LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2024**

PCH 1503 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 13-11-2024 Dept. No. Max. : 100 Marks

Time: 01:00 pm-04:00 pm

SECTION A

Answer ANY FOUR of the following **4 x 10 = 40 Marks**

1. Explain Wien's displacement and Planck's radiation laws of black body radiation.
2. (a) Derive the wave function and energy for a particle in a rectangular three dimensional box. (7)
   (b) Find the zero point energy of an electron in a one dimensional box of length 1.0 Å. (3)
3. (a) Express the spherical polar coordinates (5, 20º, 150º) in terms of Cartesian coordinates. (5)
   (b) Show that the wave function, $\psi = x\,e^{-x^2/2}$ is an eigenfunction of the operator,

   $\hat{O} = \frac{-d^2}{dx^2} + x^2$ and find the eigenvalue. (5)
4. Set up Schrodinger wave equation for a simple harmonic oscillator and solve it for the energy eigen values.
5. Find the commutator for (i) L_x and L_y and (ii) x and p_x. (6+4)
6. (a) State and explain perturbation theorem. (7)
   (b) What is a Slater determinant? (3)
7. (a) Find the Huckel molecular orbitals and energies for allyl anion. (5)
   (b) What are coulomb and exchange integrals? How are they obtained? (5)
8. (a) What are abelian point group? Mention any two point groups that are related to optical activity. (4)
   (b) How will you prove that $\pi \rightarrow \pi^*$ transition in formaldehyde is electronically allowed using the following character table? (6)

Character table for C_{2v} point group

	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

SECTION B

Answer ANY THREE of the following **3 x 20 = 60 Marks**

9. (a) Outline the postulates of quantum mechanics. (6)
   (b) Derive time independent Schrodinger wave equation. (8)
   (c) Illustrate quantum mechanical tunneling with examples. (6)
10. (a) Work out the polar and azimuthal wave equations from Schrodinger equation of a rigid rotor and solve them to get the Spherical harmonics. (10)
    (b) The work function of barium metal is 2.48 eV. If the light of 400 nm is shined on the barium cathode, calculate the maximum velocity of the ejected electrons. (6)
    (c) What are orthogonal and orthonormal functions? (4)

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

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

$$\psi_{1s}=\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_o}\right)^{3/2} e^{-\left(\frac{Zr}{a_0}\right)}$$ (6)

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

12. (a) For a particle in an infinitely deep one dimensional potential box of length L, apply the trial wave function $\psi = N\ x\ (L^2 - x^2)$ to calculate the energy. (8)

(b) Obtain the ground state term symbol for sodium. Suggest a possible electronic configuration for the term symbol $^3P_2$. (5)

(c) Outline the salient features of VB (Heitler-London) theory as applied to Hydrogen molecule. (7)

13. (a) Write down the secular determinant for ethylene and butadiene molecules and obtain expressions for energy levels of ethylene using Hückel's method. (8)

(b) Highlight the importance of variation method in the determination of energy of MO for Hydrogen molecular ion. (5)

(c) Deduce the IR and Raman active vibrational modes of trans-N_2F_2 molecule and Prove that the molecule obeys mutual exclusion principle. The C_{2h} character table is given below. (7)

C_{2h}	E	C_2	i	σ_h		
A_g	+1	+1	+1	+1	R_z	x^2, y^2, z^2, xy
B_g	+1	-1	+1	-1	R_x, R_y	xz, yz
A_u	+1	+1	-1	-1	z	-
B_u	+1	-1	-1	+1	x, y	-

14. (a) List out the symmetry elements and symmetry operations of OF_2 and HCl molecules. (6)

(b) State the postulates of great orthogonality theorem and construct the character table for C_{3v} point group. (8)

(c) Work out the hybridization scheme for σ bonding by boron in BF_3 molecule for D_{3h} symmetry. The D_{3h} character table is provided. (6)

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