Reg. No ..... Name **18P245**

MSc DEGREE END SEMESTER EXAMINATION- APRIL 2018

SEMESTER 2 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

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

(For Regular - 2017 Admission)

Time : Three Hours Max. Marks: 75

Section A
Answer any 10 (2 marks each)

1. Given the following space part of an approximate wavefunction for Li^+ ion: $1/\sqrt{2}$ [1s(1)2p$_1$(2) + 2p$_1$(1)1s(2)], write a physically possible spin part for this wavefunction.
2. Show that the probability of having three electrons in 1s orbital is zero.
3. Describe the physical significance of each of the terms that appears in the Fock operator.
4. Determine the term symbol of the ground state of C_2.
5. Electrons in bonding molecular orbitals render stability to the bond. Why?
6. Explain the MO diagram of CO.
7. Derive the valence bond functions for the LiH molecule considering it to be 60% covalent and 40% ionic.
8. What are the criteria of a transition state?
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 Z matrix for water and HF molecules.
12. What do you mean by single point energy calculation? What do you expect the single point energy value for hydrogen atom in eV units.
13. What do you mean by trajectory in a molecular dynamics simulation?

(2 x 10 = 20)

Section B
Answer any 5 (5 marks each)

14. State and prove the variation theorem.
15. Explain Roothaan's concept of basis functions
16. What electronic energy is 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. Show that *sp* hybrid orbitals are equivalent and are directed 180° from each other.
18. Show that c_1 = c_2 in the ground state valence bond wave function of hydrogen molecule, given by

$$\psi_{VB} = c_1\psi_1 + c_2\psi_2.$$

19. A hybrid orbital has 25% *s*- and 75% *p*-character. Construct the wave functions for this set of hybrid orbitals.
20. Explain the relation between variation principle and SCF procedure

21. Write the Z matrix of methane. How pdb format of methane differ from Z matrix?

(5 x 5 = 25)

Section 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. Discuss the Molecular Orbital treatment of H_2^+ ion. Sketch the molecular orbitals formed and explain the bonding.
24. Distinguish between potential energy diagram and potential energy surface. Compare and contrast the potential energy diagrams of ethane and butane. Explain how the potential energy diagram of butane can be generated using Gaussian software.
25. Explain the principle and computational procedure using Gaussian/Gamess to obtain the potential energy diagram of keto-enol tautomerism in acetaldehyde

(15 x 2 = 30)