[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 7182 **L**

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. on the top immediately 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. A molecule's geometry can be described in terms of both Cartesian coordinates and Internal Coordinates. Using the example of a water molecule, explain the difference between these coordinate systems.

   b. Construct the Z-matrix of nitrous acid (HNO_2) using appropriate labels.

   c. Why are nuclear coordinates, and not electronic coordinates the parameters that define molecular geometry? State and explain the approximation which forms the basis for this.

   d. Formulate the Hamiltonian for H_2^+ molecule ion, and explain the terms involved.

   e. The choice of the best computational chemistry method that can be employed to solve a particular system is a compromise between_____ and _____

   Arrange the computational chemistry methods (Molecular Mechanics, *Ab-initio*, DFT, and Semi-Empirical) in
   (i)Increasing order of accuracy (ii) Decreasing order of computational time

   f. Can you exactly solve the Schrödinger equation for the H_2 molecule? Why/why not?

P.T.O.

g. Justify the following statement with an appropriate explanation:
"Computational chemistry offers several advantages over *wet chemistry*; however, it cannot completely replace it."

2. a. De-abbreviate the following terms. (5)
   i. MP2
   ii. INDO
   iii. AMBER
   iv. DFT
   v. OPLS

   b. What is a potential energy surface? Using the ozone-isoozone PES, explain the following terms (5)
   i. Global minimum
   ii. Local minimum
   iii. Intrinsic reaction coordinate
   iv. Saddle point/Transition state

   c. Define the term "*forcefield*". Describe briefly the terms of a typical molecular mechanics force field. Write the expression for energy and state clearly what each term represents. (5)

3. a. Match the statements in **Column A** to those in **Column B** to make correct complete statements. Write the complete correct statement in your answer book. (10)

Column A	Column B
i) The second-derivative of energy with respect to geometric parameters (d^2E/dq^2)	a) Includes a correction term (a perturbational adjustment) by allowing electrons to avoid each other
ii) A minimum on a PES	b) Determines the reactivity of a system
iii) A first-order saddle point on a PES	c) Promotion of electrons from occupied to virtual MOs improves energy by treating electron correlation properly
iv) Hartree-Fock (HF) method	d) Overestimates binding energy by imposing B's basis set on A and A's basis set on B while optimizing molecule AB
v) HOMO-LUMO gap	e) Used to treat expanded electron clouds found in anionic systems, or molecules containing heteroatoms

vi) MP2 energy	f) Does not treat electron correlation properly
vii) Configuration interaction (CI)	g) All vibrational frequencies are real
viii) BSSE	h) Replace core electrons with an effective potential to solve transition-metal based systems easily
ix) Diffuse functions (+)	i) All vibrational frequencies except the one along the IRC are real.
x) Effective Core Potential	j) Force-constant matrix Hessian

b. Differentiate between Slater-type and Gaussian-type orbitals. (5)

4. a. For Semi-Empirical methods, answer the following questions briefly in one-two lines each: (5)

   i. Define parametrization.

   ii. Why these methods are called "*semi-empirical*"?

   iii. Are semi-empirical (SE) methods based on quantum mechanics or classical mechanics?

   iv. Discuss two salient features of the CNDO method.

   b. With the help of a potential energy diagram of ethane (potential energy Vs H-C-C-H torsional angle), explain the stability of various conformations of ethane. (5)

   c. Mention which computational method is the most accurate way of modeling (5)
   i. Proteins and nucleic acids
   ii. Organic compounds containing 5-10 carbon atoms
   iii. Nucleophilic behaviour of molecules
   iv. Dynamic motion of NaCl crystal when dissolved in water
   v. Computationally efficient yet accurate optimization of an organic compound containing 15 carbon atoms

5. a. Distinguish between (5)
   i. *Ab-initio* vs DFT method/calculations.
   ii. CHARMM vs MM1 methods (*on the basis of which system they are best designed for*)

   b. What are the main types of "*ensembles*" in a molecular dynamics calculation? State the Ergodic hypothesis. (5)

   c. In a force-field, what do you understand by the terms "transferability" and "atom-type"? Why does parameterizing a force field for transition state present special problems? (5)

P.T.O.

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

   a. Diffuse functions (+) and Polarization functions (*)

   b. Leap-Frog and Verlet Algorithm

   c. Molecular Dynamics Vs Molecular Mechanics

   d. Lennard-Jones Potential Energy function in MM

   e. Basis sets, minimal valence basis set STO-3G

   f. Periodic Box in a MD simulation