[This question paper contains 4 printed pages.]

Your Roll No.....

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Sr. No. of Question Paper : 7859

Unique Paper Code : 2173540021

Name of the Paper : DSE: Computational Chemistry

Name of the Course : **B.Sc. (Prog.) with Chemistry Major**

Semester : VIII

Duration : 2 Hours

Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. at an appropriate place on receipt of this question paper.
2. Question number 1 is compulsory.
3. Attempt FOUR questions in all.
4. All questions carry equal marks.

1. Attempt **any five** (3 marks each) (5 x 3 = 15)

   a. State the Born-Oppenheimer approximation. Give any two points to justify why this approximation is the cornerstone of computational chemistry.

   b. Construct the Z-matrix of C_2H_2 using appropriate labels.

   c. What is geometry optimization? Should calculations from first principles (*ab – initio*) be always preferred over semi-empirical calculations which make use of experimental data? Why/Why not?

   d. Formulate the Hamiltonian for a hydrogen atom, and explain the terms involved. Which term in the Schrödinger equation makes it difficult to solve for multi-electron systems?

   e. What are basis sets? An *ab-initio* calculation on C_2H_4 involves a total of 14 basis functions, while a semi-empirical calculation on it involves only 12 basis functions. Justify.

P.T.O.

f. Out of the force-field methods AMBER, CHARMM, MM3, OPLS, choose which one is the most accurate way of modeling :
(i) Hydrocarbons (ii) Bulk Liquids (iii) Proteins and Nucleic Acids

g. Write the Lennard-Jones potential energy function used to represent non-bonded interactions between two atoms in a molecular mechanics force-field. Also draw the relevant plot.

2. a. De-abbreviate the following terms. (5)

i. UFF

ii. HOMO

iii. PM3

iv. GTO

v. CNDO

b. Write the expression for a typical "molecular mechanics" potential energy function. Predict the number of bond-stretching, angle bending, torsional and non-bonded interaction terms for the propane molecule in a typical force-field. Explain the origin of the bond-stretching and angle bending terms. (5)

c. What is a *Hessian*? How can you characterize a stationary point as a minimum, a maximum or a saddle point from the eigenvalues of a Hessian? (5)

3. a. Match the quantum-mechanical methods in **Column A** to their approach in **Column B** to make correct complete/meaningful pairs. Write the complete pair in your answer book. (5)

Column A	**Column B**
i) HF	a) Electron-density based rather than wavefunction
ii) MP2	b) Linear combination of electron promotion configurations
iii) DFT	c) Mean-field (average-field) approximation method
iv) CI	d) Highly accurate correlation method
v) CC	e) Post Hartree-Fock method including perturbation correction

b. With the help of a potential energy diagram of *n*-butane (potential energy VS C-C-C-C torsional angle), explain the stability of various conformations of *n*-butane. (5)

c. Mention the underlying principle of DFT. What makes DFT calculations computationally less expensive than wavefunction-based *ab initio* methods? State the strengths and limitations of DFT. (5)

4. a. In MD simulation, how does the Leap-Frog algorithm work? List its two advantages and disadvantages. (5)

b. Define the term "parametrization" in Semi-Empirical methods. Explain any one semi-empirical method in detail. (5)

c. Distinguish between Slater-type and Gaussian-type orbitals. (5)

5. a. What is a Potential Energy Surface? How many dimensions are needed to depict the potential energy diagram of H_2, H_2O and HOF? What is a hypersurface? (5)

b. State the Ergodic hypothesis. Discuss the four main types of ensembles in a molecular dynamics simulation. (5)

c. How are semi-empirical methods different from molecular mechanics methods? Support your answer with examples of systems where they are best used. (5)

6. Write short notes on **any three** of the following 3 x 5

a. Diffuse functions vs Polarised functions

b. Basis Set Superposition Error

c. Effective Core Potential

d. Terms *forcefield*, *atom-type* and *transferability* in a molecular mechanics calculation

e. Periodic Box in an MD simulation

f. Computational chemistry softwares and the parameters that can be investigated using them.

(300)