PG Even Semester Examination, May 2025

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 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 eigenfunction 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

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

(c) Show that the probability of finding a particle in a one-dimensional box of Length L in region $x = \frac{L}{4}\ to\ \frac{3L}{4}$ is $\frac{1}{2}$ 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-orderenergy 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

(a) Zero-point energy.

(b) Maximum vibrational energy.

(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 Larmo rprecession 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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the true value given by aone-dimensional box. 4

(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 which are 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