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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 :

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

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

$R_H = 109,667.58$ 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 : 5×2=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.

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