# M. Sc. Chemistry Examination, 2023

(1st Semester, CBCS)

## Paper: I

## [ Theoretical Chemistry ]

Time : Two Hours Full Marks : 40

(20 marks for each Unit)

Use a separate answer script for each Unit.

## UNIT – 1011

1. a) Define a hermitian operator. Show that a projection operator of the type $|\phi><\phi|$ is hermitian.

   b) Construct the first excited singlet state wave function of He atom in terms of spin orbitals which satisfy Pauli Exclusion Principle. Assuming spin orthonormality and no spin-orbit interaction, evaluate its energy in terms of two-electron integrals.

   c) Prove that the quantum averages: $< l_x >$ and $< l_y >$ vanish for spherical harmonics $\{Y_{l,m_l}\}$ as orthonormal basis functions.

   d) Using ladder operators for the spin of an electron, construct Pauli spin matrix representations of $\hat{s}_x$ and $\hat{s}_y$ operators.

e) The wave function of $3d_{z^2}$ orbital of H atom is given as $\psi_{3d_{z^2}} = Ar^2 e^{-\frac{r}{3}}\left(3\cos^2\theta - 1\right)$, where A is a constant. Find the point at which the probability density of the $3d_{z^2}$ orbital will be highest. 2+3+2+2+3

2. a) If the Hamiltonian of a one-dimensional quantum system is not time dependent, the wave function $\psi(x,t)$ remains stationary — Justify. 4

b) i) Write down the trial variational wave function for $H_2^+$ in the ground state. After the variational treatment one gets bonding and antibonding orbitals. Write down these molecular orbitals and energies in terms of Coulomb, Resonance, and overlap integrals.

ii) Assuming overlap integral value of 0.5 a.u. at equilibrium bond distance, show that there is an accumulation of electron density in between two atoms of $H_2^+$ for the bonding molecular orbital. 2+2

**UNIT – 1012**

3. Construct the character table of $C_4$ with proper explanation (Area 1 and Area II only). Use this character table to construct the π-MOs of $C_4H_4$. Find the energy of these MOs applying Huckel's approximation. 4+4+4



4. Write a reducible representation for the motional degrees of freedom of $NCl_3$ molecule (Point group, $C_{3v}$). Decompose the representation using reduction formula. The character table of $C_{3v}$ point group is given below. 4

| $C_{3v}$ | E | $2C_3$ | $3\sigma_v$ |
|---|---|---|---|
| $A_1$ | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | –1 |
| E | 2 | –1 | 0 |

5. Show that any group of order 4 is an Abelian group. 2

6. Identify the point groups for following molecular species (any two): 2

i) Cis-$[Co(NH_3)_4F_2]^+$

ii) $C_3H_3^+$

iii) $SF_4$

iv) Staggered form of ferrocene 2