2025/FYUG/ODD/SEM/
CHMDSC–301T/464

FYUG Odd Semester Exam., 2025

CHEMISTRY

(5th Semester)

Course No. : CHMDSC–301T

(Quantum and Photochemistry)

Full Marks : 70
Pass Marks : 28

Time : 3 hours

The figures in the margin indicate full marks for the questions

UNIT—I

1. Answer any *two* of the following questions : 2×2=4

(a) Calculate the de Broglie's wavelength of an electron if it moves with a velocity which is $\frac{1}{10}$th of the velocity of light and was accelerated by a potential of 100 volt.

(b) What will happen if the walls of the 1-D box are suddenly removed?

(c) If $\hat{A}$ and $\hat{B}$ are two operators such that $[\hat{A}, \hat{B}] = 1$, then find the value of $[\hat{A}, \hat{B}^2]$.

2. Answer any *one* of the following questions : 10

(a) (i) Derive Planck's radiation formula. 5

(ii) Show that Planck's radiation law reduces into Rayleigh-Jeans equation when λ or T is large. 2

(iii) The threshold wavelength for photoelectric emission in tungsten is 2300 Å. What wavelength of light must be used in order to eject electrons with a maximum energy of 1·5 eV? 3

(b) (i) Show that Hermitian operator has real eigenvalues. 3

(ii) Solve the Schrödinger's wave equation for a particle of mass m confined in a 1-D box of length a and moving along x-axis. 4

(iii) Determine the degree of degeneracy of the energy level $17h^2/8ma^2$ of a particle of mass m in a 3-D cubical box of length a. 3

UNIT—II

3. Answer any *two* of the following questions : 2×2=4

(a) Is the occurrence of the zero-point energy in a SHO consistent with the Heisenberg uncertainty principle?

(b) Draw the potential energy diagram for a simple harmonic oscillator (SHO).

(c) Give an example of a rigid rotor and find the kinetic energy (KE) of the molecule.

4. Answer any *one* of the following questions : 10

(a) Write the Schrödinger wave equation for 1-D simple harmonic oscillator (SHO) and solve it to find the *(i)* normalized wave function and *(ii)* expression for energy. 2+5+3=10

(b) Obtain an expression for *(i)* solution of ϕ dependent equation, *(ii)* solution of θ dependent equation and *(iii)* energy of rigid rotator, by considering quantum mechanical approach. 4+4+2=10

UNIT—III

5. Answer any *two* of the following questions : 2×2=4

(a) State variation theorem.

(b) Define exchange and Coulomb integral.

(c) What is inversion? Define gerade and ungerade orbitals.

6. Answer any *one* of the following questions : 10

(a) Apply LCAO-MO theory to H_2^+ ion to derive secular determinant. Solve it to find the energy levels and corresponding normalized wave functions. 6+2+2=10

(b) *(i)* Write the Hamiltonian of H_2 molecule in terms of VBT and solve the Schrödinger equation to determine the energy levels of H_2 molecule. 6

(ii) Write the electronic configuration of O_2^+, O_2, O_2^- and O_2^{2-} and hence arrange them in order of increasing bond dissociation energy. 4

UNIT—IV

7. Answer any *two* of the following questions : 2×2=4

(a) Explain the concept of free valence.

(b) Show that π-bond energy in ethylene is 2β.

(c) Which is more stable $C_5H_5^+$ or $C_5H_5^-$ and why?

8. Answer any *one* of the following questions : 10

(a) *(i)* Considering quantum mechanical approach, calculate the bond angle in sp^3 hybridization taking methane as an example. 4

(ii) Explain simple Hückel theory for the cyclic conjugated systems and find the normalized wave function and energy. 6

(b) *(i)* Apply simple Hückel theory to allyl system to calculate—

1. electron densities;
2. bond order;
3. free valence. 6

(ii) Show that delocalization energy in butadiene system is 0·472β and calculate the electron densities. 2+2=4

UNIT—V

9. Answer any *two* of the following questions : 2×2=4

(a) Define one einstein and show that—

$$\text{one einstein} = \frac{0 \cdot 1197}{\lambda} \text{ J mol}^{-1}$$

where λ is the wavelength of the absorbed light.

(b) What is chemiluminescence? Give one example.

(c) For a photochemical reaction, $A \rightarrow B$, 1×10^{-5} mol of B is formed by absorption of 6 J energy at 3600 Å. Calculate the quantum efficiency of the reaction.

10. Answer any *one* of the following questions : 10

(a) *(i)* Draw Jablonski diagram depicting various photophysical processes occurring in the excited state and differentiate between—

1. fluorescence and phosphorescence;
2. internal conversion and intersystem crossing. 4+2+2=8

(ii) Write four points of difference between thermal reaction and photochemical reaction. 2

(b) (i) Give two examples of photochemical reactions with high- and low-quantum yields, with two reasons for each and explain the mechanism of photochemical reaction. 2+2=4

(ii) Explain the difference between photosensitization and quenching, giving suitable example. 4

(iii) Write the proposed mechanism of the photochemical reaction between H_2 and Br_2. 2

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