

**M. SC. (CHEMISTRY)/M. SC.
(ANALYTICAL CHEMISTRY)
(MSCCHEM/MSCANCHEM)**

Term-End Examination

December, 2024

**MCH-018 : QUANTUM CHEMISTRY AND GROUP
THEORY**

Time : 2 Hours

Maximum Marks : 50

Note : (i) *Attempt any **five** questions.*

(ii) *All questions carry equal marks.*

(iii) *You may use the following wherever required :*

$$h = 6.626 \times 10^{-34} \text{ J-s;}$$

$$m_e = 9.11 \times 10^{-31} \text{ kg; } \quad c = 3.0 \times 10^8 \text{ ms}^{-1};$$

$$R_H = 109,667.58 \text{ cm}^{-1};$$

$$\int_0^\infty x^3 e^{-ax} dx = \left[\frac{x^3}{a} - \frac{3x^2}{a^2} + \frac{6x}{a^3} - \frac{6}{a^4} \right]$$

1. Answer any *five* of the following : $5 \times 2 = 10$
- (a) State de Broglie's idea of matter waves and give its significance for quantum mechanical systems.
 - (b) What is an orthonormal set of wave functions ?
 - (c) What are commuting operators ? What is the significance of commutation of operators ?
 - (d) "The energies of $3s$, $3p$ and $3d$ orbitals of helium atom are not equal whereas for hydrogen atom these are equal." Comment.
 - (e) "Confinement leads to quantisation." Justify with a suitable example.
 - (f) Give the rationale for transforming the Schrödinger wave equation for relative motion of electron with respect to the nucleus in a hydrogen atom from Cartesian coordinates to spherical polar coordinates.
 - (g) What is a reducible representation ?

2. (a) (i) Ascertain whether $f(x) = e^{\pm\beta x}$ is a well defined wave function in the limits $-\infty < x < \infty$ or not ? Give reasons. 2
- (ii) Show that the Hermitian operators give real values of the observables. 3
- (b) (i) Derive the expression for the difference in the energies of the consecutive energy levels of a particle of mass ' m ' confined to a one-dimensional box of length l . 2
- (ii) Calculate the difference in the energies of the ground state and the first excited state of an electron confined to a one-dimensional box of length 1 nm. 3
3. (a) Define particle in a three-dimensional box model system and formulate SWE for it. 5

- (b) (i) Use the Rodrigue's formula given below to determine the expressions for the Hermite polynomials $H_0(x)$ and $H_1(x)$: 2

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n} (e^{-x^2})$$

- (ii) Use the following recursion relation along with the values of $H_0(x)$ and $H_1(x)$ determined above to get the expression for $H_3(x)$: 3

$$H_{n+1}(x) = 2xH_n(x) - 2n H_{n-1}(x)$$

4. (a) (i) Determine the wave number of light emitted when an electron in hydrogen atom makes a transition from $n = 4$ energy level to $n = 2$ energy level. 3
- (ii) Give the significance of the rotational quantum number J in the rigid rotor model. How does it relate to the rotational energy levels ? 2

- (b) The normalized radial wave function for the ground state of hydrogen atom is :

$$\psi_{1,0} = 2 \left(\frac{1}{a_0} \right)^{3/2} e^{-r/a_0}$$

Calculate the average value of the distance of the electron in 1s orbital of hydrogen atom. 5

5. (a) Formulate the Schrödinger wave equation for a helium atom. Give the estimated ground state energy of helium atom determined by ignoring interelectron repulsion as an approximation. 5
- (b) Construct the group multiplication table for the C_{2V} point group by taking a suitable molecule as an example. 5
6. (a) State and prove variation theorem. How is it used to estimate the ground state energy of a system ? 5

- (b) (i) State Born-Oppenheimer approximation and outline its significance. 2
- (ii) Describe the process of covalent bond formation according to valence bond theory by taking hydrogen molecule as an example. Give valence bond trial wave function for H_2 molecule. 3
7. (a) (i) What are the basic requirements of linear combination of atomic orbitals-molecular orbital (LCAO-MO) approach ? 3
- (ii) A molecular orbital is given by : 2
- $$\psi = 0.45\phi_A + 0.25\phi_B$$
- calculate the proportions of each atomic orbital in the molecular orbital.
- (b) (i) Give MO energy level diagram for HF molecule. 2

- (ii) The four HMO wave functions for butadiene are given below : 3

$$\psi_1 = 0.60\chi_1 + 0.37\chi_2 - 0.37\chi_3 - 0.60\chi_4$$

$$\psi_2 = 0.60\chi_1 - 0.37\chi_2 - 0.37\chi_3 + 0.60\chi_4$$

$$\psi_3 = 0.37\chi_1 + 0.60\chi_2 + 0.60\chi_3 + 0.37\chi_4$$

$$\psi_4 = 0.37\chi_1 - 0.60\chi_2 + 0.60\chi_3 - 0.37\chi_4$$

Arrange these wave functions in the order of increasing energy and justify your answer.

× × × × × × ×