ST. JOSEPH'S COLLEGE (AUTONOMOUS), BANGALORE-27
M.Sc. CHEMISTRY, III SEMESTER
SEMESTER EXAMINATION: OCTOBER 2019
CH-9318 - PHYSICAL CHEMISTRY

Time: 2½ hours   Max.Marks:-70

This paper contains 2 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 an electron in the hydrogen atom is determined with an accuracy of 0.001 nm. What is the uncertainty in the velocity of the electron. (mass of electron: $9.1x10^{-31}$ kg; h = 6.62 $x10^{-34}$J.s).
2. Given = and = find the commutator of and for an arbitrary function f(x).
3. For a particle moving under no potential barrier give (i) Hamiltanian operator and (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? What is its signficance?
6. Distinguish between π-electron bonding energy and delocalization energy.
7. Explain the coupled representation of angular momentum.
8. Give eigen value equations for orbital motion and spin motion.

PART-B

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

9. a) What are Hermitian operators? Show that eigen functions of a Hermitian operator corresponding to different eigen values are orthogonal.
   b) Set-up 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) The wave functions obtained by solving Schrodinger equation for simple harmonic oscillator are where where n = 0,1,2 ...... and is known as Hermite polynomial and y = .
   (i) calculate the first four wave functions and
   (ii) sketch first four normalized wave functions and square of them for the harmonic oscillator.
   (b) For the hydrogen atom
      (i) calculate spherical harmonics for n = 1, l = 0, m = 0 and n = 2, l = 0, m = 0.
      (ii) calculate radial wave functions for n =1, l = 0 and n = 2, l = 0 and
      (iii) using the above data give wave functions ψ_{100} and ψ_{200}. (6+6)

11. a) Explain the need for approximate methods to solve Schrodinger equation. State and prove the method of variation.
   b) By applying Heitler-London theory for hydrogen molecule derive symmetric and antisymmetric orbital wave functions with respect to ion exchange. Mention the shortcomings of Heitler-London treatment of hydrogen molecule. (6+6)

12. a) Define Ladder operators. Show that commutes with but not with . Show that lowers the eigen value of from k_m to (k_m - ħ).
   b) Using HMO theory for cyclopropenyl systems
      (i) calculate the allowed energy levels (ii) sketch the ground state π-electron distribution and
      (iii) determine total π-electron energies and delocalization energies. (6+6)

13. a) For a particle moving in a box of length 'a' the normalized wave function is given by . Determine the average value of the position of the particle.
   b) Using Huckel approximation, find four HMOs of butadiene. (Given: $x_1 = x_2 = \pm$ 1.612 and $x_3 = x_4 = \pm$ 0.618). Sketch the graphical plots of these HMOs.
   c) Briefly discuss the extended Huckel theory. (4+4+4)

14. a) Prove that for the ground state of H_2^+ ion the orbital energies E_1 = and E_2 = .
   b) Explain SCF method for the determination of wave functions and energy of many electron systems. (6+6)

PART-C

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

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

16. i) Calculate the values of J associated with the term symbol ^3D.
    ii) From the following identify the most stable states. Give reasons.
    $^1S_0$, $^3S_1$, $^3P_0$, $^3P_1$, $^3P_2$ and $^1D_2$ (2+3)

17. i) β-Carotenes are highly conjugated polyenes found in many vegetables. β-Carotene has maximum absorption of light that occurs at 480 nm. If this transition corresponds to an n = 11 to n = 12 transition of electron in a particle in a box system, what is length of the molecular box? (Given: mass of the electron = 9.1×10^{-31}kg, h = 6.626×10^{-34}J.s, c = 3×10^{8} m/s)
    ii) For a particle in three dimensional box having dimensions $L_x = L_y = L_z = 1 \times 10^{-15}$m calculate the energy of the particle in the (2,1,1) state. If the length of the box along x-axis is changed from 1×10^{-15}m to 1.5×10^{-15} m calculate the energy of the particle in the (2,1,1) state. (mass of the particle = 9.1×10^{-31}kg, h = 6.626×10^{-34}J.s). (2.5+2.5)