Reg. No ..... Name **18P146**

M.Sc DEGREE END SEMESTER EXAMINATION - NOVEMBER 2018

SEMESTER 1 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY

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

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

Time : Three Hours Max. Marks: 75

Section A
Answer any 10 (2 marks each)

1. Give the expression for reduction formula. Explain the terms in it.
2. State the selection rule for IR spectroscopy based on the principles of group theory
3. The vibrational mode of a molecule of C_{3v} point group belong to E symmetry. Can this vibrational mode be IR active? Justify
4. What are similarity transformations? what are the similarity transformations of C_2 point group
5. Determine a representation of C_{2v} point group by taking the CH bonds of dichloromethane as basis vectors. Is it reducible or irreducible?
6. Deduce the matrix representation for reflection about the xy, xz planes and find their prodcut.
7. What are eigen functions and eigen values. Give example.
8. Calculate the commutator [x, d/dx]
9. Calculate the expectation value of energy of a particle in 1 D box described by the wave function $(2/a)^{1/2} \sin(n\pi x/a)$.
10. Zero point energy of a rigid rotator is zero. Is this against the uncertainty principle?
11. Sketch the rough graphs of Ψ and of Ψ^2 for the n = 4 and n =5 particle-in-a-box states.
12. In what respects the quantum mechanical harmonic oscillator differs from classical oscillator.
13. What are the permitted values of quantum number n? Explain, why a zero value is not permitted?

(2 x 10 = 20)

Section B
Answer any 5 (5 marks each)

14. Define SALC. Generate the SALC orbitals of water molecule with bond vectors as basis.
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}
$\Gamma(R) - N_2F_2$	12	0	0	4
$\Gamma(R)$ – 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. Systematically determine the point group staggered ferrocene. List the elements of the point group.
18. Show that Schrodinger wave equation is an Eigenvalue equation
19. β-carotene is a linear polyene in which 10 single and 11 double bonds are in conjugation along a chain of 22 carbon atoms. If we take each C-C bond length to be about 140 pm, then the length of the molecular box in β-carotene is 2.94 nm. Estimate the wavelength of light absorbed by this molecule from its ground state to next higher excited state.
20. Discuss the physical origin of quantum mechanical tunnelling. Identify two chemical systems where tunnelling might play a role.
21. (a)The infrared absorption spectrum of $^{1}H^{35}Cl$ has its strongest band at 8.65×10^{13} Hz. Calculate the force constant of the bond in this molecule. (b) Find the approximate zero-point vibrational energy of $^{1}H^{35}Cl$.

(5 x 5 = 25)

Section C
Answer any 2 (15 marks each)

22. Generate the matrix representations of PCl_5 molecule with bond vectors as basis. Determine the hybridization of P in PCl_5 molecule using the applications of group theory. Given D3h character table.

D3h	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic
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)

23. State the Great Orthogonality theorem. Based on the theorem derive the character table for C_{2h} 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)