# CHAPTER 8
# ELECTRONS IN ATOMS
## PRACTICE EXAMPLES

**1A** Use $c = \lambda\nu$, solve for frequency. $\nu = \dfrac{2.9979\times10^{8}\ \text{m/s}}{690\ \text{nm}}\times\dfrac{10^{9}\ \text{nm}}{1\ \text{m}} = 4.34\times10^{14}\ \text{Hz}$

**1B** Wavelength and frequency are related through the equation $c = \lambda\nu$, which can be solved for either one.

$$\lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{91.5\times10^{6}\ \text{s}^{-1}} = 3.28\ \text{m} \quad \text{Note that Hz} = \text{s}^{-1}$$

**2A** The relationship $\nu = c/\lambda$ can be substituted into the equation $E = h\nu$ to obtain $E = hc/\lambda$. This energy, in J/photon, can then be converted to kJ/mol.

$$E = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\,\text{J s photon}^{-1}\times2.998\times10^{8}\ \text{m s}^{-1}}{230\,\text{nm}\times\dfrac{1\,\text{m}}{10^{9}\,\text{nm}}}\times\frac{6.022\times10^{23}\ \text{photons}}{1\,\text{mol}}\times\frac{1\,\text{kJ}}{1000\,\text{J}} = 520\ \text{kJ/mol}$$

With a similar calculation one finds that 290 nm corresponds to 410 kJ/mol. Thus, the energy range is from 410 to 520 kJ/mol, respectively.

**2B** The equation $E = h\nu$ is solved for frequency and the two frequencies are calculated.

$$\nu = \frac{E}{h} = \frac{3.056\times10^{-19}\ \text{J/photon}}{6.626\times10^{-34}\ \text{J}\cdot\text{s/photon}} = 4.612\times10^{14}\ \text{Hz}$$

$$\nu = \frac{E}{h} = \frac{4.414\times10^{-19}\ \text{J/photon}}{6.626\times10^{-34}\ \text{J}\cdot\text{s/photon}} = 6.662\times10^{14}\ \text{Hz}$$

To determine color, we calculate the wavelength of each frequency and compare it with *text* Figure 8-3.

$$\lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{4.612\times10^{14}\ \text{Hz}}\times\frac{10^{9}\ \text{nm}}{1\ \text{m}} = 650\ \text{nm} \quad \text{orange}$$

$$\lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{6.662\times10^{14}\ \text{Hz}}\times\frac{10^{9}\ \text{nm}}{1\ \text{m}} = 450\ \text{nm} \quad \text{indigo}$$

The colors of the spectrum that are not absorbed are what we see when we look at a plant, namely in this case blue, green, and yellow. The plant appears green.

**3A** We solve the Rydberg equation for $n$ to see if we obtain an integer.

$$n = \sqrt{n^2} = \sqrt{\frac{-R_H}{E_n}} = \sqrt{\frac{-2.179\times10^{-18}\ \text{J}}{-2.69\times10^{-20}\ \text{J}}} = \sqrt{81.00} = 9.00$$

This is $E_9$ for n = 9.

**3B**

$$E_n = \frac{-R_H}{n^2}$$

$$-4.45\times10^{-20}\ \text{J} = \frac{-2.179\times10^{-18}\ \text{J}}{n^2}$$

$$n^2 = 48.97 \Rightarrow n = 7$$

**4A** We first determine the energy difference, and then the wavelength of light for that energy.

$$\Delta E = R_H\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = 2.179\times10^{-18}\ \text{J}\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = 4.086\times10^{-19}\ \text{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{8}\ \text{m s}^{-1}}{4.086\times10^{-19}\ \text{J}} = 4.862\times10^{-7}\ \text{m} \text{ or } 486.2\ \text{nm}$$

**4B** The longest wavelength light results from the transition that spans the smallest difference in energy. Since all Lyman series emissions end with $n_f = 1$, the smallest energy transition has $n_i = 2$. From this, we obtain the value of $\Delta E$.

$$\Delta E = R_H\left(\frac{1}{n_i^{\,2}}-\frac{1}{n_f^{\,2}}\right) = 2.179\times10^{-18}\ \text{J}\left(\frac{1}{2^2}-\frac{1}{1^2}\right) = -1.634\times10^{-18}\ \text{J}$$

From this energy emitted, we can obtain the wavelength of the emitted light: $\Delta E = hc/\lambda$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626\times10^{-34}\ \text{J s}\times2.998\times10^{8}\ \text{m s}^{-1}}{1.634\times10^{-18}\ \text{J}} = 1.216\times10^{-7}\ \text{m} \text{ or } 121.6\ \text{nm (1216 angstroms)}$$

