Uva Wellassa University, Sri Lanka
End Semester Examination – September 2011
SCT 333-2 Computational Chemistry

Time: Two (02) hours

Total four (04) questions.
Answer **all** questions.
Use of standalone scientific calculators is allowed.
All symbols carry standard meanings.
Use of standard symbols without a definition is allowed

Question 1

(a). (10 Marks) Define a force field in a molecular mechanics calculation. List two types of commonly used force fields in modern computer codes.

(b). (10 marks) 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). $Fe(CO)_4$

(c). (40 marks) Sketch a plot of the force field for rotation of ethane about its C-C axis. Sketch the energy of ethane as the torsion angle varies from 0° to 360°. What is a simple functional form that would have the same qualitative shape as your plot?

(d). (40 marks) 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°. What is the total energy of the system?

Question 2

(a). (50 marks) Define following terms and describe their role in molecular mechanics

Newton-Raphson's method

Steepest Descent method

(b). (50 marks) A molecular mechanics force field for a bond and a bond angle is defined as $E = k_s x^2 + k_b y^2 - k_{sb} xy$. where x is the bond displacement, $x = r - r_{eq}$, and y is the bond angle displacement, $y = \theta - \theta_{eq}$. The force field parameters are given by k_s = 500 kcal mol^{-1} Å^{-2} r_{eq} = 1.25 Å k_b = 250 kcal mol^{-1} radian^{-2} θ_{eq} = 1.53 radians k_{sb} = 100 kcal mol^{-1} Å^{-1} radian^{-1}. The initial geometry is specified by x_{init} = 0.70 Å and y_{init} = 0.30 radians. Consider the y coordinate to be fixed at its initial value; that is, consider variation in the x coordinate only. Using one step of the Newton-Raphson energy minimization technique, determine the next value of the x coordinate.

Question 3

(a). (10 marks) What is the Hamiltonian operator for the CH_4 molecule within the Born-Oppenheimer approximation? Express the operators in atomic units.

(b). (05 marks) Write down the Slater determinant for the wave function of electrons in C atom (Z = 6).

(c). (05 marks) "The energy of a molecule calculated by HF theory is always higher than the true energy" Why (explain in one sentence)?

(d.) (20 marks) State the approximations made in Hartree – Fock (HF) Method. State HF equation for a single electron in a many electron system. Identify all operators therein (no derivations are required).

(e). (60 marks) Introducing a basis set transform the HF equation into Roothann - Hall equation (Show all work).

Question 4

(a) (25 marks) Define the following:

(i) Basis function (ii) Primitive Gaussian (iii) Basis set

(iv) Cusps behavior

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

(b) (25 marks) Describe a minimal basis set for ethanol, including the total number of atomic orbitals.

(c) (25 marks) Describe the 6-31G basis set for ethanol, including the total number of atomic orbitals.

(d) (25 marks) Describe the 6-311G** basis set for ethanol, including the total number of atomic orbitals.

46