12/12/19 M

[This question paper contains 8 printed pages]

Your Roll No. : .....

Sl. No. of Q. Paper : **7397** **J**

Unique Paper Code : 32171502

Name of the Course : **B.Sc.(Hons.) Chemistry**

Name of the Paper : Physical Chemistry - V : Quantum Chemistry and Spectroscopy

Semester : V

Time : 3 Hours ***Maximum Marks : 75***

Instructions for Candidates :

(i) Write your Roll No. on the top immediately on receipt of this question paper.

(ii) Attempt any **six** questions in all.

(iii) Question No. **1** is compulsory. Each part of Question No. **1** carries **3** marks.

(iv) Each part of the rest of the questions carries **4** marks.

(v) Attempt all parts of a question together.

(vi) Use of scientific calculators is allowed but they cannot be shared.

(vii) Logarithmic tables can be provided if required.

P.T.O.

Physical Constants

Planck's constant	6.626×10^{-34} Js
Velocity of light	3×10^{8} ms^{-1}
Avogadro's number	6.023×10^{23}
Mass of electron	9.1×10^{-31} kg
Nuclear Magneton	5.05×10^{-27} JT^{-1}
Bohr Magneton	9.27×10^{-24} JT^{-1}
Boltzmann Constant	1.38×10^{-23} JK^{-1}

1. Attempt any **five** of the following :

(a) How will the rotational spectra change when ^{12}C in $^{12}C^{16}O$ is replaced by ^{13}C ?

(b) Write the Hamiltonian for H_2 molecule and explain each term.

(c) The term 'state' and 'energy level' are not synonymous in wave-mechanics. Explain. How many states and energy levels lie in the energy range of $E < 10h^2/8ml^2$?

(d) The function given below are defined in the internal x=–a and x=+a as follows :

$f(x) = N(a^2 - x^2)$

Assuming the value of the function to be zero for x<–a and x>+a, calculate the Normalization constant N.

(e) Show that the Morse Potential :

$V = D[1 - exp\{a(r_{eq} - r)\}]^2$

is reducible to harmonic potential for the lower vibrational levels. Also show that the force constant is given as $k = 2Da^2$.

(f) What are the essential conditions for a molecule to show IR Spectra. Which of the following will be IR active : O_2, CO_2, CO and SO_2.

(g) Homonuclear diatomic molecule, Br_2, is microwave inactive but is rotational Raman active. Why ?

2. (a) Show that the probability of finding the particle in a one-dimensional box in the region L/4 and 3L/4 is ½ if n is even, and

$\frac{1}{2} + \frac{(-1)^k}{n\pi}$ if n is odd.

(b) A particle of mass m moves in a three-dimensional box of sides a, b, c. If the potential is zero inside and infinity outside the box, give the expressions for the energy eigenvalues and wavefunctions for a particle in a 3-D box. What is the zero point energy of the system ? What is the degeneracy of the first and second excited states ?

(c) Evaluate the expectation values of <x> and <p> for the ground state of the harmonic oscillator.

Given : Normalized wavefunction :

$\Psi\left(\sqrt{\frac{a}{\pi}}\right)^{1/2} \cdot e^{-ax^2/2}$;

Standard integral : $\int_{-\infty}^{\infty} x^2 e^{-ax^2} . dx = \left(\frac{1}{2a}\right)\left(\frac{\pi}{a}\right)^{1/2}$

P.T.O.

3. (a) For a one-electron homonuclear diatomic molecule the values of some relevant integrals are given below :

$$\int \Phi_A \hat{H} \Phi_A d\tau = -3 \text{a.u.} \qquad \int \Phi_B \hat{H} \Phi_B d\tau = -3 \text{ a.u.}$$

$$\int \Phi_A \hat{H} \Phi_B d\tau = -3/2 \text{ a.u.} \qquad \int \Phi_A \Phi_B d\tau = 1/2$$

where Φ_A and Φ_B are the normalized set of basis functions for an LCAO wavefunction. Find the energy of the bonding molecular orbital and find the normalized wavefunction.

