Registration Number:

Date & session:

ST.JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc (CHEMISTRY) – I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2022
(Examination conducted in December 2022)
CH 7321 – PHYSICAL CHEMISTRY I (QUANTUM CHEMISTRY)

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

This paper contains 2 printed pages and 3 parts

PART-A

Answer any EIGHT of the following questions **(2x8=16marks)**

1. Obtain an expression for $\hat{p}_x$ from the electronic wave function, $\psi = Ae^{\pm\frac{2\pi ix}{\lambda}}$.
2. Show that the function $\psi_1 = \sqrt{\frac{1}{\pi}}\cos nx$ and $\psi_2 = \sqrt{\frac{1}{\pi}}\sin nx$ are orthogonal to each other in the interval 0 to 2π.
3. Calculate the de Broglie wavelength of a particle of mass 1x 10^{-28} kg moving with a velocity of 1x10^{9} ms^{-1} (h= 6.626 x 10^{-34} Js).
4. α and β are the spin states of an electron. For a pair of electrons, build the four possible combined spin states that are symmetric or antisymmetric.
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. Sketch $r^2 R_{n,l}{}^2(r)$ against r for 3s and 2p orbitals of H atom.
7. Write the Hamiltonian for He atom. Identify the perturbation component of the operator.
8. Evaluate the commutator, $\left[L_y^2, L_z\right] = i\hbar\left[L_y L_x + L_x L_y\right]$.
9. Plot the angular momentum vector $\vec{j}$ and its possible z-component vectors $\vec{j}_z$ for j=2. What is the magnitude of $\vec{j}$?
10. Draw the π-electron energy distribution of cyclopropenyl anion and cyclopropenyl radical system in the energy levels α+2β, α-β and α-β and predict the system that would be more stable. The ground state π electron energy of ethylene is (2α+2β).

PART-B

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

11. a) Show that the eigenfunctions belonging to different eigen values of a Hermitian operator are mutually orthogonal.
    b) For a particle rotating in a sphere the Hamiltonian is
    $\hat{H} = -\frac{h^2}{8\pi^2 mr^2}\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]$. 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.

c) Determine the energy eigen value of H-atom corresponding to the radial function $R_{1,0}$ (r) in atomic units using the eigen value equation given below. Compare the result obtained with the Bohr's energy for 1s orbital of H atom.

$$\left[-\frac{h^2}{8\pi^2 m}\left\{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)-\frac{l(l+1)}{r^2}\right\}-\frac{Ze^2}{(4\pi\varepsilon_0)r}\right]R_{n,l}=ER_{n,l},\ R_{1,0}(r)=2e^{-r}a.u. \qquad (3+6+3)$$

12. a) Using Huckel molecular orbital theory, find the π-MO wave functions, the energy levels and resonance stabilization energies for cyclobutadiene system. Based on these results explain why this molecule is unstable.
    b) Derive a general expression to calculate the first order correction to energy in perturbation theory. (8+4)

13. a) 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?
    b) Discuss the Heitler-London valence bond treatment of H_2 molecule. (4+8)

PART-C

Answer any TWO of the following questions (2x5=10marks)

14. a) Show that the function $\psi = e^{i(k_1x+k_2y+k_3z)}$ is an eigenfunction for the operator $-\frac{h^2}{4\pi^2}\nabla^2$.
    b) Evaluate the commutator operator $\left[\hat{p}_x, \hat{x}^n\right]$. (3+2)

15. a) For a particle in n=3 state, in a one dimensional potential well of length L, find the probability that the particle is in the region $0 \leq x \leq L/4$.
    b) Identify the term symbols of an atom with the configuration $1s^2\ 2s^2 2p3d$. (2+3)

16. a) Give the secular equations for benzene using HMO theory.
    b) Calculate the effective nuclear charge of i) 1s electron and ii) 2p electron of Ne (Z=10). (3+2)

Some relevant formulas

$$e^{\pm ikx} = \cos kx \pm i \sin kx$$
$$e^{ikx} + e^{-ikx} = 2\cos kx$$
$$e^{ikx} - e^{-ikx} = 2i \sin kx$$

$$2\sin^2 x = \cos 2x$$
$$\int \sin^2 x dx = \frac{1}{2}x - \frac{1}{4}\sin 2x$$
$$\int \sin x.\cos x.dx = \frac{1}{2}\sin^2 x$$