M. Sc. (Chemistry) Examination, 2023

(4th Semester)

Paper: XIII–P

[Physical Chemistry Special]

Time : Two Hours Full Marks : 40

(20 marks for each unit)

Use a separate answer script for each unit.

Unit: P-4131

1. a) Derive the analytical form of the square of the total spin angular momentum operator $(\hat{S}^2)$ using a Slater determinantal function of a $(n_\alpha + n_\beta)$ electron system (n_α and n_β are the number of α and β spin electrons). 6

   b) Find the number of possible spin multiplets of a 6 electron system using Branching rule. 2

   c) Show, taking suitable example, that many electron wavefunction with spin orbitals must be antisymmetric to satisfy Pauli exclusion principle. 3

   d) Elucidate the Hartree Fock Self Consistent Field (HF-SCF) procedure to solve the Schrodinger equation for many electron atoms. What is the physical significance of Fock operator? 6+1

Or

What are the approximations used in Hückel Molecular Orbital (HMO) theory? Using HMO theory, calculate the energy levels for cyclobutadiene and butadiene. 3+2+2

e) Evaluate the expression of H_{ij} in terms of one and two electron integrals, when $D_i = \left(\left|\phi_1\bar{\phi}_1\phi_2\phi_3\right|\right)$ and $D_j = \left(\left|\phi_1\bar{\phi}_1\phi_2\phi_4\right|\right)$. 2

Unit: P-4132

2. Answer ***any four*** questions :

a) What is meant by the phenomenon of eletrocapilarity? Show that Helmholtz-Perrin model would be satisfactory for electrocapillarity curve which is a perfect parabola. 1+4

b) Can one measure the changes of the potential difference across an electrode-solution interface? 'The equivalent circuit for an electrified interface is a capacitor and resistor connected in parallel' – justify the statement. $1\frac{1}{2}+3\frac{1}{2}$

c) Mention the advantages of using mercury for measuring interfacial tension at an electrode-solution interface. Derive Lippmann equation to show that the slope of the electrocapillarity curve at

any cell pontential is equal to the charge density of the electrode. $1\frac{1}{2}+3\frac{1}{2}$

d) Give a brief account of the Temkin isotherm in relation to molecular adsorption in an electrochemical system. What is the limitation of this isotherm? 4+1

e) Derive an expression for the capacity of an interface in the presence of contact adsorption and hence, explain the appearance of 'capacitance hump'. 4+1

f) Show that the potential decays exponentially due to space charge inside the semiconductor and hence, explain that at high concentration of the charge carriers, the semiconducting behavior is turned into the metallic character. $3\frac{1}{2}+1\frac{1}{2}$