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

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

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

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

(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

(3)

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 $\psi_2(x) = N_2x(a^2 - x^2)$ 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 deuterio 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.

$1 + 1 + 2\frac{1}{2} = 4\frac{1}{2}$

(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.

$\frac{1}{2} + 2 + 2 = 4\frac{1}{2}$

(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
