

**PG EVEN SEMESTER EXAMINATION, 2023****CHEMISTRY**

2nd Semester

Course No. : CHM - 554

**(Quantum Chemistry and Molecular Spectroscopy)**

Full Marks : 70

Pass Marks : 28

Time : 3 hours

*The figures in the margin indicate full marks for the questions**(Answer five questions, selecting one from each unit)*UNIT - I

1. (a) What is a Hermitian operator? Show that the eigenfunction of a Hermitian operator corresponding to different eigenvalues are orthogonal to each other. 1 + 3 = 4
- (b) Show that the operator for linear momentum ( $\widehat{p}_x$ ) is Hermitian. 3
- (c) Consider the momentum of the particle in a box. The wave function for the system is

$$\psi_n(x) = (2/a)^{1/2} \sin \frac{n\pi x}{a}$$

Show that the wave function  $\psi_n(x)$  is an eigenfunction of  $(\widehat{p}_x)^2$  but not of  $(\widehat{p}_x)$ . 4

*( Turn Over )*

(2)

- (d) What is normal and anomalous Zeeman effect? 3
2. (a) Show that:  $[\widehat{L}_x, \widehat{L}_y] = \frac{ih}{2\pi} \widehat{L}_z$  3
- (b) Solve the Schrodinger wave equation for a particle in one dimensional box and find the expression for the energy. 4
- (c) What is meant by quantum mechanical tunnelling? Derive the expression of the transmission coefficient for particle to tunnel through a potential barrier. 1+6=7

UNIT - II

3. (a) State and prove the variation theorem. 1+4=5
- (b) If  $\widehat{H}$  is the Hamiltonian and using the trial function for  $H_2^+$  molecule ion, calculate the energies of bonding and antibonding orbitals. 6
- (c) "Delocalised allyl structures are stable than the localised allyl structure." Explain. 3
4. (a) What is perturbation theory? Derive the expression for the first-order wave function correction for nondegenerate energy levels. 1+5=6
- (b) Using the Hückel Molecular Orbital Theory, 2+2+4=8
- (i) Draw the energy level diagrams of cyclopropenylcarbonium ion, radical, carbanion.

(5)

absorption peaks observed and comment on the structure and name of the compound. 4

UNIT - V

9. (a) The basic principles of NMR and ESR are the same but their techniques are considerably different. Explain 2
- (b) Why spin magnetic moments do not orient in the direction of MF and also do not occupy the lowest energy level? 3
- (c) Discuss the factor that determines the shielding constant value. 2
- (d) Discuss the coupling between two nuclei A and X joined by a pair of bonding electrons. 4
- (e) Why most of the organic molecules with unpaired spin, the coupling constants are of the order of 2-20 MHz which is smaller than the H-atom (1400 MHz)? 3
10. (a) Derive an expression for the spin level of an H atom in a magnetic field. 5
- (b) Obtain the second-order hyperfine energy of isotropic interaction between a proton and an electron. Illustrate the allowed and forbidden transitions diagrammatically with energy values. 6+3=9

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UNIT - IV

7. (a) Explain the basic principle of Raman spectroscopy based on both classical and quantum theory with specific diagram. 6

- (b) Explain Raman activity of vibration for H<sub>2</sub>O and CO<sub>2</sub> molecule in the light of symmetry of polarizability ellipsoid. 5

- (c) For a molecule AB<sub>2</sub> the following spectroscopic data are available. Predict the geometry of AB<sub>2</sub> molecule and assign the observed lines to specific molecular vibrations showing all different possible modes. 3

Wave number (cm <sup>-1</sup> )	Infrared	Raman
1330	Inactive	Active
2349	Active (PR)	Inactive
667.3	Active (PQR)	Inactive

8. (a) What do you mean by fundamental absorption, overtones and hot bands in the IR spectroscopy? 5

- (b) What are P, Q and R branches of the vibration-rotation spectrum? Show the transition diagrammatically. 5

- (c) Following characteristics absorption peaks have been observed in the infrared spectrum of an organic compound having formula, A<sub>2</sub>B<sub>6</sub>C

(i) strong band at 3300 cm<sup>-1</sup> (ii) band at 2965 cm<sup>-1</sup> (iii) band at 2920 cm<sup>-1</sup> (iv) band at 1050 cm<sup>-1</sup>. Assign on the

- (ii) Calculate the π electron delocalization energy relative to the ethene molecule.

- (iii) Determine the three HMOs wave functions of the cyclopropenyl system.

UNIT - III

5. (a) Write short note on the radiative and nonradiative processes occurring in the photochemical excited states using Jablonski diagram. 5

- (b) Discuss the rotational spectrum of diatomic rigid rotator and compare with non-rigid rotator. 4 + 2 = 6

- (c) Calculate rotational constant of (i) H<sub>2</sub> and (ii) HCl. The H-H and H-Cl bond length is 136 pm. 3

6. (a) Write an account on different types of electronic transitions on chemical analysis of electronic spectroscopy considering solvent effect. 5

- (b) Write short notes on the following: 3 + 3 = 6

(i) Born Oppenheimer Approximation

(ii) Franck-Condon Principle

- (c) A substance when dissolved in water at 10<sup>-3</sup> M concentration absorb 10 % of an incident radiation in a path length of 1 cm. What should be the concentration of the solution in order to absorb 90% of the same radiation? 3