12.12.18 (M)

This question paper contains 7 printed pages]

Roll No. | | | | | | | | | | | |

S. No. of Question Paper : 45

Unique Paper Code : 32171502 I

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

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

Semester : **V**

Duration : **3 Hours** Maximum Marks : **75**

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

Answer *six* questions in all.

Question No. **1** is compulsory.

Attempt at least *two* questions from each section.

Attempt all parts of a question together.

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

Logarithmic tables can be provided if required.

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} mol^{-1}
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}

P.T.O.

1. Attempt any *five* :

(*a*) What is the essential condition for a molecule to be microwave active ? Which of the following molecules will show a microwave rotational spectrum : H_2, HCl, CH_4, SF_6.

(*b*) Determine whether or not the operators $x^2\frac{d^2}{dx^2}$ and $\frac{d^2}{dx^2}$ commute. What is the significance of commutation ?

(*c*) If A and B are two atoms bonding along the z-axis, predict giving reasons which of the following orbitals can combine :

(*i*) $2s$(A) and $2p_z$(B)

(*ii*) $1s$(A) and $2s$(B).

(*d*) Explain briefly the appearance of hot bands in the infra-red spectroscopy. Explain the effect of increase in temperature on the intensity of hot bands.

(*e*) The bond length decreases on removing an electron from O_2 but increases on removing an electron from N_2. Explain.

(*f*) Explain the significance of Born-Oppenheimer approximation. Write the Hamiltonian operator for hydrogen atom using Born-Oppenheimer approximation.

(*g*) What is accidental degeneracy ? Explain with an example. 3×5

Section A

2. (*a*) Find the expectation values of (*i*) x (*ii*) p_x (iii) p_x^2 for a particle of mass m, in a one-dimensional box of length l, having the solution :

$$\Psi_n = \sqrt{\frac{2}{l}}\sin\left(\frac{n\pi x}{l}\right).$$

Give the physical significance of each expression.

(*b*) Prove that the solutions with $n = 1$ and $n = 2$ for a particle in a box are orthogonal to each other.

(*c*) Determine the value of x at which the ground state wave function, Ψ for the harmonic oscillator exhibits a maxima. Given :

$$\Psi = \left(\frac{a}{\pi}\right)^{\frac{1}{4}} \exp\left(\frac{-\alpha x^2}{2}\right). \qquad 6,3,3$$

3. (*a*) Determine the energy of H atom using the trial wave function $\Psi = e^{-ar}$ where a is an adjustable parameter and r is the distance of the electron from the nucleus. Given :

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

(*b*) Discuss Bohr correspondence principle with respect to the behaviour of wave function of simple harmonic oscillator (SHO). Illustrate using its probability density plots.

(*c*) Sketch R(r) and $4\pi r^2 R^2(r)$ *Vs.* r/a_0 for $3p$ orbital for hydrogen atom. Calculate the number of radial nodes in this orbital. 6,3,3

4 (*a*) Molecular orbital theory gives equal weightage to covalent and ionic structure whereas valence bond theory ignores ionic character. Explain using the trial wave function of H_2 molecule.

(*b*) Benzene may be taken as a two-dimensional box of edge length 0.4 nm consisting of six π electrons. Calculate the energy required for the promotion of an electron from the ground to the first excited state of benzene.

(*c*) Normalize the given wave function :

$$\Phi_m = \exp(i\, m\, \phi)$$

What is the significance of quantum number m with respect to hydrogen atom ? 6,3,3

5 (*a*) A rigid rotator consists of two particles of mass m_1 and m_2 joined by a rigid rod of length, r. Based on classical considerations, show that the total energy of a rigid rotator is $L^2/2I$, where L is the angular momentum and I is the moment of inertia. How does this result differ from quantum mechanical result ?

(*b*) Define Hermitian operator. Show that $\frac{d^2}{dx^2}$ is a Hermitian operator.

(*c*) Under what conditions, the wave function Ψ is said to be an acceptable wave function ? What is the physical significance of Ψ^2 ? 6,3,3

Section B

6. (*a*) Given that the nuclear spin quantum number of $^{12}C_6$ is zero and that of $^1H_1$ is half :

(*i*) Calculate the nuclear angular momentum of these nuclei.

(*ii*) How many different energy states do these nuclei have in a magnetic field ?

(*iii*) Calculate the magnetic moment of $^1H_1$. Given : $g = 5.585$.

P.T.O.

(*b*) What are the characteristics of TMS which makes it useful as a reference in PMR spectrum ?

(*c*) Based on free electron model, calculate the wave number for the longest wavelength transition in pentadienyl radical. Given : C – C is 154 pm; C=C is 135 pm. 6,3,3

7. (*a*) A molecule AB_2 has the following infrared and Raman spectra :

$\bar{\nu}$ (cm^{-1})	Infra-red	Raman
519	Active	Active (polarized)
1151	Active	Active (polarized)
1361	Active	Active (depolarized)

Giving proper explanation arrive at the geometry of the molecule. Assign the wave numbers to specific vibrations.

(*b*) The vibrational wave number of the following molecules in their $v = 0$ states are : HCl : 2885 cm^{-1}; DCl : 1990 cm^{-1}; D_2 : 2990 cm^{-1} and HD : 3627 cm^{-1}. Using the concept of zero point energy calculate the energy change in kJ mol^{-1} of the reaction :

$$HCl + D_2 \rightarrow DCl + HD.$$

(*c*) Stokes and anti-Stokes lines in pure rotational Raman spectrum have similar intensities while Stokes lines are more intense than anti-Stokes lines in vibrational Raman spectrum. Explain. 6,3,3

8. (*a*) The low resolution NMR spectrum of $C_5H_{10}O_2$ exhibits three absorptions at δ values of 3.2, 2.1 and 1.2 with relative intensities 1 : 3 : 6 respectively. Predict the structure of the molecule giving reasons. Draw and explain the NMR spectrum expected under high resolution.

(*b*) Discuss the concept of natural line width of spectral line. It is quiet significant in case of ESR compared to that of electronic transition, explain.

(*c*) Sketch the ESR spectra of *p*-benzoquinone in low resolution and high resolution. 6,3,3

9. Write short notes on any *three* of the following :

(*a*) Larmor precession

(*b*) Effect of isotopic substitution on rotational spectrum.

(*c*) Variation theorem

(*d*) Spin-spin coupling 4×3