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5 SEM TDC CHM M 7 (N/O)

2016

(November)

CHEMISTRY

(Major)

Course : 507

(Symmetry and Quantum Chemistry)

(New Course)

Full Marks : 48
Pass Marks : 14

Time : 2 hours

The figures in the margin indicate full marks for the questions

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

(a) In MO method, the orbitals are represented by the symbols

(i) n, l, m

(ii) s, p, d, f

(iii) π, p_x, p_y, p_z

(iv) $\sigma, \pi, \sigma^*, \pi^*$

(Turn Over)

(b) When scattering angle $\phi = 0$, then Compton shift will be

(i) zero

(ii) 0·0242 Å

(iii) 0·0484 Å

(iv) 0·0726 Å

(c) 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) $n-l-1$

(d) The normalized wave function for a particle in one-dimensional box is

(i) $\sqrt{\frac{8}{l^3}} \sin \frac{n\pi x}{l}$

(ii) $\left(\frac{2}{l}\right)^{1/2} \sin \frac{n\pi x}{l}$

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

(iv) $\left(\frac{1}{l}\right)^{1/2} \sin \frac{n\pi x}{l}$

(e) NO_2 molecule has symmetry elements E, C_2, σ_v, σ_v', the point group to which it belongs is

(i) C_{2v}

(ii) C_{3v}

(iii) $C_{\infty v}$

(iv) D_{2h}

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

(a) Write down the Hamiltonian operators for H_2^+ and H_2 molecule.

(b) Explain rotation-reflection axis (S_n) in symmetry.

(c) Explain why the bond order of H_2^- is less than that of H_2.

(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) Explain the distribution of energy in the spectrum of a black-body radiation.

(Turn Over)

(f) Calculate the energy required for a transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ for an electron in a cubic hole of a crystal having edge length 1Å.

(g) Calculate the zero-point vibrational energy of a one-particle, one-dimensional system, if $E_v = \left(v + \frac{1}{2}\right) h\nu_0$.

UNIT—I

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

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

(b) With a neat sketch, find the symmetry elements, operations and point groups of the following :

$[PtCl_4]^{2-}$, CO_2, BF_3

(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) Give the reducible representation of character table for C_{3v} point group.

UNIT—II

Answer any *two* questions : $9 \times 2 = 18$

4. (a) Explain the meaning of the term 'degenerate energy levels' by taking the example of particle in a cubical box. What would happen to the degeneracy when the cubical box is distorted? 3

(b) Evaluate the expectation value of energy of a particle in a one-dimensional box of width a and infinite height with potential energy zero inside the box. 4

(c) What do you understand by an orthonormal set of wave functions? 2

5. (a) For a particle of mass m in a one-dimensional box of length a, show that ψ_1 and ψ_2 are orthogonal. 4

(b) What are linear and Hermitian operators? Give one example of each. 3

(c) Write down the equation showing Hamiltonian operator for one-dimensional harmonic oscillator. 2

(Turn Over)

6. *(a)* 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, prove that

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

(b) Prove that 1s wave function of hydrogen atom given by

$$\psi_{1s} \text{ i.e. } \psi_{1,0,0} = \frac{1}{\sqrt{\pi} a_0^{3/2}} e^{-r/a_0}$$

is a normalized wave function where a_0 represents Bohr radius.

(c) Write down Schrödinger wave equation for H-atom.

UNIT—III

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

Or

Give the ground state molecular orbital configuration of CN and CN^+. State also their bond order and magnetic character.

(b) Write the differences between bonding and antibonding molecular orbitals.

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