[This question paper contains 8 printed pages]

Your Roll No. : .....

Sl. No. of Q. Paper : **5620 I**

Unique Paper Code : 2173012018

Name of the Paper : DSE : Computational Methods & Molecular Modelling

Name of the Course : **B.Sc.(Hons.) Chemistry**

Semester : VI

Time : 3 Hours ***Maximum Marks : 90***

Instructions for Candidates :

(a) Write your Roll No. on the top immediately on receipt of this question paper.

(b) Attempt **six** questions in **all.**

(c) **All** questions carry equal marks.

1. (a) (i) How are molecular mechanics and quantum mechanical methods complementary ? 2

(ii) What is the significance of the Born - Oppenheimer approximation in ab initio calculations ? 2

P.T.O.

(iii) Which method is best for modeling time-dependent behaviour of molecules ? 1

(A) Hartree-Fock

(B) Molecular Dynamics

(C) Monte Carlo

(D) PM3

(b) Explain why introducing a vacuum around a simulation box is not suitable for modeling bulk system. How do periodic boundary conditions help in addressing this issue ? 5

(c) How are force fields parameterized in molecular mechanics ? Explain. 5

2. (a) (i) Describe the role of Slater determinants in ab initio quantum chemistry. 2

(ii) Why are semi-empirical methods faster than ab initio methods ? 2

(iii) Specify a commonly DFT functional for calculating molecular geometries. 1

(b) Explain the basic idea of the Zero Differential Overlap (ZDO) approximation and discuss its role in reducing the computational cost in semi-empirical methods. 5

(c) What computational methods are used to determine electronic properties of molecules in excited states and how do they differ from those used for ground states ? 5

3. (a) (i) What do you understand by the term reaction coordinate ? 2

(ii) Which of the following method/s is/are used for identifying stationary points in PES ? 2

(A) Multigrid variant method

(B) Hartree Fock method

(C) Steepest descent method

(D) Hessian Matrix method

(i) A and B

(ii) C and D

(iii) A, B, and C

(iv) A, C and D

(iii) In computational modeling, steepest descent method is used for/as 1

(b) Using Hückel MO theory, compute the resonance energies and compare the stability of propenyl anion and radical. The π molecular orbitals are given as : 5

$$\Psi_1 = 1/2\varphi_1 + \left(\sqrt{2}\right)/2\varphi_2 + 1/2\varphi_3$$

$$\Psi_2 = 1/\sqrt{2}\varphi_1 - 1/\sqrt{2}\varphi_3$$

$$\Psi_3 = 1/2\varphi_1 - \left(\sqrt{2}\right)/2\varphi_2 + 1/2\varphi_3$$

(c) What are the Bonded and Non bonded energy terms represent in a molecular mechanics force field ? 5

4. (a) (i) What physical quantity is used in DFT instead of wave functions to describe a system ? 2

(ii) Differentiate between Restricted (RHF) and Unrestricted Hartree-Fock methods (UHF) ? 2

(iii) Which method is most commonly used in computational chemistry to compute frontier molecular orbital energies from the following methods given below : 1

(A) Molecular mechanics

(B) Monte Carlo simulation

(C) Density Functional Theory (DFT)

(D) Thermo gravimetric analysis

(b) What is the Basis function ? Discuss how the choice of Basis functions affects the accuracy and cost of a quantum chemical calculation. 5

(c) Plot the following stationary points in a potential energy diagram :

(i) Molecule AB has energy –17.2 kcal mol^{-1}.

(ii) Molecule A—B has energy 4.9 kcal mol^{-1}.

(iii) Molecule BA has energy –9.8 kcal mol^{-1}.

How can you differentiate between AB and A—B in terms of vibrational frequencies ? Apart from the stability, what information does values of vibrational frequency give ? 5

5. (a) (i) What does a computed vibrational frequency close to 0 cm^{-1} usually indicate about the nature of the potential energy surface ? 2

(ii) In an SCF calculation, what happens if convergence is not reached and how can this impact the outcome of the simulation ? 2

(iii) The HOMO-gap is an indicator of ..... energy. 1

(b) Given the function $f(x,y) = x^2 - 2y^2 - 4y + 6$ determine the determinant of the Hessian matrix at the point (0, 0). 5

(c) Write appropriate diagrams, distinguish between : 5

(i) Global Minimum

(ii) Local Minimum

(iii) Saddle Point

6. (a) (i) How does the Hartree-Fock method approximate the solution to the Schrödinger equation ? 2

(ii) What is meant by electron correlation in quantum chemistry ? 2

(iii) The Hessian matrix provides information about which of the following : 1

(a) Spin information

(b) First derivatives of energy

(c) Second derivatives of energy

(d) Transition states

(b) Among the following methods, suggest the most efficient one for simulating a macromolecule of ~50 atoms, giving reasons : 5

(i) Semi-empirical

(ii) Ab initio

(iii) Molecular Mechanics

(c) Compare and contrast Slater-Type Orbitals (STOs) and Gaussian-Type Orbitals (GTOs). 5

7. (a) (i) What is a "hilltop" on a potential energy surface ? Explain with a sketch. 2

(ii) Expand the following acronyms : 2

(A) MMFF

(B) SCF

(iii) The expression : Number of Cartesian coordinates – Number of internal coordinates = ? refers to what molecular quantity ? 1

(b) The methods that are generally used for the optimization of molecular geometries are the 'Steepest Descent' and 'Newton – Raphson' method. Briefly outline the advantages and disadvantages of these two techniques. 5

(c) Define Intrinsic Reaction Coordinates (IRC). How does it help map the reaction path between reactants and products ? 5

8. (a) (i) What is the Hessian matrix and how is it useful in computational chemistry ? 2

(ii) How are vibrational frequencies calculated from quantum mechanical methods ? 2

(iii) As per Density Functional Theory, energy is a functional of 1

(b) Write a brief note on the Self-Consistent Field (SCF) method and its significance in electronic structure calculations. 5

(c) Though AM1 and PM3 methods yield reasonable geometries, they often fail for hydrogen-bonded systems. Explain why. 5

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