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5 SEM TDC CHM M 7 (N/O)

2017

(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 quantum mechanical operator for kinetic energy is

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

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

(b) A particle is moving in a 1-D box, N_n is the number of nodes in a state with quantum number n. The ratio of $N_{n=2} : N_{n=1}$ has a value

(i) 1

(ii) 2

(iii) 3

(iv) ∞

(c) The energy required to excite (to first excited state) a particle of mass m confined in a length l is

(i) $\frac{3h^2}{8ml^2}$

(ii) $\frac{h^2}{8ml^2}$

(iii) 0

(iv) h^2

(d) The eigenvalue of the function $\psi = 8e^{4x}$ for the operator $\frac{d^2}{dx^2}$ is

(i) 16

(ii) 32

(iii) 8

(iv) 4

(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 : $2\times5=10$

(a) What is the matrix representation of rotation-reflection axis (S_n) in symmetry?

(b) Briefly describe Compton effect.

(c) Distinguish bonding molecular orbitals from antibonding molecular orbitals.

(d) Show that the functions $\psi_1 = \left(\frac{1}{2\pi}\right)^{1/2}$ and $\psi_2 = \left(\frac{1}{\pi}\right)^{1/2} \cos x$, in the interval $x = 0$ to $x = 2\pi$, are orthogonal to each other.

(e) Hermitian operators have real eigenvalues. Explain.

(f) Show that the energy levels in a simple harmonic oscillator are equally spaced.

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) $CHCl_3$

(ii) NH_3

(iii) PCl_5

(b) Construct the character table for C_{2v} point group. 3

(c) What are dihedral planes of symmetry? Explain with example. 2+1=3

(d) Distinguish Abelian groups from non-Abelian groups by taking a suitable example. 3

UNIT—II

Answer any *two* questions : 9×2=18

4. (a) A wave function is described by $\psi(\theta) = \sin\theta$, where θ can change continuously from 0 to 2π. Show whether it is normalized or not. If it is not, then find the normalizing factor. 2+2=4

(b) Show that $\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$ is an eigenfunction of ∇^2. What is the eigenvalue? 2+1=3

(c) Verify that the operator ∇^2 is linear. 2

5. (a) Solve Schrödinger's wave equation for a particle moving freely in a one-dimensional box. Find the eigenfunction and energy also. 5

(b) 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 $0 \le x \le \frac{a}{4}$. What is the limiting probability when $n \to \infty$? 3+1=4

6. (a) Define rigid rotator. Write the Schrödinger's wave equation for this system and separate the variables. 1+4=5

(b) Sketch the variation of radial probability density against the distance from the nucleus for $2s$ state for hydrogen atom. 2

(c) Determine the degree of degeneracy of the energy level $\frac{6h^2}{8ma^2}$ of a particle in a cubical box. 2

UNIT—III

7. (a) Explain the valence bond treatment for H_2 molecule. 4

Or

Compare the MO and VB treatment of hydrogen molecule in the ground state.

(b) Write the MO configuration of CN^- ion 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) A wave function ψ satisfies the equation

$$\int_{+\infty}^{-\infty} \psi^* \psi \, dx = 1$$

The function is said to be

(i) orthogonal

(ii) diagonal

(iii) normalized

(iv) None of the above

(b) The point group of H_2O is

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

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

(c) The eigenvalue of the function $\psi = e^{4x}$ for the operator $\frac{d^2}{dx^2}$ is

(i) 16 (ii) 32

(iii) 8 (iv) 4

(d) The bond order of O_2^{2-} is

(i) 3·0

(ii) 2·5

(iii) 2·0

(iv) 1·0

(e) The lowest energy of a quantum mechanical harmonic oscillator is $\frac{1}{2}h\nu$. It is referred to as

(i) ground-state energy

(ii) zero-point energy

(iii) vibrational energy

(iv) All of the above

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

(a) Explain rotation-reflect axis in symmetry.

(b) Calculate the zero-point vibrational energy of a one-particle, one-dimensional system if $E_\upsilon = \left(\upsilon + \frac{1}{2}\right)h\nu$.

(c) Explain why wave theory fails to explain black-body radiation.

(d) What do you understand by eigenfunction and eigenvalue?

(e) Determine the degree of degeneracy of the level $\frac{17h^2}{8ma^2}$ of a particle in a cubical box.

(f) What are symmetric and antisymmetric wave functions?

UNIT—I

3. Answer any *three* questions from the following : $3 \times 3 = 9$

(a) What is multiplication table? Construct the multiplication table for C_{2v} point group. 3

(b) Write the symmetry elements and point groups of the following : $1 \times 3 = 3$

(i) $CHCl_3$

(ii) NH_3

(iii) PCl_5

(c) What are dihedral planes of symmetry? Explain with example. $2+1=3$

(d) Write a short note on any *one* of the following : 3

(i) Character table

(ii) Reducible and irreducible representations

(iii) Great orthogonality theorem

UNIT—II

Answer any *two* questions : 9×2=18

4. (a) A wave function is described by $\psi(\theta) = \sin\theta$, where θ can change continuously from 0 to 2π. Show whether it is normalized or not. If it is not, then find the normalizing constant. 2+2=4

(b) Show that $\psi = \sin(k_1 x)\sin(k_2 y)\sin(k_3 z)$ is an eigenfunction of ∇^2. What is the eigenvalue? 2+1=3

(c) Differentiate between linear and non-linear operators. 2

5. (a) ψ_i and ψ_j represent the wave functions corresponding to two different states of a particle in a box. Show that they are orthogonal to each other. 3

(b) Sketch ψ and ψ^2 for the states $n = 3$ and $n = 4$ of a particle in a one-dimensional box. 3

(c) An oxygen molecule is confined in a cubical box of volume $1 \cdot 00 \text{ m}^3$. Assuming the average energy of the molecule is $\frac{3}{2}kT$, where k is the Boltzmann constant, find the value of $n = (n_x^2 + n_y^2 + n_z^2)$ for the molecule at $T = 300$ K. 3

6. (a) Write down Schrödinger's wave equation for H-atom in polar coordinates. 2

(b) The distance between the atoms of a diatomic molecule is r and its reduced mass is μ. If the angular momentum is L and moment of inertia is I, then prove that kinetic energy, $T = \frac{L^2}{2\mu I^2}$. 3

(c) Calculate the most probable distance, r_{mp} of the electron from the nucleus in the ground state of hydrogen atom, given that the normalized ground-state wave function is

$$\psi_{1s} = \frac{1}{\sqrt{\pi} a_0^{3/2}} (\exp)^{(-r/a_0)}$$ 4

UNIT—III

7. *(a)* Explain the valence bond treatment for H_2 molecule. 4

Or

Compare the MO and VB treatment of hydrogen molecule in the ground state.

(b) Write down the MO configuration of CO molecule. Determine its bond order and predict magnetic character. 2

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