

[4]

- 5) i) Distinguish between photovoltaic and photo synthetic cells by showing schematic energy diagrams.
- (ii) Explain the reasons behind dye-sensitization of semiconductor photoelectrodes with the help of schematic energy diagrams for both n and p-type materials. 4+3

OR

- (i) Derive an expression for the capacitance of an intrinsic semiconductor immersed in an electrolyte solution, as a function of carrier density and potential.
- (ii) What is the effective thickness of space charge region within the semiconductor ? 5+2

Ex/M.Sc/CHEM/4/XIII/P-4131/2018(S)

M. Sc. CHEMISTRY EXAMINATION, 2018

(4th Semester, Special Supplementary)

PHYSICAL CHEMISTRY SPECIAL

PAPER - XIII-P

Time : Two hours

Full Marks : 50

(25 marks for each unit)

Use a separate answer script for each unit

UNIT - P- 4131

Answer *question no. 1* and any *one* from questions 2 and 3.

1. (a) Using Branching rule, find out the number of independent spin functions for a 6 electron system.

$1\frac{1}{2}$

- (b) Deduce the analytical form of the square of the total spin angular momentum operator (\hat{S}^2) for a n-electron system in which n_α and n_β are the numbers of α and β -spin electrons, respectively. 5

- (c) Write down the Slater-Condon rules. Derive an expression for the energy expectation value of the wave function

$$\Psi = \frac{1}{\sqrt{2}} (|\bar{\phi}_1\phi_2\phi_3| - |\phi_1\bar{\phi}_2\phi_3|)$$

using Slater-Condon rules

6

[Turn over

[2]

2. (a) What is Born-Oppenheimer approximation ? 2
- (b) Write down the steps involved in the Hartree-Fock Self-Consistent Field calculations for a molecule under Born-Oppenheimer approximation. 4
- (c) Construct the Configuration Interaction (CI) wave function formed by the ground and doubly excited states of H₂. Show that the CI wave-function corresponding to the lowest energy tends to the correct dissociation. 5
- (d) Write down the deficiencies of Koopmans' theorem. 1½
3. (a) Write down the approximations used in the Huckel Molecular Orbital Theory. Applying this theory, calculate the delocalization energy of cyclopropenyl radical. 5½
- (b) A long chain polyene may behave like a conductor of electricity—Justify using Huckel approximation. 4
- (c) Establish the quantum mechanical virial theorem for bound stationary states. 3

[3]

UNIT - P-4132

4. Answer *any three* :
- a) What is an electro-capillary curve ? What information can you obtain from such a curve ? Define 'surface excess'. 2+2+2
- b) i) Show that the parallel plate condenser model can explain electro-capillary curve which is perfect parabola.
- (ii) How can the electrocapillary measurements be used to determine the extent of contact adsorption on the surface of the electrode ? 3+3
- c) Prove that for a polarizable interphase, where the terms bear usual significance.
- $$d\gamma = -q_M dV - \frac{q_M}{Z_j F} d\mu_j - \sum \Gamma_i d\mu_i \quad 6$$
- d) Show that the extent of adsorption of a neutral organic molecule at an electrode 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

[Turn over