Reg. No ..... Name .....

M. Sc. DEGREE END SEMESTER EXAMINATION - OCTOBER 2019

SEMESTER 1 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

COURSE : **16P1CHET04 / 16P1CPHT04 : QUANTUM CHEMISTRY AND GROUP THEORY**

(For Regular - 2019 Admission and Supplementary - 2016/2017/2018 Admissions)

Time : Three Hours Max. Marks: 75

Section A
Answer any 10 (2 marks each)

1. In molecules with center of symmetry, IR active vibrations are not Raman active. Explain
2. Derive a reducible representation for C_{3v} point group using the C-H bonds of methoxide anion
3. What are direct product representations of a point group? Illustrate with C_{2v} point group
4. Identify the point group of the molecules with following set of operations (a) {E, $C_{2(z)}$, $C_{2(x)}$, $C_{2(y)}$, i, $S_{(xy)}$, $S_{(xz)}$, $S_{(yz)}$ } (b) {E, $8C_3$, $3C_2$, $6S_4$, $6s_d$}
5. Explain the concept Block diagonalisation.
6. Verify that wave functions of a particle in 1D box of width *a* and infinite height are orthogonal.
7. What is Hamiltonian operator ? Write the Hamiltonian operator for an atom resides in a room with 3-dimensions.
8. Why does $\Psi^*\Psi$ have to be everywhere real, nonnegative, finite and of definite value ?
9. Zero point energy of a rigid rotator is zero. Is this against the uncertainty principle?
10. Sketch the rough graphs of Ψ and of Ψ^2 for the n = 4 and n = 5 states for a particle-in 1-D-box.
11. Calculate the probability that a particle in one-dimensional box of length 'a' is found to be between 0 and a/2.
12. Apply the free electron model to the 6π electron system-hexatriene. Assuming that the length of hexatriene molecule is 867 pm, show that the first electronic transition is predicted to occur at $2.8 \times 10^4 cm^{-1}$.
13. Define Bohr radius

(2 x 10 = 20)

Section B
Answer any 5 (5 marks each)

14. Determine the type of hybridization in methane molecule using the character table for Td point group.

Td	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)

15. Prove the mutual exclusion principle using the given reducible representations of trans N_2F_2 and trans dichloro ethylene molecules

C_{2h}	E	C_2	i	σ xz
Γ(R) – N_2F_2	12	0	0	4
Γ(R) – trans dichloro ethylene	18	0	0	6

16. What are reducible and irreducible representations of a group? Find a reducible representation of the group by taking p orbitals of 1,3 butadiene molecule.
17. Write the operations of C_{2h} point group. Construct the group multiplication table for this group and find the subgroups. Give an example of a molecule that belongs to this group.
18. Prove that $[L^2, L_x] = 0$.
19. Discuss the physical origin of quantum mechanical tunnelling. Identify two chemical systems where tunnelling might play a role.
20. To a good approximation, the microwave spectrum of $H^{35}Cl$ consists of a series of equally spaced lines, separated by 6.26×10^{11}Hz. Calculate the bond length of $H^{35}Cl$.
21. Write the Legendre polynomial expression in spherical harmonics. Show that (a) the associated Legendre polynomial P_l /m/ vanishes whenever /m/ > l (b) the P_l /m/ reduce to Legendre polynomial Pl when m = 0.

(5 x 5 = 25)

Section C
Answer any 2 (15 marks each)

22. Determine the symmetris of the vibrational modes of $CHCl_3$ molecule and determine which one are IR and Raman active using normal co-ordianate analysis.
23. What are character tables? State the theorem concerning the irreducible representations of a group. And use the theorem to derive the character table for C_{2v} point group.
24. (a)Show that the variables in the Schrödinger equation for a cubic box may be separated and the overall wavefunctions expressed as X(x) .Y(y). Z (z). (b) Deduce the energy levels and wavefunctions. (c) Show that the wavefunctions are orthonormal (d) what is the degeneracy of the level with $E = 14h^2/8ml^2$
25. Solve the Schrodinger equation for hydrogen atom . Discuss the solutions in detail

(15 x 2 = 30)