**5A**

$$E_\text{f} = \frac{-Z^2\times R_\text{H}}{n_\text{f}^{\,2}} = \frac{-4^2\times2.179\times10^{-18}\ \text{J}}{3^2}$$

$E_\text{f} = -3.874\times10^{-18}$ J

$$E_\text{i} = \frac{-Z^2\times R_\text{H}}{n_\text{i}^{\,2}} = \frac{-4^2\times2.179\times10^{-18}\ \text{J}}{5^2}$$

$E_\text{i} = -1.395\times10^{-18}$ J

$\Delta E = E_\text{f} - E_\text{i}$

$\Delta E = (-3.874\times10^{-18}\ \text{J}) - (-1.395\times10^{-18}\ \text{J})$

$\Delta E = -2.479\times10^{-18}$ J

To determine the wavelength, use $E = h\nu = \frac{hc}{\lambda}$; Rearrange for $\lambda$:

$$\lambda = \frac{hc}{E} = \frac{(6.626\times10^{-34}\ \text{J s})\left(2.998\times10^{8}\ \frac{m}{s}\right)}{2.479\,x10^{-18}\ J} = 8.013\times10^{-8}\ \text{m} \text{ or } 80.13\ \text{nm}$$

**5B** Since $E = \frac{-Z^2\times R_\text{H}}{n^2}$, the transitions are related to $Z^2$, hence, if the frequency is 16 times greater, then the value of the ratio $\frac{Z^2(\text{?-atom})}{Z^2(\text{H-atom})} = \frac{Z_?^2}{1^2} = 16.$

We can see $Z^2 = 16$ or $Z = 4$ This is a Be nucleus. The hydrogen-like ion must be $Be^{3+}$.

**6A** Superman's de Broglie wavelength is given by the relationship $\lambda = h/m\nu$.

$$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\text{J}\cdot\text{s}}{91\text{kg}\times\frac{1}{5}\times2.998\times10^{8}\text{m/s}} = 1.21\times10^{-43}\,\text{m}$$

**6B** The de Broglie wavelength is given by $\lambda = h / m\nu$, which can be solved for $\nu$.

$$\nu = \frac{h}{m\lambda} = \frac{6.626\times10^{-34}\ \text{J s}}{1.673\times10^{-27}\ \text{kg}\times10.0\times10^{-12}\ \text{m}} = 3.96\times10^{4}\ \text{m/s}$$

We used the facts that $1\ \text{J} = \text{kg m}^2\text{s}^{-2}$, $1\text{pm} = 10^{-12}\ \text{m}$ and $1\ \text{g} = 10^{-3}\ \text{kg}$

**7A** $p = (91\ \text{kg})(5.996\times10^{7}\ \text{m s}^{-1}) = 5.4\underline{6}\times10^{9}\ \text{kg m s}^{-1}$

$\Delta p = (0.015)(5.4\underline{6}\times10^{9}\ \text{kg m s}^{-1}) = 8.2\times10^{7}\ \text{kg m s}^{-1}$

$$\Delta x = \frac{h}{4\pi\,\Delta p} = \frac{6.626\times10^{-34}\ \text{J s}}{(4\pi)(8.2\times10^{7}\ \frac{\text{kg m}}{\text{s}})} = 6.4\times10^{-43}\ \text{m}$$

**7B** $24\ \text{nm} = 2.4\times10^{-8}\ \text{m} = \Delta x = \dfrac{h}{4\pi\,\Delta p} = \dfrac{6.626\times10^{-34}\ \text{J s}}{(4\pi)(\Delta p)}$

Solve for $\Delta p$: $\Delta p = 2.2\times10^{-27}\ \text{kg m s}^{-1}$

$(\Delta v)(m) = \Delta p = 2.2\times10^{-27}\ \text{kg m s}^{-1} = (\Delta v)(1.67\times10^{-27}\ \text{kg})$ Hence, $\Delta v = 1.3\ \text{m s}^{-1}$.

**8A.** To calculate the probability percentage of finding an electron between 50 and 75 pm for an electron in level 6 ($n$ = 6, # nodes = 6-1 = 5), one must integrate the probability function, which is the square of the wave function between 50 and 75 pm:

Probability function:

$$\psi_6^2 = \frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)$$

$$\int_{50}^{75}\frac{2}{L}\sin^2\left(\frac{n\pi}{L}x\right)dx = \left[\frac{2}{L}\left(\frac{x}{2} - \frac{1}{2(n\pi/L)}\cdot\sin\left(\frac{n\pi}{L}x\right)\cdot\cos\left(\frac{n\pi}{L}x\right)\right)\right]_{50}^{75}$$

$$= 0.499\overline{9} - 0.333\overline{3} = 0.166\overline{6}$$

The probability is 0.167 out of 1, or 16.7%. Of course, we could have done this without any use of calculus by following the simple algebra used in Example 8-8. However, it is just more fun to integrate the function. The above example was made simple by giving the limits of integration at two nodes. Had the limits been in locations that were *not* nodes, you would have had no choice but to integrate.

