LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – **NOVEMBER 2019**

PCH 1503/17/18PCH1MC03 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 05-11-2019 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

Answer ALL questions **(10 × 2 = 20)**

1. Convert the point (−3,6, 8) in cartesian coordinate to cylindrical coordinate.
2. Which of the following is an acceptable wave function? e^{-x^2} *or* e^{-x}.
3. Calculate the kinetic energy of the photoelectron emitted with energy 3.10 eV. (Given that ϕ = 2.13 eV).
4. Find out the value of $H_3(y)$ and their corresponding normalization factor of a harmonic oscillator.
5. Mention the significance of Slaters determinant.
6. Obtain the ground state term symbol for Nitrogen atom.
7. What is coulomb integral? Mention the operator involved.
8. Prove that the four C_2 axes in the D_{2h} point group constitute two different classes.
9. Show that the p_z orbital belongs to totally symmetric representation in C_{2v} character table.
10. Identify the equivalent of the following combined operations: $C_2(z)$ and σ_v (xz).

Part-B

Answer any EIGHT questions. **(8 × 5= 40)**

11. Find out whether the operator d/dr is Hermitian for the following eigen functions of a spherically symmetric systems (i) $\psi_1 = e^{-r}$ (ii) $\psi_{12} = e^{-2r}$.
12. Discuss the postulates of quantum mechanics.
13. Write down the Schrödinger wave equation for simple harmonic oscillator and obtain their Hermite polynomial equation.
14. The first line in the rotation spectrum of CO has a frequency of 3.8424 cm^{-1}. Calculate the rotational constant and C-O bond length.
15. Apply variation theorem to the probability of finding the particle in one dimensional box of length 'l' using the trial wave function, $\psi = Nx\,(L - x)$.
16. Obtain the value of the commutator $[x, p_x]$ and mention its significance.

17a. Calculate the zero-point energy of HI molecule. Given the force constant = 314.14 N m^{-1}.

b. Write down the Hamiltonian for helium atom. (3+2)

18. How many irreducible representations are possible for PF_5 molecule? Mention their dimensions.
19. Generate the reducible representation of NH_3 molecule for its vibrational modes using the C_{3v} character table.

	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)

20. C_{3v} and C_{3h} point groups have the same order but yet their classes are different. Justify.
21. Solve the Secular determinant for 1,3-butadiene to obtain MO energies.
22. Obtain the Slater determinants for the excited state of Helium atom.

Part-C

Answer any FOUR questions. **(4 × 10= 40)**

23. a. Derive the time-independent Schrodinger wave equation.
    b. Show that the function $F = cosax\ cosby\ coscz$ is an eigen function of ∇^2 and obtain its eigen value. (6+4)

24. a. Derive the expressions for wave function and energy for a particle in a rectangular box.
    b. Obtain the value of $P_{1,0}(\theta)$ and $P_{2,1}(\theta)$. (5+5)

25. Write down the Hamiltonian and Schrödinger wave equation for hydrogen like atoms. Obtain the value of radial function for (i) $R_{2,0}(r)$ and ii) $R_{2,1}(r)$.

26. a. Show that the following wave function for *2s* orbital is normalized:

$$\psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{z}{a_0}\right)^{\frac{3}{2}} \left(2 - \frac{Zr}{a_0}\right) e^{-\frac{2Zr}{a_0}}.$$

    b. Using HMO theory obtain the resonance energy for allyl cation. (5+5)

27. a. Construct the C_{2v} character table using Great orthogonality theorem and prove that any two irreducible representations are orthogonal.
    b. Offer an explanation for the Mulliken symbols A' and E_u. (7+3)

28. a. Show that the energy integral $H_{ab} = SE + S(e^2/r_{AB}) + K$.
    b. Determine using direct product representation whether $\pi \rightarrow \pi^*$ transition is allowed in ethylene. The D_{2h} character table is provided for reference. (4+6)

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	