LOYOLA COLLEGE (AUTONOMOUS), CHENNAI – 600 034

M.Sc. DEGREE EXAMINATION - CHEMISTRY

FIRST SEMESTER – NOVEMBER 2013

CH 1814/1808 - QUANTUM CHEMISTRY & GROUP THEORY

Date : 11/11/2013 Dept. No. Max. : 100 Marks

Time : 1:00 - 4:00

Part-A

Answer all the questions. Each question carries two marks.

1. Give the limits of spherical coordinates.
2. Compare zero point energy of a particle in one and three dimensional boxes of same length.
3. Write an expression for the wave function of a particle confined to move in a cubical box of edge length 'l' having energy $12h^2/8ml^2$.
4. Show that d/dx is a linear operator whereas √ is not.
5. Solve φ_m equation for hydrogen atom, when m = 0.
6. Mention the importance of radial density function with an example.
7. Show that the product of Δx and Δp for a particle obey uncertainty principle.
8. Prove that the presence of S_n axis of even order generates $C_{n/2}$ axis.
9. Identify the point group of m – dichlorobenzene.
10. What are the improper axes of symmetry present in D_{2d} and D_{3d} point groups?

Part-B

Answer eight questions. Each question carries five marks.

11. Discuss the magnetic and catalytic properties of transition elements.
12. Derive the expressions for wave function and energy for a particle in one dimensional box. If the work function of chromium is 4.40 eV, then calculate the kinetic energy of electrons emitted from the chromium surface that is irradiated with UV radiation of wavelength 200 nm. What is the stopping potential for these electrons?
13. Explain Bohr's correspondence principle.
14. Show that the function $\cos ax \cos bx \cos cz$ is an eigen function of $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$.
15. Describe simple harmonic oscillator model.
16. Determine the possible electronic configuration of the element whose ground state term symbol is $^4S_{3/2}$.
17. Solve the radial eigen function for $R_{2,0}(r)$.
18. Normalize the trial wave functions $\Psi_g = c_1[\Psi_{1s}(A) + \Psi_{1s}(B)]$ and $\Psi_u = c_2[\Psi_{1s}(A) - \Psi_{1s}(B)]$.
19. The normalized wave function for the 1S orbital of hydrogen atom is $\Psi_{1s} = 1/(\pi)^{1/2}(Z/a_0)^{3/2}\exp(-Zr/a_o)$. Show that the most probable distance of the electron is a_0.

20. Explain how the symmetry operations of water molecule form a cyclic group.
21. H_2O_2 molecule belongs to C_2 point group. Make out the number and dimensionality of the irreducible representations.
22. $PCl_3$and PCl_5 molecules have different point groups. – Justify.

Part-C

Answer four questions. Each question carries ten marks.

23. a) State and explain the postulates of quantum mechanics.
    b) The wave function for a particle in one dimensional box is $\sin n\pi x/a$. Normalize this function in the interval (0,a). (7+3)
24. a) Explain quantum mechanical tunneling with two experimental evidences for it.
    b) When a particle of mass 9.1×10^{-31} kg in a certain one dimensional box goes from n = 5 level to n=2 level, it emits a photon of frequency 6×10^{14} s^{-1}. Find the length of the box. (6+4)
25. Use the method of separation of variables to break up Schrodinger equation for a rigid rotor into ordinary angular equations. Discuss the nature and characteristics of the solution of each.
26. a) Show that the operators L^2 and Lz commute.
    b) Apply variation principle to get an upper bound to the ground state energy of the particles in a 1D box of length a, using the trial function $\Psi = x^2(a-x)$. (5+5)
27. a) Determine the energy of the orbitals of hydrogen molecular ion in terms of energy and overlap integrals.
    b) Give the assumptions of Huckel molecular orbital theory. (7+3)
28. Work out the hybridization scheme for σ bonding by boron in BF_3 molecule for D_{3h}symmetry. Use the D_{3h} character table 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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