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# 5 SEM TDC CHMN (CBCS) C 12

## 2024

( November )

## 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 degeneracy of a particle of mass $m$ confined in a 3-D box having energy level equal to $\frac{19h^2}{8ma^2}$ is

*(i)* 7 *(ii)* 19

*(iii)* 6 *(iv)* 3

(b) The wavefunction $\psi = e^{ax^2}$ in the range $-\infty < x < \infty$ where $a$ is a finite quantity is

(i) acceptable wave function

(ii) not acceptable wave function

(iii) eigenfunction of $\frac{d}{dx}$

(iv) a normalized wave function

(c) Intersystem crossing refers to

(i) transition between two states of a system

(ii) radiationless transition between states of different spin multiplicities

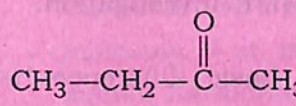
(iii) transition between excited and ground states with same multiplicities

(iv) All of the above





(d) The number of NMR signal formed by



is

(i) 2

(ii) 3

(iii) 4

(iv) 5

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

(a) State whether the function

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

is an eigenfunction of the operator $\nabla^2$. If it is an eigenfunction, find the eigenvalue.

(b) Determine the normalization constant of the function $\psi = x^2$ in the range $0 \le x \le k$, where $k$ is a constant.

(c) Microwave studies are done only in gaseous state. Explain.

(d) Explain why the nuclei $^{1}H$ and $^{13}C$ are suitable for NMR investigation.

(e) What is the basic difference between fluorescence and phosphorescence?

(f) Determine the value of $[x, P_x]$.

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

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

(b) Write the conditions for acceptability of wave function. Prove that $\tan x$ is not acceptable wave function in the range $0 \leq x \leq \pi$. 2+2=4

(c) Write Schrödinger's wave equation for rigid rotator system and separate the variables. 4

(d) (i) Write down the Schrödinger's wave equation for H-atom in Cartesian and polar coordinates. 1+1=2





(ii) What is zero-point energy? Calculate zero-point energy of a molecule if it is considered as a simple harmonic oscillator. 1+1=2

(e) (i) Prove that the eigenvalues of Hermitian operator are real. 2

(ii) Calculate the value of $\left[x, \frac{d^2}{dx^2}\right]$. 2

(f) Sketch the variation of radial wave function and radial probability distribution against the distance from the nuclei *(i)* 2*S* and *(ii)* 2*P*. 2+2=4

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

(a) Show that the lines in the rotational spectra of a diatomic molecule are equispaced under rigid rotator approximation. 4

(b) The C—H vibration (stretching) in chloroform occurs at 3000 $cm^{-1}$. Calculate the C—D frequency (stretching) in deuterated chloroform. Suppose force constant remains same during isotopic substitution. 4

(c) (i) What are *P*, *Q* and *R* branches of vibration-rotation spectra? 3

(ii) Why is electronic spectrum a band spectrum? 1

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

(i) Larmor frequency

(ii) Bathochromic shift

(e) (i) Why is TMS used as a reference standard in NMR spectra? 2

(ii) Draw the high and low resolution NMR spectra of the ethanol. 2

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

(a) What are photochemical reactions? Write the difference between photochemical and thermal reactions. Discuss the reason for low and high quantum yields of photochemical reaction. ½+2+2=4½

(b) State and explain Lambert-Beer law. Write the significance of molar extinction coefficient. 4½





(c) (i) Write short notes on any one of the following : 2

1. Actinometry
2. Chemiluminescence

(ii) A certain system absorbs $3\times10^{20}$ 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. 2½

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