Reg. No.: ____________________

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY, I SEMESTER
SEMESTER EXAMINATION: OCTOBER 2019
CH-7318 - PHYSICAL CHEMISTRY I (QUANTUM CHEMISTRY)

Time: 2½ hours **Max. Marks:** 70

This paper contains ***two*** *printed pages and* ***three*** *parts A, B and C*

PART-A

Answer any **SIX** of the following: 6 x 2 = 12 marks

1. The position of the electron in hydrogen atom is determined with an accuracy of 0.001 nm. What is the uncertainty in the linear momentum of the electron? (h = 6.62 x10^{-34} Js)
2. Given $\hat{A} = x$ and $\hat{B} = \frac{d}{dx}$, find $[\hat{A}, \hat{B}]$.
3. For a particle moving under no potential barrier, give (i) Hamiltonian operator; (ii) expression for the wavelength.
4. Calculate the spacing between E_1 and E_2 energy levels of a particle of mass 10^{-30} kg in a one-dimensional box of 0.1 nm length.
5. What is Born-Oppenheimer approximation?
6. Distinguish between π-electron bonding energy and delocalization energy.
7. Give the coupled representation of angular momenta of two electrons.
8. Write the eigen value equations for (i) orbital motion; (ii) spin of an electron.

PART-B

Answer any **FOUR** of the following: 4 x 12 =48 marks

9. (a) Show that (i) eigenvalues of a Hermitian operator are real; (ii) eigen functions of a Hermitian operator corresponding to different eigen values are orthogonal.
   (b) Arrive at the time-independent Schrodinger wave equation from the equation of a standing wave. Give any three properties of an acceptable wave function. (6+6)
10. (a) For H atom, calculate spherical harmonics and radial functions when n = 1, l = 0, M = 0; and n = 2, l = 0, M = 0. Using these arrive at the wave functions, ψ_{100} and ψ_{200}.
    (b) The wave functions obtained by solving Schrodinger equation for simple harmonic oscillator are $\psi = NH_n(y)\exp\left(-\frac{y^2}{2}\right)$, where n = 0,1,2 ....; $y = \sqrt{\beta}x$; $\beta = \frac{4\pi^2 \nu m}{h}$ and $H(y) = (-1)\exp(y^2)\frac{d^n}{dy^n}\exp(-y^2)$. Evaluate the first four wave functions and sketch the first two wave functions and their squares. (6+6)
11. (a) Explain the need for approximate methods to solve Schrodinger equation in most cases of interest to chemistry. State and prove variation theorem.
    (b) Applying Heitler-London theory for hydrogen molecule, derive the symmetric and antisymmetric orbital functions. (6+6)

12. (a) Show that (i) $\hat{J}_+$commutes with $\hat{J}^2$ but not with $\hat{J}_z$; (ii) $\hat{J}_-$ lowers the eigen value of $\hat{J}_z$ from k_m to $(k_m - \hbar)$.
(b) Using HMO theory, arrive at the allowed energy levels for cyclopropenyl system. Calculate (i) total π-electron energies; (ii) delocalization energies of cyclopropenyl cation and anion. (6+6)

13. (a) Set up the Schrodinger equation for a particle moving on a sphere. Separate the variables to arrive at the θ and ϕ- equations.
(b) The roots of Huckel secular determinant for butadiene are x = 1.618, –1.618, 0.618, and –0.618. Find the four HMOs of butadiene.
(c) Briefly discuss the extended Huckel theory. (4+5+3)

14. (a) Prove that for the ground state of H_2^+ ion the orbital energies are

$$E_1 = (H_{AA}+H_{AB})/(1+S) \text{ and } E_2 = (H_{AA}-H_{AB})/(1-S).$$

(b) Explain SCF method for the determination of wave functions and energy of many electron atoms. (6+6)

PART-C

Answer any **TWO** of the following: 2 x 5 = 10 marks

15. (a) Calculate the effective nuclear charge for 3s and 3p electrons of sulphur.
(b) Give the Slater determinant for the ground state of Be atom. (3+2)

16. (a) Calculate the values of J associated with the term symbol ^3D.
(b) Arrange the following in the increasing order of energy. Give reasons.
$^1S_0$, $^3S_1$, $^3P_0$, $^3P_1$, $^3P_2$ and $^1D_2$ (2+3)

17. (a) β-Carotene, a conjugated polyene, has maximum absorption of light at 480 nm. If this absorption corresponds to an n = 11 to n = 12 transition assuming electron in a in a 1D box model, what is the length of this molecule?
(b) An electron is confined in a cubic 3D potential well having dimensions Lx = Ly = Lz = 1 x 10^{-15} m. Calculate the energy of the particle in the (2,1,1) state. What happens to this energy if the length of the box along x-axis is changed to 1.5 x 10^{-15} m?
(mass of electron = 9.1 x 10^{-31}kg, h = 6.62 x 10^{-34}Js, c = 3 x 10^8 ms^{-1}) (3+2)
