Total number of printed pages–6

4 SEM PG CHM (CBCS) PC–V 406

2026

(June)

CHEMISTRY

Paper : Core–406

(Physical Chemistry–V)

Full Marks : 60

Time : Three hours

The figures in the margin indicate full marks for the questions.

Use separate booklet for ***UNIT–I*** *and* ***UNIT–II.***

UNIT–I

(Advanced Quantum Chemistry)

(Marks : 30)

1. What is a Slater determinant ? 1

2. Define a unitary matrix. 1

3. If $\hat{A}$ is a Hermitian operator, find whether $\left(\hat{A}+\hat{A}^{\dagger}\right)$ is Hermitian operator ? 1

4. Answer ***any three*** questions : 4×3=12

(a) Define density matrix $(P_{\lambda\sigma})$. Derive an expression for the closed-shell Fock operator in terms of $P_{\lambda\sigma}$. 1+3=4

(b) Show that the electron affinity for adding an electron to the virtual spin orbital (χ_r) is the negative of the orbital energy of that virtual orbital, $E_0^N - E_r^{N+1} = -\varepsilon_r$.

(c) Find an expression for the Fock matrix $(F_{\mu\nu})$ in terms of density matrix $(P_{\nu\mu})$, core Hamiltonian (H^{core}) and a set of two-electron integrals.

(d) Show that the sum of orbital energies is not equal to the total energy. Give reasons. 3+1=4

(e) What are closed-shell restricted spin orbitals? Convert the spin-orbital expression for orbital energies $\varepsilon_i = \langle \chi_i | h | \chi_i \rangle + \sum_b^N \langle \chi_i \chi_b \| \chi_i \chi_b \rangle$ to a closed-shell expression. 1+3=4

5. Answer ***any three*** questions : 5×3=15

(a) Give *one* example of a *one*-electron and *two*-electron operator. Show that for the matrix element of *one*-electron operator O_1, $\langle \Psi_a^r | O_1 | \Psi_b^s \rangle$

$= \langle r|h|s \rangle$ if $a = b, r \neq s$

$= -\langle b|h|a \rangle$ if $a \neq b, r = s$

$= 0$ if $a \neq b, r \neq s$

2+3=5

(b) What are the Roothaan equations? Explain each term involved. Why are the equations solved iteratively?

(c) What is Computational Chemistry? How is it different from 'wet lab' Chemistry? Briefly explain *any three* methods used in Computational Chemistry. 2+3=5

(d) Define an electron density. What is Density Functional Theory, and what are its advantages over wave function-based theories? 2+3=5

(e) What is a *Z*-matrix representation in Computational Chemistry? Demonstrate the *Z*-matrix representation of water molecule. How can a relaxed and rigid potential energy surface be distinguished? 3+2=5

UNIT–II

(Advanced Statistical Mechanics)

(Marks : 30)

6. Answer ***any three*** of the following questions : 5×3=15

(a) Taking the examples of one-dimensional harmonic oscillator and a particle in a cubical box, find the correspondence principle between quantum and classical partition functions.

(b) Derive the expression of Maxwell-Boltzmann velocity distribution assuming that translation and rotation can be treated classically.

(c) For the one-dimensional ising model prove that

$$\frac{(\theta-\alpha)(1-\theta-\alpha)}{\alpha^2} = e^{-w/k_BT}$$

(d) Prove that for an imperfect gas

$$B_3(T) = 4b_2^2 - 2b_3$$

(e) Starting from the following equilibrium $2(01) \rightleftharpoons (11) + (00)$, derive the Langmuir isotherm and prove the symmetry property $y(\theta)y(1-\theta) = 1$.

7. Answer ***any three*** of the following questions : 3×3=9

(a) Discuss the Verlet algorithm to integrate the equations of motion in Molecular Dynamics simulation.

(b) Derive the Metropolis acceptance criteria in a Monte Carlo simulation.

(c) How temperature is defined in Molecular Dynamics simulation? Discuss the Andersen thermostat method. ½+2½=3

(d) Discuss the role of importance sampling in Monte Carlo simulations.

(e) Explain the balance condition and detailed balance condition in Monte Carlo simulations. Discuss their significance.

8. Answer ***any three*** of the following questions : 2×3=6

(a) What are the essential properties a good random number generator must satisfy?

(b) What is periodic boundary condition? Discuss its role in computer simulations.

(c) What is phase space? Define phase integral and explain its significance in statistical mechanics. ½+1½=2

(d) Write the expression of configuration integral for a real gas. Modify this expression for an ideal gas. 1+1=2