2014

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer any *five* questions : 5×5=25

(a) Deduce Planck's formula in connection with blackbody radiation experiment. 5

(b) For a particle moving in a 3-D box of lengths *a*, *b* and *c*, where potential energy is zero, find the energy expression and wave function. 5

(c) For a particle in 1-D box, show that the average value of momentum along *x*-axis is zero. Find the wavelength of a radiation emitted when a particle of mass $9 \cdot 0 \times 10^{-31}$ kg in a one-dimensional box of length 3 Å undergoes transition from $\eta = 3$ level to the ground level. 2½+2½

(d) The threshold wavelength for photoelectric emission in tungsten is 2300 Å. Calculate wavelength of radiation that must be used to eject electron with maximum kinetic energy of $1 \cdot 5$ eV. State how Einstein explained the results of photoelectric effect observed by Lenward. 3+2

(e) Normalize the function $\cos \frac{n\pi x}{a}$ within the interval $0 \le x \le a$, where n is a constant. Find the lowest energy of a particle with mass $9 \cdot 0 \times 10^{-31}$ kg enclosed in a three-dimensional box of lengths $1 \cdot 0 \times 10^{-15}$ m, $2 \cdot 0 \times 10^{-15}$ m and $3 \cdot 0 \times 10^{-15}$ m assuming potential energy to be zero. 2+3

(f) Treating the π-electrons in butadiene as particles in one-dimensional box, calculate the lowest absorption frequency of the absorbed radiation, given that the length of the butadiene molecule to be $0 \cdot 56$ nm. 5

(g) Answer the following questions in brief :

(i) Which of the following sets of quantum numbers gives rise to real hydrogen like wave function?

(1) $n = 2, l = 1, m_l = -1$

(2) $n = 2, l = 1, m_l = +1$

(3) $n = 2, l = 1, m_l = 0$

State reason. 1

(ii) State how many folds a particular energy level of free axis rigid rotator will be degenerated. 1

(iii) Consider an atom with an excited state where it spends 10^{-8} s and then comes back to the ground state. Calculate the uncertainty in the energy of excitation. 2

(iv) Define linear operator. 1

2. Answer any *four* questions : 5×4=20

(a) Calculate the average value of potential energy of electron of H-atom in 1s state. 5

(b) State the Hund's set of rules for deciding the relative energies of state in a system containing equivalent electrons. Determine the term symbols for—

(i) $L = 2, \; S = \frac{1}{2}$;

(ii) $L = 1, \; S = \frac{3}{2}$. 5

(c) Find the operators for x-, y- and z-components of angular momentum. Which physical quantity is represented by Hamiltonian operator? Find operator for kinetic energy in x-dimension. 3+1+1

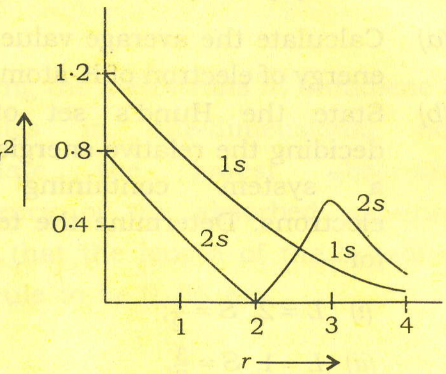
(d) The Hamiltonian for hydrogen atom and the 1s wave function in atomic units are

$$\hat{H} = -\frac{1}{2}\nabla^2 - \frac{1}{r}$$

$$\psi_{1s} = \frac{1}{\sqrt{\pi}} e^{-r}$$

respectively. Calculate the ground-state energy of hydrogen atom in SI units. Express your result also in electron volts. 4+1

(e) For a chemist, ψ^2 (probability density) is of more interest than ψ. Variation of ψ^2 with r for various states (of 1s and 2s) of H-atom is shown below :



However, Bohr's theory predicts that the electron in 1s state of H-atom is to be found at $r = a_0$ (Bohr radius). Solve this confusion and also draw actual radial probability at different values of r for H-atom. 5

(f) (i) A hydrogen-like wave function is given below with r in atomic units :

$$\psi = \frac{\sqrt{2}}{81\sqrt{\pi}} Z^{3/2} (6 - Zr)\, Zr \exp(-Zr/3) \cos\theta$$

Determine the quantum numbers n, l and m_l just from this expression. 1½

(ii) State Pauli's principle of anti-symmetric wave functions. 1

(iii) What do you mean by complete wave function? Write the complete wave function for ground state of He-atom. 1½+1

3. Answer any *three* questions : 5×3=15

(a) Use LCAO-MO theory to solve the Schrödinger equation for the electron of H_2^+ to find the normalized wave functions and corresponding energy expressions. 5

(b) (i) From the molecular orbital energy-level diagram of CO, explain whether the molecule is paramagnetic or not. 2

(ii) Show that $[\hat{x}, \hat{p}_x] = i\hbar$. 3

(c) Use Hückel method to explain the stability of benzene molecule. 5

(d) Calculate the rotational energy of CO molecule in the first excited state considering it to be rigid rotator, given that the bond length of CO is 113 pm. 5

(e) (i) A homonuclear diatomic molecule has the ground state molecular orbital configuration

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 1\pi_u^4\ 3\sigma_g^2\ 1\pi_g^2$$

(1) What is the net number of bonding electrons?

(2) What will be the spin multiplicity for the ground state?

(3) What would be the spin multiplicity of the resulting molecule ion if one goes out of the $1\pi_g$ level? 1½

(ii) Predict the stability of HeH molecule on the basis of molecular orbital theory. 1½

(iii) Explain why HCl is more polar than HF on the basis of energy of atomic orbitals. 2

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