5 SEM TDC CHM M 7 (N/O)

2018

(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 wave function which is acceptable in quantum mechanics is

(i) $\psi = x$ (ii) $\psi = x^2$

(iii) $\psi = \sin x$ (iv) $\psi = e^x$

(b) The de Broglie wavelength of an electron moving with $\frac{1}{10}$th of the velocity of light is

(i) $2 \cdot 42 \times 10^{-11}$ m

(ii) $2 \cdot 42 \times 10^{-11}$ cm

(iii) $2 \cdot 42 \times 10^{-10}$ m

(iv) None of the above

(c) Quantum mechanical operator for momentum is

(i) $\frac{h}{2\pi i}\nabla$

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

(iii) $\frac{h}{2\pi i}$

(iv) $\frac{\hbar}{2i}\nabla$

(d) Quantum mechanical operator must be

(i) linear

(ii) Hermitian

(iii) Neither (i) nor (ii)

(iv) Both (i) and (ii)

(e) The point group of $[PtCl_4]^{2-}$ is

(i) D_{4h}

(ii) D_{3h}

(iii) D_{5h}

(iv) C_{4v}

(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) What are the main differences between VBT and MOT?

(c) Show that the function $\psi = \cos ax \cos by \cos cz$ is an eigen-function of the Laplacian operator. Find the corresponding eigenvalue.

(d) Show that the length of a one-dimensional box is an integral multiple of $\lambda/2$, where λ is the wavelength associated with the particle wave.

(e) Calculate the expectation value of p_x (linear momentum along x direction) for a particle in a one-dimensional box of length a.

(f) What do you understand by the terms 'eigenfunction' and 'eigenvalue'?

(Turn Over)

UNIT—I

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

(a) Set up the group multiplication table for C_{2v} point group.

(b) Write down the symmetry elements and point groups of the following : 1×3=

(i) CO_2

(ii) BF_3

(iii) BrF_5

(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) Write down the matrix representation for σ operation taking *x*, *y*, *z* as bases.

UNIT—II

Answer any *two* questions : 9×2=18

4. (a) (i) The functions given below are defined in the interval $x = -a$ and $x = +a$ as follows :

$$F_1(x) = N_1(a^2 - x^2)$$
$$F_2(x) = N_2 x(a^2 - x^2)$$

Assuming the value of the function to be zero for $x < -a$ and $x > +a$, calculate the values of normalization constants N_1 and N_2. 3+3=6

(ii) Show that the functions $F_1(x)$ and $F_2(x)$ in the above problem are orthogonal. 3

(b) (i) Solve Schrödinger's wave equation for a particle moving freely in a three-dimensional cubic box. Find the eigenfunction and energy. 4+1+1=6

(ii) Determine the energy required for a transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ state for an electron in a cubic hole of a crystal with 10^{-8} cm edge-length. 3

(c) (i) 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*, then prove that

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

(ii) Calculate the probability density for a 1s-electron at the nucleus of H-atom. Given

$$\psi_{1s} = \left(\frac{z^3}{\pi a_0^3}\right)^{1/2} e^{-zr/a_0}$$

$$a_0 = 0 \cdot 529 \text{ Å}$$

(iii) Set up Schrödinger's wave equation for a simple harmonic oscillator. "The zero-point energy of a simple harmonic oscillator cannot be zero." Explain. 2+1

UNIT—III

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

(b) Explain with a diagram, the formation of bonding and anti-bonding molecular orbitals on the basis of LCAO approximation.

Or

Draw the MO configuration of NO molecule and predict its magnetic character.