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(November)

CHEMISTRY

(Major)

Course : 507

(Symmetry and Quantum Chemistry)

The figures in the margin indicate full marks for the questions

(New Course)

Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answer from the following : 1×5=5

(a) The wave function which is acceptable in quantum mechanics is

(i) $\psi = x$ *(ii)* $\psi = x^2$

(iii) $\psi = \sin x$ *(iv)* $\psi = e^x$

(b) The de Broglie wavelength of an electron moving with $\frac{1}{10}$th of the velocity of light is

(i) $2 \cdot 42 \times 10^{-11}$ m

(ii) $2 \cdot 42 \times 10^{-11}$ cm

(iii) $2 \cdot 42 \times 10^{-10}$ m

(iv) None of the above

(c) Quantum mechanical operator for momentum is

(i) $\frac{h}{2\pi i}\nabla$ *(ii)* $-\frac{h^2}{8\pi^2 m}\nabla^2$

(iii) $\frac{h}{2\pi i}$ *(iv)* $\frac{\hbar}{2i}\nabla$

(d) Quantum mechanical operator must be

(i) linear

(ii) Hermitian

(iii) Neither *(i)* nor *(ii)*

(iv) Both *(i)* and *(ii)*

(e) The point group of $[PtCl_4]^{2-}$ is

(i) D_{4h} *(ii)* D_{3h}

(iii) D_{5h} *(iv)* C_{4v}

2. Answer any *five* questions from the following : 2×5=10

(a) Taking NH_3 as an example of trigonal pyramid molecule, discuss symmetry operations in C_{3v} point group molecules.

(b) What are the main differences between VBT and MOT?

(c) Show that the function $\psi = \cos ax \cos by \cos cz$ is an eigen-function of the Laplacian operator. Find the corresponding eigenvalue.

(d) Show that the length of a one-dimensional box is an integral multiple of $\lambda/2$, where λ is the wavelength associated with the particle wave.

(e) Calculate the expectation value of p_x (linear momentum along x direction) for a particle in a one-dimensional box of length a.

(f) What do you understand by the terms 'eigenfunction' and 'eigenvalue'?

UNIT—I

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

(a) Set up the group multiplication table for C_{2v} point group.

(b) Write down the symmetry elements and point groups of the following : 1×3=3

(i) CO_2

(ii) BF_3

(iii) BrF_5

(c) State, without any derivation, the five rules about irreducible representation of a group and their characters by making use of 'great orthogonality theorem'.

(d) Write down the matrix representation for σ operation taking x, y, z as bases.

UNIT—II

Answer any *two* questions : 9×2=18

4. *(a)* *(i)* The functions given below are defined in the interval $x = -a$ and $x = +a$ as follows :

$$F_1(x) = N_1(a^2 - x^2)$$

$$F_2(x) = N_2 x(a^2 - x^2)$$

Assuming the value of the function to be zero for $x < -a$ and $x > +a$, calculate the values of normalization constants N_1 and N_2. 3+3=6

(ii) Show that the functions $F_1(x)$ and $F_2(x)$ in the above problem are orthogonal. 3

(b) *(i)* Solve Schrödinger's wave equation for a particle moving freely in a three-dimensional cubic box. Find the eigenfunction and energy. 4+1+1=6

(ii) Determine the energy required for a transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ state for an electron in a cubic hole of a crystal with 10^{-8} cm edge-length. 3

(c) *(i)* The distance between the atoms of a diatomic molecule is r and its reduced mass is μ. If its angular momentum is L and moment of inertia is I, then prove that

$$\text{kinetic energy, } T = \frac{L^2}{2\mu I^2}$$ 3

(ii) Calculate the probability density for a 1s-electron at the nucleus of H-atom. Given

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0}$$

$$a_0 = 0 \cdot 529 \text{ Å}$$ 3

(iii) Set up Schrödinger's wave equation for a simple harmonic oscillator. "The zero-point energy of a simple harmonic oscillator cannot be zero." Explain. 2+1=3

