

**LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034****M.Sc. DEGREE EXAMINATION – CHEMISTRY****FIRST SEMESTER – JULY 2024****PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY**

Date: 13-06-2024

Dept. No.

Max. : 100 Marks

Time: 10:00 AM - 01:00 PM

SECTION A – K1 (CO1)**Answer ALL the questions****(5 x 1 = 5)****1 Define the following**

- a) Volume element for spherical coordinate system
- b) Bohr's correspondence principle
- c) Pauli's exclusion principle
- d) Dihedral point group
- e) Overlap integrals

SECTION A – K2 (CO1)**Answer ALL the questions****(5 x 1 = 5)****2 Fill in the Blanks**

- a) The coordinate system applied to describe a diatomic molecule is _____.
- b) The magnitude of the most probable distance of the electron from nucleus of hydrogen atom is _____.
- c) Born-Oppenheimer approximation separates _____.
- d) The number of symmetry operations present in C_{2v} point group are _____.
- e) The Coulomb integrals provide _____.

SECTION B – K3 (CO2)**Answer any THREE of the following****(3 x 10 = 30)**

- 3 (a) Find whether the wave function, $\psi = e^{-8x}$ is an eigen function of the operator, $\hat{O} = \frac{d^2}{dx^2}$.
(b) Explain the postulates of quantum mechanics. (4+6)
- 4 (a) Illustrate quantum mechanical tunneling with suitable examples.
(b) The force constant of $^{79}\text{Br}^{79}\text{Br}$ is 240 Nm^{-1} . Calculate the fundamental vibrational frequency and zero-point energy of Br_2 molecule. (5+5)
- 5 (a) Sketch the radial plot for 3s orbital and also find the angular and radial nodes for 3s orbital.
(b) Apply variation theorem and predict the ground state energy of hydrogen atom using the trial wave function, $\psi = \exp(-\alpha r)$. (5+5)
- 6 (a) Write the symmetry operations and mention the point group for CHCl_3 molecule.
(b) What are Slater and Secular determinants? Mention their significance. (5+5)
- 7 (a) Explain the three important approximations of Huckel LCAO-MO theory.
(b) How will you compare the number of classes present in C_{3v} and C_{3h} point groups? (6+4)

SECTION C – K4 (CO3)

Answer any TWO of the following **(2 x 12.5 = 25)**

- 8 Derive Time-independent and Time-dependent Schrodinger wave equations.
- 9 Set up the Schrodinger wave equation for a simple harmonic oscillator and solve it for the energy eigen values.
- 10 (a) Show that the wave functions describing 1s orbital is normalized.
 Given: $\Psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-\frac{Zr}{a_0}}$
 (b) State Hohenberg - Kohn theorem. (6+6.5)
- 11 (a) Deduce the IR and Raman active modes of vibrations of trans-N₂F₂ molecule and Prove that the molecule obeys mutual exclusion principle. The C_{2h} character table is given below.

C _{2h}	E	C ₂	i	σ _h		
A _g	+1	+1	+1	+1	R _z	x ² , y ² , z ² , xy
B _g	+1	-1	+1	-1	R _x , R _y	xz, yz
A _u	+1	+1	-1	-1	Z	-
B _u	+1	-1	-1	+1	x, y	-

- (b) Illustrate the application of molecular orbital theory to H₂⁺ system. (6.5 + 6)

SECTION D – K5 (CO4)

Answer any ONE of the following **(1 x 15 = 15)**

- 12 (a) Evaluate the commutator for the angular momentum operators L_x and L_y.
 (b) Deduce the wave function and energy for a particle in a one dimensional box. (10+5)
- 13 (a) Determine the order, class and point group of BrF₅ molecule.
 (b) State and explain perturbation theorem.
 (c) Work out the hybridization scheme for σ bonding by boron in BF₃ molecule of D_{3h} symmetry. The D_{3h} character table is provided below. (4+5+6)

D _{3h}	E	2C ₃	3C' ₂	σ _h	2S ₃	3σ _v		
A' ₁	+1	+1	+1	+1	+1	+1	-	x ² +y ² , z ²
A' ₂	+1	+1	-1	+1	+1	-1	R _z	-
E'	+2	-1	0	+2	-1	0	(x, y)	(x ² -y ² , xy)
A'' ₁	+1	+1	+1	-1	-1	-1	-	-
A'' ₂	+1	+1	-1	-1	-1	+1	z	-
E''	+2	-1	0	-2	+1	0	(R _x , R _y)	(xz, yz)

SECTION E – K6 (CO5)

Answer any ONE of the following **(1 x 20 = 20)**

- 14 (a) Use the method of separation of variables to break up Schrodinger equation for hydrogen atom into ordinary angular equations and arrive at the solutions for each.
 (b) The equilibrium inter nuclear distance of H¹²⁷I is 160.4 pm. Calculate the rotational constant of H¹²⁷I. (13+7)
- 15 (a) Explain Wien's displacement and Planck's laws of black body radiation.
 (b) Construct the character table for C_{3v} point group.
 (c) Obtain the total π energy for allyl anion using Huckel MO theory. (6+7+7)
