2020

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 of the rest.

1. Answer ***any ten*** of the following : 1×10

(a) Write down the Schrödinger equation for the one-dimensional simple harmonic oscillator (SHO).

(b) Show that the SHO wave function $\psi_0(x) = \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\frac{\alpha x^2}{2}}$ is normalized.

(c) Write down the form of the $\hat{L}_z$ in terms of $\hat{x}, \hat{y}, \hat{z}$ and $\hat{p}_x, \hat{p}_y, \hat{p}_z$.

(d) Write down the energy expression for the rigid rotator explaining the terms and mention the admissible values of the rotational quantum number J.

(e) For the H-atom write down the *normalized* ϕ-function Φ(ϕ), mentioning the restriction on *m*.

(f) Write down the normalized radial wave function for the 1s orbital of the hydrogen atom, $R_{10}(r)$, mentioning the relevant term used.

(g) State the Born-Oppenheimer approximation qualitatively.

(h) Write the expression of the Hamiltonian operator of Lithium atom.

(i) Suppose 10 data points for each of x and $f(x)$ are given. Write down the strategy for integrating $f(x)$ using a combination of Simpson's one-third rule and Trapezoidal rule.

(j) For what order of polynomials does the Trapezoidal Rule furnish an *exact* value of the integral? Give one example.

(k) Write down the relationship between the partition function of a statistical system and its entropy.

(l) What is the dimension of the parameter β, as used in the Boltzmann distribution function?

(m) Write down the equation for thermodynamic probability of a state having a total number of particles N distributed among the different energy levels ϵ_i, with n_i in the respective energy levels.

(n) Name the *three* constant parameters characteristic of the elements of a Grand Canonical Ensemble.

(o) What should be the degeneracy of the ground state for a statistical system so that it exhibits 'residual entropy'?

2. (a) In the mathematical form of the Boltzmann distribution the sign before β is negative. Justify.

(b) Deduce the 1st-derivative Central Difference formula in connection with numerical differentiation, using the Taylor Series expansion. 2+3

3. Set up the Hamiltonian operator for $H_2^{\oplus}$ (hydrogen molecule ion) in atomic units. The LCAO – MO may be written as $\psi_{\pm} = C_1\, 1S_A \pm C_2\, 1S_B$ (terms have their usual meaning). Draw the plots of $\psi_{\oplus}^{\,2}$ and $\psi_{\ominus}^{\,2}$ against the distance of nuclear separation (R) and hence label $\psi_{\oplus}$ and $\psi_{\ominus}$ as bonding or anti-bonding molecular orbital. Give arguments for choosing $C_1 = C_2 = C$. 5

4. (a) Calculate the positive root of the equation $x^2 + 2x - 2 = 0$. Correct upto two significant figures by the Newton-Raphson method.

(b) Show that $\left[\hat{L}^2, \hat{L}_z\right] = 0$, where the terms have got their usual significance. 3+2

5. The ground state SHO wave function is given by $\psi_0(x) = (\alpha/\pi)^{1/4} \exp\left(-\alpha x^2/2\right)$. Find $\langle x \rangle$, $\langle x^2 \rangle$, $\langle p_x \rangle, \langle p_x^2 \rangle$. Hence show that the Uncertainty Principle of Heisenberg holds true for this eigenstate.

Given : $\displaystyle\int_0^{\infty} x^{2n} \exp\left(-ax^2\right) dx = \frac{1.3.....(2n-1)}{2^{n+1}} \sqrt{\frac{\pi}{a^{2n+1}}}$

$\displaystyle\int_0^{\infty} x^{2n+1} \exp\left(-ax^2\right) dx = \frac{n!}{2a^{n+1}}$ 5

6. (a) Consider the following table :

x	1·0	2·0	3·0	4·0	5·0	6·0	7·0
y	2·0	5·0	7·0	10·0	12·0	15·0	19·0

Calculate the slope and the intercept of the best fit straight line using these points.

(b) A certain molecule has a non-degenerate excited state lying 540cm^{-1} above the non-degenerate ground state. At what temperature is the population of the excited state just 10% of the ground state? 3+2

7. (a) Calculate the difference in the barometric reading between the tenth floor and ground floor of a building where each floor is 3 meter high. Express your answer in *torr*. [Given $T = 27$ºC and air is considered as a mixture of N_2 and O_2 in the mole-ratio 4 : 1, N = 14, O = 16, at. wt.]

(b) Given : $\psi_{2p+1} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a}\right)^{5/2} re^{-r/2a}.\ \sin\theta.e^{i\phi}$

$\psi_{2p-1} = \frac{1}{8\sqrt{\pi}}\left(\frac{1}{a}\right)^{5/2} re^{-r/2a}.\ \sin\theta.e^{-i\phi}$

(for hydrogen atoms)

Find the real wave functions by taking two suitable combinations of the above two functions. 3+2

8. (a) With the help of a suitably labelled diagram, briefly explain the principle of 'Adiabatic-Demagnetization'.

(b) From Boltzmann distribution, show that if the energy of the *three* consecutive levels are in arithmetic progression, the number of particles in the respective energy levels will be in geometric progression. 3+2

9. (a) From the Boltzmann distribution function, prove that $U = -RT^2 \frac{d\ln q}{dT}$, terms have their usual significance.

(b) Taking trial function, $\psi = e^{-cx^2}$ for the ground state of one-dimensional harmonic oscillator, find the optimum value of the parameter 'c' for the ground state, using the Variation Method.

$$\left[\text{Given : } (i)\int_0^\infty x^n e^{-qx}dx = \frac{n!}{q^{n+1}},\ \ n>-1,\ q>0;\ \ (ii)\int_0^\infty e^{-bx^2}dx = \frac{1}{2}\left(\pi/b\right)^{1/2},\ b>0\right]$$ 2+3

10. (a) Write down the LCAO – MO wave function for H_2 molecule. Comment on its limitation in describing the dissociation limit. Suggest an improvement with the VB treatment.

(b) State Planck's formulation of the Third law of Thermodynamics and explain the same. 3+2

11. The spherical harmonic $Y_{+1}^{-1}(\theta,\phi)$ is given as $(3/8\pi)^{1/2}\sin\theta.e^{-i\phi}$. Show that Y_{+1}^{-1} is normalized and also that it is orthogonal to Y_0^0. Make use of de Moivre's Theorem in the latter case. 5

12. (a) State and explain the Nernst Heat Theorem.

(b) Write down the Schrödinger equation for the rigid rotator in three dimensions in spherical polar coordinates. Separate the variables. 2+3

Please Turn Over

13. (a) Consider a system 'A' consisting of subsystems 'A_1' and 'A_2' for which $W_1 = 1\times10^{20}$ and $W_2 = 2\times10^{20}$.

(i) What is the numerical configuration available to the combined system?

(ii) Compute the entropies S, S_1 and S_2.

(iii) What is the significance of this result?

(b) What do you understand by the classical turning point of an one-dimensional harmonic oscillator? 3+2
