BIRLA INSTITUTE OF TECHNOLOGY AND SCIENCE, PILANI
II Semester, 2017-2018

Course No.: CHEM F111 Course Title: General Chemistry Max. Marks: 15

Assignment Set 1 *[based on Lecture Nos.: 4 –12 in the course handout]*

Instructions to the students: The following problems should be solved as home assignment within a week of distribution.

Q. No. 1 (a) An electron is moving in a cyclic ring (i.e., having two-dimensional rotational motion). If the absorption occurs at a wavelength of 260 nm for a change in rotational level (m_ℓ) from 3 to 4, then calculate the diameter of the ring (in Å). [6]

(b) By what factor will the vibrational frequency of HI changes, when hydrogen is replaced by deuterium. Assume that the Iodine atom does not move and the vibration is solely to the motion of H or D atom. [4]

(c) Calculate the probability density at the nucleus for an electron in a hydrogen atom with n = 1, l = 0, and m_l = 0. [5]

Q. No. 2 (a) Treat a rotating HI molecule as a stationary I atom around which an H atom circulates in a plane at a distance of 161 pm. Calculate (i) the moment of inertia of the molecule, (ii) the greatest wavelength of the radiation that can excite the molecule into rotation. [6]

(b) Calculate Z_{eff} for a 1s electron in He, if the first ionization energy of He is 24.6 eV. [4]

(c) Calculate the probability of finding the electron in a volume of 6.5 pm^3 centered on the nucleus in a hydrogen atom. [5]

Q. No. 3 (a) Calculate the difference in the adjacent energy levels of a harmonic oscillator of mass 1.4 x 10^{-25} kg and force constant is 300 Nm^{-1}. [5]

(b) A hydrogen atom is in a state described by $\psi = N\, r^2(c_1 - c_2 r + c_3 r^2)\exp(-r/5a_0)\sin 2\theta \cos\varphi$. Answer the following: [10]

(i) Find the number of angular nodes in the orbital.

(ii) Find the number of radial nodes in the orbital.

(iii) Find the magnitude of the angular momentum in the units of ħ in the given state.

(iv) Identify the orbital.

(v) What is the value of $|m_l|$ for this orbital?

(vi) What are the other possible form of the wavefunction that has same $|m_l|$ value but uncertainty in the sign of m_l? Write the general form of the orbital.

Q. No. 4 Consider an electron in the ground state of the hydrogen atom.

(a) At what value of the radius does the probability density fall to one tenth of its maximum value? [5]

(b) What is the probability of finding the electron in a spherical shell of thickness 0.001 nm, at a distance a_0 from the nucleus? [5]

(c) What is the probability that an electron in the Ψ_{1s} orbital of hydrogen will be within a radius of 0.1 Å from the nucleus? [5]

Q. No. 5 (a) The Humphreys series is a group of lines in the spectrum of the hydrogen atom, with the shortest wavelength line at 3281.4 nm. (i) What are the transitions involved? (ii) What is the longest wavelength transition in this series? (iii) At what wavelength will the longest wavelength transition take place in the corresponding series for He^+? [7]

(b) Identify the orbitals corresponding to wavefunctions Ψ_1 and Ψ_2 for hydrogen like atom as given below by identifying n, l, m_l. [4]

$\Psi_1 = 1/8 \,.\, (64Z^3/\pi a_0^3)^{1/2}\, e^{-2zr/2a0})$; $\Psi_2 = 1/8 \,.\, (2Z^3/\pi a_0^3)^{1/2}\, (zr/\, a_0)\, e^{-zr/2a0} \cos\theta)$

(c) A line in the Balmer series of the emission spectrum of atomic hydrogen is observed at a wavelength of 486.3 nm. Deduce the upper state principal quantum number for this transition. [4]

Q. No. 6 (a) Consider the electronic configuration $3p^1 3d^1$. (i) Obtain all possible term symbols, (ii) What would be possible terms if the 3d electron is excited to 4p sub-shell? (iii) What would be the possible terms if the electronic configuration were $3s^2$? [4+3+2]
(b) Consider electronic transition from ***3d*** to ***2p*** state of hydrogen atom. (i) What are possible term-symbols of the states involved in this transition? (ii) Do mention any two allowed transitions. Selection rule for atomic transition is: $\Delta L = \pm 1$ and $\Delta J = 0, \pm 1$. [4+2]

Q. No. 7 (a) Which of the following transitions between terms are allowed in the normal electronic emission spectrum of a many electron atom: (i) $^2P_{3/2} \rightarrow {}^2S_{1/2}$; (ii) $^3P_0 \rightarrow {}^3S_1$; (iii) $^3D_3 \rightarrow {}^1P_1$ [6]
(b) What are the allowed total angular momentum quantum numbers of a composite system in which $j_1=5$ and $j_2=3$? [3]
(c) What information does the term symbol $^3F_4$ provide about angular momentum of an atom? [3]
(d) Suppose that an atom has five electrons in different orbitals. What are the possible values of total spin quantum number S? What is the multiplicity in each case? [3]

Q. No. 8 (a) If two of the hybridized orbitals (ϕ_1 and ϕ_2) of a central atom is
$\phi_1 = s - (1/2)^{1/2}p_x + (3/2)^{1/2}p_y$ and $\phi_2 = s - (1/2)^{1/2}p_x - (3/2)^{1/2}p_y$; Write the
(i) hybridization of central atom
(ii) normalization constant for the given orbitals and
(iii) prove that these two hybridized orbitals are orthogonal, assuming that unhybridized atomic orbitals are orthonormal. [2+2+5]
(b) Write down the ground state electron configuration H_2^-, N_2, and O_2. Also calculate bond order for each system. [6]

Q. No. 9 (a) Between O_2 and C_2, which molecules gets stabilized (i) by addition of an electron and (ii) by removal of an electron? Give the reason for each of your answer in one sentence. [5]
(b) Write the expression for wave function of bonding molecular orbital (ψ_{BMO}) of a heteronuclear diatomic molecule AB, assuming that the contribution of atomic orbital of A (ψ_A) is 80% and that of atomic orbital of B (ψ_B) is 20%. [5]
(c) Valence Bond theory consider the molecular wavefunction in terms of product of atomic orbitals. Consider H_2 molecule as an example, at infinite inter atomic separation, each hydrogen atom (H_A and H_B) has its own independent wavefunctions. Answer the following questions:
(i) Write the mathematical expression of wavefunction for bonding ($\Psi+$) and antibonding ($\Psi-$) molecular orbital. [2]
(ii) Identify the region of constructive and destructive interference. [2]
(iii) How many nodes are possible during the formation of bonding and antibonding molecular orbital? [1]

Q. No. 10 (a) Give the valence bond wavefunction of H_2O in terms of the orbitals on the O atom that are used to form bonds. Predict, on the basis of valence bond theory, whether you would expect H_2O to be linear or bent. [5]
(b) A bonding molecular orbital (BMO) of a molecule AB is expressed as:
$\Psi_{MO} = c_A\phi_A + c_B\phi_B$
where, ϕ_A and ϕ_B are the atomic orbitals centered on atoms A and B, respectively. Determine the coefficients c_A and c_B if on average, the electron spends 65% of its time at atom A and 35% at atom B, assuming negligible overlap. [5]
(c) Determine the value of normalization constant for anti-bonding molecular orbital of H_2^+ molecule. Given that the value of overlap integral (S) between the atomic orbitals ϕ_{1Sa} and ϕ_{1Sb} is 0.59. [5]

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