[This question paper contains 4 printed pages.]

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

Sr. No. of Question Paper : 5841 **K**

Unique Paper Code : 2172013503

Name of the Paper : QUANTUM CHEMISTRY AND COVALENT BONDING

Name of the Course : **B.Sc. (H) 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 any **six** questions out of **eight**.
3. Attempt all parts of a question together.
4. Use of scientific calculators and log tables is allowed.

Physical constants

Atomic mass unit	:	1.66×10^{-27} kg
Planck's constant	:	6.626×10^{-34} J s
Velocity of Light	:	3×10^{8} m s^{-1}
Boltzmann constant	:	1.381×10^{-23} J K^{-}
Mass of Electron	:	9.1×10^{-31} kg
Avogadro's number	:	6.022×10^{23} mol^{-}

Standard Integrals

$\int_0^{\infty} x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$ for $n > 1$

$\int_0^{\infty} e^{-\alpha x^2} dx = \left(\frac{\pi}{4\alpha}\right)^{1/2}$

$\int_0^{\infty} x^{2n} e^{-\alpha x^2} dx = \frac{1.3.5...(2n-1)}{2^{n+1}\alpha^n} \left(\frac{\pi}{\alpha}\right)^{1/2}$ for $n > 1$

P.T.O.

1. (a) (i) Write the properties of a function that make it acceptable as a wave function solution of Schrodinger wave equation.

   (ii) A particle in a one-dimensional box moving under a constant potential in a space has no boundaries. Will the energy be quantized in such a case? Explain.

   (b) Apply the variation theorem to the wave function $\psi(x) = x(L^2 - x^2)$, where $0 \leq x \leq L$ to a particle of mass m in a one-dimensional box and estimate the ground state energy. Is the wave function a suitable choice for a particle in a one-dimensional box problem? Explain.

   (c) Naphthalene may be considered to be a rectangle of length 0.8 nm and breadth 0.4 nm. Write the wave function corresponding to the highest occupied level for naphthalene. Using free electron model calculate the energy required by the electron to go to the first excited state.

(5,5,5)

2. (a) A particle of mass '*m*', attached to a flexible spring, undergoes simple harmonic oscillations.

   (i) Give the expression for energy level based on quantum mechanical treatment.

   (ii) What is the energy difference (ΔE) between two successive energy levels?

   (iii) What is the zero point energy of the system? Explain its significance.

   (b) Given that the ground state normalized wave function for the harmonic oscillator is

$$\psi_0 = \left(\frac{\sqrt{\alpha}}{\pi^{1/2}}\right)^{1/2} \exp\left(-\frac{\alpha x^2}{2}\right)$$

   (i) Determine the value of x at which the ground-state function of the harmonic oscillator exhibits the maximum. Predict the value of x at which the probability of finding the particle is maximum. Compare this value with that predicted by the classical treatment.

   (ii) Evaluate the expectation value of kinetic energy for harmonic oscillator in ground state.

(5,5,5)

3. (a) What are Hermitian operators? Show that the eigenvalues of a Hermitian operator are always real.

   (b) Determine whether the following functions are eigen functions of the operator, $\hat{L}_z = -i\hbar\frac{d}{d\phi}$. Evaluate the eigen values if applicable.

   (i) $\psi = \exp(im\phi)$

   (ii) $\psi = 6\cos m\phi$

(c) Find the commutator of position operator ($\hat{x}$) and momentum operator ($\hat{p}_x$). What is its physical significance? State the name of the principle it verifies.

(5,5,5)

4. (a) Write the simplest trial wave functions for H_2 molecule using VBT and MOT. Compare the merits and demerits of the above two methods.

(b) Calculate the bond order of the following molecular ions and compare the strength of their bonds with their respective neutral molecules.

Be_2^+, Be_2^-, F_2^+, F_2^-

(c) Explain the molecular orbital formation in the LiH molecule using the LCAO approach with the help of MO diagram. Discuss the overlap of atomic orbitals involved and indicate which combinations lead to bonding and antibonding orbitals.

(5,5,5)

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 treatment, 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? Write the Schrodinger equation for the rigid rotator in spherical polar co-ordinates.

(b) Normalize the given wave function for Hydrogen atom:

$\Phi = A \exp\,(im\phi)$

What is the significance of quantum number 'm' with respect to hydrogen atom?

(c) Show that for hydrogen atom, the wave functions for 1s and 2s orbitals are orthogonal.

Given: $\psi_{1,0,0} = 2\left(\frac{1}{a_0}\right)^{3/2} \exp\left(\frac{-r}{a_0}\right).\frac{1}{\sqrt{4\pi}}$

and $\psi_{2,0,0} = \left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right) \exp\left(\frac{-r}{2a_0}\right).\frac{1}{\sqrt{4\pi}}$

(5,5,5)

6. (a) Derive the following expression using LCAO-MO treatment for H_2^+, starting from trial wavefunction $\psi = C_1 1s_A + C_2 1s_B$:

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

(Here α is the Coulomb integral, β is the resonance integral and S is the overlap integral)

(b) What are the essential conditions for atomic orbitals to form bonds in homonuclear diatomic molecules? Which of the following atomic orbitals will overlap to form molecular orbitals in a homonuclear diatomic molecule?

(i) 1s and 2s
(ii) $2p_x$ and $3p_z$
(iii) 3s and $3p_z$

(c) Verify that the wave functions of a particle of mass '*m*' in a one-dimensional box of length '*a*' are orthonormal.

(5,5,5)

7. (a) Calculate the average distance of 2s electrons from the nucleus of hydrogen atom. The normalised wave function for 2s electron in hydrogen atom is

$$\psi_{2,0,0} = \left(\frac{1}{2a_0}\right)^{3/2}\left(2-\frac{r}{a_0}\right)\exp\left(\frac{-r}{2a_0}\right)\cdot\frac{1}{\sqrt{4\pi}}$$

(b) How does the study of particle in a three-dimensional box lead to the concept of degeneracy. Show with the help of energy level diagram.

(c) State the Born-Oppenheimer approximation. Write the Hamiltonian operator for Li atom after applying the Born-Oppenheimer approximation explaining all the terms.

(5,5,5)

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

(a) Configuration interaction

(b) Zeeman and anomalous Zeeman effect

(c) Bonding and antibonding molecular orbitals

(d) Bohr's Correspondance Principle

(5,5,5)