University Chemistry Quiz 2

2014/10/16

1. (10%) In the particle in a two-dimensional box, the particle is confined to a rectangular box with side dimensions L_x and L_y. The energy levels for this system are given by

$$\mathrm{E}(n_x, n_y) = \frac{h^2}{8m}\left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2}\right]$$

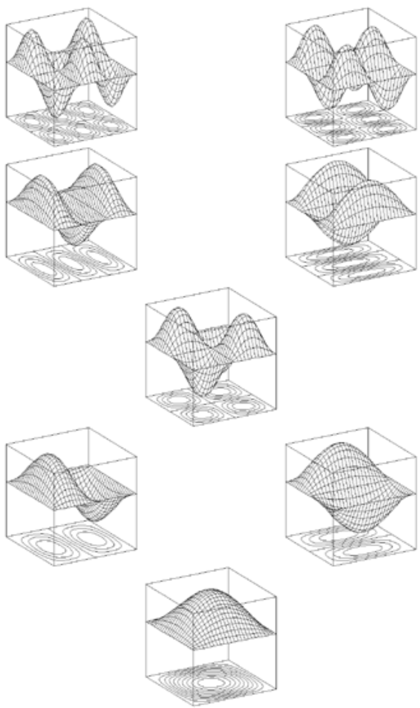
where the three quantum numbers (n_x and n_y) can be any set of two strictly positive integers. The wavefunction corresponding to the state (n_x, n_y) is

$$\psi(\mathrm{x}, \mathrm{y}) = \left(\frac{4}{L_x L_y}\right)^{\frac{1}{2}} \sin\left(\frac{n_x \pi x}{L_x}\right) \sin\left(\frac{n_y \pi y}{L_y}\right)$$

If the box is square ($L_x = L_y$), determine the set of two quantum numbers for the five lowest energy levels. (Some energy levels may consist of several degenerate quantum states.)

Sol.

The five lowest energy levels for a two-dimensional particle in a box correspond to the following sets of quantum numbers: (n_x=1, n_y=1), (n_x=1, n_y=2), (n_x=2, n_y=1), (n_x=2, n_y=2), (n_x=3, n_y=1), (n_x=1, n_y=3), (n_x=3, n_y=2), (n_x=2, n_y=3). These wavefunctions are plotted below with the lowest energy wavefunction at the bottom. Notice that the states (n_x=1, n_y=2) and (n_x=2, n_y=1) have the same energy as do the states (n_x=1, n_y=3) and (n_x=3, n_y=1) and the states (n_x=3, n_y=2) and (n_x=2, n_y=3).



2. (10%) The electron configuration of a neutral atom is $1s^22s^22p^63s^2$. Write a complete set of quantum numbers for each of the electrons.

Sol.

There are a total of twelve electrons:

Orbital	n	l	m_l	m_s
1*s*	1	0	0	$+\frac{1}{2}$
1*s*	1	0	0	$-\frac{1}{2}$
2*s*	2	0	0	$+\frac{1}{2}$
2*s*	2	0	0	$-\frac{1}{2}$
2*p*	2	1	1	$+\frac{1}{2}$
2*p*	2	1	1	$-\frac{1}{2}$
2*p*	2	1	0	$+\frac{1}{2}$
2*p*	2	1	0	$-\frac{1}{2}$
2*p*	2	1	−1	$+\frac{1}{2}$
2*p*	2	1	−1	$-\frac{1}{2}$
3*s*	3	0	0	$+\frac{1}{2}$
3*s*	3	0	0	$-\frac{1}{2}$

The element is magnesium.

3. (10%) Indicate which of the following sets of quantum numbers in an atom are unacceptable and explain why: (a) [1, 0, 1/2, 1/2], (b) [3, 0, 0, +1/2], (c) [2, 2, 1, +1/2], (d) [4, 3, -2, -1/2], and (e) [3, 2, 1, 1].

Sol.

(a) is incorrect because the magnetic quantum number m_l can have only whole number values.

(c) is incorrect because the maximum value of the angular momentum quantum number l is $n - 1$.

(e) is incorrect because the electron spin quantum number m_s can have only half-integral values.

