PG (CBCS) EVEN SEMESTER EXAMINATION, 2023

CHEMISTRY

2nd Semester

Course No. : CHMCC - 204

(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

(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.

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 constant 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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(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_2 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^{-3} 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

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_2O and CO_2 molecule in the light of symmetry of polarizability ellipsoid. 5

(c) For a molecule AB_2 the following spectroscopic data are available. Predict the geometry of AB_2 molecule and assign the observed lines to specific molecular vibrations showing all different possible modes. 3

Wave number (cm^{-1})	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_2B_6C

(i) strong band at 3300 cm^{-1} (ii) band at 2965 cm^{-1} (iii) band at 2920 cm^{-1} (iv) bond at 1050 cm^{-1}. Assign on the