Reg. No..... Name.....

M.SC. DEGREE END SEMESTER EXAMINATION NOVEMBER 2016

SEMESTER **– 1: CHEMISTRY**

COURSE: **16P1CHET04 – 16P1CPHT04 –: QUANTUM CHEMISTRY AND GROUP THEORY**

Time: Three Hours Max. Marks: 75

Section A

*Answer **any** **ten** questions. Each question carries **2** marks*

1. Prove that the two operators commute if they have common complete set of eigen functions.
2. Explain Hermitian operator with an example.
3. For a particle in a cube how many states have an energy of $\frac{14h^2}{8ma^2}$?
4. The energy of SHO is $\frac{13}{2}h\upsilon$. At what point Hermite polynomial is terminated?
5. What is the magnitude of angular momentum of an electron that occupies the following orbital:
   i) 1s ii) 2p iii) 3d iv) 3s
6. Evaluate the commutator $\left[\hat{x}, \hat{p}_x\right]$
7. Sketch the polar diagram of the function sinθ cosφ in the xy-plane. (θ and φ are spherical polar coordinates)
8. Show that the wave function $\psi = (\sin\theta)(e^{i\varphi})$ is an eigen function of $\hat{L}_z$, where $\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$. What is the eigen value?
9. Differentiate between reducible and irreducible representations.
10. What are the different kinds of operations generated by Sn (n=odd) operation?
11. Comment on the statement: '*A molecules that has no improper rotation axis must be dissymmetric*'.
12. Prove by matrix method, $C_{2(z)}.i = i.\ C_{2(z)} = \sigma_{(xy)}$
13. What is transition moment integral? What is its significance?

(2 × 10 = 20)

Section B

*Answer **any** **Five** questions. Each question carries **5** marks*

14. The radial wave function for the 1s orbital of a hydrogen atom is $R_{1s} = Ae^{-r/a_0}$. Find the normalization constant. Given $\int x^n e^{-ax} dx = \frac{n!}{a^{n+1}}$

15. What are spherical harmonics? Why these are named so? Explain with examples.

16. If the electron in butadiene of length 0.56Å is assumed to be similar to a particle in a 1-dimensional box, determine the minimum energy of excitation to the level n=5.

17. State and explain various postulates of quantum mechanics.

18. Draw the geometries of the following molecules, their symmetry elements and assign the point group:
a) $CHCl_3$ b) Ferrocene c) C_6H_6

19. Derive the matrix representation of rotation operation using the basis (x,y,z).

20. What are the symmetry operations in the point group C_{2v}? Give an example and construct its group multiplication table.

21. HCHO belongs to C_{2v} point group. Find the allowed electronic transitions of the molecule.

(5 × 5 = 25)

Section C

*Answer **any** **Two** questions. Each question carries **15** marks*

22. a) Solve the Schrodinger equation for particle on a ring.
b) Show that the energy of the particle is quantized. What is the degeneracy of the energy levels of the particle on a ring? (10 + 5)

23. a) Solve the Schrodinger equation of simple harmonic oscillator and arrive at the energy and wave function expressions.
b) The strongest IR band of CO occurs at $\bar{\upsilon}$ = 2143 cm^{-1}. Find the force constant of this molecule under the harmonic oscillator approximation
(10 + 5)

24. a) State the Great Orthogonality Theorem and apply this to construct the character table for C_{3v} point group.
b) Reduce the C_{3v} representation Γ_a [5 2 -1].
(10 + 5)

25. a) Using group theory, obtain the selection rules for vibrational transitions in IR and Raman spectroscopy.

b) Examine the IR and Raman activities of the vibrations of the water molecule. (7 + 8)

(15 × 2 = 30)

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