LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **APRIL 2022**

PCH 1503 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 18-06-2022 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

PART – A

Answer ALL Questions: **10 x 2 = 20 Marks**

1. Mention the limits and volume element for spherical polar coordinates.
2. Which of the following operators are linear? (i) ∇^2 and $\sqrt{}$.
3. State Bohr's correspondence principle.
4. What is the degree of degeneracy for the particle in a cubic box with energy values of $17h^2/8ma^2$?
5. State variation theorem.
6. Mention the significance of Born-Oppenheimer's approximation.
7. Obtain the ground state term symbol for a halogen atom.
8. State Pauli's exclusion principle as applicable to Fermions.
9. Obtain the multiplication table for C_{2v} point group.
10. Mention the possible C_n symmetry operations in a trigonal planar molecule.

PART – B

Answer Any EIGHT Questions: **8 x 5 = 40 Marks**

11. (a) Which of the following are acceptable wave functions? Justify (i) $-x^2$ (ii) $\cos\theta$?

    (b) Normalize the following wave function: $e^{in\theta}$ in the interval of $[0,2\pi]$.

12. Deduce the expression for Rayleigh-Jeans and Stefan's law from Planck's radiation law.
13. Arrive at the Hamiltonian for simple harmonic oscillator.
14. Calculate the length of the γ-carotene molecule containing 11 conjugated double bonds and 10 single bonds and a transition wave length of 4600 Å.
15. Apply variation theorem to predict the ground state energy of hydrogen atom using the trial wave function, $\psi = e^{-\alpha r}$.
16. Obtain the value of $[L_x^2, L_x]$ and $[x, p_x]$. Mention their significance.
17. Apply Huckel's method to calculate the total energy in ethylene molecule.
18. Show that the Slater determinant for the ground state of Helium atom is antisymmetric with respect to the exchange of two electrons.

19. Obtain expressions for the energy levels of 1,3-butadiene using Secular determinant.

20. Predict the point group of eclipsed ethane. Mention its symmetry elements and operations.

21. Obtain the matrix representation for the reflection operation performed in YZ plane.

22. Illustrate similarity transformation with two examples.

PART – C

Answer Any FOUR Questions: **4 x 10 = 40 Marks**

23. (a) State and explain the postulates of quantum mechanics.

    (b) Derive time-independent Schrödinger wave equation. **(4+6)**

24. (a) Write the Schrodinger wave equation for a rigid rotor. Using the method of separation, separate the equation into two independent equations with only one variable each.

    (b) The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond (atomic mass of ^{35}Cl = 34.9688 u). **(7+3)**

25. (a) Write the Schrodinger wave equation for hydrogen atom in spherical polar coordinates. Obtain the solution for radial equation.

    (b) Draw radial plot for 1s and 2p orbitals. **(6+4)**

26. (a) Mention the significance of Slater and secular determinant.

    (b) State variation theorem and determine the energies of the bonding and anti-bonding orbitals of hydrogen molecular ion using variation principle. **(5+5)**

27. (a) Highlight the salient features of Huckel's approximations in Molecular orbital theory.

    (b) Obtain the reducible representation for the hybridization scheme of ammonia (NH_3) molecule.

    (5+5)

28. Find the symmetries of the IR and Raman active vibrational modes of trans-N_2F_2 molecule. Its character table is provided here.

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	

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