LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

FIRST SEMESTER – **NOVEMBER 2022**

PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 28-11-2022 Dept. No. Max. : 100 Marks

Time: 01:00 PM - 04:00 PM

	SECTION A		
	Answer ALL the questions		
1	**Answer the following**		**(5 x 1 = 5)**
a)	Mention the limits and Laplacian for spherical coordinates.	K1	CO1
b)	How many degenerate energy levels lie in $11h^2/8mL^2$ for a particle in a cubic box of length L?	K1	CO1
c)	Write the Hamiltonian for H_2^+ ion.	K1	CO1
d)	Identify the number of reflection planes present in a molecule of C_{4v} point group.	K1	CO1
e)	Mention the operator involved in resonance integral.	K1	CO1
2	**Answer the following**		**(5 x 1 = 5)**
a)	Find the accelerating potential for an electron with de Broglie wavelength of 5 Å.	K2	CO1
b)	Predict the value of $H_0(q)$.	K2	CO1
c)	Write the Slater determinant for the ground state configuration $1s^2$.	K2	CO1
d)	What is the point group of $BFCl_2$ molecule?	K2	CO1
e)	Mention the significance of coulomb integral.	K2	CO1
	SECTION B		
	Answer any THREE of the following		**(3 x 10 = 30)**
3	(a) State and explain the postulates of quantum mechanics. (b) Which of the following operators are linear? $()^2$ and d^2/dx^2. Justify. **(5+5)**	K3	CO2
4	Write the Schrödinger wave equation for rigid rotator in terms of spherical angular coordinates. Using the method of separation, separate them into two independent variables such as P(θ) and Z(Φ) and obtain the solution for Φ equation.	K3	CO2
5	(a) For a particle in an infinitely deep one-dimensional potential box of length L, apply the trial wave function $\psi = Nx(L^2-x^2)$ to calculate the energy and obtain the percentage of error. (b) State the Pauli's exclusion principle for ground state electronic configuration of lithium atom. **(6+4)**	K3	CO2
6	a) List the symmetry elements and operations of cyclopropane molecule. b) Obtain the matrix representation for the refelection operation σ_{yz}. **(5+5)**	K3	CO2
7	a) Obtain the reducible representation relating to the prediction of hybridisation scheme in CH_3Cl molecule. b) Evaluate the overlap integral S_{12} in the formation of H_2^+ ion when the distance of separation between the nuclei of two 1S orbitals is 1.32 Å. Given the first Bohr radius 0.529 Å. **(5+5)**	K3	CO2
	SECTION C		
	Answer any TWO of the following		**(2 x 12.5 = 25)**
8	(a) Write the conditions for acceptable wave functions. Identify the acceptable wave functions among the following and justify: (i) x^4 (ii) $\tan\theta$. (b) Show that $\psi = \sin(5x)\sin(8y)\sin(2z)$ is an eigen function of ∇^2 and find the eigen value? (c) Predict the value of $[x, p_x^2]$ and mention its significance. **(4.5+4+4)**	K4	CO3

9	(a) Calculate the length of the γ-carotene molecule which is a conjugated system having 10 double bonds (+ 9 single bonds) and a transition wave length of 4300 Å. (b) Write the Hamiltonian and Schrödinger wave equation for hydrogen like atom. Draw the radial plots for n = 3 and l = 1. **(5+7.5)**	K4	CO3
10	(a) Explain Born-Oppenheimer approximation and write Kohn-Sham equation. (b) Using the concept of Great Orthogonality theorem and construct D_{2h} character table. **(5+7.5)**	K4	CO3
11	(a) What is variation integral? How is it used to determine the energies associated with the trial function $\psi = c_1\psi_{1a} + c_2\psi_{1b}$ in the formation of H_2^+ ion? (b) Explain the evaluation of the average energy integrals H_{aa} and H_{ab}. **(6.5+6)**	K4	CO3
SECTION D			
Answer any ONE of the following **(1 x 15 = 15)**			
12	(a) Derive time dependent Schrödinger wave equation. (b) With the help of perturbation theorem, predict the ground state energy of helium atom. (c) Obtain the value of $L_1(\rho)$ and $P_1(x)$. **(6+5+4)**	K5	CO4
13	(a) Write the requirement of Hartree-Fock self-consistent field method. (b) Identify the symmetries of IR and Raman vibrational modes of trans-2-butene using the C_{2h} character table provided. Verify whether this molecule obeys mutual exclusion principle and mention the significance of the Mulliken symbols of modes. **(3+12)** 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 |	K5	CO4
SECTION E			
Answer any ONE of the following **(1 x 20 = 20)**			
14	(a) Derive the expressions for wave function and energy for a particle in 1-D box of length l. **(6)** (b) Obtain the Hamiltonian for simple harmonic oscillator. Prove that the operator $p_x = (h/2\pi i)\ d/dx$ is Hermitian. **(8)** (c) The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond (mass of ^{35}Cl = 34.9688 u). **(6)**	K6	CO5

15	a) Apply variation theorem to predict the ground state energy of hydrogen atom using the trial wave function, $\psi = e^{-\alpha r}$. b) Using Huckel molecular orbital theory, solve the secular determinants for ethylene and allyl radical. Calculate the total π-electron energy and the stabilisation energy. c) Discuss the application of direct product principle to verify whether the π → π* transition is allowed in HCHO molecule. The C_{2v} character table is given for reference. **(5+8+7)**	K6	CO5

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
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