LOYOLA COLLEGE (AUTONOMOUS) CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2024

PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 13-11-2024   Dept. No.   Max. : 100 Marks
Time: 01:00 pm-04:00 pm

SECTION A – K1 (CO1)

	Answer ALL the questions	**(5 x 1 = 5)**
1	**Answer the following**	
a)	Write the degree and order of the differential equation, $\dfrac{d^2 y}{dx^2}+4\dfrac{dy}{dx}+2\,y=0.$	
b)	State Bohr's correspondence principle.	
c)	Indicate the Slater determinant for beryllium atom.	
d)	How many C_3 axis are present in $CHCl_3$ molecule?	
e)	Write the Hamiltonian operator for any molecule.	

SECTION A – K2 (CO1)

	Answer ALL the questions	**(5 x 1 = 5)**
2	**Fill in the blanks**	
a)	The integral of odd functions between the symmetric limits is equal to _____.	
b)	The expression of wave function for a particle in 2D square box with n =1 is _____.	
c)	The true energy is always _____ than the energy predicted based on the trial wave function.	
d)	The sum of the diagonal elements of a square matrix is called _____.	
e)	$(A_1)^2$ x $(B_1)^2$ x $(B_2)^2$ = _____.	

SECTION B – K3 (CO2)

	Answer any THREE of the following	**(3 x 10 = 30)**
3	(i) Show that the operators, L^2 and L_x commute with each other. (5) (ii) When a clean surface of lithium metal having the work function of 2.30 eV is irradiated with light of wavelength 300 nm, calculate the threshold frequency of the metal and velocity of the ejected photoelectrons. (5)	
4	(i) Derive the wave function and energy for a particle in a rectangular three-dimensional box. (7) (ii) Find the zero point energy of an electron in a one-dimensional box of length 1.0 Å. (3)	
5	(i) Write the Schrodinger equation for H-atom and obtain the expression for its energy. (7) (ii) Convert the Cartesian coordinate, (4, 16, 2) into spherical polar coordinates. (3)	
6	(i) identify the Mulliken notation for the following irreducible representation: (4) E Cn nC$_2$ i σ$_h$	

1	1	-1	-1	-1	

(ii) List down the symmetry elements and operations of toluene and S=C=O molecules.   (6)

7	Work out the hybridization scheme for σ bonding by P atom in PF_5 molecule using the D_{3h} character table given below.

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
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 C – K4 (CO3)

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

8	(i) Derive time-dependent Schrodinger wave equation. (8.5)
	(ii)What are orthogonal and orthonormal functions? (4)

9	(i) Use the method of separation of variables to break up Schrodinger equation for a rigid rotor into ordinary angular equations and write the solutions for each. (9)
	(ii) Draw the radial plot for 3s and 2p orbitals and indicate the nodes. (3.5)

10	(i) State and explain perturbation theorem. (6.5)
	(ii) Predict the point group for eclipsed forms of ferrocene. Write the associated operations of the S_5 axis. (6)

11	(i) Obtain the expression for overlap and coulomb integrals using MO theory. (5)
	(ii) How will you prove the electronically allowed and forbidden transitions in formaldehyde using the ter table?
	(7.5)

Character table for C_{2v} point group

	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear, rotations	quadratic
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

SECTION D – K5 (CO4)

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

12 (i) Find whether the wave function, $\psi = x\,e^{-ax^2}$ is an eigen function of the operator,

$\hat{O} = \dfrac{d^2}{dx^2} - 4a^2 x^2$. (5)

(ii) Explain quantum mechanical tunneling and mention any two evidences for it. (6)

(iii) Evaluate the length of hexatriene chain, which has an absorption maximum at 3009 Å. (4)

13 (i) State Hohenberg - Kohn theorem and write Kohn-Sham equation. (5)

(ii) Predict the point group, order and class for the molecule, trans-$[Pt(Cl)_2(Br)_2]$. (5)

(iii) Find the symmetry of the IR and Raman vibrational modes of ammonia molecule using the following character table. (5)

	E	$2C_3$ (z)	$3\sigma_v$	linear, rotations	quadratic
A_1	1	1	1	z	x^2+y^2, z^2
A_2	1	1	-1	R_z	
E	2	-1	0	$(x, y)\ (R_x, R_y)$	$(x^2-y^2, xy)\ (xz, yz)$

SECTION E – K6 (CO5)

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

14 (i) Solve the Schrodinger equation for a simple harmonic oscillator and obtain its energy levels. (10)

(ii) Outline the postulates of quantum mechanics. (5)

(iii) Show that the wave function describing 1s orbital of hydrogen atom is normalized where

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} \left(\frac{Z}{a_o}\right)^{3/2} e^{-\left(\frac{Zr}{a_0}\right)}$$ (5)

15 (i) For a particle in an infinitely deep one-dimensional potential box of length L, apply the trial wave function $\psi = N \times (L^2 - x^2)$ to calculate the energy using variation theorem. (7)

(ii) Construct the character table for C_{2h} point group using the Great Orthogonality theorem. (6)

(iii) Write down the secular determinant for 1,3-butadiene molecule using Hückel's method and obtain expressions for their energy levels. (7)