2016

CHEMISTRY

(Major)

Paper : 5.1

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

(The symbols used signify their usual meanings)

1. Answer in brief (any *seven*) : 1×7=7

(a) Define eigenvalue and eigenfunction.

(b) State true or false with reason :

$\hat{O}[f(x) + g(x)]$ is always equal to $\hat{O}f(x) + \hat{O}g(x)$.

(c) Find the expression for the Hamiltonian operator for a particle of mass m in x-dimension.

(d) For a particle in one-dimensional box of length a, where potential energy is zero, the wave function is

$\psi = N \sin \frac{n\pi x}{a}$, N = normalization constant

State why the value of the quantum number n cannot be zero.

(e) State what you mean by spin-orbital.

(f) Find the value of the orbital angular momentum of an electron in d-orbital.

(g) Write the term symbol for H_2 in ground state.

(h) Give the schematic plots of ψ and $|\psi|^2$ against coordinate for $n = 2$ state of a particle in one-dimensional box of length a where potential energy is zero.

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

(a) What do you mean by eigenvalue equation? Write with example what the constant in the eigenvalue equation indicates.

(b) Show that the average value of momentum of a particle described by the wave function e^{ikx} is $\hbar k$, where k is a constant.

(c) Explain how many folds a particular energy level of the free axis rigid rotator is degenerate.

(d) The associated Legendre function is defined by

$$P_l^{|m|}(w) = \frac{1}{2^l\, l!}(1-w^2)^{|m|/2}\frac{d^{l+|m|}}{dw^{l+|m|}}(w^2-1)^l$$

The solution of the Schrödinger equation for H-atom also involves this type of function $P_l^{|m|}(\cos\theta)$. Find the values of the function when the value of the quantum number l is 1.

(e) A particle with mass m is moving in one-dimensional box of length a where the potential energy is zero. Show that the wavelength associated with the particle is $\frac{2a}{n}$.

3. (a) Write the quantum numbers on which radial wave function and the angular wave function of H-like atom depend. Discuss what information can be obtained from the plots of radial wave function and square of the radial wave function. 1+4=5

Or

Write in brief about Russell-Saunders coupling of angular momenta. Find the term symbols for the ground state and the first excited state of He atom. 2+1+2=5

(b) Write the general expression for the Hamiltonian of a molecule. Explain how Born-Oppenheimer approximation can be applied to separate the Schrödinger equation for a molecule into electronic and nuclear Schrödinger equations. 1+4=5

Or

Write the MO wave functions and the corresponding energy values for the electron of hydrogen molecule ion. Using these, explain how the potential energy diagram is constructed. State what information can be obtained from this diagram. 1+3+1=5

(c) Solve the electronic Schrödinger equation of H_2^+ using LCAO-MO method to find the energies and the MO wave functions. 5

Or

Discuss how Heitler-London method is an improvement over the MO method for H_2. 5

4. Answer either *(a)*, *(b)* and *(c)* or *(d)*, *(e)* and *(f)*: 10

(a) Show graphically how energy is distributed among different wavelengths emitted by a blackbody at a definite temperature. Deduce Planck's radiation law which can explain the above experimental observation. 1+4=5

(b) The work function for Na metal is 1·82 eV. Calculate its threshold frequency. 2

(c) Find the lowest kinetic energy of an electron in a three-dimensional box of lengths 1×10^{-13} cm, 2×10^{-13} cm and 3×10^{-13} cm assuming potential energy to be zero. 3

Or

(d) Consider a particle with mass m moving in a box of lengths a, b and c along x-, y- and z-axes respectively. Assume that the potential energy inside the box is zero, and outside it is infinity. Solve the time-independent Schrödinger equation for the particle to get the values of the wave function and the energy. 4

(e) It is found that the surface of the sun radiates as a blackbody with λ_{max} of 480 nm. Calculate the surface temperature of the sun. 3

(f) Show that the wave function for the particle in one-dimensional box, where potential energy is zero, is not an eigenfunction of the momentum operator $\hat{p}_x$; but it is an eigenfunction of $\hat{p}_x^2$. 3

5. Answer *either (a)* and *(b)* or *(c)*, *(d)* and *(e)* : 10

(a) Define radial distribution function. Find an expression for the radial distribution function for s-orbital. Prove that the maximum probability of finding the electron of H-atom is at a distance equal to the first Bohr radius of H-atom. 1+2+3=6

(b) Consider an atom with two electrons, one in *p*-orbital and the other in *d*-orbital. Find the symbols for the terms arising out of the coupling between the angular momenta of the two electrons. 4

Or

(c) Write the approximate spatial function and the possible spin functions for the electrons of the ground state He-atom. Applying Pauli's antisymmetry principle, find the acceptable ground state complete wave function of the He-atom. 2+3=5

(d) The wave function for the ground state H-atom is Ne^{-r/a_0}. Find the value of the normalization constant *N*. 2

(e) Calculate the average value of the potential energy of the electron of H-atom in ground state. 3

6. Answer *either (a)* and *(b)* or *(c)*, *(d)* and *(e)* : 10

(a) Write the secular determinant for benzene on the basis of Hückel molecular-orbital theory. Using this theory, explain how delocalization of π-electrons stabilizes the benzene molecule. 1+5=6

(b) Write the basis of classifying the molecular orbitals as *g* or *u*. Can the molecular orbitals of a heteronuclear diatomic molecule be assigned as *g* or *u*? Answer stating reason. Distinguish between σ- and π-molecular orbitals using symmetry concept. 1+1+2=4

Or

(c) State how the Coulomb integrals and the resonance integrals are represented in Hückel molecular orbital method. Using this theory, deduce the expressions for the energies and the corresponding π-molecular orbital wave functions of ethene. 1+5=6

(d) Consider that the valence-bond wave-function of ground state HF molecule is obtained from 1s orbital of H atom and $2p_z$ orbital of F atom. Write the

unnormalized valence-bond wave functions for the molecule considering it to be *(i)* purely covalent and *(ii)* purely ionic. 2

(e) Draw the molecular orbital energy-level diagram of CO. Find its bond order. 2

Standard integral :

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

★★★