(b) Calculate the average distance of the electron from the nucleus of H atom in the 2s state.

$$\Psi_{200} = \left(\frac{1}{\sqrt{32\pi}}\right)\left(\frac{1}{a0}\right)^{\frac{3}{2}}\left(2-\frac{r}{a0}\right)e^{-r/2a0}$$

$$\left(\text{Given} : \int_0^\infty r^n e^{-ar} . \, dr = \frac{n!}{(a)^{n+1}}\right)$$

(c) What do you understand by the term transition probability ? Depict the energy levels and probability densities for the first four levels of a harmonic oscillator with the help of a diagram.

4. (a) Show that if two operators $\hat{A}$ and $\hat{C}$ are Hermitian, then their product $(\hat{A}\,\hat{C})$ is also Hermitian if and only if $\hat{A}$ and $\hat{C}$ commute.

(b) Write down the normalized Valence Bond wavefunction and Molecular Orbital wavefunction for H_2 molecule. Compare the expressions obtained and explain configuration interaction.

(c) Arrive at the following expression for H_2^+ :

$$E_+ = \frac{\alpha+\beta}{1+S}$$

(where α is the coulomb integral, β is the resonance integral and S is the overlap integral) using LCAO-MO treatment.

5. (a) The pi electrons of a conjugated molecule can be regarded as moving in a particle in a box, where the box length is somewhat more than the length of the conjugated chain. For butadiene, take this length as 7.0 Å and estimate the wavelength of the light absorbed when a pi-electron is excited from the highest occupied to the lowest vacant level. The experimental value is 217 pm.

(b) Find the commutator of position and momentum operator and give its physical significance, giving the name of the principle it verifies.

(c) Gilliam et al. (1950) measured the first line in the rotational spectrum of CO as 3.84235 cm^{-1}. Calculate the rotational constant, moment of inertia and find out which rotational state of CO would be most populated at 300 K ?

6. (a) What are the selection rules for observing IR spectra of an anharmonic oscillator ? Derive the expressions for energy required for fundamental transition and first overtone.

(b) Dissociation energy of $^{12}C^{16}O$ is 1.107×10^{6} $Jmol^{-1}$. The anharmonicity constant of the molecule is 5.860×10^{-3}. Find :

(i) equilibrium frequency of vibration

(ii) force constant of the molecule

(c) The line spacing (on each side of the band origin ω_0) in PR spectrum of CO_2 is 4B instead of the usual 2B as observed in case of HCN. Briefly explain.

7. (a) A molecule A_2B_2 shows IR and Raman spectra as tabulated below :

cm^{-1}	IR	Raman
3374	-	strong, polarized
1974	-	strong, polarized
3287	Active (PR)	-
612	-	weak, polarized
729	Active (PQR)	-

Predict the shape of the molecule and assign the various observed lines to the appropriate normal modes of vibrations.

(b) Show that the separation between the maximum in P and R branches of a vibration rotation spectrum of a heteronuclear diatomic molecule is approximately given as :

$$\Delta\nu = \sqrt{\frac{8kTB}{hc}}$$

where the symbols have their usual meanings.

(c) Distinguish between Fluorescence and Phosphorescence.

8. (a) r_{eq}'' and r_{eq}' are internuclear distance of a diatomic molecule in the ground and excited states respectively. Three cases arise :

$r_{eq}'' = r_{eq}'$, $r_{eq}'' > r_{eq}'$ and $r_{eq}'' >> r_{eq}'$.

Discuss the intensity distribution in absorption spectra of any **two** cases using Franck Condon principle along with potential energy diagrams.

(b) Of the two molecules, N_2 and O_2, which will show an ESR spectrum and why ? Show the hyperfine structure of Methyl radical ($\cdot CH_3$) in ESR spectrum, giving the intensities of the peaks.

(c) (i) In a spectrometer operating at 1 T, the NMR frequency of ^{19}F is 40.06MHz. Calculate its magnetogyric ratio/ gyromagnetic ratio.

(ii) Show the low and high resolution NMR spectrum of acidified ethanol.

9. Write short notes on (any **three**) :

(a) Born Oppenheimer Approximation

(b) Variation Principle

(c) Dissociation and Predissociation

(d) Larmor Precession