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Solution to the Assigned Problems of Workshop 3
Chem. 103, Spring 2014

Chapter 3: Quantum theory and Electronic structure of Atoms
Home-assigned problems (total of 21): 3.15, 3.17, 3.19, 3.47, 3.49, 3.51, 3.57, 3.59, 3.67, 3.71, 3.72, 3.73, 3.74, 3.95, 3.97, 3.99, 3.101, 3.117, 3.119, 3.121, 3.123.

3.15 a. **Setup:** We are given the frequency of an electromagnetic wave and asked to calculate the wavelength. Rearranging Equation 3.3 of the text to solve for wavelength gives:

$$\lambda = \frac{c}{\nu}$$

Solution: Substituting the frequency and the speed of light (3.00×10^8 m/s) into the above equation, the wavelength is:

$$\boldsymbol{\lambda} = \frac{c}{\nu} = \frac{3.00\times10^{8}\ \text{m/s}}{8.6\times10^{13}\ \text{/s}} = 3.5\times10^{-6}\ \text{m} = \mathbf{3.5 \times 10^{3}\ nm}$$

b. **Setup:** We are given the wavelength of an electromagnetic wave and asked to calculate the frequency. Rearranging Equation 3.3 of the text to solve for frequency gives:

$$\nu = \frac{c}{\lambda}$$

Solution: Because the speed of light is given in meters per second, it is convenient to first convert wavelength to units of meters. Recall that 1 nm = 1×10^{-9} m (see Table 1.3 of the text). We write:

$$566\ \text{nm}\times\frac{1\times10^{-9}\ \text{m}}{1\ \text{nm}} = 566\times10^{-9}\ \text{m or } 5.66\times10^{-7}\ \text{m}$$

Substituting in the wavelength and the speed of light (3.00×10^8 m/s), the frequency is:

$$\boldsymbol{\nu} = \frac{c}{\lambda} = \frac{3.00\times10^{8}\ \text{m/s}}{566\times10^{-9}\ \text{m}} = 5.30\times10^{14}\ \text{/s} = \mathbf{5.30\times10^{14}\ Hz}$$

3.17 Since the speed of light is 3.00×10^8 m/s, we can write:

$$(1.3\times10^{8}\ \text{mi})\times\frac{1.61\ \text{km}}{1\ \text{mi}}\times\frac{1000\ \text{m}}{1\ \text{km}}\times\frac{1\ \text{s}}{3.00\times10^{8}\ \text{m}} = \mathbf{7.0\times10^{2}\ s}$$

Think About It: Would the time be different for other types of electromagnetic radiation?

3.19
$$\lambda = \frac{c}{\nu} = \frac{3.00\times10^{8}\text{ m/s}}{9{,}192{,}631{,}770\text{ s}^{-1}} = 3.26\times10^{-2}\text{ m} = \mathbf{3.26\times10^{7}\ nm}$$

This radiation falls in the **microwave region** of the spectrum. (See Figure 3.1 of the text.)

3.47 Note that we use more significant figures than we usually do for the values of *h* and *c* for this problem.

$$E = \frac{hc}{\lambda} = \frac{(6.6256\times10^{-34}\text{ J}\cdot\text{s})(2.998\times10^{8}\text{ m/s})}{656.3\times10^{-9}\text{ m}} = \mathbf{3.027\times10^{-19}\ J}$$

3.49 **Strategy:** We are given the initial and final states in the emission process. We can calculate the energy of the emitted photon using Equation 3.8 of the text. Then, from this energy, we can solve for the frequency of the photon, and from the frequency we can solve for the wavelength.

Solution: From Equation 3.8 we write:

$$\Delta E = -2.18\times10^{-18}\text{ J}\left(\frac{1}{n_\text{f}^2}-\frac{1}{n_\text{i}^2}\right) = -2.18\times10^{-18}\text{ J}\left(\frac{1}{3^2}-\frac{1}{4^2}\right) = -1.06\times10^{-19}\text{ J}$$

The negative sign for ΔE indicates that this is energy associated with an emission process. To calculate the frequency, we will omit the minus sign for ΔE because the frequency of the photon must be positive. We know that:

$$\Delta E = h\nu$$

Rearranging the equation and substituting in the known values:

$$\nu = \frac{\Delta E}{h} = \frac{1.06\times10^{-19}\text{ J}}{6.63\times10^{-34}\text{ J}\cdot\text{s}} = 1.60\times10^{14}\text{ s}^{-1} \text{ or } \mathbf{1.60\times10^{14}\ Hz}$$

We also know that $\lambda = \frac{c}{\nu}$. Substituting the frequency calculated above into this equation gives:

$$= \frac{(3.00\times10^{8}\text{ m/s})}{1.60\times10^{14}\text{ s}^{-1}} = 1.88\times10^{-6}\text{ m} = \mathbf{1.88\times10^{3}\ nm}$$

This wavelength is in the infrared region of the electromagnetic spectrum (see Figure 3.1 of the text).

