Total number of printed pages–7

1 (Sem–4) CHE 3

2025

CHEMISTRY

Paper : CHE0400304

(Theoretical Chemistry)

Full Marks : 45

Time : Two hours

The figures in the margin indicate full marks for the questions.

1. Answer the following questions as directed : 1×5=5

   (i) State function Ψ of a system must be an eigenfunction of the operator H. *(State whether the statement is True* ***or*** *False)*

   (ii) Show whether the operator $\hat{A}$ in the equation $\hat{A}\Psi = \Psi^2$ is linear or not.

(iii) At what distance is the radical probability maximum for 1s orbital? What is the distance called?

(iv) The first derivative of each particle in a box stationary state wave function is discontinuous at

(a) midpoint $(a/2)$

(b) $(a/3, 0)$

(c) $a/4$

(d) end point $(0, a)$

(Choose the correct option)

(v) Closed shell configuration is always represented by the term symbol _____.

(Fill in the blank)

2. Answer ***any five*** from the following questions : $2\times5=10$

(i) If $\hat{A} = 3x^2$ and $\hat{B} = d/dx$, show that $\hat{A}$ and $\hat{B}$ do not commute.

(ii) Normalize the function in the given range $\cos \pi x / a \; ; -a \le x \le a$.

(iii) Define complementary observable with *one* example.

(iv) State why the eigenfunction of an operator should be single-valued and continuous.

(v) Write how the molecular orbitals of a homonuclear diatomic molecule can be classified a σ and π.

(vi) Show that the wave function for a particle in one-dimensional box of length a, where the potential energy is zero, is not an eigenfunction of the linear momentum operator.

(vii) Considering the sun as black-body radiator calculate the temperature of its surface for the maximum wavelength of emitted radiation 480*nm*. (Given Wein's displacement constant is 2.88 *mmK*)

(viii) Give the values of L and S in ^1D.

(ix) What do you mean by orbital ? State the differences between an orbit and an orbital.

(x) Write the expression of Debye equation. Why the alkali metal atoms have high polarizability volume ?

3. Answer ***any four*** from the following questions : 5×4=20

(i) Determine which of the following functions are eigenfunctions of the operator d/dx :

(a) e^{-ikx}

(b) $\cos kx$

(c) $\sin x$?

Determine the Eigenvalue wherever appropriate.

(ii) What is a Hermitian operator ? Show that the eigenvalue of a Hermitian operator is real ? 2+3=5

(iii) The wavefunction for the electron in the ground state of hydrogen atom is $\psi = \left(\pi a_0^3\right)^{-1/2} e^{-r/a_0}$, where a_0 is the radius of Bohr orbit. Calculate the probability of finding the electron somewhere between 0 and $2a_0$. What is the probability beyond $2a_0$? 4+1=5

(iv) Write down the Schrödinger equation for a particle of mass m moving in three -dimensions and state the properties of wave function to have physical significance. What do you mean by orthonormal wave function ? 1+2+2=5

(v) Derive the term symbols inner for the excited state configuration of Helium $(2s^1 2p^1)$ and arrange the terms in increasing order of energy. 3+2=5

(vi) Write, what you mean by radial distribution function ? Find an expression for the radial distribution function. Give the plot of radial distribution function against the radial distance from the nucleus for 1s orbital. State how this plot differs from the plot of square of the radial function against the radial distance. 1+2+1+1=5

(vii) Calculate the zero-point vibrational energy of HCl if its force constant is 516 Nm^{-1}.

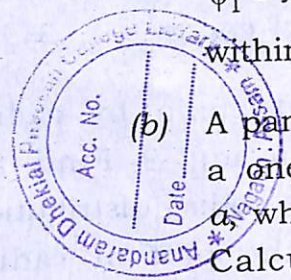
(viii) What is meant by polarizability of a molecule ? Derive the Clausius-Mossotti equation. 1+4=5

4. Answer ***any four*** from the following questions : 10×1=10

(i) (a) Show that the following sets of functions are orthogonal

$\psi_1 = x$ and $\psi_2 = x^2$

within the interval $-k \le x \le k$. 3

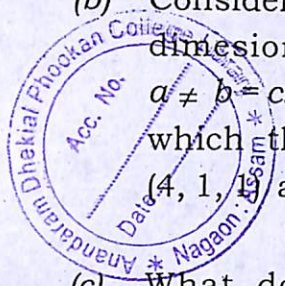


(b) A particle of mass m is moving in a one-dimensional box of length a, where potential energy is zero. Calculate the average kinetic energy of the particle. 4

(c) An electron is confined to a molecule of length $10^{-9}m$. Considering the electron to be a particle in one-dimensional box, where $V = 0$, calculate its minimum energy. 3

(ii) Discuss the valence bond treatment of hydrogen molecule.

(iii) (a) What do you mean by degeneracy ? Determine the degree of degeneracy of the energy level $17h^2/8ma^2$ of a particle in a cubical box. 1+3=4



(b) Consider a particle in a three-dimesional box of dimensions $a \neq b = c$. Find the condition under which the levels (2, 2, 1) and (4, 1, 1) are doubly degenerated. 4

(c) What do you mean by space quantization ? 2

(iv) (a) How van-der forces affect in boiling point in isomers ? Explain briefly by taking pentane as example. 2

(b) Discuss the temperature method for measurement of dipole moment. 4

(c) Discuss how dipole moment of a molecule helps in distinguishing (i) linear and non-linear molecules, (ii) *cis-*, *trans* isomer. 4

———