LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – APRIL 2023

PCH 1503 – QUANTUM CHEMISTRY AND GROUP THEORY

Date: 04-05-2023   Dept. No.   Max. : 100 Marks
Time: 09:00 AM - 12:00 NOON

PART A

Answer ALL questions   **(10 x 2 = 20 marks)**

1. Predict the eigen value of the function e^{x^2} with an operator $\frac{d^2}{dx^2}$.
2. Mention the conditions for well-behaved wave functions.
3. State Bohr's correspondence principle.
4. Determine the wave length of light absorbed when an electron in a linear molecule 10 Å long makes a transition from the energy level n = 1 to n = 2.
5. What is the need of approximation method for obtaining solutions to the wave equation?
6. Mention the significance of Secular determinant.
7. What are resonance and coulomb integrals?
8. Obtain the trace of the matrix corresponding to the operation C_6^3.
9. Identify the equivalent operation to the operations i) S_4^2 ii) S_6^4.
10. Predict the Mulliken symbol for a two-dimensional representation that is anti-symmetric with respect to horizontal plane.

PART B

Answer any EIGHT questions   **(8 x 5 = 40 marks)**

11. State and explain the postulates of quantum mechanics.
12. (a) Normalize e^{i5x} in the interval of $(-\pi, \pi)$.
    (b) Which of the following operators is linear, ∇^2 and $\sqrt{}$?
13. Arrive the Hamiltonian for simple harmonic oscillator.
14. Derive the expressions for wave function and energy of a particle in 1-D box of length l.
15. The wavenumber of the fundamental vibrational transition of $^{35}Cl_2$ is 564.9 cm^{-1}. Calculate the force constant of the bond (m(^{35}Cl) = 34.9688 u).
16. State and explain variation theorem.
17. Obtain the value of $[x, p_x^2]$. Mention its physical significance.
18. Give the assumptions of Huckel molecular orbital theory and apply it to ethylene molecule.
19. Find the Huckel molecular orbitals and obtain the energies for allyl radical.
20. Mention the proper and improper axes of rotations possible in Benzene molecule.
21. How are the symmetry operations of D_{3h} point group classified?
22. Predict the number of irreducible representations and their dimensions for *trans*-N_2F_2 molecule.

PART C

Answer any FOUR questions   **(4 x 10 = 40 marks)**

23. (a) Derive time-independent Schrödinger wave equation.   (5+5)
    (b) State Wien's displacement law.

24. Write down the Schrödinger wave equation for rigid rotator in terms of spherical angular coordinates. Using the method of separation, separate them into two independent variables such as P(θ) and Z(φ).

25. (a) Write down the Hamiltonian and Schrödinger wave equation for hydrogen like atoms.
    (b) With the help of perturbation theorem, predict the ground state energy of Helium atom.   (5+5)

26. Illustrate the importance of variation method to obtain the energy of the molecular orbitals of hydrogen molecular ion and also show that the energy integral
    $H_{ab} = SE + S(e^2/r_{AB}) + K$.

27. a) Calculate the total π-electron energy and delocalization energy for 1,3-butadiene molecule.
    b) Obtain the reducible representation to determine the molecular vibrations in PCl_3 molecule.   (6+4)

28. Work out the hybridization scheme for σ bonding by boron in BCl_3 molecule using the D_{3h} character table provided.

D_{3h}	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$		
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)

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