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Name of the Paper : DSE: COMPUTATIONAL METHODS &
   MOLECULAR MODELLING
Name of the Course : B.Sc. (Hons.) Chemistry
Semester : 4/6
Duration : 3 hrs
Maximum Marks : 90

Answer six questions in all. All questions carry equal marks.

1. a. **(i)** What is the main assumption behind molecular mechanics?
   (ii) Name two ensembles commonly used in molecular dynamics.
   (iii) Which method would you choose to study the folding of a protein? **(2,2,1)**

 b. Describe the Zero Differential Overlap (ZDO) approximation used in many semi-empirical methods. **(5)**

 c. Write down a typical molecular mechanics potential energy function used in macromolecular simulations, and explain each term involved. **(5)**

2. a. **(i)** Name any two commonly used semi-empirical methods.
   (ii) Why is the choice of functional critical in DFT calculations?
   (iii) In ab initio methods, which of the following is true?
   a) They rely heavily on experimental data.
   b) They are fully based on first principles without empirical parameters.
   c) They are only applicable to metals.
   d) They ignore electron correlation completely. **(2,2,1)**

 b. How do polarized basis sets differ from unpolarized basis sets, and why are polarized basis sets often preferred in molecular calculations? **(5)**

 c. Describe the Hartree-Fock (HF) method. What are the main approximations made in HF calculations? **(5)**

3. a. **(i)** Briefly explain the concept of "convergence" in an SCF calculation. Why is it important?

   (ii) Expand the following acronyms:
    a) AMBER
    b) PM3

   (iii) Which of the following is NOT an advantage of the SCF method?
    a) It provides a good approximation to the electronic structure of molecules.
    b) It can be used to calculate molecular properties like dipole moment and charge distribution.
    c) It is computationally expensive for large systems with heavy elements.
    d) It gives exact solutions for many-electron systems.
     (2,2,1)

 b. The occupied Hückel π molecular orbitals for C2 and C3 of 1,3- butadiene are:
   $\Psi_1 = 0.371\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.371\phi_4$
   $\Psi_2 = 0.602\phi_1 + 0.371\phi_2 - 0.371\phi_3 - 0.602\phi_4$

Determine the bond order between the C2 and C3 carbon atoms, and evaluate the atomic charges on these two carbon atoms.

(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)

4. a. **(i)** What is the significance of the minimum energy points on a Potential Energy Surface (PES)?
(ii) Explain the difference between a relaxed PES and a rigid PES.
(iii) In the Hartree-Fock method, the total electronic wavefunction is expressed as a
_____ .   **(2,2,1)**

b. What is an Intrinsic Reaction Coordinate (IRC)? Explain its role in studying reaction mechanisms.   **(5)**

c. Although the simple Hückel method (SHM) predicts identical resonance energies for the cyclopropenyl cation, radical, and anion, actual resonance energies tend to decrease as more π electrons are added. What accounts for this discrepancy?

(5)

5. a. **(i)** What condition must the energy gradient satisfy at the optimized geometry?
(ii) Why are exchange-correlation functionals essential in DFT calculations?
(iii) The electron excitation from HOMO to LUMO in UV-Vis spectroscopy corresponds to:
a) Nuclear transition
b) $\pi \rightarrow \pi^*$ or n $\rightarrow \pi^*$ transitions
c) Vibrational transitions
d) Ionization   **(2,2,1)**

b. What are the advantages of using internal coordinates or z-matrix? Construct the z-matrix for an ethane molecule by using appropriate labels.   **(5)**

c. How can electrostatic potential maps assist in understanding the packing of molecules in crystalline solids?   **(5)**

6. a. **(i)** How would you choose an appropriate basis set for studying the geometry optimization of a highly charged ionic species?
(ii) When modeling the dipole moment of a molecular ion, why would it be necessary to include polarization functions in the basis set?
(iii) Monte Carlo simulations rely on _____ sampling techniques to explore configuration space.   **(2,2,1)**

b. Describe the construction of a Slater determinant for a two-electron system and explain how it maintains the antisymmetry of the wavefunction.   **(5)**

c. How can computational chemistry predict the heat of hydrogenation and its relevance to reaction optimization?   **(5)**

7. **a.**   **(i)** How can the activation energy of an isomerization reaction be computed using Density Functional Theory (DFT)?
    (ii) What is the relationship between atomic charges and electrostatic interactions in molecular systems?
    (iii) Semi-empirical methods are faster than ab initio methods because they:
    a) Use a smaller basis set
    b) Ignore all electron interactions
    c) Include approximations based on experimental data
    d) Only study isolated atoms   **(2,2,1)**

  b.   Using Hückel molecular orbital theory, calculate the π-electron charge localized on all the carbon atoms (φ_2) of the propenyl cation and anion.
    The π molecular orbitals are given as:
$$\Psi_1 = 1/2 \; \varphi_1 + (\sqrt{2})/2 \; \varphi_2 + 1/2 \; \varphi_3$$
$$\Psi_2 = 1/\sqrt{2} \; \varphi_1 - 1/\sqrt{2} \; \varphi_3$$
$$\Psi_3 = 1/2 \; \varphi_1 - (\sqrt{2})/2 \; \varphi_2 + 1/2 \; \varphi_3$$
                                                                     (5)

  c.   Discuss the challenges associated with the introduction of a simulation box in Molecular Dynamics simulations and explain how they are addressed.   **(5)**

8. **a.**   **(i)** How can computational methods be used to simulate UV-Vis spectra of organic molecules?
    (ii) Apply Hückel Molecular Orbital (HMO) theory to determine the molecular orbitals and their energies for the ethylene (C_2H_4) molecule, given that the β value for ethylene is -30 kJ/mol.
    (iii) A Hessian matrix is a square matrix of _____ of energy with respect to atomic positions.   **(2,2,1)**

  b.   Given the function $f(x,y)=3x^2+y^2+5y$ calculate the gradient of the function at the point (0,0).   **(5)**

  c.   Discuss the significance of vibrational analysis in computational chemistry, and explain how it aids in the characterization of molecular structures.   **(5)**