LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

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

FIRST SEMESTER – NOVEMBER 2007

CH 1808 - QUANTUM CHEMISTRY & GROUP THEORY

AD 16

Date : 31/10/2007 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

PART-A

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

1. If Ae^{-ax} is an eigen function of the operator d^2/dx^2, what is its eigen value?
2. Show that the first two members of Legendre Polynomials, x and ½ $(3x^2-1)$ are mutually orthogonal over [-1,1]
3. Define a well-behaved function in quantum mechanics.
4. How are energy and length expressed or measured in atomic units?
5. Write the time-dependent Schrodinger wave equation for a single particle in 1-D in stationary state.
6. What is a node? Draw the radial distribution plot for 3s orbital of H-atom and indicate where the nodes are.
7. Differentiate quantum mechanically a 'fermion' from a 'boson'.
8. Write the Hamiltonian operator for the H_2 molecule defining each term involved in it.
9. List the symmetry elements of pyridine molecule.
10. Identify the point groups for the following molecules:
    (a) HCl (b) CH_3Cl (c) CH_2Cl_2 d) IF_7

PART-B

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

11. What do you understand by "Postulates of Quantum Mechanics"? State and explain any two of them.
12. What is a hermitian operator? Show that the eigen value of a hermitian operator is real.
13. Illustrate the significance of Bohr's Correspondence Principle taking any quantum mechanical model.
14. Explain briefly with a suitable example: (a) quantum mechanical tunneling
    (b) Principle of Mutual Exclusion (3+2)
15. (a) Show that [d/dx, x] = 1
    (b) What are the values of $[\mathbf{x},\mathbf{p}_x]$ and $[\mathbf{L}^2,\mathbf{L}_x]$? What is their physical significance? (2+2+1)
16. What is Slater determinant? Taking He atom in its excited state ($1s^1$, $2s^1$) write the four Slater determinants.
17. Define and explain the overlap, coulomb and resonance integrals which are found in solving H_2^+ problem using the LCAO method?
18. State the Variation Theorem. Apply the variation method to get an upper bound to the ground state energy of particle in a 1-D box using the trial function $\psi = x(a^2-x^2)$, where a is the length of the box. Compare your result with the true value. (2+3)
19. CO absorbs energy at 768 m^{-1}. The absorption can be attributed to the J=1 to J=2 transition. Using the expression for the energy of the rigid rotor, calculate the moment of inertia and the internuclear distance.
20. $\psi = (2a/\pi)^{1/4}\exp(-ax^2)$ is an eigen function of the hamiltonian operator
    $H = -(h^2/8\pi^2m)\, d^2/dx^2 + (1/2)\, kx^2$ 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 $E = (1/2)h\nu$. (4+1)

21. (a) Explain the concept of "Group' in group theory with an example.
(b) When do we say two symmetry operations are in the same class? Illustrate with a suitable example. (3+2)

22. (a) Give the reduction formula and define the terms used.
(b) Give the meaning of (i) A_u (ii) E" with their subscripts and superscripts, which represent the irreducible representations in a character table. (2+3)

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) For the butadiene molecule, calculate the λ_{max} on the basis of a particle in a 1-D box of length 5.0 Å. (7+3)

24. Discuss the Pauli Exclusion Principle in quantum mechanics applied to He atom in its ground state. (10)

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 allyl cation. Obtain therefrom expressions for the energy levels and the wave functions. (3+7)

27. a) Write briefly on Born-Oppenheimer approximation.
b) Calculate the energy in cm^{-1} of the first two energy levels of a particle in a box and their energy difference for (a) an electron in a box of 2Å in length (b) a ball-bearing of mass 1g in box of 1 cm length. Compare the results and on their basis enunciate the Bohr's Correspondence Priniciple. (4+6)

28. Find the number, symmetry species of the infrared and Raman active vibrations of CCl_4, which belongs to T_d 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, $f(R) = -1 + 2\cos(2\pi/n)$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2+z^2$
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		$(2z^2-x^2-y^2; x^2-y^2)$
T_1	3	0	-1	1	-1	(R_x,R_y,R_z)	
T_2	3	0	-1	-1	1	(x,y,z)	(xy, yz, zx)

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