3.51

$$\Delta E = -2.18\times10^{-18}\ \text{J}\left(\frac{1}{2^2}-\frac{1}{n_i^2}\right)$$

n_f is given in the problem but we need to calculate ΔE. The photon energy is:

$$E = \frac{hc}{\lambda} = \frac{(6.63\times10^{-34}\ \text{J}\cdot\text{s})(3.00\times10^{8}\ \text{m/s})}{434\times10^{-9}\ \text{m}} = 4.58\times10^{-19}\ \text{J}$$

Since this is an emission process, the energy change ΔE must be negative, or -4.58×10^{-19} J.

Substitute ΔE into the following equation, and solve for n_i.

$$-4.58\times10^{-19}\ \text{J} = -2.18\times10^{-18}\ \text{J}\left(\frac{1}{2^2}-\frac{1}{n_i^2}\right)$$

$$\frac{1}{n_i^{\,2}} = \left(\frac{-4.58\times10^{-19}\ \text{J}}{2.18\times10^{-18}\ \text{J}}\right)+\frac{1}{2^2} = -0.210+0.25 = 0.040$$

$$\boldsymbol{n_i} = \frac{1}{\sqrt{0.040}} = \mathbf{5}$$

3.57 **Strategy:** We are given the mass and the speed of the honey bee and asked to calculate the de Broglie wavelength. We need the de Broglie equation, which is Equation 3.11 of the text. Note that because the units of Planck's constant are J·s, *m* must be in kg and *u* must be in m/s (1 J = 1 kg·m^2/s^2).

Solution: Because mass in this problem is given in g and speed is given in mph, we must first convert these to kg and m/s, respectively.

$$m = 8.45\ \text{g}\times\frac{1\ \text{kg}}{1000\ \text{g}} = 0.00845\ \text{kg}$$

$$u = \frac{6.28\ \text{mi}}{1\ \text{h}}\times\frac{1.61\ \text{km}}{1\ \text{mi}}\times\frac{1000\ \text{m}}{1\ \text{km}}\times\frac{1\ \text{h}}{3600\ \text{s}} = 2.81\ \text{m/s}$$

Using these values in Equation 3.11 we write:

$$\lambda = \frac{h}{mu} = \frac{6.63\times10^{-34}\ \text{J}\cdot\text{s}}{(0.00845\ \text{kg})(2.81\ \text{m/s})} = 2.79\times10^{-32}\ \text{m}\times\frac{100\ \text{cm}}{1\ \text{m}} = \mathbf{2.79\times10^{-30}\ cm}$$

3.59 **Strategy:** Use Equation 3.11 to calculate velocity from the de Broglie wavelength:

$$\lambda = \frac{h}{mu}$$

Setup: Solving Equation 3.11 for velocity gives:

$$u = \frac{h}{\lambda m}$$

Planck's constant, *h*, is 6.63 × 10^{-34} J·s or 6.63 × 10^{-34} kg·m^2/s. For the purpose of making the unit cancellation obvious, the mass must be in kilograms and the wavelength in meters.

The mass of neutron is 1.67493 × 10^{-24} g (Table 2.1). The mass in kilograms is:

$$1.67493\times10^{-24}\ \text{g}\times\frac{1\ \text{kg}}{1\times10^{3}\ \text{g}} = 1.67493\times10^{-27}\ \text{kg}$$

The wavelength is 10.5Å. The wavelength in meters is:

$$10.5\ \text{Å}\times\frac{1\times10^{-10}\ \text{m}}{1\ \text{Å}} = 1.05\times10^{-9}\ \text{m}$$

Solution:

$$u = \frac{h}{\lambda m}$$

$$u = \frac{6.63\times10^{-34}\ \text{kg}\cdot\text{m}^2/\text{s}}{(1.05\times10^{-9}\ \text{m})(1.67493\times10^{-27}\ \text{kg})} = \mathbf{377\ m/s}$$

3.67 Rearranging Equation 3.13 to solve for the uncertainty in velocity, *Δu*, we write:

$$\Delta u \geq \frac{h}{4\pi m\Delta x} = \frac{6.63\times10^{-34}\ \text{J}\cdot\text{s}}{(4\pi)(2.80\times10^{-3}\ \text{kg})(6.75\times10^{-7}\ \text{m})} \geq \mathbf{2.79\times10^{-26}\ m/s}$$

This uncertainty is far smaller than can be measured. Therefore, we are able to determine the speed of a macroscopic object with great certainty using a visible wavelength of light.

