[This question paper contains 2 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 3014 **L**

Unique Paper Code : 2173522007

Name of the Paper : DSE: Quantum Chemistry and Spectroscopy

Name of the Course : **B.Sc. (Prog.)**

Semester : IV/VI

Duration : 2 Hours Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **four** questions.
3. Attempt **all parts** of a question together.
4. Use of scientific calculators is allowed.

Physical Constants

Planck's constant 6.626×10^{-34} *Js*

Velocity of light 3×10^{8} *m/s*

Atomic mass unit 1.661×10^{-27} *kg*

Avagadro's number 6.023×10^{23} mol^{-1}

Mass of electron 9.109×10^{-31} *kg*

1. (a) Which of the following mathematical functions are acceptable wavefunctions in the intervals given?
   (i) $\psi = \tan x \ (0, 2\pi)$
   (ii) $\psi = e^{-x} \ (0,\infty)$
   (iii) $\psi = \frac{\sin x}{x} \ (0,\infty)$
   (b) Write the expression for *Hamiltonian operator* for He-atom and explain each term.
   (c) Draw a schematic sketch of the first four wavefunctions and their probability density plots of a particle in 1-D box.
   (d) Write the Schrödinger wave equation for particle in one dimensional box. Define its boundary conditions. Show that the energy levels are quantized. How the energy levels of particle in one dimensional box are different from that of the free particle?
   (3,3,4,5)

2. (a) Can "zero point energy" of particle in 1-D box be zero? Explain with suitable reasons.
   (b) What is meant by Simple Harmonic Oscillator? Write Hamiltonian Operator for a particle executing simple harmonic motion at any instant.
   (c) Which of the following functions are eigen functions of d^2/dx^2:
   (i) Sin 3x (ii) $5x^2$
   Give the eigen value wherever appropriate.
   (d) An electron is constrained to move in a one-dimensional box of length 0.15 nm.
   Calculate: (i) the energy corresponding to the levels n= 1, 2, 3
   (ii) the energy absorbed when this electron undergoes a transition from E_1 to E_2 and E_2 to E_3. (3,3,4,5)

P.T.O.

3. (a) Write the mathematical expressions for the momentum operator $\widehat{p_x}$ and potential energy operator $\hat{V}$.
   (b) Give any four characteristics of a *well-behaved* wave function.
   (c) What is normalization of the wavefunction? Normalize the wavefunction $\psi_n(x) = A \sin\left(\frac{n\pi x}{L}\right)$ for a particle in 1-D box of length 'L'.
   (d) Name and explain the theory which forms the basis for the electronic spectra of conjugated systems. What is the minimum excitation energy for linear molecule butadiene, given that the average C-C bond distance is 140 pm? (3,3,4,5)

4. (a) Define Lambert - Beer's Law. What are its limitations?
   (b) IR signal for stretching of C-C bond is at lower frequency than C=C bond. True or False. Give reasons.
   (c) Write short note on any *two* of the following:
      (i) Franck Condon principle
      (ii) Auxochromes and Chromophore
      (iii) Hypsochromic and hyperchromic shift
   (d) The $^{1}H^{35}Cl$ molecule shows pure rotational lines at the following frequencies (cm^{-1}) 20.7, 41.5, 62.0, 83.0, 103.8. Calculate the bond distance of HCl. ($m_H = 1.673 \times 10^{-27}$kg, $m_{Cl} = 58.06 \times 10^{-27}$kg) (3,3,4,5)

5. (a) Sketch fundamental vibrations of CO_2 molecule. Which of them will be IR active?
   (b) How would isotopic substitution ^{16}O by ^{18}O alter the microwave spectrum of $C^{16}O$?
   (c) How many translational, rotational and vibrational degree of freedom are there in H_2O and CH_4 molecules?
   (d) The fundamental vibration frequency of $^{14}N^{16}O$ is observed at 1870 cm^{-1}. Calculate the zero-point energy and force constant of the molecule. (3,3,4,5)

6. (a) Indicate with the help of the Jablonski diagram, the various processes by which the excited electronic states get deactivated. What is the difference between fluorescence and phosphorescence?
   (b) A molecule XY is studied by microwave spectroscopy under the rigid rotator approximation. Draw its schematic line spectrum. What is the structural information that can be obtained from this spectrum?
   (c) State the conditions for a molecule to be rotationally and vibrationally active. Which of the following molecules HCl, N_2, CO, H_2O? Will give rise to observable rotational and vibrational spectra.
   (d) Calculate the transmittance, absorbance and the molar excitation coefficient of a solution which absorbs 90% of a certain wavelength of light when the beam passes through a 1 cm cell which contains a solution of molarity 0.25M. (3,3,4,5)