2015

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

(Symbols signify their usual meanings)

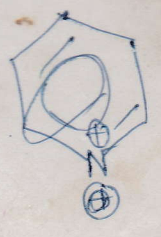
1. Answer in brief : $1\times7=7$

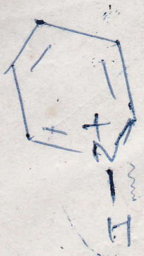
   (a) Find the eigenvalue of the operator $\frac{d^2}{dx^2}$ if the eigenfunction is $\cos 2x$.

   (b) The H-like wavefunctions corresponding to $n=2$, $l=1$, $m_l=\pm1$ are imaginary. But the orbitals cannot be imaginary. State how the orbitals are found out corresponding to these quantum numbers.

   (c) The ground state electronic configuration of H_2^+ is $(1s\sigma_g)^1$. Write the term symbol.

   (d) Show whether the operator $\hat{O}$ in the equation $\hat{O}\psi=\psi^2$ is linear or not.





(e) The normalization condition is $\int \psi^2 \, d\tau = 1$. State what this condition actually means.

(f) Show whether the function e^{-x} is well-behaved or not within the limit $-\infty \le x \le \infty$.

(g) If the state function of a system is ψ, write the expression for the expectation value of a physical quantity denoted by M.

2. Answer the following questions (any *four*) : 2×4=8

(a) Normalise the H-like function $\psi = e^{-n}$.

(b) Show that the functions $\sin \frac{\pi x}{a}$ and $\cos \frac{\pi x}{a}$ are orthogonal within the limit $0 \le x \le a$.

(c) For the two equivalent electrons $(2p^2)$ of ground state carbon atom, the terms are as follows :

$$^1D_2, \; ^3P_2, \; ^3P_1, \; ^3P_0, \; ^1S_0$$

Using Hund's rule, explain which will be the ground term.

(*Continued*)

(d) Show that the wavefunction for a particle in one-dimensional box of length a, where the potential energy is zero, is not an eigenfunction of the linear momentum operator in one dimension.

(e) It is required that the eigenfunction of an opeator representing a physical quantity should be single valued, continuous and quadratically integrable. State why the function should be single-valued and continuous.

3. Answer the following questions : 5×3=15

(a) State Pauli's antisymmetry principle. Using this principle, show that no two electrons of an atom can have all the four quantum numbers alike. 1+4=5

Or

What do you mean by complete wavefunction? Using the complete wavefunctions of the first excited He-atom, identify the singlet and triplet states. 1+4=5

(b) Write what you mean by radial distribution function. Find an expression for the radial distribution function. Give the plot of radial distribution function against the radial distance from the nucleus for 1s orbital. State how this plot differs from the plot of square of the radial function against the radial distance. 1+2+1+1=5

Or

Write the general expressions for the magnitude and z-component of angular momentum. Write what you mean by space quantisation of angular momentum. Discuss with diagram the orientations of angular momentum of magnitude $\sqrt{2}\hbar$ in presence of applied magnetic field in z-direction. 1+2+2=5

(c) Answer either *(i)* or *(ii)* and *(iii)* :

(i) Calculate the zero-point vibrational energy of CO molecule assuming it to be a harmonic oscillator if the force constant of the bond between the two atoms is 1840 Nm^{-1}. Find the energy difference between two consecutive vibrational levels taking the same assumption. 3+2=5

Or

(ii) Find the average value of the distance of the electron from the nucleus of the ground state H-atom. 3

(iii) According to Huckel theory, the energies of the six delocalized π molecular orbitals of benzene are $\alpha + 2\beta$, $\alpha + \beta$ (doubly degenerate), $\alpha - \beta$ (doubly degenerate) and $\alpha - 2\beta$ respectively. Find the energy of the π-electrons of the molecule. 2

4. Answer *either* (a) and (b) or (c) and (d) :

(a) Write in brief about the experimental observation of the photoelectric effect as observed by Lennard. State how classical physics fails to explain these results. Write how Einstein explained these. 3+2+2=7

(b) A cosmic ray photon with energy $h\nu$ is scattered through 90° by an electron initially at rest. The scattered photon has wavelength twice as that of the incident photon. Find the wavelength of the incident photon. 3

Or

(c) Show that the Compton shift, observed when a beam of monochromatic X-ray impinges on carbon block and gets scattered, depends on the angle through which scattered radiation is observed; but does not depend on the wavelength of the incident radiation. 6

(d) Show that the total energy of all the radiations emitted by a blackbody is proportional to the 4th power of the absolute temperature of the blackbody. 4

5. Answer *either* (*a*) and (*b*) or (*c*) and (*d*) :

(*a*) Using the MO wavefunction of H_2, discuss the drawback of the MO theory. Write how Heitler-London modified the wavefunction. Discuss about the correct form of the wavefunction for bonding in H_2 taking into account of resonance. 3+1+3=7

(*b*) Show that the maximum probability of finding the electron of H-like atom in the ground state is at a distance of a_0/z from the nucleus. 3

Or

(*c*) Write the basic assumptions of Huckel molecular orbital theory. Using this theory, explain how the formation of π-molecular orbital stabilizes the ethene molecule. 2+5=7

(*d*) For a particle in a one-dimensional box of length *a*, find the probability of finding the particle in the region $0 \le x \le a/4$ in the ground state. 3

6. Answer *either* (*a*), (*b*) and (*c*) or (*d*), (*e*) and (*f*) :

(*a*) Let a cubic box of edge length 1 nm, within which potential energy is zero, contain 10 electrons. Considering ground state, explain with diagram how these electrons occupy the different states. 3

(Continued)

(b) Write the angular function for s-orbital and hence explain why s-orbital is spherically symmetric. 1+2=3

(c) Taking the example of H_2^+, explain how the potential energy diagram can be constructed. What information regarding characterization of a bond can be obtained from this diagram? 3+1=4

Or

(d) Taking $2p_z$ orbital as example, explain why *p*-orbital is dumbbell in shape. 3

(e) Find the operator for kinetic energy in *x*-dimension. Hence deduce an expression for the kinetic energy in the ground state of a particle in one-dimensional box with zero potential energy. 1+3=4

(f) Draw the molecular orbital energy-level diagram of HF. Write the molecular orbital wavefunctions involved. 1+2=3

Standard integrals :

$$\int_0^\infty x^n e^{-ax}\, dx = \frac{n!}{a^{n+1}}$$

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \frac{\pi^4}{15}$$

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