



ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27
M.Sc. CHEMISTRY - I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2021
(Examination conducted in January-March 2022)

CH 7318/CH7321 - PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY)

Time- 2 ½ hrs

Max Marks-70

This question paper contains 2 printed pages and 3 parts

PART-A

Answer any **SIX** of the following questions

6x2=12

1. What is Born-Oppenheimer approximation?
2. Which of the following functions are eigen functions of $\frac{d^2}{dx^2}$? (i) $6\cos 4x$ (ii) $5x^2$ (iii) $3e^{-5x}$. In cases where the function is eigen function, state the eigen value.
3. Given the energy levels of the cyclobutadiene molecule to be $\alpha+2\beta$, α (doubly degenerate) and $\alpha-2\beta$, calculate the delocalization energy and predict the stability of the molecule. The ground state π electron energy of ethylene is $(2\alpha+2\beta)$.
4. Give two examples of quantum mechanical tunnelling.
5. The wave function for H_2 molecule arrived at in molecular orbital theory is $\Psi = [\frac{1}{2(1+S)}][1S_A(1) 1S_A(2)+ 1S_B(1) 1S_B(2)+ 1S_A(1) 1S_B(2)+ 1S_A(2) 1S_B(1)]$. Why is this function unrealistic?
6. Verify the uncertainty relation with respect to the motion of a particle in a 1D box of length 'L'.
7. Give the HMO secular determinant of butadiene molecule.
8. Plot the angular momentum vector \vec{j} and its possible z-component vectors, \vec{j}_z for $j = 3/2$. What is the magnitude of \vec{j} ?

PART-B

Answer any **FOUR** of the following questions

4x12=48

9. (a) For a particle moving on the surface of a sphere the Hamiltonian is
$$\hat{H} = \frac{-\hbar^2}{8\pi^2mr^2} \left[\frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial\phi^2} \right]$$
 Set up the Schrodinger equation for a rigid rotor using the above equation and separate the variables to arrive at the θ and ϕ equations. Solve the ϕ equation to get the normalized eigen functions.
(b) Set up the Schrodinger equation for a particle confined in a 1D potential well. Solve the equation to get the wave functions and expression for energy (No normalization required).
(c) Compute the first three vibrational energies of a simple harmonic oscillator and find the energy difference ΔE between successive energy levels. (5+4+3)
10. (a) Prove that the eigen values of a Hermitian operator are real. Examine if $\frac{d^2}{dx^2}$ is Hermitian with the functions $\psi = e^{ix}$ and $\phi = \sin 2x$.
(b) What are linear operators? Verify if the operator ∇^2 is linear.
(c) State the postulates of quantum mechanics. (5+3+4)
11. (a) The normalized radial function for H-like atom is given by

$$R_{nl}(\rho) = N_{nl} \cdot \rho^l \cdot e^{-\rho/2} \cdot L_{n+l}^{2l+1}(\rho)$$

where N_{nl} , the normalization factor = $-\sqrt{\left(\frac{\rho}{r}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}$; $\rho = \frac{2Zr}{na_0}$; a_0 is the Bohr radius;

$L_{n+l}^{2l+1}(\rho)$ is the associated Laguerre polynomial of order $2l+1$; n and l are the quantum numbers. The polynomials are derived from the generating function $L_k^p(\rho) = \frac{d^p}{d\rho^p} \left[e^\rho \cdot \frac{d^k}{d\rho^k} (\rho^k \cdot e^{-\rho}) \right]$, where $k = n+l$ and $p = 2l+1$. Work out the normalized radial functions $R_{1,0}$, $R_{2,0}$, and $R_{2,1}$. What is the degree of polynomial for each of the functions?

(b) State variation theorem. Using the trial wave function $\psi = Nx(L^2-x^2)$ to a particle in a one-dimensional box with infinite potential walls, calculate the ground state energy. What is the percentage error in energy in comparison to the energy calculated by solving the Schrodinger equation without using approximation method? (6+6)

12. (a) Show how the energy of the He atom in its ground state is obtained using variation method.

(b) Derive a general expression to calculate the first order correction term for the energy of the system.

(c) Evaluate $[L^2, L_z]$ and comment on the physical significance of the result (4+4+4)

13. (a) Arrive at the expression for the energies of the bonding and the antibonding molecular orbitals of H_2^+ ion in terms of H_{AA} , H_{BB} and S using the LCAO-MO approximation.

(b) Discuss the Heitler-London valence bond treatment of H_2 molecule. (6+6)

14. (a)(i) Using the Huckel molecular orbital theory, set up the secular determinant and arrive at the normalized wave functions and energy levels of the π - molecular orbitals for the allyl system. Draw the HMOs and indicate the number of nodes in each case. Calculate the delocalization energies of the allyl carbonium ion, allyl radical and allyl carbanion and predict their order of stability. The ground state π electron energy of ethylene is $(2\alpha+2\beta)$.

(b) Show that the ladder operator, \hat{j}_+ , has no effect on the eigen value of \hat{j}^2 but it increases the eigen value of the operator \hat{j}_z by $\frac{h}{2\pi}$. (7+5)

PART-C

Answer any **TWO** of the following questions

2x5=10

15. (a) What are the term symbols for the $1s^2 2s^2 2p^1$ electronic configuration of boron

(b) Calculate the first four energy levels of a particle in a 3D potential well of dimensions $2L_x = 2L_y = L_z$. Indicate the degenerate states if any. (2+3)

16. (a) Write the antisymmetric wave function for Be atom in the Slater determinant form.

(b) Calculate the effective nuclear charge for 3s and 2p electrons of nitrogen (Atomic no.= 6). (3+2)

17. (a) Solution to the secular determinant for benzene in HMO treatment are $x = \pm 2, \pm 1$ and ± 1 , where $x = \alpha - E/\beta$. Calculate the value of β if the resonance stabilization energy of benzene is 143.1 kJmol^{-1} .

(b) Evaluate $\left[\hat{x}^n, \frac{d^2}{dx^2} \right]$. (3+2)