3.71 **Strategy:** What are the relationships among n, ℓ, and m_ℓ?

Setup: The angular momentum quantum number ℓ can have integral (i.e. whole number) values from 0 to $n - 1$. In this case $n = 2$, so the allowed values of the angular momentum quantum number, $\boldsymbol{\ell}$, are **0**, corresponding to an *s* orbital; and **1**, corresponding to a *p* orbital.

Each allowed value of the angular momentum quantum number labels a subshell. Within a given subshell (label ℓ) there are $2\ell + 1$ allowed energy states (orbitals) each labeled by a different value of the magnetic quantum number. The allowed values run from $-\ell$ through 0 to $+\ell$ (whole numbers only). For the subshell labeled by the angular momentum quantum number $\boldsymbol{\ell = 1}$, the allowed values of the magnetic quantum number, m_ℓ, are **–1, 0, and 1**. For the other subshell in this problem labeled by the angular momentum quantum number $\boldsymbol{\ell = 0}$, the allowed value of the magnetic quantum number is **0**.

Solution: If the allowed whole number values run from –1 to +1, are there always $2\ell + 1$ values? Why?

3.72 are given the principal quantum number, $n = 3$. The possible ℓ values range from 0 to (n – Thus,
e are three possible values of ℓ: 0, 1, and 2, corresponding to the *s*, *p*, and *d* orbitals,
ectively. The values of m_ℓ can vary from $-\ell$ to ℓ. The values of m_ℓ for each ℓ value are:

$\boldsymbol{\ell = 0: m_\ell = 0}$ $\boldsymbol{\ell = 1: m_\ell = -1, 0, 1}$ $\boldsymbol{\ell = 2: m_\ell = -2, -1, 0, 1,}$

3.73 **For $n = 4$, the allowed values of ℓ are 0, 1, 2, and 3 [$\ell = 0$ to ($n - 1$), integer values].** These ℓ values correspond to the **4*s*, 4*p*, 4*d*, and 4*f* subshells**. These subshells each have **1, 3, 5, and 7 orbitals, respectively** (number of orbitals = $2\ell + 1$).

3.74 **The allowed values of ℓ are 0, 1, 2, 3, and 4.** These correspond to the **5*s*, 5*p*, 5*d*, 5*f*, and 5*g* subshells**. These subshells each have **one, three, five, seven, and nine orbitals, respectively**.

3.95 The electron configurations for the elements are

a. N: $1s^2 2s^2 2p^3$ There are **three *p*-type electrons**.

b. Si: $1s^22s^22p^63s^23p^2$ There are **six *s*-type electrons**.

c. S: $1s^22s^22p^63s^23p^4$ There are **no *d*-type electrons**.

3.97 For aluminum, there are **two 2*p* electrons missing**. The electron configuration should be $\mathbf{1s^22s^22p^63s^23p^1}$.

For boron, there are **too many 2*p* electrons**. The electron configuration should be $\mathbf{1s^22s^22p^1}$.

For fluorine, there are **too many 2*p* electrons**. The correct electron configuration is $\mathbf{1s^22s^22p^5}$. (The configuration shown is that of the F^- ion.)

3.99 To determine the number of unpaired electrons, we must look at the electron configuration of each of the elements. Since a *p* shell has 3 orbitals, according to Hund's rule once all of the orbitals are singly occupied, additional electrons will have to pair with those already in orbitals (see Section 3.9 of text).

B: $1s^22s^22p^1$ There is **one unpaired electron**.

C: $1s^22s^22p^2$ There are **two unpaired electrons**.

N: $1s^22s^22p^3$ There are **three unpaired electrons**.

O: $1s^22s^22p^4$ There are **two unpaired electrons**.

F: $1s^22s^22p^5$ There is **one unpaired electron**.

