PG Even Semester Examination, May 2025

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 right margin indicate full marks for the question. Answer any five questions selecting one from each unit.

UNIT-I

1. (a) Derive the expression for the wave function and total energy of a particle in a Three-dimensional box. Explain the concept of degeneracy. 4+2=6

   (b) A particle in a box cannot have zero energy quantum mechanically. Explain. 3

   (c) Show that the ground state wave function $\Psi_0 = (\frac{2\alpha}{\pi})^2 e^{-\alpha x^2}$ is an eigen function of the operator corresponding to a one-dimensional harmonic oscillator with eigenvalue $\frac{1}{2}h\vartheta_0$. (where $\alpha^2 = (\frac{\pi}{h})^2 km$) 5

2. (a) What is a Hermitian operator? Show that the eigenfunctions of a Hermitian operator corresponding to different eigenvalues are orthogonal to each other. 2+3=5

(b) Show that: $[x^n, p_x] = -\frac{h}{2\pi i} n x^{n-1}$, where n is a positive integer. 2

(c) Show that: $[\widehat{L_x}, \widehat{L_y}] = \frac{ih}{2\pi}\widehat{L_z}$ 3

(d) Show that the probability of finding a particle in a one-dimensional box of Length L in region $x = \frac{L}{4}\ to\ \frac{3L}{4}$ if n is even and $\frac{1}{2} + \frac{(-1)^k}{n\pi}$ if n is odd (=2k+1, where k=0, 1, 2, 3....). 4

UNIT-II

3. (a) State and prove the variation theorem. 1+3=4

(b) What do you mean by linear combination of atomic orbitals (LCAO) approximation?2

(c) Explain the molecular orbital (MO) treatment of the H_2 molecule with a proper description of two-centered Coulomb, exchange and overlap integrals. 8

4. (a) What is perturbation theory? Derive the expression for the first-order energy and wave function correction for a nondegenerate system. 1+3+3=7

(b) Consider a trial function ψ= x(L-x) for a particle in a one-dimensional box of length L. Apply the variation method to get an upper bound to the ground state energy of the particle, and compare the result with the true value given by a one-dimensional box. 4

(c) Force constant of the ^{14}N-^{16}O bond. 6

(d) A CCl_4 solution of sulphur is excited with 1064 nm. (a) Calculate the position of the Rayleigh scattering line in cm^{-1}. (b) A sharp Raman spectral peak appears at 9620 cm^{-1}. Comment whether it is Stokes or anti-Stokes. 2+1=3

UNIT-V

9. (a) Discuss the magnetic Hamiltonian of an H atom 6

(b) What is a basic spin function? Obtain the zero-order energies of the H-atom. 5

(c) Why are most of the organic molecules with unpaired spin, the coupling constant is of the order of 2-20 MHz, which is smaller than the H-atom (1400 MHz)? 3

10. (a) Discuss how nuclear and electronic spins are almost equally distributed between two energy levels. 4

(b) What is Larmor Precession? Explain that the Larmor precession frequency is the separation between energy levels. 4

(c) What is fine coupling and hyperfine coupling? 2

(d) Discuss the effect of the magnetic field on the energy level of the methyl and hydroxyl nuclei of methanol. 4

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(c) Write the secular determinant of cyclobutadiene in terms of coulomb(α) and resonance(β) integrals of Huckel molecular orbital theory and show the energy level in a graphical sketch. Calculate its pi-delocalization energy relative to the energy of two ethylene molecules. 1+1+1=3

UNIT-III

5. (a) Briefly describe the Franck-Condon principle. 4

(b) Show that the spectral lines of a rigid diatomic molecule are equispaced. 3

(c) Predict the first three lines in the rotational spectrum of O_2 if the equilibrium bond distance of O_2 is 1.21 Å. The mass of each O atom is 16 a.u. 4

(d) Show that the spectrum of heavier species will show smaller separation. 3

6. (a) Two consecutive pure rotational lines of HBr are separated by 17 cm^{-1}. (a) Calculate the moment of inertia. (b) Calculate the internuclear distance of HBr. 4

(b) Differentiate symmetric top, spherical top, and asymmetric top molecules. 3

(c) Calculate the ratio of the number of molecules present in the first and ground rotational states of a molecule that has the rotational constant B value of 4.2 cm^{-1} at 300 K. 3

(d) Why is phosphorescence at room temperature a rare event? 2

(e) Define the terms (a) Electromagnetic spectrum, (b) Microwave spectroscopy. 2

UNIT-IV

7. (a) Write down the expression for the potential energy and vibrational energy of a diatomic molecule considering the Morse oscillator of vibration. (b) Draw the potential energy versus displacement diagram of a harmonic and an anharmonic oscillator. 3+2=5

(b) Show the different vibrational modes of H_2O. Which of these vibrational modes are IR active? 2+1=3

(c) The frequency of vibration of $^{1}H^{35}Cl$ is 3000 cm^{-1}. Calculate the force constant of the H-Cl bond. 3

(d) What are hot, fundamental, and overtone bands in vibrational spectroscopy? 3

8. (a) Show the different vibrational modes of CO_2. Which of these vibrational modes are IR active and Raman active? 3

(b) What are the Stokes and anti-Stokes lines in the Raman spectrum? 2

(c) The fundamental band and the first overtone of $^{14}N^{16}O$ appear at 1876 cm^{-1} and 3724 cm^{-1}, respectively. Find

(a) Zero-point energy.

(b) Maximum vibrational energy.