



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – APRIL 2024

PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 12-04-2024

Dept. No.

Max. : 100 Marks

Time: 09:00 AM - 12:00 NOON

SECTION A – K1 (CO1)

Answer ALL the questions

(5 x 1 = 5)

1 Answer the following

- a) Define an orthonormal set.
- b) Represent graphically, the wave function, ψ for the state $n = 3$ for a particle in one dimensional box.
- c) Write Kohn - Sham equation.
- d) Mention any two point groups that are related to optical activity.
- e) Whether the vibrations of 'g' modes are Raman active?

SECTION A – K2 (CO1)

Answer ALL the questions

(5 x 1 = 5)

2 Fill in the blanks

- a) Euler's formula is _____.
- b) The expression for finding the ground state energy of a particle in a 2D square box is _____.
- c) The Hamiltonian operator for a perturbed system in terms of an unperturbed system is _____.
- d) The symbol for a one dimensional representation that is symmetric with respect to σ_v is _____.
- e) The overlap integral is defined as _____.

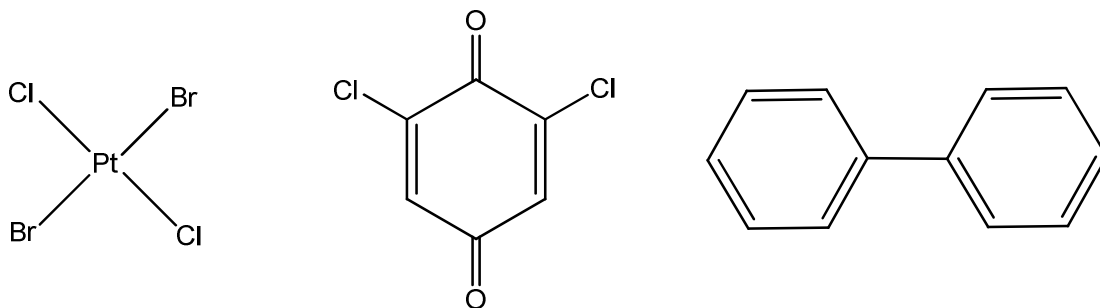
SECTION B – K3 (CO2)

Answer any THREE of the following

(3 x 10 = 30)

- 3** (a) Write the postulates of quantum mechanics.
(b) Show that Balmer series occurs between 3646 Å and 6563 Å. (6+4)
- 4** (a) Illustrate the quantum mechanical tunneling with examples.
(b) A particle of mass 2×10^{-26} g is confined in a one dimensional box of length 4.00 nm. Find wavelength of the photon emitted when the particle goes from $n = 3$ to $n = 2$ level. (5+5)
- 5** Write the Schrodinger equation to be solved for hydrogen atom and solve it for its energy using a simple solution, which assumes the wave function to depend only on the distance r and not on the angles θ and ϕ .

- 6 Predict the point group of the following molecules and determine their order and class.



Which of the above molecules possess dipole moment?

- 7 (a) Normalize the following molecular orbital: $\psi_1 = C(1s_a + 1s_b)$.
 (b) Obtain the possible hybridization scheme of BF_3 molecule using group theory. The D_{3h} character table is provided. (4+6)

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$		
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 C – K4 (CO3)

Answer any TWO of the following

(2 x 12.5 = 25)

- 8 (a) Derive time-dependent Schrodinger wave equation.
 (b) The temperature of a fire ball in a thermonuclear explosion can reach a temperature of about 10^7 K. What value of $\lambda_{\max}$ does this correspond to? (8.5+4)
- 9 Use the method of separation of variables to break up Schrodinger equation for a rigid rotor into ordinary equations and write the solutions for each.
- 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) C_{3v} and C_{3h} point groups have the same order, yet classes are different. Prove. (6.5+6)
- 11 (a) Highlight the importance of variation method in the determination of energy of MO for Hydrogen molecular ion.
 (b) Write down the secular determinant for ethylene and allyl cation using Hückel's method. (6.5+6)

SECTION D – K5 (CO4)

Answer any ONE of the following

(1 x 15 = 15)

- 12** (a) How distant is the point, (5, 20°, 150°) away from the origin?
 (b) Derive the wave function and energy for a particle in a rectangular three dimensional box. (5+10)
- 13** (a) Explain the following: (i) Hartree-Fock Self consistent Field (ii) Pauli principle of anti-symmetric wave function.
 (b) Construct the character table for C_{3v} point group.
 (c) Deduce the IR and Raman active modes of vibrations of CH_4 molecule. The T_d character table is given below: (5+5+5)

Character table for T_d point group

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linear, rotations	quadratic
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)

SECTION E – K6 (CO5)

Answer any ONE of the following

(1 x 20 = 20)

- 14** (a) Evaluate the commutator for the angular momentum operators, L_x and L_y .
 (b) The force constant for $H^{79}Br$ is 392 Nm^{-1} . Calculate the fundamental vibrational frequency and zero point energy of $H^{79}Br$.
 (c) Sketch the radial plot for 2p orbital and also find the angular and radial nodes for 2p orbital. (10+6+4)
- 15** (a) Apply variation theorem to predict the ground state energy of hydrogen atom using the trial wave function, $\psi = e^{-\alpha r}$.
 (b) Determine the symmetry operations and their classes of PCl_5 molecule.
 (c) Find the Huckel molecular orbitals and energies for cyclobutadiene. (7+5+8)
