



LOYOLA COLLEGE (AUTONOMOUS), CHENNAI-600034

M.Sc. DEGREE EXAMINATION-CHEMISTRY

FIRST SEMESTER-NOVEMBER 2015

CH-1814: QUANTUM CHEMISTRY AND GROUP THEORY

Date : 07/11/2015

Time : 01:00-04:00

Dept.

Max: 100 Marks

Part-A

Answer ALL questions.

(10 × 2 = 20)

- Determine whether the following functions are odd or even. Justify your answer.
(i) $e^{-x^2} \cos x$ (ii) $x^2 \sin x$
- Rigel, the brightest star in constellation Orion, has approximately a blackbody radiation spectrum with a maximum wave length of 145 nm. Estimate the surface temperature of Rigel.
- What is quantum mechanical tunneling?
- Show that the eigenvalues of Hermitian operators are real.
- Obtain the ground state atomic term symbol for carbon.
- State variation principle. Mention its significance.
- Mention any two point groups that obey mutual exclusion principle.
- Why is a molecular plane always identified to form a class by itself?
- Mention the significance of Secular determinant.
- Write down the Hamiltonian for Hydrogen molecular ion.

Part-B

Answer any EIGHT questions.

(8 × 5 = 40)

- Convert the Cartesian coordinate $(-1, 1, -\sqrt{2})$ into spherical polar coordinates.
- Derive time independent Schrodinger wave equation from time dependent equation.
- The force constant for H^{79}Br is 392 Nm^{-1} . Calculate the fundamental vibrational frequency and zero point energy of H^{79}Br .
- Use the method of separation of variables to break up Schrodinger equation for a rigid rotor into ordinary angular equations and write the solutions for each.
- Show that for a 1s orbital of a hydrogen like ion, the most probable distance from the nucleus to electron is a_0/Z .
- State Pauli's antisymmetric principle and illustrate it for the ground state of helium atom.
- Evaluate the commutator for angular momentum components L_x and L_z .
- Classify the symmetry operations of i) NH_3 ii) H_3BO_3 .
- How will you arrive at the matrix representation for S_n operation?
- What are the features that distinguish the Huckel method from other LCAO methods?
- A molecule is found to have 5 classes of 8 symmetry operations. Work out the number and the dimensionality of the irreducible representations.
- What are coulomb and exchange integrals? How are they obtained?

Part-C

Answer any **FOUR** questions.

(4 × 10 = 40)

- 23a. Explain the postulates of quantum mechanics.
- b. Show that the wave function, $\psi = xe^{-x^2/2}$ is an eigenfunction of the operator,
 $\hat{O} = -\frac{d^2}{dx^2} + x^2$ and find the eigenvalue. (6+4)
- 24a. Derive the wave function and energy for a particle in a rectangular three dimensional box.
- b. Determine the wave length of light absorbed when an electron in a linear molecule of 11.8 Å long makes a transition from the energy level, $n = 1$ to $n = 2$. (7+3)
- 25a. Evaluate the first order correction to the energy term when an electric field of strength 'F' is applied to a particle in a one dimensional box of length 'l'.
- b. Draw the radial distribution plot for 3d and 4s orbitals of H-atom and indicate the nodes. (8+2)
- 26a. Outline the construction of the character table for C_{3v} point group.
- b. Find the Huckel molecular orbitals and energies for allyl radical. (6+4)
27. How is the energy of the orbitals of hydrogen molecular ion determined through energy and overlap integrals?
- 28a. Prove that one of the operations of the symmetry element S_6 corresponds to C_3 axis independently.
- b. Predict the Mulliken symbols for the irreducible representations T_1, T_2, T_3 in the D_3 character table shown below. (4+6)

D_3	E	$2C_3 (z)$	$3C'_2$		
T_1	+1	+1	+1	-	x^2+y^2, z^2
T_2	+1	+1	-1	z, R_z	-
T_3	+2	-1	0	$(x, y) (R_x, R_y)$	$(x^2-y^2, xy) (xz, yz)$
