Reg. No ..... Name **21P2045**

M. Sc DEGREE END SEMESTER EXAMINATION - JULY 2021

SEMESTER 2 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE : **16P2CHET08 / 16P2CPHT08 : THEORETICAL AND COMPUTATIONAL CHEMISTRY**

(For Regular - 2020 Admission & Supplementary - 2019/2018/2017/2016 Admissions)

Time : Three Hours Max. Marks: 75

PART A

Answer any 10 (2 marks each)

1. Is the trial wave function $\Phi\left(x\right)=\left(\frac{x}{a}-\frac{x^3}{a^3}\right)+\alpha\left(\frac{x^5}{a^5}-\frac{1}{2}\left(\frac{x^7}{a^7}\right)\right),\ 0<x<a$ a suitable choice for the calculations using variation method, for a particle in 1-D box problem? Justify your answer.
2. Describe the physical significance of each of the terms that appears in the Fock operator.
3. If the normalised variation function $\Phi=\left(3/l^3\right)^{\frac{1}{2}}x$ for $0\leq x\leq l$ is applied to the particle-in-a-one-dimensional-box problem, one finds that the variational integral equals zero, which is less than the true ground-state energy. What is wrong?
4. What are the allowable spin functions for a two-electron system?
5. Write down the wavefunctions corresponding to singlet and triplet state of H_2 molecule.
6. Illustrate non-crossing rule with an example.
7. Determine the term symbols for He_2 and He_2^+.
8. What is meant by model chemistry? Explain with an example.
9. What are Kohn-Sham orbitals?
10. The total energy calculated for the same molecule by an HF and MP2 method are different when the same basis set is used. Give reasons.
11. Write the components of an input file.
12. What is the principle involved in molecular dynamics simulation.
13. What are the different interactions that are accounted for in the Molecular Mechanics force field?

(2 x 10 = 20)

PART B

Answer any 5 (5 marks each)

14. Explain the variation treatment for the ground state of helium atom.
15. Write a note on HFSCF theory.
16. What is the electronic energy predicted by the independent electron approximation for the Lithium atom in its ground state? What is the experimental value for the total electronic energy, given that the first and second ionization energies are 0.198 a.u. and 2.778 a.u?
17. Solve the secular determinant for butadiene to obtain the Molecular Orbital energies.
18. Prove that the simple molecular orbital theory over emphasizes ionic terms.
19. Prove that the three sp^2 hybrid orbitals are directed at angles of 120° with respect to one another.
20. Explain the different types of basis sets with examples for each.
21. Write a note on semi-empirical methods

(5 x 5 = 25)

PART C

Answer any 2 (15 marks each)

22. Explain first order perturbation theorem. Illustrate the application of perturbation theory to particle in a 1-D box with slanted bottom.

23. Write down and solve the secular determinant for the π system of ethylene and allyl radical in the Hückel model. Determine the coefficients for the $2p_z$ atomic orbitals on each of the carbon atoms and make a sketch of molecular orbitals.
24. Explain the basic principles of computational chemistry based on Density Functional Theory (DFT)
25. How do you obtain the IR spectrum of water molecule using computational chemistry calculation? Explain the principle, procedure and output of the calculation.

(15 x 2 = 30)