(d) Calculate the ionization potential (IP) & electron affinity (EA) of the central bond where MO energies of a molecule with 4 pi electrons is given as

$\alpha+1.5\beta$, $\alpha+0.5\beta$, $\alpha-0.5\beta$, $\alpha-1.5\beta$ where β = -25 kJ/mol (3,4,4,4)

[This question paper contains 8 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 261 **L**

Unique Paper Code : 2173012018

Name of the Paper : DSE: COMPUTATIONAL METHODS & MOLECULAR MODELLING

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

Semester : VI

Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all.
3. **All** questions carry equal marks.

1. (a) Molecular Mechanics (MM) is unable to describe bond breaking processes. Explain.

   (b) What is parametrizing the force field in molecular mechanics?

   (c) Geometry optimization is necessary before performing molecular dynamics or quantumchemical calculations. Explain.

   (d) Calculate the Hessian matrix at the point (1,0) of the following multivariable function :

   $f(x,y) = y^4+x^3+3x^2+4y^{2-}4xy-5y+8$ (3,4,4,4)

2. (a) What is the role of periodic boundary conditions (PBC) in simulations?

   (b) Explain the factors that determine the choice of time step in Molecular Dynamics and describe the problems associated with inappropriate time step selection.

7. (a) Explain the concept of Intrinsic Reaction Coordinate (IRC) and how it helps trace the reaction pathway.

   (b) Explain how Gaussian functions are used to approximate atomic orbitals in minimal basis sets. Give an example.

   (c) What is meant by the term 'correlation energy'? What methods can be used to calculate energies including correlation effects?

   (d) Discuss the importance of antisymmetry principle in quantum chemistry. (3,4,4,4)

8. (a) Vibrational frequencies are calculated to characterize Stationary points in PES, comment.

   (b) What are electrostatic potential maps? Give their significance.

   (c) How Zero Differential Overlap (ZDO) approximation in semi-empirical methods reduces the computational cost.

6. (a) Why is the Born-Oppenheimer approximation significant in ab initio methods?

(b) One of the functional forms to represent torsional angles in MM force field is the following :

$$\upsilon(\omega) = \sum_{n=0}^{N} \frac{V_n}{2} [1 + \cos(n\omega - \gamma)]$$

What does various symbols represent in this equation?

(c) What does a saddle point in a potential energy surface indicate? How will you differentiate between a minimum and a saddle point?

(d) What are the advantages of using internal coordinates or z-matrix? Construct a Z-matrix for formaldehyde. (3,4,4,4)

(c) What is the concept and purpose of core-electron replacement with (a)s

(d) For a system with potential energy $E = 3x^2 + y^2 + 5y$, compute the gradient and explain its significance in energy minimization. (3,4,4,4)

3. (a) Write the extended form of the following :

(i) MM4

(ii) OPLS

(iii) BIO+

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

$$\Psi_1 = 1/2\ \varphi_1 + (\sqrt{2})/2\ \varphi_2 + 1/2\ \varphi_3$$
$$\Psi_2 = 1/\sqrt{2}\ \varphi_1 - 1/\sqrt{2}\ \varphi_3$$
$$\Psi_3 = 1/2\ \varphi_1 - (\sqrt{2})/2\ \varphi_2 + 1/2\ \varphi_3$$

(c) Why is DFT extensively used in computational chemistry? Explain the concept and importance of electron density in DFT.

(d) Different computational techniques vary in accuracy and computational cost. Given the methods: MMF, AMI, HF/STO-3G, and B3LYP/6-31G*, which method would be most suitable for the following applications :

(i) Biomolecular systems,

(ii) Small organic molecules,

(iii) Large organic frameworks and

(iv) Reactivity studies involving electron donation. (3,4,4,4)

4. (a) How does Density Functional Theory (DFT) differ from Time-Dependent DFT (TD-DFT) in calculating electronic properties?

(b) Distinguish between Relaxed PES and Rigid PES.

(c) Why are thermostats and barostat essential for simulating real systems?

(d) Semi-empirical methods are faster than ab initio methods. Explain. (3,4,4,4)

5. (a) How do atomic charges influence electrostatic interactions between atoms in molecular systems?

(b) Expand and explain the following acronyms :

(i) MMFF

(ii) BSSE

(c) Discuss a first order derivative method to attain the energy minimization in molecules.

(d) The Hartree-Fock (HF) method is a specific type of Self-Consistent Field (SCF) method used in quantum chemistry. Explain. (3,4,4,4)