

2018

PG Even Semester (CBCS) Exam., May—2018

CHEMISTRY

(2nd Semester)

Course No. : CHMCC-204

(Quantum Chemistry and Molecular Spectroscopy)

Full Marks : 70Pass 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 eigenvalues of a Hermitian operator are real. 1+2=3
- (b) The ground state wave function for hydrogen atom is

$$100 \quad \frac{1}{r_0^3} \exp \frac{r}{a_0}$$

Show that the radial probability density is maximum at $r = a_0$. 4

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- (c) Using the function

$$\exp \frac{1}{2} x^2$$

as an eigenfunction of the simple harmonic oscillator, calculate the eigenvalue.

Here, k is the force constant and

$$\frac{2 (mk)^{\frac{1}{2}}}{h} \quad 3$$

- (d) Using

$$(x) \quad -\frac{1}{4} \exp \frac{x^2}{2}$$

as variation of trial wave function and as the variable parameter, determine the best possible ground state energy of the quartic oscillator with the potential function of $V(x) = cx^4$. 4

2. (a) What is unitary operator? Show that eigenvalues of a unitary operator have modulus one. 1+2=3

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(3)

- (b) Obtain the solution for ground state of the harmonic oscillator and show that for a diatomic oscillator

$$\frac{1}{2} \sqrt{\frac{k}{\mu}}$$

where, ω is the frequency and μ is the reduced mass. 3

- (c) Show that : 3+3=6

(i) $[L_x, L_y] = i\hbar L_z$

(ii) $[L^2, L_z] = 0$

- (d) Write short notes on 'Zeeman effect' and 'Paschen-Back effect'. 2

UNIT—II

3. (a) State and prove the upper bound (variation) theorem. 5
- (b) Discuss the basic features of valence bond (VB) theory taking hydrogen molecule ion (H_2^+) as an example. 5
- (c) In cyclopropenyl system, the carbonium ions will be more stable than the radical or carbanion. Justify with proper explanation. 4

(4)

4. (a) Set up a Hückel theory secular determinant for butadiene in terms of coulomb (H_{ii}) and resonance (H_{ij}) integrals. Calculate its π -electron delocalization energy relative to the energy of two ethylene molecules. Present the graphical sketches of four HMOs of butadiene. 6
- (b) Explain briefly whether the valence bond theory or molecular orbital theory provides an unsatisfactory value of dissociation energy (D_e) for hydrogen molecule. 4
- (c) "Delocalized allyl structures are stable than localized allyl structures." Justify the statement with proper explanation. 4

UNIT—III

5. (a) Discuss the verification of Beer-Lambert law from the rate of excitation expression

$$a_m a_m^* = \frac{8\pi^3}{3h^2} |f_{lm}|^2 I \nu$$

where the symbols have their usual significances. 8

- (b) " $n \rightarrow \pi^*$ absorption exhibits blue shift in polar solvent compared to non-polar solvent." Justify or criticise. 4

(5)

- (c) A dye solution of concentration of 0.01 g/cc absorbs 40% of blue light in a cell of thickness 1 cm. What should be the concentration to ensure a 90% absorption in the same cell? 2
6. (a) “*d-d* transitions are forbidden but become partially allowed due to vibronic coupling.” Explain. 4
- (b) State and explain ‘Kasha’s rule’ in emission spectroscopy. Cite one example while ‘Kasha’s rule’ becomes violated. 4
- (c) What is meant by Born-Oppenheimer approximation? Explain its limitations. 4
- (d) For a compound, $\tau_f = 0.1$ and $\tau_{nr} = 10$ ns. Calculate k_r and k_{nr} . 2

UNIT—IV

7. (a) Derive the expressions for fundamental absorption and the first and second overtone absorptions in the IR spectrum of a diatomic molecule undergoing anharmonic oscillator. 8
- (b) Show that at room temperature, the transitions originating at $v=1$ or more may be neglected in vibrational spectroscopy. 3

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(6)

- (c) The IR stretching frequency of free OH bond is 3600 cm^{-1} . Calculate the isotopic shift, when hydrogen is labelled with deuterium. 3
8. (a) Explain the principle of Raman spectroscopy based on quantum theory with a schematic diagram. 7
- (b) What are meant by ‘hot bands’ in IR spectroscopy? 3
- (c) Explain the ‘rule of mutual exclusion’. Explain also the Raman activity of vibration in CO_2 in the light of symmetry and polarizability ellipsoid. 1+3=4

UNIT—V

9. (a) Discuss the interaction between a magnetic field and spin of electron and proton. Obtain an expression relating frequency and magnetic field. 3+2=5
- (b) The basic principles of NMR and ESR are same but their techniques are considerably different. Explain. 4
- (c) What is chemical shift? By taking example of methanol, explain in detail the NMR spectra. 2+3=5

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10. (a) What are the basic spin functions?
Obtain the second-order hyperfine energy of isotropic interaction between a proton and an electron. Illustrate the allowed and forbidden electronic resonance transitions diagrammatically with energy values. $2+7+3=12$
- (b) What is Larmor precession? 2
