# LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – APRIL 2010

**CH 1808 - QUANTUM CHEMISTRY & GROUP THEORY**

Date & Time: 29/04/2010 / 1:00 - 4:00 Dept. No. Max. : 100 Marks

**PART-A**

**ANSWER ALL QUESTIONS (10 × 2 = 20)**

1. Show that the function $\Psi(x,y,z) = \sin ax \sin by \sin cz$ (where a,b,c are constants) is an eigen function of the Laplacian Operaator $\nabla^2$. What is its eigen value?
2. The accepted wave function Φ for a rigid rotor is $N\exp(\pm im\varphi)$ for $0 \le \varphi \le 2\pi$. Determine N.
3. Show that the energy $E = 11h^2/8ma^2$ of a particle in a cubic box of side 'a' is triply degenerate.
4. What is a well-behaved or acceptable wave function in quantum mechanics?
5. Under what conditions an electron would give a continuous or discrete spectrum? Why?
6. What is a node? Sketch a rough graph of $\psi^2$ for n=3 for a particle in 1-D box, and v =3 for the harmonic oscillator model. Indicate the nodes.
7. $[\mathbf{L^2},\mathbf{L_x}]$ =? What is its physical significance?
8. Write the Hamiltonian operator for the $H_2^+$ molecular ion in atomic units defining each term involved in it.
9. Explain the principle of mutual exclusion with an example.
10. Identify the point groups for the following molecules:
    (a) $Br_2$ (b) $CH_3Br$ (c) $[Co(NH_3)_6]^{3+}$ d) $IF_5$

**PART-B**

**ANSWER ANY EIGHT QUESTIONS (8 × 5 = 40)**

11. Derive the Schroedinger time-independent wave equation from the time-dependent one.
12. What is a hermitian operator and its significance? Show that eigen functions corresponding to two different eigen values of a hermitian operator are orthogonal.
13. Show that in spherical polar coordinates the operator for the Z-component of angular momentum becomes $\mathbf{L_z} = -i\hbar\delta/\delta\varphi$. Show that the function $\Phi = Ae^{im\varphi}$ are eigen functions of $\mathbf{L_z}$ while the functions $\Phi = A\sin m\varphi$ or $\Phi = A\cos m\varphi$ are not. Evaluate the normalization constant A in the equation $\Phi = Ae^{im\varphi}$.
14. Show that the wave function describing the 1s orbital of H-atom is normalized, given: $\Psi_{1s} = (1/\sqrt{\pi})\,(Z/a_0)^{3/2}\exp(-Zr/a_0)$. [Useful integral: $_0{}^{\infty}\int x^n e^{-ax}dx = n!/a^{n+1}$]
15. Illustrate Bohr's Correspondence Principle and its significance taking any quantum mechanical model.
16. The force constant of $^{79}Br^{79}Br$ is 240 $Nm^{-1}$. Calculate the fundamental vibrational frequency and the zero-point energy of the molecule.
17. Explain quantum mechanical tunneling with a suitable example.
18. Define and explain the overlap, coulomb and resonance integrals which are found in solving $H_2^+$ problem using the LCAO method?
19. $\psi = (2a/\pi)^{1/4}\exp(-ax^2)$ is an eigen function of the hamiltonian operator
    $H = -(h^2/8\pi^2 m)\, d^2/dx^2 + (1/2)\, kx^2$ for the 1-D Simple Harmonic Oscillator.

    a) Find the eigenvalue E of $H\Psi = E\Psi$
    b) Show that the above obtained eigen value in terms of the classical frequency $\nu = (1/2\pi)\sqrt{(k/m)}$ and the constant $a = (\pi/h)(km)^{1/2}$ is $E = (1/2)h\nu$.

20. With an example explain: (a) Spherical Harmonics (b) Born-Oppenheimer Approximation.
21. Define a "Group' and a 'Class' in group theory? Explain with a suitable example each.
22. Define the three parts of a term symbol and write the term symbols arising out of the excited configuration of carbon: $1s^2 2s^2 2p^1 3p^1$.

**PART-C**

**ANSWER ANY FOUR QUESTIONS (4 × 10 = 40)**

23. a) Set up the Schroedinger equation for a particle in 1-D box and solve it for its energy and wave function.
    b) A cubic box of 10Å on the side contains 12 electrons. Applying the simple particle in a box model, calculate the value of ΔE for the first excited state of this system. (7+3)
24. (a) Illustrate the variation method with an example.
    (b) State the Pauli Exclusion Principle for electrons and show how it is applied to He atom in its ground state. (4+6)
25. Discuss the Molecular Orbital treatment of $H_2$ molecule and explain how the Valance Bond (Heitler-London) method overcomes some of the difficulties of MO theory. (10)
26. a) What are the three important approximations that distinguish the HMO method from other LCAO methods.
    b) Write down the secular determinant obtained on applying Huckel's method to 1,3-butadiene and obtain expressions for the energy levels. (3+7)
27. a) Write the Schroedinger equation to be solved for H atom and solve it for its energy using a simple solution, which assumes the wave function to depend only on the distance r and not on θ and φ.
    b) The wave function of 1s orbital of $Li^{2+}$ is $\Psi_{1s} = (1/\sqrt{\pi})\,(Z/a_0)^{3/2}\exp(-Zr/a_0)$, where $a_0$ is the most probable distance of the electron from the nucleus and Z is the atomic number. Show that the average distance is $a_0/2$. [Help: $\int_0^\infty x^n e^{-qx} = n!/q^{n+1}$] (4+6)

28. Find the number, symmetry species of the infrared and Raman active vibrations of $NH_3$, which belongs to $C_{3V}$ point group. State how many of them are coincident.
(You may, if you wish, use the table of f(R) given below for solving this).

| Operation: | E | σ | i | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $S_3$ | $S_4$ | $S_5$ | $S_6$ | $S_8$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| f(R): | 3 | 1 | -3 | -1 | 0 | 1 | 1.618 | 2 | -2 | -1 | 0.382 | 0 | 0.414 |

For any $C_n$, $f(R) = 1 + 2\cos(2\pi/n)$, For any $S_n$, $f(R) = -1 + 2\cos(2\pi/n)$

| $D_{3V}$ | E | $2C_3$ | $3\sigma_v$ | | |
|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | z | $x^2 + y^2$, $z^2$ |
| $A_2$ | 1 | 1 | -1 | $R_z$ | |
| E | 2 | -1 | 0 | (x,y) ($R_x$,$R_y$) | ($x^2 - y^2$,xy) (xz,yz) |

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