**8B.** We simply note here that at $n$ = 3, the number of nodes is n-1 = 2. Therefore, a box that is 300 pm long will have two nodes at 100 and 200 pm.

**9A**

$$50.\ \text{pm}\times\frac{1\ \text{m}}{1\times10^{12}\ \text{pm}} = 5.0\times10^{-11}\ \text{m}$$

$$\Delta E = E_{\text{excitedstate}} - E_{\text{ground state}}$$

$$E = \frac{n^2h^2}{8mL^2}$$ Where n=energy level, h=Planck's constant, m= mass, L=length of box

$$\Delta E = \frac{3^2 h^2}{8mL^2} - \frac{5^2 h^2}{8mL^2}$$

$$\Delta E = \frac{-16\ h^2}{8\ mL^2} = \frac{-16(6.626\times10^{-34}\,\text{Js})^2}{8(9.109\times10^{-31})(5.0\times10^{-11})^2}$$

$$\Delta E = -3.86\times10^{-16}\ \text{J}$$

The negative sign indicates that energy was released / emitted.

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626\times10^{-34}\,\text{Js})(3.00\times10^{8}\,\text{ms}^{-1})}{3.86\times10^{-16}\,\text{J}}$$

$$\lambda = 5.15\times10^{-10}\,\text{m}\times\frac{10^9\ \text{nm}}{1\ \text{m}} = 0.515\ \text{nm} = 0.52\ \text{nm}$$

**<u>9B</u>**

$$24.9\ \text{nm}\times\frac{1\ \text{m}}{10^9\ \text{nm}} = 2.49\times10^{-8}\ \text{m}$$

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\ \text{Js})(3.00\times10^{8}\ \text{ms}^{-1})}{2.49\times10^{-8}\ \text{m}}$$

$$\Delta E = 7.98\times10^{-18}\ \text{J}$$

$$\Delta E = \frac{2^2 h^2}{8mL^2} - \frac{1^2 h^2}{8mL^2}$$

$$\Delta E = \frac{3\ h^2}{8\ mL^2}$$

$$7.98\times10^{-18}\,\text{J} = \frac{3(6.626\times10^{-34}\,\text{Js})^2}{8(9.109\times10^{-31})(L)^2}$$

$$L^2 = 2.265\times10^{-20}$$

$$L = 1.50\times10^{-10}\ \text{m} = 150.\ \text{pm}$$

**<u>10A</u>** Yes, an orbital can have the quantum numbers n=3, $\ell$=0 and $m_\ell$=0. The values of $\ell$ can be between 0 and n-1. The values of $m_\ell$ can be between $\ell$ and $-\ell$ encompassing zero. The three quantum numbers given in this question represent a 3s orbital.

**<u>10B</u>** For an orbital with n = 3 the possible values of $\ell$ are 0, 1, and 2. However, when $m_\ell$=1, this would omit $\ell$=0 because when $\ell$=0, $m_\ell$ must be 0. Therefore in order for both quantum numbers of n=3 and $m_\ell$=1 to be fulfilled, the only $m_\ell$ values allowed would be $\ell$=1 and 2.

**<u>11A</u>** The magnetic quantum number, $m_\ell$, is not reflected in the orbital designation. Because $\ell = 1$, this is a $p$ orbital. Because $n = 3$, the designation is $3p$.

**11B** The H-atom orbitals 3*s*, 3*p,* and 3*d* are degenerate. Therefore, the 9 quantum number combinations are:

| | $n$ | $\ell$ | $m_\ell$ |
|---|---|---|---|
| 3*s* | 3 | 0 | 0 |
| 3*p* | 3 | 1 | -1,0,+1 |
| 3*d* | 3 | 2 | -2,-1, 0,+1,+2 |

Hence, n = 3; l = 0, 1, 2; $m_l$ = -2, -1, 0, 1, 2

**12A** (3,2,-2,1) **$m_s$ = 1** is incorrect. The values of $m_s$ can only be + ½ or – ½.
(3,1,-2, ½ ) **$m_\ell$ = -2** is incorrect. The values of $m_\ell$ can be +1,0,+1 when $\ell$=1
(3,0,0, ½ ) All quantum numbers are allowed.
(2,3,0, ½ ) $\ell$ = 3 is incorrect. The value for $\ell$ can not be larger than n.
(1,0,0,- ½ ) All quantum numbers are allowed.
(2,-1,-1, ½ ) $\ell$ = -1 is incorrect. The value for $\ell$ can not be negative.

