[This question paper contains 2 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 2954 **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) Determine whether each of the following wavefunctions are acceptable or not as a state function over the indicated intervals.
   (i) e^{-x} $(0, \infty)$
   (ii) e^{-x} $(-\infty, \infty)$
   (iii) $\sin x$ $(0, 2\pi)$

   (b) Write the expression for *Hamiltonian operator* for H-atom and explain each term.
   (c) Draw a schematic sketch of the first four wavefunctions and their probability density plots of a harmonic oscillator.
   (d) Solve Schrodinger wave equation for a particle of mass 'm' moving in a 1-D box of length 'l' and find the expression for wavefunction and energy of the particle. Also, normalize the wavefunction. (3,3,4,5)

2. (a) Why n=0 is not allowed in the equation $E = \frac{n^2h^2}{8mL^2}$?

   (b) Show that $\psi = 3\cos 2x$ is an eigenfunction of the operator $\frac{-h^2}{4\pi^2}\frac{d^2}{dx^2}$. What is the eigenvalue?
   (c) Explain the following:
   (i) Bohr's Correspondence principle
   (ii) Operators in quantum mechanics
   (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 hexatriene, given that the average C-C bond distance is 140 pm? (3,3,4,5)

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3. (a) Write the mathematical expressions for the position operator $\hat{x}$ and kinetic energy operator $\hat{T}_x$.
   (b) Give the physical significance of ψ and ψ^2.
   (c) For a free particle, how can you show that its energy is not quantized. What is the restriction imposed on its energy? Why energy is not allowed to take negative values?
   (d) Calculate the percentage change in the energy of a particle of mass m in a one-dimensional box of edge length L when the edge length is decreased by 10%. (3,3,4,5)

4. (a) Discuss Frank Condon Principle in detail.
   (b) Explain the terms inter system crossover, internal conversion and primary process.
   (c) Which of the following molecules can exhibit a pure infrared spectrum: Cl_2, NH_3, CO_2, C_6H_6, H_2O, $CHCl_3$? Explain briefly.
   (d) For $^1H^{35}Cl$ molecule, the wave number of rotations for J=2 rotational state is 120 cm^{-1}. Calculate moment of inertia and the bond length of the molecule. (3,3,4,5)

5. (a) Arrange and explain the following in the ascending order of value of rotational constant: $H^{35}Cl$, $D^{35}Cl$, $D^{37}Cl$.
   (b) On what factors does the vibrational frequency of a molecule depend? What is order of decreasing vibrational frequency for carbonyl bond in HCHO, CH_3CHO, CH_3COCH_3? Justify your answer.
   (c) Describe in detail the factors responsible for the broadening of spectral lines.
   (d) When an incident beam of wavelength 3000 Å was allowed to pass through 2 mm thick pyrex glass, the intensity of the radiation was reduced to one-tenth of its initial value. What part of the same radiation will be absorbed by 1 mm thick glass? (3,3,4,5)

6. (a) What is the effect of polar solvents on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic transitions?
   (b) Explain the factors responsible for intensity of spectral lines in spectroscopy.
   (c) Derive and show that the population maximum at the nearest integral J value is $J_{max} = \sqrt{\frac{K_B T}{2hcB}} - \frac{1}{2}$
   (d) The fundamental vibrational frequency of $^1H^{19}F$ is 4141.3 cm^{-1}. Calculate the force constant of the H-F bond. Also, predict the fundamental vibrational frequency of DF.

(3,3,4,5)