S.No. of question Paper:

Unique Paper code   : 32171502

Name of the course   : B.Sc. (Hons) Chemistry

Name of the paper   : Quantum Chemistry & Spectroscopy

Semester   : V

Duration   : 3 hours

Maximum Marks   : 75

Instruction for Candidate:

1. **Attempt any FOUR questions in all.**
2. **Each question carries 18.75 marks and has four parts.**
3. **Preferably attempt all parts of a question together.**
4. **Please show all calculations as each step carries marks.**
5. **Use of scientific calculators is allowed.**
6. **This question paper consists of FIVE pages.**

Physical constants

Atomic mass unit	$1.66 \times 10^{-27} kg$
Planck's constant	$6.626 \times 10^{-34} Js$
Velocity of light	$3 \times 10^8 ms^{-1}$
Boltzmann constant	$1.381 \times 10^{-23} JK^{-1}$
Mass of electron	$9.1 \times 10^{-31} kg$
Avogadro's number	$6.023 \times 10^{23} mol^{-1}$
Nuclear magneton	$5.05 \times 10^{-27} JT^{-1}$
Bohr magneton	$9.274 \times 10^{-24} JT^{-1}$

1. (a) Determine whether the following functions are acceptable or not acceptable as state functions over the interval indicated. Give reasons.

Function	Interval
$(1 - x^2)^{-1}$	$(-1, +1)$
$exp(-x)$	$(0, \infty)$

(b) Are the following functions eigen functions of the given operators?

Function	Operator
$\left\{ sin\left(\frac{3\pi x}{4}\right) \right\}$	$\left(-\frac{h^2}{8m}\frac{d^2}{dx^2} + 0.8 \right)$
$\{exp(-x^3/2)\}$	$\left(\frac{d^2}{dx^2}\right)$

If yes calculate the eigen values.

(c) Explain the different modes of vibration in the following two polyatomic molecules: water and carbon dioxide. Are they all both IR and Raman active? Explain your answer.

(d) Using the quantum mechanical treatment for the hydrogen atom explains the following conclusions:
(i) The energy of relative motion of the hydrogen atom is quantized and this energy is related generally to the distance of electron from the nucleus and does not depend on angular orientation.
(ii) s orbitals are spherically symmetrical, but the p orbitals are dumbbell shaped.

(5, 5, 5, 3.75)

2. (a) A particle of mass m exists in a one-dimensional box of length a. Using the trial wave function $\psi_{trial} = Ax\left\{1 - \left(\frac{x}{a}\right)\right\}$ evaluate the energy associated with the lowest energy level and comment on whether this trial wave function is an acceptable function according to the variation theorem.

(b) Show that the wave functions describing the $1s$ atomic orbital and the $2s$ atomic orbital for the hydrogen atom are orthogonal. Given that:

$$\psi_{1s} = (\pi a_0^3)^{-\frac{1}{2}} exp(-r/a_0) \text{ and } \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{1}{a_0}\right)^{3/2} \{2 - (r/a_0)\} exp\left(\frac{-r}{2a_0}\right)$$

where a_0 is Bohr's radius and $\int r^n exp(-ar)\, dr = n!/a^{(n+1)}$.

(c) Calculate the two possible values of energy for the ^{1}H nucleus placed in an external magnetic field of $5.50T$. What will be the value of ΔE for the splitting observed? Calculate the value of the electromagnetic radiation frequency required to induce a transition corresponding to ΔE. Calculate the relative population of the two states in equilibrium at $300K$. ($g_n = 5.585$)

(d) Prove that if the operators $\hat{A}$ and $\hat{B}$ have the same set of eigen functions then the operators must commute. (5, 5, 5, 3.75)

3. (a) A linear molecule whose moment of inertia is $I = 7.16 x 10^{-46} kgm^2$ is analysed by a Raman spectrometer using incident radiation at $435nm$. Draw the expected stick-line spectrum under Raman rotational spectroscopy. Where will the first Stokes and Anti-Stokes line appear?

(b) Draw the ψ and ψ^2 patterns for various levels of the Simple Harmonic Oscillator. What conclusions can be drawn from these patterns? How do these compare and contrast with the classical model.

(c) A particle of mass m exists in a cubical box of length a. What is the degeneracy of the state which has energy $\dfrac{27\,h^2}{8ma^2}$? Write the mathematical expressions corresponding to the degenerate functions to show that they are different eigen functions.

