5 SEM TDC CHM M 7

2013

(November)

CHEMISTRY

(Major)

Course : 507

(Symmetry and Quantum Chemistry)

Full Marks : 48
Pass Marks : 19

Time : 3 hours

The figures in the margin indicate full marks for the questions

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

(a) The H_2O molecule belongs to C_{2v} point group. It does not possess

(i) C_2 symmetry axis

(ii) C_4 symmetry axis

(iii) σ_v plane

(iv) E

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

(i) magnetic quantum number

(ii) spin quantum number

(iii) azimuthal quantum number

(iv) None of the above

(c) The bond order of O_2^+ is

(i) 3·0

(ii) 2·5

(iii) 2·0

(iv) 1·0

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

(i) wavelength

(ii) frequency

(iii) intensity

(iv) None of the above

(e) 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

(Continued)

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) Show that the following functions are orthogonal to each other :

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

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

(c) Calculate the eigenvalue of the function $\psi = \sin 7x$, where operator $\frac{d^2}{dx^2}$ is operated upon it.

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

(e) Write a short note on Bravais lattice.

(f) Hermitian operators have real eigen-values. Explain.

UNIT—I

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

(a) Write short notes on symmetry elements and symmetry operations.

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

(i) CO_2

(ii) C_2H_4

(iii) PCl_5

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

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

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

UNIT—II

Answer any *two* questions : 9×2=18

4. *(a)* What are eigenfunctions and eigenvalues? Normalize the function $\psi = x^2$ over the interval $0 \leq x \leq k$, where k is a constant. 3

(b) 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

(c) Deduce the equation showing Hamiltonian operator for one-dimensional harmonic oscillator. 3

5. (a) Deduce the Schrödinger's wave equation on the basis of classical wave concept. 3½

(b) 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. 3½

(c) Determine the degree of degeneracy of the energy levels $\frac{17h^2}{8ma^2}$ of a particle in a three-dimensional box. 2

6. (a) Solve the 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

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

UNIT—III

7. Explain on the basis of LCAO-MO theory how a single electron can bind two hydrogen nuclei to form a stable hydrogen molecule ion. 4

8. What are the main differences between VBT and MOT? 2

Or

Draw the MO energy-level diagram for any *one* of the following molecules and find the bond order : 2

(a) CO molecule

(b) NO molecule

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