4. (10%) Only a fraction of the electrical energy supplied to a tungsten light bulb is converted to visible light. The rest of the energy shows up as infrared radiation (that is, heat). A 75-W light bulb converts 15.0 percent of the energy supplied to it into visible light (assume the wavelength to be 550 nm). How many photons are emitted by the light bulb per second? (1 W = 1 J s^{-1} and h = 6.626 x 10^{-34} J s)

Sol.

Since 1 W □ 1 J s^{-1}, the energy output of the 75-W light bulb in 1 second is 75 J. The actual energy converted to visible light is 15 percent of this value (0.15 × 75 = 11 J).

First, we need to calculate the energy of one 550 nm photon. Then, we can determine how many photons are needed to provide 11 J of energy.

The energy of one 550 nm photon is:

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}\ \mathrm{J\,s})(3.00 \times 10^{8}\ \mathrm{m\,s^{-1}})}{550 \times 10^{-9}\ \mathrm{m}} = 3.62 \times 10^{-19}\ \mathrm{J}$$

The number of photons needed to produce 11 J of energy is:

$$11\ \mathrm{J} \times \frac{1\ \text{photon}}{3.62 \times 10^{-19}\ \mathrm{J}} = \mathbf{3.0 \times 10^{19}\ photons}$$

5. (10%) An electron in the hydrogen atom makes a transition form an energy state of principal quantum number n_1 to the n = 2 state. If the photon emitted has a wavelength of 434 nm, what is the value of n_1? (R_H = 3.290 x 10^{15} s^{-1})

Sol.

Equation 1.15 yields the energy of the photon absorbed for different transitions. For an emission, Equation 1.15 can be written:

$$E_{\text{photon}} = \frac{Z^2 e^4 m_e}{8h^2 \varepsilon_0^2}\left[\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right]$$

Energy equals Planck's constant times the speed of light divided by the wavelength:

$$E = \frac{hc}{\lambda}.$$

We can use this relationship to modify the above equation.

$$\frac{hc}{\lambda} = \frac{Z^2 e^4 m_e}{8h^2 \varepsilon_0^2}\left[\frac{1}{n_{\text{final}}^2} - \frac{1}{n_{\text{initial}}^2}\right]$$

We can now solve for one over n_{initial}.

$$\frac{1}{n_{\text{initial}}} = \sqrt{\frac{1}{n_{\text{final}}^2} - \frac{8h^3\varepsilon_0^2 c}{Z^2 e^4 m_e \lambda}} = \sqrt{\frac{1}{2^2} - \frac{8(6.626\times10^{-34}\ \text{J s})^3(8.8542\times10^{-12}\text{C}^2\ \ \text{J}^{-1}\ \text{m}^{-1})^2\left(3.0\times10^8\ \ \text{m s}^{-1}\right)}{(1)^2\,(1.602\times10^{-19}\ \ \text{C})^4(9.109\times10^{-31}\ \ \text{kg})\left(434\times10^{-9}\ \ \text{m}\right)}} = 0.20 = \frac{1}{5}$$

Hence, ***n***

6. (10%) Why do the 3s, 3p and 3d orbitals have the same energy in a hydrogen atom but different energies in a many-electron atom?

Sol.

In the many-electron atom, the 3*p* orbital electrons are more effectively shielded by the inner electrons of the atom (that is, the 1*s*, 2*s*, and 2*p* electrons) than the 3*s* electrons. The 3*s* orbital is said to be more "penetrating" than the 3*p* and 3*d* orbitals. In the hydrogen atom there is only one electron and hence there can not be any shielding, so the 3*s*, 3*p*, and 3*d* orbitals have the same energy.

7. (10%) Arrange the following isoelectronic species in order of (a) increasing ionic radius and (b) increasing ionization energy: O^{2-}, F^-, Na^+, Mg^{2+} .

Sol.

This is an isoelectronic series with ten electrons in each species. The nuclear charge interacting with these ten electrons ranges from +8 for oxygen to +12 for magnesium . Therefore the +12 charge in Mg^{2+} will draw in the ten electrons more tightly than the +11 charge in Na^+, than the +9 charge in F^-, than the +8 charge in O^{2-}. Recall that the largest species will be the *easiest* to ionize.

