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

(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.

(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 $E_v = \left(v + \frac{1}{2}\right) h\omega_0$.

UNIT—I

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

(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 : 9×2=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

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

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

(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. 4

(c) Write down Schrödinger wave equation for H-atom. 2

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. 4

Or

Give the ground state molecular orbital configuration of CN and CN^+. State also their bond order and magnetic character. 4

(b) Write the differences between bonding and antibonding molecular orbitals. 2

(Continued)

(Old Course)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

(a) The quantum number accounts for the Zeeman effect is

(i) magnetic quantum number

(ii) azimuthal quantum number

(iii) spin quantum number

(iv) None of the above

(b) The operator corresponding to the total energy of a system, written as a sum of kinetic and potential energies is called

(i) momentum operator

(ii) kinetic energy operator

(iii) Hamiltonian operator

(iv) None of the above

(c) Bonding energy of a diatomic molecule depends on

(i) internuclear repulsions

(ii) nuclear electronic attractions

(iii) interelectronic repulsions

(iv) All of the above

(d) The maximum kinetic energy of the photoelectrons varies directly with

(i) intensity

(ii) frequency

(iii) wavelength

(iv) None of the above

(e) A molecule belonging to C_{3v} point group possesses

(i) E, $2C_3$ and $3\sigma_v$

(ii) E, $2C_3$ and $2\sigma_v$

(iii) E, $3C_3$ and $2\sigma_v$

(iv) E, $3C_3$ and $3\sigma_v$

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

(a) Discuss the following with reference to symmetry elements and symmetry operations :

(i) $CHCl_3$

(ii) CO_2

(b) Discuss the symmetry elements and symmetry operations of BF_3.

(c) Calculate the eigenvalue of the function $\psi = \cos 5x$, where the operator $\frac{d^2}{dx^2}$ is operated upon it.

(d) Discuss orthogonality with the following functions :

(i) $\left(\frac{1}{\pi}\right)^{1/2} \cos nx$

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

(e) Hermitian operators have real eigenvalues. Explain.

(f) Taking water as an example of symmetric angular molecule, discuss symmetry operations in C_{2v} point group molecule.

UNIT—I

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

(a) Write short notes on symmetry elements and point group.

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

(c) Determine Γ_v for C_{3v} point group.

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

(e) A group has the following irreducible representations :

$$A_1, A_2, B_1, B_2, E_1, E_2$$

(i) What is the order of the group?

(ii) How many classes are there in the group?

UNIT—II

Answer any *two* questions : 9×2=18

4. *(a)* What are eigenfunctions and eigenvalues? Normalize the function $\psi = x^3$ over the interval $0 \leq x \leq k$, where k = constant. 3

(Continued)

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

(c) Solve Schrödinger's wave equation for a particle in a one-dimensional box and find its energy. 3

5. (a) State two postulates of quantum mechanics. 2

(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 $0 \leq x \leq \frac{a}{3}$. What is the limiting probability when $x \to \infty$? 3

(c) Write a short note on radial and angular parts of wave functions. 4

6. (a) A helium atom is in excited state. It has two electrons a and b. One electron is in 1s orbital while the other is in 2s orbital.

(i) Give the two possible wave functions (ψ).

(ii) Mention all four product combinations of the orbital and spin wave functions if the spins are α and β. 3

(b) State two significant experimental observations concerning photoelectric effect. Explain the observations with the help of classical theory or any other theory of light. 3

(c) Derive a dimensionless algebraic equation for harmonic oscillator by quantum mechanical treatment. 3

UNIT—III

7. (a) What are the main differences between VBT and MOT? 2

(b) Explain why H_2 molecule is more stable than H_2^+ molecule. 2

(c) Draw the MO energy-level diagram for any one of the following and find the bond order : 2

(i) NO^+ molecule

(ii) N_2 molecule

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