2019

PG Even Semester (CBCS) Exam., May—2019

CHEMISTRY

(2nd Semester)

Course No. : CHMCC–204

(Quantum Chemistry and Molecular Spectroscopy)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

Answer **five** questions, taking **one** from each Unit.

UNIT—I

1. *(a)* What is Hermitian operator? Show that the eigenfunction of a Hermitian operator corresponding to different eigenvalues of orthogonal. 1+3=4

(b) A trial wave function $Nx(a - x)$ for a particle in a one-dimensional box of length a with infinite walls considering the function shows a single maximum between the ends of the box. Use it to calculate the ground state energy. 4

(c) Write short notes on the following : 2+4=6

(i) Spin-orbit interaction

(ii) L–S coupling and j-j coupling

2. *(a)* Show that linear momentum operator is Hermitian and components of linear momenta commute with each other. 2½+2½=5

(b) Treating -electrons in conjugated systems as particles moving in a one-dimensional box, calculate the lowest absorption frequency (in cm ^{1}) and wavelength (nm) of absorbed light for the molecule of butadiene; the length of the molecule is 0.56 nm. What is the total ground state energy of the molecule? 5

(c) A particle of mass m 1 0 10^{26}g is confined to move in a box of length 2 0 Å. What is the probability of finding the particle between 1 6000 Å and 1 6001 Å? Calculate for n 1 and n 2. 4

UNIT—II

3. *(a)* Explain the molecular orbital (MO) treatment of hydrogen molecule (H_2) with proper description of two-centre coulomb, exchange and overlap integrals. 9

(b) Calculate the -bond energy of ethylene molecule. Write down the bonding and anti-bonding -orbitals with graphical representation. 5

4. *(a)* Discuss the basic features of valence bond (VB) theory taking hydrogen molecule (H_2) as an example. Show the potential energy curve of H_2. 5

(b) "Delocalised allyl structures are stable than localised allyl structures." Justify the statement with proper explanation. 5

(c) Write a short note on Born-Oppenheimer approximation. Point out its limitation. 4

UNIT—III

5. *(a)* Show that for a transition between two stationary states, the rate of development of the excited state is an exponential function of time. 12

(b) What is the difference between static and dynamic quenchings in fluorescence spectroscopy? 2

6. *(a)* Show that extinction co-efficient of *n* — *(~ 10) is much lower than that of — *(~ 1000). 4

(b) State and explain Kasha's rule in fluorescence spectroscopy. Hence, state the basic features of an emission spectrum. 2+4=6

(c) "*n * absorption exhibits blue shift in polar solvent compared to non-polar solvent." Justify or criticise. 4

UNIT—IV

7. *(a)* Obtain the energy expression of a diatomic vibrator taking into the consideration of Born-Oppenheimer approximation. Write down the selection rule and derive the expression for PQR branch. 5+1+2=8

(b) Show that the diatomic molecule can never have zero vibrational energy. 3

(c) The force constant of $^{79}Br^{79}Br$ is 240 cm^{-1}. Calculate the fundamental vibrational frequency and zero point energy $^{79}Br^{79}Br$. 3

8. *(a)* Explain the principle of Raman spectroscopy based on both classical and quantum theories with a schematic diagram. 4+4=8

(b) How many fundamental vibrations are possible for H_2S and CO_2 molecules? Depict diagrammatically the symmetry and fundamental vibration of both these molecules. 3

(c) Explain the rule of mutual exclusion with an example. 3

UNIT—V

9. *(a)* What is chemical shift? Explain the factors influencing the chemical shift with one suitable example in each case. 2+5=7

(b) Discuss the effect of relaxation process on line width of NMR spectral lines. 4

(c) Explain the term 'diamagnetic anisotropy' by taking suitable example. 3

10. *(a)* Obtain the basic functions of electron and nuclei. Write the zero-order of energy values for the states and draw the first-order spin energy levels of H-atom and depict the allowed e.s.r. transition. 2+2+4=8

(b) Write short notes on the following : 3+3=6

(i) Dipolar interaction

(ii) Larmor precession

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