

M. Sc DEGREE END SEMESTER EXAMINATION - OCT 2020 : FEBRUARY 2021**SEMESTER 1 : CHEMISTRY / PHARMACEUTICAL CHEMISTRY****COURSE : 16P1CHET04 / 16P1CPHT04 : QUANTUM CHEMISTRY AND GROUP THEORY***(For Regular - 2020 Admission and Supplementary - 2016/2017/2018/2019 Admissions)*

Time : Three Hours

Max. Marks: 75

PART A**Answer any 10 (2 marks each)**

- In molecules with center of symmetry, IR active vibrations are not Raman active. Explain
- Is it possible to find the symmetries of bending vibrations and stretching vibrations of a molecule separately? Explain
- Deduce the matrix representation for reflection about the xy, xz planes and find their product.
- Write the multiplication table for C_3 point group? What type of point group is it?
- What are direct product representations of a point group? Illustrate with C_{2v} point group
- Whether d/dx and d/dy commute with each other. Justify your answer
- Calculate the expectation value of energy of a particle in 1 D box described by the wave function $(2/a)^{1/2} \sin(n\pi x/a)$.
- What is a well behaved function? Explain
- Discuss the physical origin of quantisation of energy for a particle confined to move in a one-dimensional box.
- Define zero-point energy. Provide an example for zero-point energy.
- For butadiene, $CH_2=CH-CH=CH_2$, take the box length as 7.0 \AA and apply the free electron model to estimate the wavelength of light absorbed when a pi electron is excited from the highest occupied to the lowest vacant box level.
- For a particle in a cubic box, what is the degree of degeneracy of the energy levels with the following values of $h^2 / 8ma^2$? (a) 9 (b) 12 (c) 14 (d) 27
- State Uhlenbeck and Goudsmit electron spin postulates in quantum mechanics.

(2 x 10 = 20)**PART B****Answer any 5 (5 marks each)**

- Determine the symmetries of the vibrational modes of NH_3 molecules using cartesian coordinates
- 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
$\Gamma(R) - \text{trans dichloro ethylene}$	18	0	0	6

- 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.
- Derive the group multiplication table for C_{3v} point group.
- Solve the Schrödinger wave equation for a particle in one-dimensional box
- Point out the similarities and differences between the one-dimensional particle-in-a box and the harmonic-oscillator wavefunctions and energies.

20. The force constant of $^{79}\text{Br}^{79}\text{Br}$ is 240 Nm^{-1} . Calculate the fundamental vibrational frequency and zero-point energy of Br-Br, approximating the molecular vibration as that of a harmonic oscillator.
21. Discuss the radial and angular Schrodinger equation of hydrogen atom depend on the variables r, θ, φ and its solutions

(5 x 5 = 25)

PART C

Answer any 2 (15 marks each)

22. Explain the symmetry selection rules for IR and Raman Spectra. What is the significance of third and fourth area of character table of a point group in spectroscopy. Determine the IR and Raman Active vibrational modes of ammonia molecule using character table.
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. Solve the Schrödinger equation for a rigid rotator. Discuss the results.
25. Solve the Schrodinger equation for hydrogen atom . Discuss the solutions in detail

(15 x 2 = 30)