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

Time: 2 ½ hours   **Max. Marks: 70**

*This question paper has **two** printed pages and **three** parts*

PART A

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

1. Position and linear momentum of a particle was measured simultaneously. If the uncertainty in position was 100 nm, calculate the minimum uncertainty in linear momentum. (Planck's constant, $h = 6.626 \times 10^{-34}$ Js)
2. Plot R(r) *vs* r curves for 1s, 2s and 3p orbitals of hydrogen atom.
3. State variation theorem.
4. Write the Slater determinant for C (atomic no = 6) in diagonalized form.
5. Give the generalized quantum mechanical definition of angular momentum.
6. Explain Born-Oppenheimer approximation qualitatively (without mathematical details).
7. What is the fundamental difference between molecular orbital theory and valence bond theory of chemical bonding?
8. The energies of π-MOs of cyclobutadiene are $\alpha+2\beta$, α, α and $\alpha-2\beta$. If the energy of the bonding π-MO of ethylene is $\alpha+\beta$, calculate the delocalization energy of cyclobutadiene.

PART B

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

9. a) Show that the eigen functions of a Hermitian operator are orthogonal to each other.
   b) What is the physical significance of the quantum mechanical state function, ψ? Based on this significance, state the conditions for ψ to be well-behaved.
   c) State the postulates of quantum mechanics. Show that the time-dependent Schrödinger equation is not needed to get the energy of the system, provided the state functions are chosen to be stationary functions.   (3+3+6)

10. a) The solutions of Schrödinger equation for a particle of mass m in a 1D-potential well of length L are $\psi = \sqrt{2/L}\sin(n\pi x/L)$ and $E = n^2 h^2/8mL^2$, where $n = 1, 2, 3, ...$ Solve the Schrödinger equation for the same particle in a 3D-potential well of lengths L_x, L_y and L_z along x, y and z respectively to get normalized wave functions and energy of the particle. Plot (to scale) the first six energy levels when $L_x = L_y = L_z$. Indicate degeneracies where applicable.
    b) Given the potential energy of a harmonic oscillator, $V = 2\pi^2 \nu^2 m x^2$, set up the Schrödinger equation for a particle of mass m executing harmonic oscillation along x. Show that the solutions for this equation are $\psi = NH_n(y)\exp(-y^2/2)$, where $H_n(y)$ is Hermite polynomial; $y = \sqrt{\beta}x$ and $\beta = 4\pi^2 \nu m/h$.   (6+6)

11. a) Evaluate the spherical harmonics, $\psi_{\ell,M}(\theta,\phi)$, for $\ell = 0$, M = 0; and $\ell = 1$, M = −1.
    b) The solutions of the ϕ, θ and r – equations of H-like atoms are:
    $$F(\phi) = N_1 exp(iM\phi); \quad P(\theta) = N_2(1/2^l \cdot l!)(1 - cos^2\theta)^{\frac{|M|}{2}} \frac{d^{(l+|M|)}}{d(cos\theta)^{(l+|M|)}}(cos^2\theta - 1)^l;$$
    $$R(r) = N_3\, \rho^l \exp(-\rho/2)\frac{d^{(2l+1)}}{d\rho^{(2l+1)}}\left\{\exp(\rho)\frac{d^{(n+l)}}{d\rho^{(n+l)}}[\rho^{(n+l)}\exp(-\rho)]\right\}, \text{ where } \rho = \frac{2Zr}{na_0}.$$
    Arrive at the allowed values of the quantum numbers, $n, l\ and\ M$ and the relationships between these quantum numbers.

c) For a general system, whose Hamiltonian is $\hat{H}_0 + \lambda\hat{H}'$, where $\hat{H}'$ is the perturbation operator, derive the expression for the first order correction term in energy. (4+4+4)

12. a) Employing Hückel molecular orbital theory, get the π-MOs and the π-energy level diagram of allyl system. Show that the allyl cation and allyl anion are equally stable.
b) Describe, in brief, Hartree's self-consistent field (SCF) method for multielectron atoms. How does Hartree-Fock SCF method improve the above method? (6+6)

13. a) Given $k_j \geq k_m^2$; $\hat{J}^2(\hat{J}_{+/-}\phi) = k_j(\hat{J}_{+/-}\phi)$; $\hat{J}_z(\hat{J}_{+/-}\phi) = (k_m \pm \hbar)(\hat{J}_{+/-}\phi)$, where k_j and k_m are the eigen values of $\hat{J}^2$ and $\hat{J}_z$ respectively, arrive at the eigen values of the operators $\hat{J}^2$ and $\hat{J}_Z$ when the nature of the eigen functions, ϕ, are not known.
b) Find the Russel-Saunders term symbols for the excited states of Be with the electronic configuration $1s^2 2s^1 2p^1$.
c) Taking the trial MO function for H_2^+ to be a linear combination of two H-1s functions and employing molecular orbital theory, arrive at the secular equations. (Need not solve the secular equations) (4+4+4)

14. a) Build the antisymmetric MO spin-orbital functions of the excited state of H_2 molecule.
b) Discuss the Heitler-London treatment of H_2 molecule based on valence bond theory. Show how the initial trial function was improved through linear combination. What is the physical significance of this linear combination? (4+8)

PART C

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

15. a) Calculate the radii of the nodal surfaces of the 2s orbitals of (i) H and (ii) Li^{2+} in atomic units. What is the physical significance of these results?
$$[\psi_{2s} = \frac{1}{4\sqrt{2\pi}} Z^{3/2} (2 - Zr) \exp\left(-\frac{Zr}{2}\right)]$$
b) Which of the following functions is/are eigen function(s) of the linear momentum operator along x?
    (i) $\sin(2x)$ (ii) $\cos(3x)$ (iii) $\cos(x) - i\sin(x)$ (iv) e^{5ix} (3+2)

16. a) Verify if $x(L-x)$ is a well-behaved state function for a particle in a 1D- potential well of length L. If yes, show that this function would yield an expectation energy greater than the true ground state energy of the particle in a 1D- potential well.
b) The term symbols for the states of excited C ($1s^2 2s^2 2p^1 3p^1$) are $^3D_1$, $^3D_2$, $^3D_3$, $^1D_2$, $^3P_2$, $^3P_1$, $^3P_0$, $^1P_1$, $^3S_1$, $^1S_0$. Arrange the states in the increasing order of energy. (3+2)

17. a) The four π-molecular orbitals of butadiene are:
$$\psi_1 = 0.372p_1 + 0.602p_2 + 0.602p_3 + 0.372p_4$$
$$\psi_2 = 0.602p_1 + 0.372p_2 - 0.372p_3 - 0.602p_4$$
$$\psi_3 = 0.602p_1 - 0.372p_2 - 0.372p_3 + 0.602p_4$$
$$\psi_4 = 0.372p_1 - 0.602p_2 + 0.602p_3 - 0.372p_4$$
Draw these orbitals. Which atom(s) would have maximum electron density in the first excited state of butadiene?
b) Write the Hückel molecular orbital secular determinant for the π-electrons of cyclopentadienyl anion. (3+2)