M. Sc. Chemistry Examination, 2022

(4th Semester)

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 *any two* questions.

1. a) Many electrons wave function written in Slater determinantal form satisfies the anti-symmetry requirement. Justify using a 3-electron system.

   b) Write down those Slater determinants which are always eigen functions of $\hat{S}^2$ by construction of a 3-electron system. Construct spin eigen functions with $S = \frac{3}{2}$ and $M_s = \frac{1}{2}$ of the same system using spin projection operator.

   c) Show that for an atom with two non-interacting electrons, the two electron wave function is the product of eigen functions of two single electrons.

   $3+7\frac{1}{2}+2$

2. a) What are Slater Condon rules? Derive an expression for the energy expectation value of the wave

function $\psi = \frac{1}{\sqrt{2}}\left(\left|\bar{f}_1 f_2 f_3\right| - \left|f_1 \bar{f}_2 f_3\right|\right)$ using Slater-Condon rules.

b) What is Koopman's theorem? Prove it for N electron atom using Hartree Fock self consistent field orbitals. 6+6$\frac{1}{2}$

3. a) Using Hückel Molecular Orbital (HMO) theory, derive general expression of energy level and wave function of a cyclic conjugated polyene having N-carbon atoms (N may be odd or even).

b) What are the approximations used in Huckel Molecular orbital (HMO) theory? Using HMO theory, calculate the energy levels for cyclobutadiene and butadiene. 5$\frac{1}{2}$+(3+2+2)

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4. Answer ***any three*** questions :

a) Distinguish chemical potential from electrochemical potential. Derive Nernst equation based on the thermodynamic principle of equilibrium. 2+4

b) Define surface excess.

Derive $d\gamma = -q_M dV - \left(q_M / Z_j F\right) d\mu_j - \sum \Gamma_i d\mu_i$ for a polarizable electrode, where γ = interfacial tension and Γ_1 = surface excess for i-th type of species and all other terms bear usual significance. 1+5

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

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

d) i) Derive an expression of potential gradient $\left(d\Psi / dx\right)$ at a distance x from an electrode structured as Gouy-Chapman double layer.

ii) Using the above equation, show that the double layer is theoretically extended up to infinity.

4$\frac{1}{2}$+1$\frac{1}{2}$

5. Answer ***any one*** question:

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

4$\frac{1}{2}$

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

b) Explain with necessary diagrams the mechanisms of action of photovoltaic, photosynthetic and photocatalytic cells. 2$\frac{1}{2}$+2$\frac{1}{2}$+2