LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - **CHEMISTRY**

FIRST SEMESTER – NOVEMBER 2011

CH 1808 - QUANTUM CHEMISTRY & GROUP THEORY

Date : 05-11-2011 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

PART-A

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

1. How much distance is away the point (5, 120˚, 60˚) from the origin?

2. Represent the following complex numbers in the form of Euler formula.

(i) $1/\sqrt{2} + (1/\sqrt{2})i$ (ii) $½ + (\sqrt{3}/2)i$

3. Normalize exp(imx) for $0 \leq x \leq 2\pi$

4. Evaluate $ABCx^3$ if $A=d^2/dx^2$, $B= x+3$ and $C = d/dx$

5. Write the Hamiltonian for H_2^+ and explain the terms involved.

6. Calculate the trace of the transformation matrix of the operation S_2.

7. Obtain the symmetry operation equivalent to each of the fol--lowing

(i) C_4^6 (ii) S_4^2

8. Suggest a possible electronic configuration for the term symbol $^3P_2$

9. What is a Hartree? Give its value.

10. Mention Born-oppenheimer approximation with an example.

PART-B

Answer any EIGHT questions (8 x 5 = 40)

11. Show that for $0 \leq x \leq a$, $\sin(2\pi/a)x$ is orthogonal to $\sin(3\pi/a)x$.

12. State and explain the postulates of quantum mechanics

13. Evaluate the following for a particle in 1D box: (i) $\langle p_x \rangle$ (ii) $p_x^2\Psi$. Comment on your results.

14. The rotational spectral lines of $^1H^{35}Cl$ are equally spaced by 20.8 cm^{-1}. Calculate the inter nuclear distance of the molecule.

15. Get an expression for the total energy of a simple harmonic oscillator in terms of its amplitude and frequency.

16. Evaluate the spherical harmonics $Y_{0,0}$.

17. Discuss the Pauli principle of anti-symmetric wave function.

18. What is a Secular determinant? Write down the determinants for the excited state of He atom.

19. Obtain the value of $[x, p_x^2]$. Mention its physical significance.

20. Outline the salient features of VB(Heitler-London) theory as applied to Hydrogen molecule.

21. The molecule ethylene belongs to D_{2h} point group. Identify the order, number and the dimensions of the irreducible representations.

22. Contruct the C_{3v} character table using great orthogonality theorem.

PART-C

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

23. Set up the Schrodinger equation for a particle in 1D box and hence solve for its energy and wave function.

24. (a) Define the following.

(i) Associated Legendre equation

(ii) Associated Legendre polynomials

(iii) Legendre polynomials

(b) Get the following polynomial functions for a rigid rotor:

(i) $P_2^1(\cos\theta)$ (ii) $P_3(\cos\theta)$

25. (a) Define the following.

(i) Hermite equation

(ii) Hermite polynomials

(b) Obtain the following Hermite polynomials for

(i) n = 0 (ii) n = 1 (iii) n = 3

26. (a) Find out the most probable distance of 1s electron of hydrogen atom using the wave function $\Psi_{1s} = 1/(\pi)^{1/2}(Z/a_0)^{3/2}\exp(-Zr/a_o)$. Calculate the values for the atoms from hydrogen to boron and offer your comments upon their ionization potentials.

(b) What are the three important approximations of Huckel LCAO-MO theory?

27. (a) State the variation principle and apply it to get an upper bound to the ground state energy of the particles in a 1D box of length a, using the trial function $\Psi = x^2(a-x)$.

(b) Find the Huckel molecular orbitals and energies for allyl radical.

28. Work out the hybridization scheme for σ bonding by boron in BF_3 molecules for D_{3h} symmetry. The D_{3h} character table is 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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