D 93036 (Pages : 3) Name..................................

Reg. **No...........................**

FIRST SEMESTER M.Sc. DEGREE EXAMINATION, DECEMBER 2015

(CUCSS)

Chemistry

CH 1C 01—THEORETICAL CHEMISTRY—I

(2010-2014 Admissions)

Time : Three Hours Maximum : 36 Weightage

Part A (Short Answer Type Questions)

Answer all **fourteen** *questions.*
Each question carries a weight of 1.

1. Which of the following functions are eigen functions of $\frac{d^2}{dx}$? What are their eigen values ?

   (a) sin $(ax) + \cos(ax)$. (b) 3 Cos 4x.

   (c) $e^{\hat{}x}$. (d) x^2.

2. Indicate which of the following functions are acceptable as wave functions :

   (a) $\psi = x$. **(b)** $\psi = \sin x$.

   (c) $\psi = e^{-x}$ **(d)** $\mathbf{w} = e^{\ x}$

3. Show that $\left[x\ ,\hat{p}_x\right]\ \frac{1}{2\pi!}\,nx^n$.

4. Explain the condition for orthogonality of a wave function.

5. The size of the nucleus is 10^{-12} cm. Treating it as a one-dimensional box, show why electron does not exist in the nucleus.

6. Write the Schrödinger equation and Hamiltonian for a particle on a sphere in spherical polar co-ordinates.

7. Define spin orbital. Write one example.

8. Obtain an approximate wave function for He atom.

9. Explain, what is meant by normalisation.

10. Set up the Huckel determinant for ethylene and get the energies allowed for the pi-electrons.

Turn over

11. Predict the relative stabilites of the species N_2, N_2 and N.

12. Determine the ground-state molecular term symbols of O_2 and O_2.

13. Plot the radial nodes of 4s, 4p, 4d and 4f hydrogen like wave functions.

14. Is wave function of H is given $1 \cdot \frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{r/a_0}$. Where do you find maximum electron density. Justify your answer.

(14 x 1 = 14 weightage)

Part B (Paragraph Type Questions)

Answer any **seven** *questions.*
Each question carries a weight of 2.

15. Using $\psi = Nx\,(a - x)$ as the trial function, obtain an expression for ground state energy of electron.

16. Develop the trial function used for the MO treatment of H. Write down the expression for the MOs and energies obtained from this trial function. Show the MO diagram of this molecule. What is the Multiplicity of the ground state of this molecule ?

17. Set up the Schrödinger wave equation for a particle in a three dimensional rectangular box.

18. What is slater determinant ? Write the slater determinants for Helium atom ground state $(1s^2)$ and the excited state $(1s^1\,2s^1)$.

19. Write equation for L^2 and L_z, in terms of spherical polar co-ordinates.

20. Compare the Cartesian and Spherical Polar Co-ordinates.

21. Apply the Schrödinger equation for a sample Harmonic Oscillator. Transform into Hermite equation.

22. Apply HMO method for butadiene. Find the energy of π molecular orbitals.

23. Discuss the bonding in H_2^+ ion according to MO theory.

24. Draw the energy level diagram of N_2 molecule. Explain with reasons whether N_2 molecule is paramagnetic or diamagnetic.

(7 x 2 = 14 weightage)

Part C (Essay Type Questions)

Answer any two questions.
Each question carries a weight of 4.

25. Apply the principle of quantum mechanics to the problem of a rigid rotator and hence obtain the energy of such a rotator and corresponding wave function.
26. Briefly explain HMO theory taking benzene molecule as an example.
27. Derive the expression for the first order perturbation energy for a particle confined to one dimensional box with slanted bottom.
28. Discuss Hartree Fock self consistent method of solving many electron atoms.

(2 x 4 = 8 weightage)