This question paper contains 4+2 printed pages]

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

S. No. of Question Paper : **813**

Unique Paper Code : **217605** **E**

Name of the Paper : **Physical Chemistry–V [CHHT-617]**

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

Semester : **VI**

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. Use of calculators is allowed but they cannot be shared. Logarithmic tables can be provided if required.

Attempt all parts of a question together.

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	9.109×10^{-31} kg
Nuclear Magneton	5.051×10^{-27} JT^{-1}
Bohr Magneton	9.275×10^{-24} JT^{-1}
Boltzmann Constant	1.38×10^{-23} JK^{-1}

P.T.O.

1. Attempt any *five* :

(*a*) Of which of the following operators is the function $e^{-x^2/2}$ an eigen function ?

$$\frac{d^2}{dx^2}, \frac{d}{dx} \text{ and } \frac{1}{x}\frac{d}{dx}.$$

(*b*) Write the Hamiltonian operator for Lithium atom explaining each term.

(*c*) Calculate :

$$\left[\hat{p}_y, \hat{x}\right].$$

What is the significance of commutation ?

(*d*) Bond length increases on removing an electron from N_2, but decreases on removing an electron from O_2. Explain.

(*e*) How would the microwave spectrum of HCl be affected if bond length was 10 times the actual value ?

(*f*) What are antistokes ? In order to increase the intensity of antistokes in Raman spectrum of a substance, should one heat or cool ? Give reason.

(*g*) Br_2 microwave inactive but is rotational Raman active. Why ?

(*h*) The center of esr spectrum of methyl radical occurs at 329.4 mT when spectrometer working at 9.23 GHz is used. Calculate the value of *g*. 5×3

Section A

2. (*a*) Normalise the function $x(a - x)$ over the range $0 \leq x \leq a$.

(*b*) For a particle confined to move in a box of length L, find the probability of finding the particle in the range $0 \leq x \leq L/4$ if it is in $n = 1$ and $n = 2$ states.

(*c*) Draw $R_{2,0}$, $R_{2,0}^2$ and $r^2R_{2,0}^2$ versues r for H atom. 4,6,2

3. (*a*) Naphthalene may be considered to be a rectangle of length 0.8 nm and breadth 0.4 nm. Using free electron model calculate the expected wave number of radiation required to give the excited state.

(*b*) Calculate the average distance of 2s electron from nucleus of hydrogen atom given :

$$\phi_{2s} = \left(\frac{1}{32\pi}\right)^{\frac{1}{2}} \left(\frac{1}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{r}{a_0}\right) \frac{-r}{e^{2a0}} \quad \text{and} \quad \int_0^\infty r^n e^{-ar}\, dr = \frac{n!}{a^{(n+1)}}$$

(*c*) State and explain the Pauli's Exclusion Principle. 5,5,2

4. (*a*) The average energy of H atom calculated on the basis of trial function :

$$\psi = e^{-\alpha x} \text{ is } \langle E \rangle = \frac{h^2 \alpha^2}{8\pi^2 m} - \frac{e^2 \alpha}{4\pi \epsilon_0}$$

where α is a variable parameter. Using variation method, calculate the ground state energy of the H atom. Is this energy greater, lesser or equal to the true energy ? Give reason for your answer.

(*b*) Show that two eigen functions of a Hermitian operator having different eigen values are orthogonal to each other.

(*c*) Calculate expectation value of momentum of a particle described by the function e^{-ikx} where x can extend from 0 to 1. 6,3,3

5. (*a*) The wave functions for Butadiene are :

$$\psi_1 = 0.37\Phi_1 + 0.61\Phi_2 + 0.61\Phi_3 + 0.37\Phi_4$$

$$\psi_2 = 0.61\Phi_1 + 0.37\Phi_2 - 0.37\Phi_3 - 0.61\Phi_4$$

$$\psi_3 = 0.61\Phi_1 - 0.37\Phi_2 - 0.37\Phi_3 + 0.61\Phi_4$$

$$\psi_4 = 0.37\Phi_1 - 0.61\Phi_2 + 0.61\Phi_3 - 0.37\Phi_4$$

Where Φ_i represent the p_z orbital of the ith carbon atom and $E_1 < E_2 < E_3 < E_4$. Calculate the bond order between C_1 and C_2 and the charge density on C_3. Give a schematic sketch of the four wave functions.

(*b*) Draw energy level diagram to explain bonding in HF molecule and write the wave functions of the molecular orbitals.

(*c*) Write the simplest trial wave function for H_2 molecule using VBT and MOT. Compare them. 6,2,4

Section B

6. (*a*) Derive the expression for V_{max} and spectroscopic dissociation energy.

(*b*) Intensities for Stokes and antiStokes lines are comparable in rotational Raman spectra but in vibrational Raman Stokes lines are more intense. Explain.

(*c*) The infrared spectrum of HCl shows the fundamental and first overtone at 2886 and 5668 cm^{-1} respectively. Calculate the fundamental vibrational frequency and the anharmonicity constant. 4,3,5

7. (*a*) How will the microwave spectrum of HCl^{35} be affected if Cl^{35} was replaced by Cl^{37} ? Illustrate your answer both qualitatively and quantitatively.

(*b*) The microwave spectrum of DI^{127} shows a series of equally spaced lines, spacing between them being 6.507 cm^{-1}. Calculate rotational constant B, moment of inertia I and bond length *r*.

(*c*) IR signal for stretching of C–C bond is at lower frequency than C = C. True or false ? Give reason. 5,5,2

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

$$r'_{eq} = r''_{eq}, r'_{eq} > r''_{eq} \text{ and } r'_{eq} >> r''_{eq}.$$

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

P.T.O.

(*b*) The nuclear *g* factor for F^{19} nucleus is 5.256 (spin 1/2). Calculate the resonance frequency when it is placed in a magnetic field of strength 1 Tesla. Also calculate the relative populations of the two spin states at 298 K.

(*c*) Explain the esr spectrum of the 1,4 benzosemiquinone radical anion. 4,4,4

9. Write short notes on any *three* of the following : 3×4

(*a*) Fluorescence

(*b*) Factors controlling width of spectral transitions

(*c*) Larmor precession

(*d*) Bohr correspondence principle.