Registration Number:

Date & Session:

ST. JOSEPH'S UNIVERSITY BENGALURU -27
M.Sc CHEMISTRY – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2023
(Examination conducted in November/December 2023)

CH 7322 : PHYSICAL CHEMISTRY-I (Quantum Chemistry)
(For current batch students only)

Time: 2 Hours **Max Marks: 50**

This paper contains 2 printed pages and 3 parts.

PART-A

Answer any **EIGHT** of the following questions **8x2=16**

1. A baseball (m=200g) is moving with a velocity of 3000cms^{-1}. If its position is located with an uncertainty of 500nm, what will be the uncertainty in its velocity? Comment on the result. [Planck's constant h = 6.625 x 10^{-34} J s].
2. Plot the angular momentum vector $\vec{J}$ and its possible z-component vectors, $\vec{J}_z$ for j = 5/2. What is the magnitude of $\vec{J}$?
3. Given $\hat{H}^0, \psi^0$ and E^0 as the Hamiltonian operator, wave function and energy of an unperturbed system, write the Schrodinger equation for the perturbed and unperturbed systems.
4. Construct all possible 2-electron wave functions for H_2 molecule using the LCAO MO with minimal basis set that are antisymmetric to electron exchange.
5. The Hermite polynomial is given by $H_n(y) = (-1)^n e^{y^2} \frac{d^n}{dy^n}(e^{-y^2})$. Evaluate $H_1(y)$ and $H_2(y)$.
6. Given the energy levels of benzene to be α+2β, α+β (two-fold degenerate), α-β (two-fold degenerate) and α-2β. Calculate the delocalization energy of benzene. The ground state π electron energy of ethylene is (2α+2β).
7. For the first two states (n=1 and n=2) find the values of the eigenfunctions of a particle in a box between -L/2 and +L/2 for x= -L/2, -L/4, and 0.
8. What is the probability of an electron found at a distance of r=0 and 3/2 a.u. from the nucleus of an H atom in the 1s state? (Given $\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$)
9. Evaluate the commutator $[\hat{L}_x, \hat{L}_y]$.
10. Which of the functions (i) Sin3x (ii) 3e^{-5x} are eigenfunctions of the momentum operator? State the eigen values.

PART-B

Answer any **TWO** of the following questions **2x12=24**

11. (a) For a particle rotating in a sphere the Hamiltonian is $\hat{H} = -\frac{h^2}{8\pi^2 mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$. 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.
(b) Starting from the quantum mechanical operator for linear momentum along x, arrive at the operators for the (i) kinetic energy along x (b) angular momentum along x.

(c) Legendre polynomials (|M|=0) for various values of l may be derived from the "generating function" $P_l(x) = \frac{1}{2^l \cdot l!} \cdot \frac{d^l}{dx^l}(x^2-1)^l$ where x=cosθ and l is an integer. Evaluate the polynomial for l=0,1 and 2. (5+3+4)

12. (a) An electron moving in a 1D box of length L is subjected to a perturbation by a uniform electric field E due to which its potential energy increases continuously as we move along the box. Find the first order correction to energy and the ground state eigen value by applying the perturbation theory. ($\int_0^{\pi} y\, sin^2 y\, dy = \frac{\pi^2}{4}$)

(b) show that the complex function $\psi = \frac{1}{\sqrt{2\pi}} e^{iM\phi}$ is an eigenfunction of $\widehat{H}$ and $\widehat{L}_z$ but the real function $\psi = \frac{1}{\sqrt{\pi}} sin\, M\phi$ is eigenfunction of $\widehat{H}$ only. What is the physical significance of the above result? (Given: $\widehat{H}$ = $-\frac{h^2}{8\pi^2 I}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right]$ and $L_z = -\frac{ih}{2\pi}\frac{d}{d\phi}$).

(c) E_1 and the doubly degenerate E_2 for the cyclopropenyl system are α+2β and α-β. Compare the stabilities of the cyclopropenyl cation, anion and radical. The ground state π electron energy of ethylene is (2α+2β). (5+4+3)

13. (a) Using the trial LCAO MO wave function $\Psi = a_1 1s_A + a_2 1s_B$, apply the linear variation method to obtain eigen values E_1 and E_2 of H_2^+ in terms of the atomic integrals. Plot E_1 and E_2 against R and comment on the nature of these curves.

(b) Employing the Huckel molecular orbital theory, get the π-MO's, the π-bond and delocalization energies, and the π-energy level diagram of the allyl system. Compare the stability of the allyl cation and allyl anion. (6+6)

PART-C

Answer any **TWO** of the following questions **2x5=10**

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

(b)Calculate the spacings between energy levels for

(i) an electron (mass= 9.1×10^{-30} kg) in a one-dimensional box of length 1.0Å and

(ii) a ball bearing (mass=1g) in a box of length 10cm.

Comment on the results. (2+3)

15. (a) Find the term symbols of an atom with the configuration $1s^2\, 2s^1 2p^1$

(b) Given the trial wave function $\frac{1}{\sqrt{2}}\phi_1 + \sqrt{\frac{3}{2}}\phi_2$, where ϕ_1 and ϕ_2 are orthonormal. Find the expectation values of the energies. (2+3)

16. (a) Show that the two MO's of H_2 given by $\Psi_{\pm} = \frac{1}{\sqrt{2(1 \pm s)}}[1s_A \pm 1s_B]$ are orthogonal.

(b) Solution to the secular determinant for benzene by HMO treatment are x=±2, ±1 and ±1, where x=α-E/β. Calculate the value of β if the resonance stabilization energy of benzene is 143.1kJmol^{-1}. (2+3)