UNIT—III

5. *(a)* Taking suitable trial wave function for hydrogen molecule ion, obtain the expressions for the possible energies and the corresponding eigenfunctions. 4

(b) Explain with a diagram, the formation of bonding and anti-bonding molecular orbitals on the basis of LCAO approximation. 2

Or

Draw the MO configuration of NO molecule and predict its magnetic character. 2

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

1. Select the correct answer from the following : 1×5=5

(a) Eigenvalues of a Hermitian operator are

(i) real

(ii) complex

(iii) imaginary

(iv) both real and imaginary

(b) The quantum mechanical operator for kinetic energy is

(i) $-\frac{h^2}{8\pi^2 m}\nabla^2$ (ii) $\frac{h}{2\pi i}\nabla$

(iii) $\frac{h}{2\pi i}\cdot\frac{d}{dx}$ (iv) V

(c) The wave function ψ satisfies the equation

$$\int_{-\infty}^{+\infty}\psi^*\psi\,dx = 0$$

The function is said to be

(i) normalized

(ii) diagonal

(iii) orthogonal

(iv) All of the above

(d) The number of nodes in the radial probability distribution curve of s-orbital of any energy level is equal to

(i) $\frac{n}{2}$ (ii) $n-1$

(iii) $n-2$ (iv) $n-l-1$

(e) The point group of NH_3 is

(i) T_d (ii) D_{2h}

(iii) C_{2v} (iv) C_{3v}

2. Answer any *five* questions from the following : 2×5=10

(a) What do you understand by eigenfunctions and eigenvalues?

(b) Differentiate between linear and non-linear operators with examples.

(c) What are the main differences between VBT and MOT?

(d) Show that e^{-ax^2} (a is a constant) is an eigenfunction of operator $\frac{1}{x}\cdot\frac{d}{dx}$. Find the eigenvalue.

(e) Write a short note on crystallographic point group.

(f) Determine the degree of degeneracy of the energy levels $\frac{14h^2}{8ma^2}$ of a particle in a three-dimensional box.

UNIT—I

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

(a) Write the symmetry elements and point groups of the following : 1×3=3

(i) H_2O

(ii) BCl_3

(iii) CO_2

(b) State, without any derivation, the five rules about irreducible representation of a group and their characters by making use of 'great orthogonality theorem'.

(c) Give the reducible representation of character table for C_{2v} point group.

(d) Write down the matrix representation for σ operation taking x, y, z as bases.

UNIT—II

Answer any *two* questions : 9×2=18

4. (a) (i) Deduce Schrödinger's wave equation on the basis of classical wave concept. 4

(ii) What is photoelectric effect? State two significant experimental observations concerning photo-electric effect. Explain the observations with the help of classical theory or any other theory of light. 1+2+2=5

(b) (i) Solve Schrödinger's wave equation for a particle in a one-dimensional box and find its energy. Why is the value $n = 0$ of the quantum number not permitted? 4+1=5

(ii) A particle of mass m is confined in a one-dimensional box of length a. Calculate the probability of finding the particle in the region $0 \le x \le \frac{a}{3}$.

What is the limiting probability when $n \to \infty$? 3+1=4

(c) (i) Write a short note on radial and angular part of wave function. 3

(ii) Calculate the probability density for a 1*s*-electron at the nucleus of H-atom. Given

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0}$$

$$a_0 = 0 \cdot 529 \text{ Å}$$ 3

(iii) Set up Schrödinger's wave equation for a simple harmonic oscillator. "The zero point energy of a simple harmonic oscillator cannot be zero." Explain. 2+1=3

UNIT—III

5. *(a)* Taking suitable trial wave function for hydrogen · molecule ion, obtain the expressions for the possible energies and the corresponding eigenfunctions. 4

(b) Draw the MO configuration of NO molecule and predict its magnetic character. 2

Or

Explain why H_2 molecule is more stable than H_2^+ ion. 2

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