LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION – CHEMISTRY

FIRST SEMESTER – NOVEMBER 2009

CH 1808 - QUANTUM CHEMISTRY & GROUP THEORY

Date & Time: 09/11/2009 / 1:00 - 4:00 Dept. No. Max. : 100 Marks

PART-A

ANSWER ALL QUESTIONS (10 × 2 = 20)

1. For the wave function $\Psi(\varphi) = Ae^{im\varphi}$, where m is an integer, for $0 \le \varphi \le 2\pi$, determine A so that the wave function is normalized.
2. Show that Ae^{-ax} is an eigen function of the operator d^2/dx^2. What is the eigen value?
3. For the hexatriene molecule, calculate λ_{max} on the basis of particle in a one-dimensional box of length equal to 7.3Å.
4. The energy of a particle moving in a 3-D cubic box of side 'a' is $13h^2/4ma^2$. How many degenerate energy levels are there and what are they?
5. What is a node? Draw the radial distribution plot for 3p orbital of H-atom and indicate where the nodes are.
6. What is the value of [$\mathbf{y}$,$\mathbf{p_y}$]? What is its physical significance?
7. When do we say two symmetry operations are in the same class? Give an example.
8. Identify the point groups for the following molecules:
   (a) H_2 (b) HBr (c) C_6H_6 (d) $Ni(CN)_4^{2-}$ (square planar)
9. Explain the terms 'hartree' and 'bohr'.
10. What is a character table? What is the meaning of B_u in a character table?

PART-B

ANSWER ANY EIGHT QUESTIONS (8 × 5 = 40)

11. Derive the time-independent Schroedinger equation from the time-dependent and prove that the property as electron density is time independent although the wave function describing an electron is time dependent.
12. The microwave spectrum of the CN radical shows a series of lines spaced by a nearly constant amount of 3.798 cm^{-1}. What is the bond length of CN?
13. What is a Hermitian operator? Show that the eigen value of a hermitian operator is real.
14. Write the Schroedinger equation for 1-D harmonic oscillator and verify if $\psi = (2a/\pi)^{1/4}\exp(-ax^2)$ is an eigen function of the Hamiltonian operator for the 1-D harmonic oscillator.
15. Calculate the most probable position of r for an electron in He^+ ion 1s orbital, given $\psi_{1s} = (1/\sqrt{\pi})(Z/a_0)^{3/2}\exp(-Zr/a_0)$.
16. Illustrate Bohr's Correspondence Principle with a quantum mechanical model.
17. Write the Hamiltonian in atomic units for H_2 molecule and explain briefly how Heitler-London and Rosen improved upon the MO theory treatment.

18. What is a Slater determinant? Write the four Slater determinants for the excited state of He atom (1s,2s).
19. Explain what a term symbol is and demonstrate its use in explaining the origin of the fine structure of the emission spectrum of sodium vapor used in street lighting.
20. State and illustrate the variation theorem applying to a suitable system. Compare the result with the true value.
21. Illustrate the following with the suitable example: (a) quantum mechanical tunneling (b) Born-Oppenheimer approximation.
22. The reducible representation obtained using the four Mn-O bonds in MnO_4 as bases is

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
	4	1	0	0	2

Reduce this into irreducible representation using the T_d character table given below and find out the nature of hybrid orbitals in MnO_4.

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,xz,yz)

PART-C

ANSWER ANY FOUR QUESTIONS **($4 \times 10 = 40$)**

23. a) Set up the Schroedinger equation for a particle in 1-D box and solve it for its energy and wave function.
 b) The bond length and the force constant of $^{1}H^{127}I$ are 0.1609 nm and $314 Nm^{-1}$ respectively. Calculate the value of the fundamental vibrational frequency and its rotational constant. (6+4)

24. (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 the angles θ and φ.
 b) Explain Spherical harmonics with a suitable example (7+3)

25. a) State Pauli Exclusion Principle applied to bosons.
 b) Illustrate the Pauli Exclusion Principle taking He atom as example and derive the acceptable wave function for the ground state of He atom. (2+8)

26. a) What are the three important approximations that the Huckel MO method uses for treatment of π-orbitals in conjugated systems?
 b) Write down the secular determinant using Huckel's method to allyl anion and obtain the expressions for the energy levels of the π electrons. (3+7)

27. (a) In solving the H_2^+ problem using the LCAO method, the lowest energy obtained is $E_+ = (H_{AA} + H_{AB}) / (1+S_{AB})$ where A and B refer to the two hydrogen nuclei. Explain each of the integrals in the above equation and their significance.
 (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 Principle. (5+5)

28. Find the number, symmetry species of the infrared and Raman active vibrations of Boron trifluoride (BF_3), which belongs to D_{3h} point group.
(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_{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)