

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 $k_s = 500 \text{ kcal mol}^{-1} \text{ \AA}^{-2}$, $r_{eq} = 1.25 \text{ \AA}$, $k_b = 250 \text{ kcal mol}^{-1} \text{ radian}^{-2}$, $\theta_{eq} = 1.53 \text{ radians}$, $k_{sb} = 100 \text{ kcal mol}^{-1} \text{ \AA}^{-1} \text{ radian}^{-1}$. The initial geometry is specified by $x_{init} = 0.70 \text{ \AA}$ and $y_{init} = 0.30 \text{ radians}$. 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 Roothaan - 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.

