

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 :

- (a)
- (i) Derive Planck's radiation formula.
 - (ii) Show that Planck's radiation law reduces into Rayleigh-Jeans equation when λ or T is large.
 - (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?
- (b)
- (i) Show that Hermitian operator has real eigenvalues.
 - (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.
 - (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

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.

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

(Turn Over)

(4)

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

(5)

UNIT—IV

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?

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

(Turn Over)

(6)

UNIT—V

9. Answer any two of the following questions :

(a) Define one einstein and show that—
one einstein = $\frac{0.1197}{\lambda} \text{ J mol}^{-1}$ 2×2=4

where λ is the wavelength of the absorbed light.

(b) What is chemiluminescence? Give one example.

(c) For a photochemical reaction, $A \rightarrow B$, $1 \times 10^{-5} \text{ mol}$ of B is formed by absorption of 6 J energy at $3600 \text{ \AA}$. 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

(7)

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

(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

2025/FYUG/ODD/SEM
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