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5 SEM TDC CHM M 7 (N/O)

2019

(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 function which is acceptable in quantum mechanics over the range x varying between 0 and 2π is

(i) $\cos x$

(ii) $\tan x$

(iii) $\cot x$

(iv) cosec x

(b) According to quantum mechanics, the correct wave function is

(i) $\psi_{1,1,0}$ (ii) $\psi_{2,1,0}$

(iii) $\psi_{2,-1,0}$ (iv) $\psi_{3,3,0}$

(c) The degree of degeneracy of the energy level

$$\frac{17h^2}{8ma^2}$$

of a particle in a cubical box is

(i) 3 (ii) 0

(iii) 2 (iv) 6

(d) $\sin(k_1x)\sin(k_2y)\sin(k_3z)$ is an eigenfunction of operator ∇^2. Eigenvalue is

(i) $-(k_1^2+k_2^2+k_3^2)$ (ii) $(k_1^2+k_2^2+k_3^2)$

(iii) 1 (iv) $(k_1^2+k_2^2)$

(e) The point group of CH_4 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) Explain rotation-reflection axis (S_n) in symmetry.

(b) Write down the Hamiltonian operator for H_2^+ ion with proper significance of each term.

(c) Write down the operators corresponding to momentum and kinetic energy.

(d) An electron is confined to a molecule of length 1 nm. Find its zero-point energy.

(e) What are orthogonal and normalized wave functions?

(f) Show that the following functions are orthogonal in the interval $0 \le x \le 2\pi$:

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

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

UNIT—I

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

(a) Write down the symmetry elements and point groups of the following :

(i) C_2H_4

(ii) $[PtCl_4]^{2-}$

(iii) $CHCl_3$

(b) Explain with suitable examples the following symmetry elements and the associated symmetry operations :

(i) Axis of rotation

(ii) Symmetry planes

(iii) Centre of inversion

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

(d) Write short notes on any *one* of the following :

(i) Great orthogonality theorem

(ii) Abelian groups and non-Abelian groups

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 a free particle in a cubical box. What would happen to the degeneracy when the cubical box is distorted? 3

(b) Deduce the Schrödinger's wave equation on the basis of classical wave concept. 3

(c) 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 $0 \leq x \leq \frac{a}{2}$. 3

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

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

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

(Turn Over)

(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 the Schrödinger's wave equations for the (i) rigid rotator and (ii) hydrogen atom in spherical polar coordinates. 3

UNIT—III

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

Or

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

(ii) State the conditions for effective combination of atomic orbitals to form molecular orbitals. 2

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

Or

Write the molecular orbital configuration of CN^- ion and predict its magnetic character.

(Old Course)

Full Marks : 48

Pass Marks : 19

Time : 3 hours

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

(a) The function which is acceptable in quantum mechanics over the range x varying between 0 to 2π is

(i) $\cos x$ *(ii)* $\tan x$

(iii) $\cot x$ *(iv)* $\operatorname{cosec} x$

(b) A wave function ψ satisfies the equation

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

The function is said to be

(i) diagonal

(ii) normalized

(iii) orthogonal

(iv) orthonormal

(c) The degree of degeneracy of the energy level

$$\frac{17h^2}{8ma^2}$$

of a particle in a cubical box is

(i) 3 *(ii)* 0

(iii) 2 *(iv)* 6

(*Turn Over*)

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

(i) Hamiltonian operator

(ii) kinetic energy operator

(iii) momentum operator

(iv) None of the above

(e) The point group of CH_4 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) Explain rotation-reflection axis (S_n) in symmetry.

(b) Write any two differences between VBT and MOT.

(c) Write down the operators corresponding to momentum and kinetic energy.

(d) Calculate the zero-point vibrational energy of a one-particle, one-dimensional system, if

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0$$

(e) What are orthogonal and normalized wave functions?

(f) Show that the energy spacing for a particle restricted in one-dimensional box is not equal.

UNIT—I

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

(a) Write down the symmetry elements and point groups of the following :

(i) C_2H_2

(ii) $[PtCl_4]^{2-}$

(iii) $CHCl_3$

(b) Explain with suitable examples the following symmetry elements and the associated symmetry operations :

(i) Axis of rotation

(ii) Symmetry planes

(iii) Centre of inversion

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

(d) Explain the terms 'reducible' and 'irreducible' representation.

UNIT—II

Answer any *two* questions : 9×2=18

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

(b) Solve Schrödinger's wave equation for a particle moving freely in a three-dimensional box. Find the eigen-function and energy. 4

(c) Explain the meaning of the term 'degenerate energy levels'. 2

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

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

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

(b) Prove that 1*s* 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 Böhr radius. 4

(c) Write down the Schrödinger's wave equations for the *(i)* simple harmonic oscillator and *(ii)* hydrogen atom. 3

UNIT—III

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

(b) Write the MO configuration of CN^- ion and predict its magnetic character. 2

Or

Write the differences between bonding and antibonding molecular orbitals.

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