(a) increasing ionic radius: Mg^{2+} < Na^+ < F^- < O^{2-}

(b) increasing ionization energy: O^{2-} < F^- < Na^+ < Mg^{2+}

8. (10%) An electron in an excited state in a hydrogen atom can return to the ground state in two different ways: (a) via a direct transition in which a photon of wavelength λ_1 is emitted and (b) via an intermediate excited state reached by the emission of a photon of wavelength λ_2. This intermediate excited state then decays to the ground state by emitting another photon of wavelength λ_3. Derive an equation that relates λ_1, λ_2, and λ_3.

   Sol.

Since the energy corresponding to a photon of wavelength λ_1 equals the energy of photon of wavelength λ_2 plus the energy of photon of wavelength λ_3, then the equation must relate the wavelength to energy.

energy of photon 1 $=$ (energy of photon 2 $+$ energy of photon 3)

Since $E = \frac{hc}{\lambda}$, then:

$$\frac{hc}{\lambda_1} = \frac{hc}{\lambda_2} + \frac{hc}{\lambda_3}$$

Dividing by *hc*:

$$\frac{1}{\lambda_1} = \frac{1}{\lambda_2} + \frac{1}{\lambda_3}$$

9. (15%) When two atoms collide, some of their kinetic energy may be converted into electronic energy in one or both atoms. If the average kinetic energy is about equal to the energy for some allowed electronic transitions, an appreciable number of atoms can absorb enough energy through an inelastic collision to be raised to an excited electronic state. ($R_H = 3.290 \times 10^{15}\ s^{-1}$)
   (a) Calculate the average kinetic energy per atom in a gas sample at 298 K.
   (b) Calculate the energy difference between the n = 1 and n = 2 levels in hydrogen.
   (c) At what temperature is it possible to excite a hydrogen atom from the n = 1 level to the n = 2 level by collision ? (The average kinetic energy of 1 mol of a gas at low pressures is 3/2 RT, where the gas constant R= 8.314 J $mol^{-1}\ K^{-1}$ and T is the absolute temperature in Kelvin.)

Sol.

(a) The average kinetic energy of 1 mole of an ideal gas is 3/2*RT*. Converting to the average kinetic energy per atom, we have:

$$\frac{3}{2}(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(298\ \text{K}) \times \frac{1\ \text{mol}}{6.022 \times 10^{23}\ \text{atoms}} = 6.171 \times 10^{-21}\ \text{J atom}^{-1}$$

(b) To calculate the energy difference between the $n = 1$ and $n = 2$ levels in the hydrogen atom, we modify Equation 1.5 of the text.

$$\Delta E = R_{\text{H}}\left(\frac{1}{n_{\text{i}}^2} - \frac{1}{n_{\text{f}}^2}\right) = (2.180 \times 10^{-18}\ \text{J})\left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

$$\boldsymbol{\Delta E = 1.635 \times 10^{-18}\ \text{J}}$$

(c) For a collision to excite an electron in a hydrogen atom from the $n = 1$ to $n = 2$ level,

$$KE = \Delta E$$

$$\frac{\frac{3}{2}RT}{N_{\text{A}}} = 1.635 \times 10^{-18}\ \text{J}$$

$$T = \frac{2}{3}\frac{(1.635 \times 10^{-18}\ \text{J})(6.022 \times 10^{23}\ \text{mol}^{-1})}{(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})} = 7.90 \times 10^{4}\ \text{K}$$

This is an extremely high temperature. Other means of exciting H atoms must be used to be practical.

10. (5%) Arrange the following elements in order of increasing first ionization energy: F, K, P, Ca, and Ne.

Sol.

The general periodic trend for first ionization energy is that it increases across a period (row) of the periodic table and it decreases down a group (column). Of the choices, K will have the smallest ionization energy. Ca, just to the right of K, will have a higher first ionization energy. Moving to the right across the periodic table, the ionization energies will continue to increase as we move to P. Continuing across to Cl and moving up the halogen group, F will have a higher ionization energy than P. Finally, Ne is to the right of F in period two, thus it will have a higher ionization energy. The correct order of increasing first ionization energy is:

K < Ca < P < F < Ne

You can check the above answer by looking up the first ionization energies for these elements in Table 2.2 of the text.