

M. Sc. CHEMISTRY EXAMINATION, 2017

(4th Semester)

PHYSICAL CHEMISTRY SPECIAL**PAPER - XIII-P**

Time : Two hours

Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - P - 4131Answer *any two* questions

1. a) Using Branching diagram, find the number of possible spin multiplets of a 7-electron system. $1\frac{1}{2}$
- b) Write the Slater determinantal form of the wave function of a 3-electron system and show that it satisfies Pauli anti-symmetry principle. 3
- c) Evaluate the expression of H_{ij} in terms of one and two electron integrals, when

$$D_i = |\varphi_1 \bar{\varphi}_1 \varphi_2 \varphi_3| \text{ and } D_j = |\varphi_1 \bar{\varphi}_1 \varphi_2 \varphi_4|. \quad 2$$
- d) What are the Slater-Condon rules ? If the wave function of a 3-electron system is represented by

$$\frac{1}{\sqrt{2}} (|\varphi_1 \bar{\varphi}_2 \varphi_3| - |\bar{\varphi}_1 \varphi_2 \varphi_3|), \text{ find out the energy expectation value using Slater-Condon rules. } \quad 6$$

OR

Elucidate the Hartree-Fock self-consistent field (HF-SCF) method to solve the Schrödinger equation for many electron atom. What is the physical significance of Fock operator ? Briefly describe the MCSCF method. Define correlation energy. $6\frac{1}{2}+1+3+2$

2. a) What is Koopman's theorem ? Using Hartree-Fock SCF orbitals, prove the theorem for a N-electron system. $6\frac{1}{2}$

OR

Write down the Kohn-Sham equations for the calculation of molecular structure with the meaning of the terms used. Elucidate the iterative procedure for solving Kohn-Sham equations in Density Functional Theory (DFT). $2+4\frac{1}{2}$

[2]

- b) Derive an expression of the transition dipole moment for a transition from the ground singlet to the lowest excited singlet state of H_2 . 3

OR

Derive the quantum mechanical Virial Theorem. 3

- c) Prove that the Configuration Interaction (CI) wave function corresponding to the lowest root of H_2 tends to the homopolar dissociation (ignore spin functions). 3

OR

State the basic principle of CI method in theoretical Chemistry. 3

3. a) What are the approximations used in Hückel Molecular Orbital (HMO) theory ? Using HMO theory, calculate the energy levels for cyclobutadiene and butadiene. $2\frac{1}{2}+2+2$
- b) Apply HMO theory to derive a general expression for the energy level and wave function of a cyclic conjugated polyene having N carbon atoms (N may be odd or even). 6

OR

For a heteronuclear diatomic molecule, calculate the energy levels by using linear variational theory and also find out the coefficient of linear combination. 6

UNIT - P - 4132

4. Answer **any three** questions :

a) Define surface excess. Derive,

$$d\gamma = -q_M dV - \frac{q_M}{Z_j F} d\mu_j - \sum_i \Gamma_i d\mu_i$$

for an electrolyte, where γ = surface tension & Γ_i = surface excess for i-th type of species at the interface and all other terms bear usual significance. 1+5

b) i) How does the contact adsorption influence the capacity of the interface ? Derive the necessary relation and explain.

ii) How is the extent of contact adsorption on the surface of an electrode determined from electrocapillary measurements ? 3+3

c) i) Show that the parallel plate condenser model can explain the electro-capillary curve which is perfect parabolic in nature.

ii) Give salient features of the Stern model of double layer and explain the total capacity at an electrode solution interface at high and low concentrations separately. 3+3

d) Show that the extent of adsorption of a neutral organic molecule at an electrode-aqueous solution interface is expected to pass through a maximum around PZC. Explain the significance of the fact that this maximum is observed at a potential slightly negative to PZC. 4+2

5. i) Derive an expression of the capacitance of an extrinsic semiconductor immersed in an electrolyte solution, as a function of potential.

ii) Show that the capacitance-potential profile is asymmetric for extrinsic semiconductor and symmetric for intrinsic semiconductor. $4\frac{1}{2}+2\frac{1}{2}$

OR

i) Distinguish between photovoltaic and photo synthetic solar cells by depicting energy diagrams.

ii) What are the advantages of using dye-sensitized over normal solar cells ? Explain the action of dye-sensitized solar cells with the help of schematic energy diagrams for both n- and p- type materials.

3+1+3