# LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

**M.Sc.** DEGREE EXAMINATION – **CHEMISTRY**

FIRST SEMESTER – **APRIL 2025**

**PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY**

Date: 28-04-2025 Dept. No. Max. : 100 Marks

Time: 09:00 AM - 12:00 PM

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|---|---|---|
| | **SECTION A – K1 (CO1)** | |
| | **Answer ALL the questions** | **(5 x 1 = 5)** |
| **1** | **Answer the following** | |
| a) | What are stationary states? | |
| b) | Write the wave function for a particle in the ground state within a 2D square box. | |
| c) | Mention the significance of Hartree-Fock method. | |
| d) | Write the resulting symmetry operation of $S_6^2$. | |
| e) | Mention the significance of secular equations. | |
| | **SECTION A – K2 (CO1)** | |
| | **Answer ALL the questions** | **(5 x 1 = 5)** |
| 2 | **Fill in the blanks** | |
| a) | The divergence of Rayleigh-Jeans law with $\nu^2$ at higher frequencies is termed as _____. | |
| b) | A symmetric wave function satisfies the condition, $\Psi(x)$ = ___. | |
| c) | The magnitude of Bohr radius (in Å) is _____. | |
| d) | The point group of allene is _____. | |
| e) | If the overall direct product transforms to the most symmetric representation of the group, then the corresponding electronic transition is _____. | |
| | **SECTION B – K3 (CO2)** | |
| | **Answer any THREE of the following** | **(3 x 10 = 30)** |
| 3 | (i) State and explain the postulates of quantum mechanics. | (5) |
| | (ii) Show that the function, $\Psi = e^{-x^2/2}$ for the operator, $x^2 - \frac{d^2}{dx^2}$ is an eigen function and find its eigen value. | (5) |
| 4 | (i) Derive the expression for wave function and energy for a particle in a one dimensional box. | (7) |
| | (ii) Show that the energy states (221), (212), (122) are degenerate for a particle in a cubical box. | (3) |
| 5 | (i) State and explain variation theorem. | (5) |
| | (ii) With the help of perturbation theorem, predict the ground state energy of Helium atom. | (5) |
| 6 | (i) Construct the character table for $C_{2v}$ point group using Great Orthogonality theorem. | (7) |
| | (ii) Obtain the transformation matrices for the symmetry operations '$S_n$' and 'i'. | (3) |
| 7 | (i) Outline the salient features of VB (Heitler-London) theory as applied to Hydrogen molecule. | (4) |
| | (ii) Obtain the symmetries of the base orbitals $\sigma_{C\text{-}O}$, $\pi_{C\text{-}O}$, $\pi^*_{C\text{-}O}$ and $n_{C\text{-}O}$ for HCHO molecule. | (6) |

## SECTION C – K4 (CO3)

**Answer any TWO of the following** **(2 x 12.5 = 25)**

8 (i) Find the commutator for the angular momentum operators, $L_x$ and $L_y$. (8.5)

(ii) Express the spherical polar coordinates (5, 20º, 150º) in terms of Cartesian coordinates. (4)

9 (i) Set up the Schrodinger wave equation for a simple harmonic oscillator and solve it for the energy eigenvalues. (8.5)

(ii) Find out the length of butadiene chain, which has an absorption maximum at 2150 Å. (4)

10 Write the Schrodinger equation for hydrogen atom and solve it for its energy and radius of the shell.

11 (i) Show that $C_{2v}$ point group is abelian. (4)

(ii) Deduce the IR and Raman active modes of vibrations of $BCl_3$ molecule. The $D_{3h}$ character table is given below. (8.5)

| $D_{3h}$ | E | $2C_3$ | $3C'_2$ | $\sigma_h$ | $2S_3$ | $3\sigma_v$ | | |
|---|---|---|---|---|---|---|---|---|
| $A'_1$ | +1 | +1 | +1 | +1 | +1 | +1 | - | $x^2+y^2, z^2$ |
| $A'_2$ | +1 | +1 | -1 | +1 | +1 | -1 | $R_z$ | - |
| E' | +2 | -1 | 0 | +2 | -1 | 0 | (x, y) | $(x^2-y^2, xy)$ |
| $A''_1$ | +1 | +1 | +1 | -1 | -1 | -1 | - | - |
| $A''_2$ | +1 | +1 | -1 | -1 | -1 | +1 | Z | - |
| E'' | +2 | -1 | 0 | -2 | +1 | 0 | $(R_x, R_y)$ | (xz, yz) |

## SECTION D – K5 (CO4)

**Answer any ONE of the following** **(1 x 15 = 15)**

12 (i) Work out the polar and azimuthal wave equations from Schrodinger equation of a rigid rotor and solve them to get the spherical harmonics. (10)

(ii) The work function of barium metal is 2.48 eV. If the light of 400 nm shined on the barium cathode, what is the maximum velocity of the ejected electrons? (5)

13 (i) Show that the wave function describing 1*s* orbital of hydrogen atom is normalized where

$$\psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-\left(\frac{Zr}{a_0}\right)}$$ (5)

(ii) State and explain Great Orthogonality theorem. (5)

(iii) Write down the secular determinant for cyclopropenyl cation using Hückel's method and obtain expressions for their energy levels. (5)

## SECTION E – K6 (CO5)

**Answer any ONE of the following** **(1 x 20 = 20)**

14 (i) Derive time-independent Schrodinger wave equation. (8)

(ii) Illustrate quantum mechanical tunneling with evidences. (7)

(iii) Show that for a particle in a three dimensional box with lengths, $l_x = l_y = l_z/2$, the energy levels 122 and 114 are accidentally degenerate. (5)

15 (i) Sketch the radial distribution plots for 2s and 3p orbitals and indicate the nodes. (4)

(ii) Predict the point group, symmetry operations, class and order for the following molecules: (8)

(a) Staggered ethane (b) Chlorobenzene

(iii) Work out the hybridization scheme for σ bonding by Br atom in $[BrF_4]^-$ molecule using the $D_{4h}$ character table given below. (8)

| | **E** | **$2C_4$ (z)** | **$C_2$** | **$2C_2'$** | **$2C_2''$** | **i** | **$2S_4$** | **$\sigma_h$** | **$2\sigma_v$** | **$2\sigma_d$** | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **$\chi_R$** | **4** | **0** | **0** | **0** | **2** | **0** | **0** | **4** | **0** | **2** | | |
| **$A_{1g}$** | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | | $x^2+y^2$, $z^2$ |
| **$A_{2g}$** | 1 | 1 | 1 | -1 | -1 | 1 | 1 | 1 | -1 | -1 | $R_z$ | |
| **$B_{1g}$** | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | 1 | -1 | | $x^2-y^2$ |
| **$B_{2g}$** | 1 | -1 | 1 | -1 | 1 | 1 | -1 | 1 | -1 | 1 | | xy |
| **$E_g$** | 2 | 0 | -2 | 0 | 0 | 2 | 0 | -2 | 0 | 0 | ($R_x$, $R_y$) | (xz, yz) |
| **$A_{1u}$** | 1 | 1 | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | | |
| **$A_{2u}$** | 1 | 1 | 1 | -1 | -1 | -1 | -1 | -1 | 1 | 1 | z | |
| **$B_{1u}$** | 1 | -1 | 1 | 1 | -1 | -1 | 1 | -1 | -1 | 1 | | |
| **$B_{2u}$** | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | | |
| **$E_u$** | 2 | 0 | -2 | 0 | 0 | -2 | 0 | 2 | 0 | 0 | (x, y) | |

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