks)

c. "The energy of a molecule calculated by HF theory is always higher than the true energy" Why (explain in one sentence).

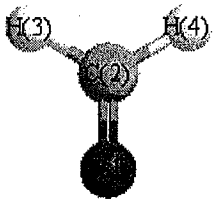
(20 marks)

d. Write short notes on following:

i. CISD
ii. NDDO
iii. ZDO
iv. RHF

(20 marks)

e. State the Z-matrix of the following molecule (given: bond lengths / angle C(2) H(4) = C(2)H(3) = 1.11 3 Å; C(2) O(1) = 1.208 Å; H(3)C(2)H(4) = 118°)



(20 marks)

02. a. Define the following:

i. Basis function

ii. Primitive Gaussian

iii. Basis set

(25 marks)

Suppose you are performing electronic structure calculations on the ethanol molecule.

b. Describe a minimal basis set for ethanol, including the total number of atomic orbitals.

(25 marks)

c. Describe the 6-31G basis set for ethanol, including the total number of atomic orbitals.

(25 marks)

d. Describe the 6-311G** basis set for ethanol, including the total number of atomic orbitals.

(25 marks)

03. a. State the approximations made in (i) Hartree method, (ii) Hartree – Fock (HF) Method. State a key difference between these methods.

(20 marks)

b. State HF equation for a single electron in a many electron system. Identify all operators therein (no derivations are required).

(20 marks)

c. How electron-electron correlation is taken into account in Hartree method and HF method.

(20 marks)

d. Introducing a basis set transform the HF equation into Roothann Hall equation (Show all work).

(40 marks)

04. a. In most molecular mechanics software packages, the bond lengths and other geometrical parameters of a molecule are determined by knowledge of the Cartesian coordinates of each atom. For example, the bond distance AB between two atoms A and B can be calculated from the equation

$$r_{AB} = \left[(x_A - x_B)^2 + (y_A - y_B)^2 + (z_A - z_B)^2\right]^{1/2}$$

where (x_A, y_A, z_A) are the Cartesian coordinates of atom A and (x_B, y_B, z_B) are the Cartesian coordinates of atom B. Consider a water molecule with atoms having the following Cartesian coordinates (in Å):

Atom	x	y	z
O	0.00	0.00	0.00
H_1	0.00	−0.65	0.60
H_2	0.00	0.65	0.60

k_{OH} = 700 kcal mol^{-1} Å^{-2}, $r_{OH,equil}$ = 0.93 Å, k_{HOH} = 100 kcal mol^{-1} radian^{-2}, $\theta_{HOH,equil}$ = 104.5°

i. What is the stretching energy of water at this geometry?

ii. What is the bending energy of at this geometry?

iii. What is the total energy of the system?

(50 marks)

b. Sketch a plot of the force field for rotation of ethane about its C-C axis. Sketch the energy of ethane as the torsional angle varies from 0° to 360°.

i. What is a simple functional form that would have the same qualitative shape as your plot in part a? If the maxima in the torsional potential of ethane occur at 0.3 kcal/mol and the minima occur at 0.0kcal/mol, construct a specific potential function to reproduce the ethane torsional potential.

ii. Explain how <u>your plot</u> from question 4(a) would change if the molecule was instead 1,2-dichloroethane.

(50 marks)

05. a. Define a force field in a molecular mechanics calculation. List two types of commonly used force fields in modern computer codes.

(20 marks)

b. Indicate whether it would be appropriate to carry out a molecular mechanics calculation using a typical force field (such as MMFF) to determine the minimized energy for the molecular systems listed below.

i. porphyrin ii. $Fe(CO)_4$

iii. a small protein molecule iv. $(H_2O)_2$

(20 marks)

c. In most force fields, the interaction between two non-bonded atoms is described using a function called the Lennard-Jones 6-12 potential. It has the form

$$E_{nb} = -\frac{A}{r^6} + \frac{B}{r^{12}}$$

Where; A and B are constants which depend on the two interacting atoms and r is the distance between them. For example, for two carbon atoms interacting, A = 745 and B = 2524840 (these parameters yield energy in kcal/mol if the distance is expressed in angstroms).

(20 marks)

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d. Sketch the non-bonded energy as a function of distance for the case of two carbon atoms. At approximately what distance does the minimum energy occur for this particular non-bonded interaction?

(20 marks)

e. Which of the two terms in the expression for the non-bonded energy is responsible for the attractive part of the interaction? Which term is responsible for the repulsive part of the interaction?

(20 marks)