LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2023**

PCH 1503 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 06-11-2023 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

PART A

Answer ALL questions. **10 x 2 = 20 marks**

1. Write the limits for spherical polar coordinates.
2. Rigel, the brightest star in constellation Orion, has approximately a blackbody radiation spectrum with a maximum wave length of 145 nm. Estimate the surface temperature of Rigel.
3. Sketch Ψ and Ψ^2 for a particle in one dimensional box when n = 2.
4. Calculate the zero point energy of a particle of mass 9.1×10^{-31} kg in a cubical box of length 10 Å.
5. Obtain the ground state atomic term symbol for fluorine.
6. Mention the need for approximation method.
7. What is the order of D_{3h} point group?
8. Write the symbol for a two dimensional representation that is symmetric with respect to inversion, *i*.
9. Mention the significance of Secular determinant.
10. Whether the vibrations of '*u*' modes are IR active? – Account.

PART B

Answer any EIGHT questions: **8 x 5 = 40 marks**

11. State the postulates of quantum mechanics.
12. The work function of barium metal is 2.48 eV. If the light of 400 nm is shined on barium cathode, what is the maximum velocity of ejected electrons?
13. How distant the point, (6, 10º, 120º) is away from the origin?
14. Derive an expression for wave function and energy for a particle in a one dimensional box.
15. Prove that the operators of any one of the angular momentum components commute with the operator of the square of angular momentum (L^2).
16. State and explain quantum mechanical tunnelling.
17. Show that the wave functions describing 1s orbital is normalized.

    Given: $\Psi_{1s} = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
18. What is Born-Oppenheimer approximation? Mention its importance.
19. List down the symmetry elements and operations of $CHCl_3$ and HI molecules.
20. State and explain Great Orthogonality theorem.
21. Explain the three important approximations of Huckel LCAO-MO theory.
22. Using the following reducible representation for CH_4 molecule, determine its possible hybridization schemes. Γ = 4 1 0 0 2. T_d character table is provided for the reference.

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

PART C

Answer any FOUR questions: **4 x 10 = 40 marks**

23. (a) Derive time independent Schrodinger wave equation.
    (b) Find the value of 'A' if A $\cos\frac{n\pi}{a}x$ is a normalised function over the interval $-a \leq x \leq a$. (Hint: $2cos^2x - 1 = cos2x$) (6+4)
24. Write the Schrodinger equation to be solved for hydrogen atom and solve it for its energy using a simple solution, which assumes the wave function to depend only on the distance r and not on the angles θ and φ.
25. Describe the rigid rotor model and obtain an expression for the energy of the same.
26. State and explain the following: (i) Variation theorem
    (ii) Pauli's exclusion principle (iii) Hohenberg - Kohn theorem. (4+3+3)
27. (a) Determine the symmetry operations and their classes for benzene molecule.
    (b) Construct the character table for C_{3v} point group. (4+6)
28. (a) Obtain the normalized trial wave functions and energies for bonding and antibonding orbitals of H_2 molecular ion.
    (b) Deduce the IR active modes of vibrations of H_2O molecule. The C_{2v} character table is given below. (5+5)

	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

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