(d) How is it possible to determine the expectation values for a particular observable if the wave function describing the system is not an eigen function of the operator corresponding to the variable? From where does this method originate? Explain with an example. (5, 5, 5, 3.75)

4. (a) The Free Electron Molecular Orbital (FEMO) model has been used to explain bonding and the HOMO to LUMO transitions in the hexa - $1,3,5 -$ triene molecule. Calculate the wave number corresponding to the $\pi \rightarrow \pi^*$ transition, given that the bond lengths are: C-C : $154pm$; C=C : $135pm$.

(b) Consider the two molecules ^{1}H^{35}Cl and ^{1}H^{37}Cl. Both the molecules are rotating within the rigid rotator approximation and vibrating within the harmonic oscillator model. Their rotational constants are B and B' respectively and their fundamental vibrational frequencies are v and v' respectively. Evaluate the ratio of (i) their rotational constants and (ii) their fundamental vibrational frequencies.

(c) The ^{1}H NMR spectra of CH_3F, CH_3Cl, CH_3Br and CH_3I are run using an instrument operating at $100MHz$. The chemical shifts of the methyl protons are observed at different values on the δ scale. Explain this difference. Will the chemical shift value change if the spectra are run using an instrument operating at $200MHz$? Explain briefly.

(d) For HCl at room temperature three vibrational signals appear at 1198nm, 1764nm and 3465nm. Identify the signals and give the expressions for the energies of transitions corresponding to these. (5, 5, 5, 3.75)

5. (a) The vibrational – rotational spectrum of $^1H^{79}Br$ consists of a series of lines in the P- and R- branches:

P-branch		R-branch	
Line	**Position / cm^{-1}**	**Line**	**Position / cm^{-1}**
P_1	2542.56	R_0	2575.55
P_2	2525.51	R_1	2591.23
P_3	2507.86	R_2	2606.61
P_4	2489.63	R_3	2621.35

(i) Draw the spectrum as per data given in the table above.
(ii) What are the values of the rotational quantum numbers J'' and J' for each of the lines observed?
(iii) Evaluate the internuclear distance for the molecule $^1H^{79}Br$
(iv) Evaluate the fundamental vibrational frequency for the molecule.

(b) A particle of mass m exists in a two-dimensional box which extends along both the x-axis and y-axis. Suppose $\psi(x, y)$ and $\varphi(x, y)$ are two degenerate functions which are solutions to this system. Show that the two possible linear combinations of these two functions are also eigen functions of the system with the same energy.

(c) The time gap between absorption and emission in Phosphorescence is much longer compared to that in case of Fluorescence. In Phosphorescence phenomenon, the absorption spectrum is generally observed at higher wave numbers compared to the emission spectrum. Explain these observations. What kind of information can be obtained from the absorption and emission Phosphorescence spectra?

(d) What is the main difficulty in solving the Schrodinger equation for the Helium atom? Briefly explain the various steps taken to overcome this problem. (5, 5, 5, 3.75)

6. (a) The vibrational energy levels of ^{23}Na^{127}I are:
$$129.3, 389.5, 651.9, 916.5 \ cm^{-1}$$
Evaluate the force constant, zero point energy and the bond dissociation energy.

(b) The $J = 2 \rightarrow J = 3$ pure rotational transition for ^{39}K^{37}Cl occurs at $22410 MHz$. Assuming that the molecule is rotating under the rigid rotator approximation, predict the frequency and the corresponding wavelength of the $J = 0 \rightarrow J = 1$ transition for both ^{39}K^{37}Cl and ^{39}K^{35}Cl molecules.

(c) Methanol has a UV absorption peak at $184nm$ with $\varepsilon = 150 \ dm^3 mol^{-1} cm^{-1}$. Calculate the transmittance of $184nm$ radiation through a $0.0010 \ mol \ dm^{-3}$ solution of methanol in a non-absorbing solvent for two different cells of length: (i) $1.0cm$ and (ii) $10.0cm$.

(d) What is the significance of continuum in the vibrational electronic spectrum of a molecule? In some of the spectra, the continuum is observed in between, followed by discrete lines. What is this phenomenon called and how does it occur?

(5, 5, 5, 3.75)