(b) Explain Larmor precession of a spinning nucleus and derive expression for precessional frequency.

(c) The spacing between the successive lines of Raman rotational spectrum of O_2 molecule is 8B while for H_2 molecule it is 4B (where B is the rotational constant). Explain. (4.5,4,4)

8. (a) What is Fermi Resonance and hot bands in IR spectroscopy.

(b) Write short notes on the following:

(i) Dissociation and Predissociation

(ii) Franck Condon principle (4.5,4+4)

[This question paper contains 8 printed pages.]

01.01.2024(M)

Your Roll No..............

Sr. No. of Question Paper : 4378 G

Unique Paper Code : 32171502

Name of the Paper : Physical Chemistry V: Quantum Chemistry & Spectroscopy

Name of the Course : B.Sc. (Hons.) CHEMISTRY

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all, **three** questions each from sections **A** and **B**.
3. Attempt all part of a question together.
4. **All** questions carry equal marks.
5. Use of a non-programmable scientific calculator is allowed.

Physical constants

Atomic mass unit	$=1.66 \times 10^{-27}$ kg
Planck's constant	$= 6.626 \times 10^{-34}$ J s
Velocity of Light	$= 3 \times 10^{8}$ m s^{-1}
Boltzmann constant	$= 1.381 \times 10^{-23}$ J K^{-1}
Mass of Electron	$= 9.1 \times 10^{-31}$ kg
Avogadro's number	$= 6.023 \times 10^{23}$ mol^{-1}
Nuclear magneton	$= 5.05 \times 10^{-27}$ J T^{-1}
Bohr magneton	$= 9.274 \times 10^{-24}$ J T^{-1}

Section A

(Quantum Chemistry)

1. (a) The uncertainty in a quantity, represented by operator A is given as under,

$$\sigma_A^2 = \langle A^2 \rangle - \langle A \rangle^2$$

For a particle in the ground state of a one-dimensional box having length, L, represented by

$$\psi = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right), \text{ determine } \sigma_x \cdot \sigma_p$$

where x and p represent position and momentum, respectively.

(c) Discuss how a simple harmonic oscillator system differs from a homonuclear diatomic molecule undergoing anharmonic oscillations in terms of energy relation and energy vs displacement curve from mean position. (4.5,4,4)

6. (a) Given that the spin quantum numbers of $^{12}C_6$, $^{1}H_1$ and $^{2}D_1$ are zero, half and one, respectively, how many different energy states do these nuclei have in a magnetic field? Which of these atoms will show peak in the NMR spectra?

(b) Draw and discuss, the low and high-resolution NMR spectrum of CH_3CHO showing the peak corresponding to the reference standard TMS.

(c) The pure microwave spectrum for $^{1}H^{35}Cl$ is observed as a series of lines at 20.7, 41.5, 62.0, 83.0, 103.8 cm^{-1}. Evaluate the rotational constant and the internuclear distance for this molecule. (4.5,4,4)

7. (a) What do you understand by the terms, 'singlet' and 'triplet'? On the basis of these terms explain why fluorescence is a rapid phenomenon as compared to phosphorescence.

(c) Why do we need to employ approximate methods to determine solution for multielectron atoms? Explain Variation principle as an approximate method` to determine approximate wave function. (4.5,4,4)

Section B

(Molecular Spectroscopy)

5. (a) A molecule AB_2 has the following infra-red and Raman spectra :

Wave number (cm^{-1})	Infrared	Raman
589	Active (PQR)	Inactive
1285	Active (PR)	Active (polarized)
2224	Active (PR)	Active (depolarized)

Giving proper explanation and arrive at the geometry of the molecule. Assign the wavenumbers to specific vibrations.

(b) The intensities of Stokes and anti-Stokes lines are similar in rotational Raman spectra. However, in the vibrational Raman spectra, the Stokes lines are more intense than the anti-Stokes lines. Explain.

Use standard integral $\int x \sin\left(\frac{\pi x}{L}\right) = \frac{L^2}{4}$ and

$$\int x^2 \sin^2\left(\frac{\pi x}{L}\right) = \left(\frac{L}{2\pi}\right)^3\left(\frac{4\pi^3}{3} - 2\pi\right).$$

(b) Prove that the functions having different real eigen values for linear momentum operator are orthogonal.

(c) Starting from $\left[\frac{d}{dx}, x\right] = 1$, use the commutator identities to find

(i) $[\hat{x}, \widehat{p_x^2}]$

(ii) $[\hat{x}, \hat{H}]$, $\hat{H}$ is Hamiltonian for a one-particle, three-dimensional system. (4.5,4,4)

2. (a) Demonstrate that the Eigen functions for the particle in a one-dimensional box are orthonormal.

$$\psi(x) = \left(\frac{2}{L}\right)^{1/2} \sin\left(\frac{n\pi x}{L}\right)$$

(b) Write Hamiltonian operators for a particle moving under constant potential 'V' in a (i) one-dimensional box and (ii) three-dimensional box.

(c) As a crude treatment for the π electrons of a conjugated polyene, the π electrons of the conjugated chain are considered as moving in a one-dimensional box across the end to end conjugated chain. Considering 1,3-butadiene as a one-dimensional box of box length, 7.0 Å, calculate the wavelength of light absorbed when a π electron is excited from the highest-occupied to the lowest-vacant level of the molecular electronic ground state. (4.5,4,4)

3. (a) Construct the Hamiltonian operator for Simple Harmonic oscillator and write the Schrodinger equation. What is the zero-point energy of this type of system?

(b) A molecule X has 10 pi electrons and it is assumed to have cubical shape with edge length 10 pm. Give the quantum numbers corresponding to the highest occupied energy levels. Based on the free electron model, calculate the longest wavelength required for transition.

(c) Normalize the following functions :

(i) $f(r) = r \exp(-a r) \quad 0 \le r \le \infty$

(ii) $f(\varphi) = N \exp(im\phi) \quad 0 \le \varphi \le 2\pi$

(4.5,4,4)

4. (a) Using linear momentum operator $\hat{p}_x, \hat{p}_y$ and $\hat{p}_z$, derive angular momentum operators, $\hat{L}_x, \hat{L}_y$ and $\hat{L}_z$. Using $\hat{L}_z = -i\frac{h}{2\pi}\left(\frac{d}{d\phi}\right)$ construct the Schrodinger equation dependent on variable φ only. Write a possible solution as an eigen function and determine eigen values.

(b) Using normalized ground state wave function for hydrogen atom

$$\psi(r) = 2\left(\frac{1}{a}\right)^{3/2} \exp\left(\frac{-r}{a}\right)$$

Determine

(i) $\langle E \rangle$

(ii) The radius of maximum radial density distribution of electron