LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRSTSEMESTER – NOVEMBER 2017

17/16PCH1MC03/CH1814/CH1808 - QUANTUM CHEMISTRY AND GROUP THEORY

Date: 08-11-2017 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

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

1. List *the first two eigen functions and the eigen values for a particle in a one dimensional box of length 'l' when the origin of the coordinate system is at the middle.*
2. *The work function of a metal is 2.91 $\times 10^{-19}$ J. Calculate the threshold wavelength of the metal.*
3. *Show that '√' is a non-linear operator.*
4. *Determine the value of normalization constant and Hermite polynomial for the vibrational quantum number, n=1.*
5. *State Euler's formula and use it to prove* $sin\theta = \frac{e^{i\theta} - e^{-i\theta}}{2i}$.
6. *Obtain the trace of the matrix for the operation* C_4^2.
7. *Identify the symmetry elements present in* H_2O_2 *molecule.*
8. *Why is it that a molecular plane always forms a class by itself?*
9. *Write the acceptable wave function for an atom with two electrons.*
10. *What is variational integral?*

Part-B

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

11. In the infrared spectrum of $^{39}K^{35}Cl$ an intense line is seen at $\bar{\upsilon}$ 378.0 cm^{-1}. Calculate the force constant and zero point energy of $^{39}K^{35}Cl$.
12. Derive the expression for wave function and energy for a particle in a three dimensional rectangular box of dimensions a, b and c.
13. Show that the wave functions describing 1s orbital are normalized.
    Given: $\Psi_{1s} = \frac{1}{\sqrt{\pi}}(\frac{Z}{a_0})^{\frac{3}{2}}e^{-\frac{Zr}{a_0}}$
14. Derive the time-independent Schrodinger wave equation.
15a. Determine the wave length (in Å) for the third line in Balmer series of hydrogen atomic spectrum.
   b. Prove that $3e^{-8x}$ is an eigen function of secondorder differentiation. Find its eigen value.
   (3+2)
16. Write the Schrodinger equation 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.
17. Show that $[L^2, L_x] = 0$.
18. Obtain the values of L, S and J for the term symbol $^3F_2$.

19. Generate the transformation matrices for the identity operation upon π and π^* orbitals and obtain their characters.
20. List down the symmetry elements and operations present in a tetrahedron.
21. How will you account for the transitions observed in the atomic spectrum of sodium?
22. Show that the total wave function that is antisymmetric in the exchange of coordinates of every pair of electrons does not violate the Pauli exclusion principle.

Part-C

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

23a. Outline the essential postulates of quantum mechanics.

b. How much is the distance of the point $(8, \frac{1}{2}, \frac{\pi}{2})$ away from the origin with the major axis of 10 units?

(6+4)

24a. Apply variation theorem to the probability of finding the particle in one dimensional box of length 'l' using the trial wave function, $\psi = x\,(l - x)$.

b. Explain quantum mechanical tunneling with evidence. (6+4)

25a. Work out the polar and azimuthal wave equations from Schrodinger equation of a rigid rotor and solve them.

b. Find the angular and radial nodes for 2p and 3d orbitals. (8+2)

26a. How will you normalize the molecular orbital in the equation $\psi = N\{\psi_{1s}(A) + \psi_{1s}(B)\}$?

b. Find the irreducible components of representations generated by a set of σ bonds present in NH_3 molecule using the C_{3v} character table provided.

(4+6)

C_{3v}	E	$2C_3$ (z)	$3\sigma_v$		
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)

27a. Describe the simple Huckel molecular treatment of 1,3-butadiene to obtain its π electronic energy.

b. What are Bosons and Fermions? (7+3)

28 a. Outline the construction of C_{2h} character table using great orthogonality theorem.

b. How are the symmetry operations in PCl_5 molecule classified?

(5+5)

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