LOYOLA COLLEGE (AUTONOMOUS), CHENNAI-600034

M.Sc. DEGREE EXAMINATION-CHEMISTRY

FIRST SEMESTER-November 2014

CH-1814: Quantum Chemistry and Group Theory

Date:

Time: Marks: 100

Part-A

Answer all the questions. Each question carries two marks.

1. Name the coordinate system that is applied to describe diatomic molecule and give its limits.
2. Sirius, one of the hottest known stars, has approximately a blackbody radiation spectrum with λ_{max} at 2600 Å. Estimate the surface temperature of Sirius.
3. Show that for a particle in a three dimensional box with lengths, $l_x = l_y = l_z/2$, the energy levels 122 and 114 are accidentally degenerate.
4. Verify,whether the energy of a rigid rotor is quantized.
5. How many symmetry operations are generated by a C_5 axis?
6. Identify the Mulliken notations for the following irreducible representations.

	E	i
	1	1
	1	-1

7. For a particle with position vector, r = 2i-3j+k in *m* and momentum vector, p = i+2j-2k in kg m/s, calculate the magnitude of the angular momentum.
8. Prove the commutation relation $[x, p_x] = ih/2\pi$.
9. Deduce the atomic term symbol for boron.
10. What is Born-Oppenheimer approximation?

Part-B

Answer any eight questions. Each question carries five marks.

11. Find the original energy level of the electron for a line in the Lyman series of hydrogen corresponding to a wavelength of 1.03×10^{-5} cm.
12. Show that the function **sin kx sinly sinmz** is an eigenfunction of Laplacian operator (∇^2) and find the eigenvalue.
13. Explain the properties of Hermitian operator.
14. Derive the expressions for wavefunction and energy for a particle in a rectangular box.

15a. Write a note on Bohr's correspondence principle. (3)

b. Sketch Ψ and Ψ^2 for a particle in one dimensional box when n = 3. (2)

16. Find all the symmetry elements and operations present in an octahedron.
17. Obtain the character of the matrix of the operations (i) $C_4^2$and (ii) S_3^5.
18. Calculate the de Broglie wavelength of the electron in the first Bohr orbit of hydrogen atom(given: r = 0.529Å).

19. Write the Slater determinant for the ground state of Helium atom. Show that it is antisymmetric with respect to the exchange of the two electrons.
20. Obtain the point at which the probability density of $3d_{z^2}$ orbital will be maximum. Given $\psi_{320} = Cr^2\exp^{(-r/3)}(3\cos^2\theta - 1)$ where C contains all the constants.
21. Derive an expression for the energy of electron in hydrogen atom.
22. Write down the secular determinant for ethylene molecule using Hückel'smethod and obtain expressions for its energy levels.

Part-C

Answer any four questions. Each question carries ten marks.

23. Derive time-dependent and time-independent Schrodinger wave equations.
24a. Explain quantum mechanical tunneling with any two evidences. (6)
b. For a particle of mass 2×10^{-26} g in one dimensional box of length 4.00 nm, calculate the wavelength of the photon emitted when the particle goes from $n = 3$ to $n = 2$ level. (4)
25a. Set up the Schrodinger wave equation for a simple harmonic oscillator and solve it for the energy eigenvalues. (7)
b. Express the Cartesian coordinates (1,0,0) in terms of spherical coordinates. (3)
26. How will you obtain the IR and Raman active vibrational modes of *trans*-1,2-dichloroethene molecule, using the C_{2h} character table provided? Prove that the molecule obeys mutual exclusion principle.

C_{2h}	E	C_2	i	σ_h		
A_g	+1	+1	+1	+1	R_z	x^2, y^2, z^2, xy
B_g	+1	-1	+1	-1	R_x, R_y	xz, yz
A_u	+1	+1	-1	-1	z	-
B_u	+1	-1	-1	+1	x, y	-

27a. Solve the radial eigenfunction for $R_{2,0}(r)$. (6)
b. Verify whether the following pair of operators commute: d^2/dx^2 and x. (4)
28. Find the first order correction to the energy term when an electric field of strength 'F' is applied to the electron in a one dimensional box of length L.
Given: $\psi = (2/L)^{1/2}\sin(n\pi x/L)$.

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