In order of increasing number of unpaired electrons, we have **B = F < C = O < N.**

3.101 To determine the number of unpaired electrons, we must look at the electron configuration of each of the elements. Those with all paired electrons are diamagnetic; and those with one or more unpaired electrons are paramagnetic.

a. **Rb**: $[Kr]5s^1$ There is **one unpaired electron**; **paramagnetic**

b. **As**: $[Ar]4s^23d^{10}4p^3$ There are **three unpaired electrons**; **paramagnetic**

c. **I**: $[Kr]5s^24d^{10}5p^5$ There is **one unpaired electron**; **paramagnetic**

d. **Cr**: $[Ar]4s^13d^5$ There are **six unpaired electrons**; **paramagnetic**

e. **Zn**: $[Ar]4s^23d^{10}$ There are **no unpaired electrons**; **diamagnetic**

3.117 **Part (b) is correct in the view of contemporary quantum theory. Bohr's explanation of emission and absorption line spectra appears to have universal validity. Parts (a) and (c) are artifacts of Bohr's early planetary model of the hydrogen atom and are *not* considered to be valid today.**

3.119 a. With $n = 2$, there are n^2 orbitals = $2^2 = 4$. $m_s = +½$, specifies 1 electron per orbital, for a total of **4 electrons** (one e^- in the 2*s* and 2*p* orbitals).

b. $n = 4$ and $m_\ell = +1$, specifies one orbital in each subshell with $\ell = 1, 2$, or 3 (i.e., a 4*p*, 4*d*, and 4*f* orbital). Each of the three orbitals holds 2 electrons for a total of **6 electrons**.

c. If $n = 3$ and $\ell = 2$, m_ℓ has the values 2, 1, 0, –1, or –2. Each of the five orbitals can hold 2 electrons for a total of **10 electrons** (2 e^- in each of the five 3*d* orbitals).

d. If $n = 2$ and $\ell = 0$, then m_ℓ can only be zero. $m_s = –½$ specifies 1 electron in this orbital for a total of **1 electron** (one e^- in the 2*s* orbital).

e. $n = 4$, $\ell = 3$ and $m_\ell = –2$, specifies one 4*f* orbital. This orbital can hold **2 electrons**.

3.121 In the case of the red light, no electrons were emitted. As a result, the ammeter showed no reading, since no current was flowing. When the light source was changed to blue light, electrons were ejected and current flowed through the circuit, as measured by the ammeter. **The frequency of the red light must be below the threshold frequency; the frequency below which no electrons can be ejected. The blue light must meet or exceed the threshold frequency.**

a. Increasing the intensity of the red light would result in **no change**. A higher intensity light will have more photons, but the energy of those photons will be the same. Below the threshold frequency no electrons can be ejected, no matter how intense the light.

b. Increasing the intensity of the blue light will result in more electrons being ejected from the metal's surface. Since blue light is above the threshold frequency, a more intense beam of light, which consists of a larger number of photons, will eject more electrons than a less intense beam of the same light. **The reading on the ammeter would be higher than it is for the lower intensity blue light**, as more current flows through the system.

c. Violet light has a higher frequency than blue light, therefore a higher energy value. As a result, it must also be above the threshold frequency. The kinetic energy of the electrons ejected from the metal will be higher than the kinetic energy for electrons ejected by blue light. As long as the frequency of the light is above the threshold frequency, the number of electrons ejected depends on the intensity of the light (the number of photons), not the frequency of the light. **The ammeter will indicate that current is flowing through the circuit.**

3.123 a. First, we can calculate the energy of a single photon with a wavelength of 633 nm.

$$E = \frac{hc}{\lambda} = \frac{(6.63 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^{8}\ \text{m/s})}{633 \times 10^{-9}\ \text{m}} = 3.14 \times 10^{-19}\ \text{J}$$

The number of photons produced in a 0.376 J pulse is:

$$0.376\ \text{J} \times \frac{1\ \text{photon}}{3.14 \times 10^{-19}\ \text{J}} = \mathbf{1.20 \times 10^{18}\ photons}$$

b. Since a 1 W = 1 J/s, the power delivered per a 1.00 × 10^{-9} s pulse is:

$$\frac{0.376\ \text{J}}{1.00 \times 10^{-9}\ \text{s}} = 3.76 \times 10^{8}\ \text{J/s} = \mathbf{3.76 \times 10^{8}\ W}$$

Compare this with the power delivered by a 100-W light bulb!
