[This question paper contains 8 printed pages.]

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

Sr. No. of Question Paper : 1113 **I**

Unique Paper Code : 2172013503

Name of the Paper : Quantum Chemistry and Covalent Bonding

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

Semester : V

Duration : 3 Hours Maximum Marks : 90

Instructions for Candidates

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

2. Attempt only **six** questions out of **eight**.

3. Use of scientific calculators and Logarithmic tables is allowed.

4. Attempt all parts of a question together.

Physical Constants

Planck 's constant	6.626×10^{-34} J s
Velocity of Light	3×10^{8} ms^{-1}
Avogadro's Number	6.022×10^{23} mol^{-1}
Mass of Electron	9.1×10^{-31} kg
Boltzmann Constant	1.38×10^{-23} J K^{-1}

1. (a) A particle of mass m, in a one-dimensional box of length a can be represented by the function, $\psi(x) = \sin\frac{n\pi x}{a}$ (n=1,2,3...). Normalize the given function $\psi(x)$ and find whether it is an eigen function of (i) p_x (ii) p_x^2.

(b) Write four properties of a function to make it acceptable as a solution of Schrodinger equation. Determine whether the following functions are acceptable or not acceptable as state functions over the interval indicated, giving appropriate reasons.

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

(c) Evaluate the commutator $[\widehat{L_x}, \widehat{L_y}]$ where $\widehat{L_x}$ and $\widehat{L_y}$, are the angular momentum operators along the x and y-direction respectively. (5,5,5)

2. (a) Are the following functions eigen functions of the operator $\widehat{\frac{d^2}{dx^2}}$? If so, give the eigen value.

(i) $f(x) = \exp\left(-\frac{x^2}{2}\right)$

(ii) $\cos 2x$

(b) Consider a particle of mass 'm' in a cubic box of edge length 'L'. What is the degeneracy of the level that has energy three times the lowest energy ? Write the mathematical expressions for the degenerate wavefunctions.

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

(i) φ_{2s}^{A} and $\varphi_{2p_z}^{B}$

(ii) φ_{1s}^{A} and φ_{2s}^{B}

(iii) $\varphi_{2p_x}^{A}$ and φ_{2s}^{B} (5,5,5)

3. (a) Write the expression for the Hamiltonian operator for the helium atom explaining briefly all the terms involved. Simplify this expression using the Bom Oppenheimer approximation. Write the expression for the corresponding Schrodinger's equation.

(b) Evaluate the expectation value of the radius, (r), at which the electron in the ground state of Hydrogen atom (Z=1) is found. Given the wave function for this state is

$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}} \left(\frac{z}{a_0}\right)^{3/2} \exp\left(-\frac{zr}{a_0}\right)$ where a_0 is the Bohr radius and $\int_0^\infty r^n \exp(-ar)\, dr = \frac{n!}{a^{(n+1)}}$.

(c) Write the electronic configuration of H_2, H_2^+ and hypothetical H_2^- species using molecular orbital theory. Explain why He_2^+ exist whereas He_2 does not. (5,5,5)

4. (a) A diatomic molecule can be treated as a simple quantum mechanical oscillator. How is the simple Schrodinger Wave Equation (SWE) modified for this system? Show that

(i) $\exp(-\beta x^2)$ is a solution to this SWE and

(ii) $E = \frac{1}{4\pi}\sqrt{\frac{k}{\mu}}$, here k is the force constant and μ is the reduced mass)

(b) What is the degeneracy of each of the following energy levels of H atom?

(i) $\frac{-e^2}{72\pi\epsilon_0 a_0}$ (ii) $\frac{-e^2}{128\pi\epsilon_0 a_0}$

(c) Explain and calculate zero point energy (ZPE) of an electron in a one dimensional box of infinite height and 1 Å length. State the Bohr's Correspondence principle. (5,5,5)

5. (a) Show that the wave functions describing the Is atomic orbital and the 2s atomic orbital for the hydrogen atom are orthogonal. Given that

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

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

where a_0 is Bohr's radius and

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

(b) Set up the Hamiltonian operator for a particle oscillating about a mean position (a simple harmonic oscillator). Explain the significance of zero-point energy of a simple harmonic oscillator.

(c) Why the quantum number 'n' cannot be assigned a zero value while solving for the particle in a 1-D box? Give the units of ψ^2 for a particle in a 1-D box.

(5,5,5)

6. (a) A particle of mass m exists in a one-dimensional box of length L. Using the trial wave function $\psi_{trial} = Nx(L-x)$ 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 operators corresponding to $\hat{x}$ and $\hat{p}_x$ do not commute. Give the physical significance of your result.

(c) What do you understand by Hermitian operators? Prove that all the eigen values of Hermitian operators are real numbers. (5,5,5)

7. (a) Write the LCAO-MO trial wave function of H_2^+, using Molecular Orbital approach. Derive the expressions for molecular orbital wave functions corresponding to the bonding and anti-bonding energy levels of H_2^+.

(b) Plot the radial probability distribution functions for an electron in hydrogen atom where $n = 1$ and $n = 2$. Explain the plots briefly.

(c) Explain the significance of orthonormality principle giving relevant mathematical expressions.

(5,5,5)

8. Write short notes on **any three** :

(a) Postulates of Quantum Mechanics

(b) Pauli's Exclusion principle (quantum mechanical approach)

(c) Configuration Interaction

(d) Variation Theorem (5,5,5)