5 SEM TDC CHMH (CBCS) C 12

2022

(Nov/Dec)

CHEMISTRY

(Core)

Paper : C–12

(Physical Chemistry, Quantum Chemistry and Spectroscopy)

Full Marks : 53
Pass Marks : 21

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Choose the correct answer from the following : 1×4=4

(a) The expression for Hamiltonian operator $\hat{H}$ is

(i) $\frac{h^2}{8\pi^2 m}\nabla^2 + V$

(ii) $-\frac{h^2}{8\pi^2 m} + V$

(iii) $\frac{h^2}{8\pi^2 m}\nabla^2 - V$

(iv) $-\frac{h^2}{8\pi^2 m}\nabla^2 - V$

(b) The eigenvalue of the function $\psi = 8e^{4x}$ is

(i) e^{4x}

(ii) 32

(iii) 8

(iv) 4

(c) The rotational spectrum of a rigid diatomic rotator consists of equally spaced lines with spacing equal to

(i) B

(ii) $2B$

(iii) $B/2$

(iv) $4B$

(d) Intersystem crossing refers to

(i) transition between two states of a system

(ii) radiationless transition between states of different spin multiplicities

(iii) transition between excited and ground states with same multiplicity

(iv) All of the above

2. Answer any *four* questions from the following : 2×4=8

(a) HBr molecule is microwave active. Explain, why.

(b) Describe Larmor frequency.

(c) Water is a good solvent for UV and visible spectroscopy, but not for IR spectroscopy. Explain.

(d) Distinguish photochemical reaction from thermal reaction.

(e) State whether the function

$$\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$$

is an eigenfunction of the operator ∇^2. If it is an eigenfunction, find eigenvalue.

UNIT—I

3. Answer any *four* questions from the following : 4×4=16

(a) Solve Schrödinger's wave equation for a particle having mass m moving freely in a one-dimensional box of length a. Find out the energy expression. 3+1=4

(b) What is a simple harmonic oscillator? Deduce an expression for the fundamental frequency of a harmonic oscillator. 1+3=4

(c) (i) What is an operator? Write quantum mechanical operator corresponding to momentum. 1+1=2

(ii) Examine if the function

$\psi_1(x) = N_1(a^2 - x^2)$ and $\psi_2(x) = N_2 x(a^2 - x^2)$

are orthogonal within $-a < x < a$. 2

(d) (i) Show that Hamiltonian operator ($\hat{H}$) for a rigid rotator is given by $\hat{H} = L^2/2I$, where L is the angular momentum and I is the moment of inertia. 2

(ii) Write the energy expression for second energy-level of a rigid rotator. 2

(e) (i) Write Schrödinger wave equation for hydrogen atom in Cartesian and polar coordinate. 1+1=2

(ii) What does the term 'degenerate level' mean? Calculate degeneracy of the level having energy $\frac{5h^2}{8ma^2}$ for a free particle moving in a two-dimensional box of two equal side lengths. 1+1=2

(f) (i) What is zero point energy? Calculate zero point energy of a molecule if it is considered as a simple harmonic oscillator. 2

(ii) Sketch and explain the wave functions for the first three energy levels for the particle in one-dimensional box. 2

UNIT—II

4. Answer any *four* questions from the following : 4×4=16

(a) Describe different types of electronic transitions with one example of each.

(b) State Frank-Condon principle. Explain the effects of change of solvents on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions. Write the significance of molar extinction coefficient. 1+2+1=4

(c) The C—H vibration (stretching) in chloroform occurs at 3000 cm^{-1}. Calculate the C—D frequency (stretching) in deutero chloroform. It is supposed force constants remain same during isotopic substitution.

(d) Write brief notes on the following : 2×2=4

(i) Chemical shift

(ii) Spin-spin coupling

(e) (i) Discuss the effect of isotopic substitution on the rotational spectra of a diatomic molecule. 2

(ii) Roughly sketch the fundamental vibrations of water molecule and show the infrared active vibrations. 2

UNIT—III

5. Answer any *two* questions from the following : 4½×2=9

(a) What is quantum yield of a photochemical reaction? Under what condition is its value 1? A certain system absorbs 3×10^{20} quanta of light per second. On irradiation for 20 minutes, 0·02 mole of the reactant was found to have reacted. Calculate the quantum yield of the reaction. 1+1+2½=4½

(b) What are photochemical reactions? Write the differences between photochemical and thermal reactions. Discuss the reasons for high and low quantum yields of photochemical reactions. ½+2+2=4½

(Continued)

(c) (i) Write a short note on any *one* of the following : 2

(1) Actinometry

(2) Chemiluminescence

(ii) Write the differences between phosphorescence and fluorescence. 2½

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