Register No:

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ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.SC. CHEMISTRY: I SEMESTER
SEMESTER EXAMINATION – JANUARY 2021
OCH /CH7318: PHYSICAL CHEMISTRY-I (QUANTUM CHEMISTRY)

Time: **2 hours and 30 minutes** **Max Marks:70**

This question paper contains 2 pages and 3 parts

PART-A

Answer any **SIX** of the following questions **6x2=12**

1. If the position of the electron in the hydrogen atom could be determined with an accuracy of 0.01 nm, what would be the uncertainty in its momentum? [Planck's constant h = 6.625 x 10^{-34} Js]
2. Plot the angular momentum vector $\vec{J}$ and its possible z-component vectors, $\vec{J}_z$ for j = 2. What is the magnitude of $\vec{J}$?
3. The Legendre polynomial (when |M| = 0) for various values of l may be derived from the generating function given by $P_l(x) = \frac{1}{2^l \cdot l!}\frac{d^l}{dx^l}(x^2-1)^l$. Derive the first two polynomials as functions of cosθ taking x = cosθ.
4. Plot the wave functions for the ground state and the first excited state of a harmonic oscillator. Mark the nodes, if any, in the functions.
5. Write the antisymmetric wave function for Be atom in the Slater determinant form.
6. Construct all possible 2-electron wave functions for H_2 molecule that are antisymmetric with respect to electron exchange.
7. Write the Hamiltonian for Helium atom. Identity the perturbation component of the operator.
8. State the postulate of quantum mechanics concerning operators for each of the physical quantities in classical mechanics with two examples.

PART-B

Answer any **FOUR** of the following questions **4x12=48**

9. (a) What are Hermitian operators? Prove that the eigen functions of a Hermitian operator corresponding to different eigen values are orthogonal.
(b) Given the potential energy of a harmonic oscillator, $V=2\pi^2\nu^2mx^2$, set up the Schrodinger equation for a harmonic oscillator and find its asymptotic solution when x is large.
(c) From the wave function of a particle wave represented by $\psi=\exp(\pm 2\pi ix/\lambda)$, derive the linear momentum operator, $\hat{p}_x$. (5+4+3)

10. (a) Prove that the function $\psi=\frac{1}{\sqrt{2\pi}}e^{iM\varphi}$ is an eigen function of the Hamiltonian operator $\hat{H}$ as well as the operator $\hat{L}_z$, for a particle in a ring. Given $\hat{H}=\frac{-h^2}{8\pi^2 I}\frac{\partial^2}{\partial\phi^2}$ and $\hat{L}_z=\frac{-ih}{2\pi}\frac{\partial}{\partial\phi}$. Give the eigen values.
(b) Set up the Schrodinger equation for a particle confined in a 1D potential well. Solve the equation to get the normalized wave functions and expression for energy. Using these solutions arrive at the energy and wave function of a particle in a cubic potential well. (4+8)

11. (a) Plot R against r, and radial distribution functions, for 1s and 2p orbitals of H atom.
(b) Construct the antisymmetric spin-orbital functions for the singlet and triplet states of excited Helium atom using the following orbital and spin functions.

Orbital functions: $\frac{1}{\sqrt{2}}$ [1s(1) 2s(2) + 1s(2) 2s(1)] , $\frac{1}{\sqrt{2}}$ [1s(1) 2s(2) - 1s(2) 2s(1)]

Spin functions: $\alpha(1)\ \alpha(2)$, $\beta(1)\ \beta(2)$, $\frac{1}{\sqrt{2}}$ [$\alpha(1)\ \beta(2)+\ \alpha(2)\beta(1)$], $\frac{1}{\sqrt{2}}$ [$\alpha(1)\ \beta(2)-\ \alpha(2)\beta(1)$]

(c) An electron moving in a 1D box of length L is subjected to a perturbation by a uniform electric field Є 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. ($\int_0^{\pi} y\, sin^2 y\, dy = \frac{\pi^2}{4}$).

(4+3+5)

12. (a) State and prove variation theorem.
(b) 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 butadiene. Draw the four HMOs and indicate the number of nodes in each case. (4+8)

13. (a) Discuss the Heitler-London valence bond treatment of H_2 molecule
(b) $\hat{J}^2$ and $\hat{J}_z$ are operators for angular momentum and its z-component with eigen values kj and k_m respectively and a common set of eigen functions $\varphi_{j,m}$. Show that
(i) $k_j \geq k_m^2$
(ii) While the operator $\hat{J}_+$ does not alter the eigen value of $\hat{J}^2$, it increases the eigen value of the operator $\hat{J}_z$ by $\frac{h}{2\pi}$. (7+5)

14. (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^+. Plot E_1 and E_2 against R and comment on the nature of these curves.
(b) Evaluate the commutator $[\hat{L}_x, \hat{L}_y]$. (8+4)

PART-C

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

15. (a) Find the term symbols of an atom with the configuration $1s^2\ 2s^2 2p^1\ 3d^1$.
(b) Calculate the effective nuclear charge for the 3d electrons of iron (Z= 26) using Slater's rules. (3+2)

16. (a) Given the energy levels of the cyclopropenyl system to be α+2β and α-β (doubly degenerate) show that the stability order in this system is cation> radical> anion. The ground state π electron energy of ethylene is (2α+2β).
(b) The wave function for H_2 molecule arrived at in molecular orbital theory is
$\psi(1s) = [\frac{1}{2(1+s)}][1S_A(1)\ 1S_A(2) + 1S_B(1)\ 1S_B(2) + 1S_A(1)\ 1S_B(2) + 1S_A(2)\ 1S_B(1)]$.
Why is this function unrealistic? (3+2)

17. (a) For a particle in a 3-dimensional box with $L_x = L_y = L_z/2$, write the expression for the energy of the particle. Find a pair of states that are accidentally degenerate.
(b) The following are the eigen functions of the Hydrogen atom in atomic units (a.u.). Identify n, l, m associated with the functions by inspection and assign orbital designations to these functions.
(i) $\psi = \frac{1}{\sqrt{\pi}} e^{-r}$ (ii) $\psi = \frac{1}{4\sqrt{2}} r e^{-r/2} \cos\theta$ (3+2)

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