LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – **CHEMISTRY**

FIRST SEMESTER – NOVEMBER 2016

16PCH1MC03 / CH 1808 / CH 1814 - QUANTUM CHEMISTRY AND GROUP THEORY

Date: 07-11-2016 Dept. No. Max. : 100 Marks

Time: 01:00-04:00

Part-A

Answer ALL questions. **(10 × 2= 20)**

1. Normalise the wave function, Ψ = $Asin(\frac{n\pi x}{a})$ for a particle in one dimensional box of length 'a'.
2. Calculate the de Broglie wave length for an electron with a kinetic energy of 100 eV.
3. State Bohr's correspondence principle.
4. Calculate the energy for the transition from n = 2 to n=3 state for an electron in a one dimensional box of length 5.78 Å.
5. Draw the radial distribution plot for 2p and 3d orbitals of H-atom and indicate the nodes.
6. Identify the symmetry elements present in $POCl_3$ molecule.
7. Obtain the characters for $2p_x$ orbital with respect to the symmetry operations of C_{2v} point group.
8. What is the Mulliken symbol for a two dimensional representation which is anti- symmetric with respect to horizontal plane?
9. How will you write the acceptable wave function for an atom containing two electrons?
10. Write the Hamiltonian for helium atom and mention the terms involved.

Part-B

Answer any EIGHT questions. **(8 × 5= 40)**

11. Calculate the wave length in Å of the second line in Paschen series of hydrogen spectrum.

12 a. Convert the coordinate, (2, $\frac{\pi}{4}$, 5) into Cartesian coordinate.

b. Show that the value of Stefan-Boltzmann constant is 5.66×10^{-8} J m^{-2} K^{-4} s^{-1} **(3+2)**

13. Determine the energy required for the transition from $n_x = n_y = n_z = 1$ to $n_x = n_y = 1$, $n_z = 2$ state for an argon atom (atomic mass = 39.95 g mol^{-1}) in a cubic container with 1.0 cm side.
14. Explain any two evidences for quantum mechanical tunneling.
15. The microwave spectrum of $^{39}K^{127}I$ consists of a series of lines with almost constant spacing of 3634 Hz. Calculate the bond length of $^{39}K^{127}I$.
16. Apply variation theorem to the probability of finding the particle in one dimensional box of length '*l*' using the trial wave function, ψ = $x\,(l - x)$.
17. If a horizontal plane of symmetry is added to D_2 point group, find the resulting point group and list its symmetry operations.

18. Predict the point group of BeF_2 and PCl_3 molecules with the list of the operations.

19. The three1s orbital of hydrogen of ammonia molecule have the character given below

E	$2C_3$	$3\sigma_v$
3	0	1

Identify the irreducible representations using the character table given below.

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

20. What are resonance and coulomb integrals? Obtain their expressions.

21. Prove that the angular momentum and kinetic energy of a particle can be measured simultaneously to an arbitrary precision.

22. Evaluate the commutator [Lz,Lx] and mention its significance.

Part-C

Answer any FOUR questions. **(4 × 10= 40)**

23 a. Explain the postulates of quantum mechanics. **(7+3)**

b. Calculate the eigenvalue, if the function, $\frac{1}{\pi}sin(3.63x)$ is an eigenfunction of operator $\frac{-h^2}{8\pi^2 m}\frac{d^2}{dx^2}$.

24. Solve the Schrodinger equation for simple harmonic oscillator and obtain its energy levels.

25. Use the method of separation of variables to break up Schrodinger equation for hydrogen atom into ordinary angular equations and write the solutions for each.

26 a. Construct C_{2h} character table using the Great orthogonality theorem.

b. What is transition probability integral? Mention its importance. **(6+4)**

27 a. How are the symmetry operations of D_{3h} point group classified?

b. Solve the secular determinantel equations of allyl cation and allyl anion for their delocalization energy. **(4+6)**

28 a. Obtain expressions for the energy of the molecular orbitals of hydrogen molecular ion using variation method.

b. Verify whether an energy state with term symbol $^2P_{5/2}$ can exist. **(7+3)**

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