

2021

## CHEMISTRY — HONOURS

Paper : CC-11

(Physical Chemistry - 4)

Full Marks : 50

*The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.*Answer **question no. 1** and **any eight** questions from the rest.

1. Answer **any ten** of the following : 1×10
- (a) All harmonic oscillator wave functions with 'v', an odd integer must have a node at the origin — justify or criticize.
  - (b) Write down the integral for the calculation of the average momentum of a simple harmonic oscillator.
  - (c) **What do you mean by micro and macro states of a system?**
  - (d) **State Sterling's approximation and mention the condition of its validity.**
  - (e) **What are the relative populations of the states of a two-level system when the temperature is infinitely high?**
  - (f) Explain why the least square method is called so.
  - (g) The  $\hat{L}^2$  eigenvalues are degenerate except for  $L = 0$ . – Justify or criticize.
  - (h) Give an example when Newton-Raphson method fails.
  - (i) **What is the physical significance of the term Partition function?**
  - (j) Justify the nomenclature of the magnetic quantum number, 'm'.
  - (k) For a hydrogen atom 2s and 2p orbitals are degenerate. — Justify or criticize.
  - (l) What is the physical basis of the Born-Oppenheimer approximation?
2. (a) Explain why any two consecutive states of a simple harmonic oscillator are orthogonal to each other.
- (b) Graphically represent  $\psi_0(x)$  and  $\psi_0^2(x)$  for a simple harmonic oscillator. Clearly indicate the classically forbidden region in your plots. Comment on your answer. 2+3

Please Turn Over

3. (a) How can the wavefunction of  $H_2$  molecule be obtained by a simple extension of the LCAO–MO's obtained for  $H_2^{\oplus}$  system? Give expressions for the bonding MO, incorporating both the spatial and spin parts.
- (b) If  $\psi = \sum_i a_i f_i$  where  $f_i$ 's are orthonormal, then establish the condition involving  $a_i$  for which  $\Psi$  will be normalized. 3+2

4. (a) Set up the hamiltonian operator for  $H_2$  molecule in atomic units.
- (b) Give the plot of  $\frac{P}{P_0}$  with height ( $z$ ) for a particular gas at two different temperatures,  $T_1$  and  $T_2$ , where  $T_1 > T_2$ .  $P$  and  $P_0$  are the pressures of the gas at height  $z$  and at sea level respectively. 2+3

5. The  $\phi$  dependent part of spherical harmonics  $F(\phi)$  for a rigid rotator satisfies the following expression :

$$\frac{1}{F(\phi)} \frac{d^2 F(\phi)}{d\phi^2} = -m^2, \quad \text{where } m \text{ is a constant.}$$

From the above equation, derive the normalized form of  $F(\phi)$ . Apply the acceptability condition of  $F(\phi)$  to find values of  $m$ . 5

6. (a) State the third law of thermodynamics. 'This law is consistent with the statistical definition of entropy' – discuss.

(b) Derive the Trapezoidal Rule for numerical integration from the geometrical standpoint. 2½+2½

7. Briefly outline how you would use the Newton-Raphson method to find the root of the equation  $x^2 - A = 0$ , where  $A$  is a constant. Solve the above equation to find the positive root when  $A = 28$ . Use the guess value = 5 to start your calculation. 5

8. (a) In  $N$  molecules are distributed among the possible non-degenerate energy levels  $\epsilon_1, \epsilon_2, \epsilon_3, \dots$  in an isolated system, show that the entropy of the system can be represented as  $S = K\beta E + NK \ln Q$  (symbols have their usual meaning). Find the value of  $\beta$  in terms of  $T$ .

(b) Central difference formula generally gives better result than backward and forward difference formula for numerical differentiation. – Explain. 3+2

9. (a) Write down the Hamiltonian operator ( $\hat{H}$ ) for the He atom in atomic units. Why is it difficult to get the ground state energy of He atom by solving the Schrödinger equation?

(b) Show that  $[\hat{L}_y, \hat{L}_z] = i\hbar L_x$ . 2+3

10. (a) Consider a Trial function of a particle in a one-dimension of corresponding ground state energy. Discuss the compliance of variational principle. Given true ground state energy as  $0.125 \frac{\hbar^2}{ml^2}$ .
- (b) Zero point energy of a simple harmonic oscillator does not violate Heisenberg's uncertainty principle – Explain. 3+2

11. (a)  $\widehat{L}_z^2 y_l^m(\theta, \phi) = m^2 \hbar^2 y_l^m(\theta, \phi)$   
 $\widehat{L}^2 y_l^m(\theta, \phi) = l(l+1) \hbar^2 y_l^m(\theta, \phi)$

All the terms in the above equations have usual significance. From the above relations, show that the only possible values for 'm', the magnetic quantum number are  $0, \pm 1, \pm 2, \dots, \pm l$ .

- (b) Give an example of quantum mechanical system for which the spacing between energy levels –
- increases as  $E$  increases
  - remains the same as  $E$  increases
  - decreases as  $E$  increases. 3+2

12. A sample consisting of 5 molecules has a total energy  $5\epsilon$ . Each molecule is able to occupy states of energy  $j\epsilon$ , with  $j = 0, 1, 2, \dots$

- Calculate the weight of the configuration in which the molecules are distributed evenly over the available states.
- Draw up a table with columns headed by the energy of the states and write beneath them all configurations that are consistent with the total energy. Calculate the weights of each configuration and identify the most probable configurations. 2+3

13. Consider an isolated system containing  $N$  molecules, distributed among the possible non-degenerate energy levels represented by  $\epsilon_1, \epsilon_2, \dots$  etc. Assuming the expression for thermodynamic probability, show that under equilibrium conditions number of molecules ( $N_i$ ) in the level  $\epsilon_i$  is given by  $N_i = A \exp(-b\epsilon_i)$ , where 'A' and 'b' are constants. 5