**12B** (2,1,1,0) **$m_s$ = 0** is incorrect. The values of $m_s$ can only be + ½ or – ½.
(1,1,0, ½ ) $\ell$ = 1 is incorrect. The value for $\ell$ is 0 when n=1.
(3,-1,1, ½ ) $\ell$ = -1 is incorrect. The value for $\ell$ can not be negative.
(0,0,0, - ½ ) n= 0 is incorrect. The value for n can not be zero.
(2,1,2, ½ ) **$m_\ell$ = 2** is incorrect. The values of $m_\ell$ can be +1,0,+1 when $\ell$=1.

**13A** (a) and (c) are equivalent. The valence electrons are in two different degenerate p orbitals and the electrons are spinning in the same direction in both orbital diagrams.

**13B** This orbital diagram represents an excited state of a neutral species. The ground state would follow Hund's rule and there would be one electron in each of the three degenerate p orbitals.

**14A** We can simply sum the exponents to obtain the number of electrons in the neutral atom and thus the atomic number of the element. $Z = 2+2+6+2+6+2+2 = 22$, which is the atomic number for Ti.

**14B** Iodine has an atomic number of 53. The first 36 electrons have the same electron configuration as Kr: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$. The next two electrons go into the $5s$ subshell $(5s^2)$, then 10 electrons fill the $4d$ subshell $(4d^{10})$, accounting for a total of 48 electrons. The last five electrons partially fill the $5p$ subshell $(5p^5)$.

The electron configuration of I is therefore $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^5$. Each iodine atom has ten $3d$ electrons and one unpaired 5*p* electron.

**15A** Iron has 26 electrons, of which 18 are accounted for by the [Ar] core configuration. Beyond [Ar] there are two $4s$ electrons and six $3d$ electrons, as shown in the following orbital diagram.

| | | $3d$ | $4s$ |
|---|---|---|---|
| Fe: | [Ar] | [↑↓][↑][↑][↑][↑] | [↑↓] |

**15B** Bismuth has 83 electrons, of which 54 are accounted for by the [Xe] configuration. Beyond [Xe] there are two $6s$ electrons, fourteen $4f$ electrons, ten $5d$ electrons, and three $6p$ electrons, as shown in the following orbital diagram.

| | | $4f$ | $5d$ | $6s$ | $6p$ |
|---|---|---|---|---|---|
| Bi: | [Xe] | [↑↓][↑↓][↑↓][↑↓][↑↓][↑↓][↑↓] | [↑↓][↑↓][↑↓][↑↓][↑↓] | [↑↓] | [↑][↑][↑] |

**16A** **(a)** Tin is in the 5th period, hence, five electronic shells are filled or partially filled.
**(b)** The $3p$ subshell was filled with Ar; there are six $3p$ electrons in an atom of Sn.
**(c)** The electron configuration of Sn is [Kr] $4d^{10}5s^2 5p^2$. There are no $5d$ electrons.
**(d)** Both of the $5p$ electrons are unpaired, thus there are two unpaired electrons in a Sn atom.

**16B** **(a)** The $3d$ subshell was filled at Zn, thus each Y atom has ten $3d$ electrons.
**(b)** Ge is in the $4p$ row; each germanium atom has two $4p$ electrons.
**(c)** We would expect each Au atom to have ten $5d$ electrons and one $6s$ electron. Thus each Au atom should have one unpaired electron.

# INTEGRATIVE EXAMPLE

**A.** **(a)** First, we must find the $u_{rms}$ speed of the He atom

$$u_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\left(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\right)\left(298\ \text{K}\right)}{4.003\times10^{-3}\,\text{kg}\cdot\text{mol}^{-1}}} = 1363\ \text{m/s}$$

Using the rms speed and the mass of the He atom, we can determine the momentum, and therefore the de Broglie's wavelength:

$$\text{mass He atom} = 4.003\times10^{-3}\ \frac{\text{kg}}{\text{mol}}\times\frac{1\ \text{mol}}{6.022\times10^{23}\ \text{atoms}} = 6.647\times10^{-27}\ \text{kg}$$

$$p = m\cdot v = \left(6.647\times10^{-27}\ \text{kg}\right)\left(1363\ \text{m/s}\right) = 9.06\times10^{-24}\ \text{kg}\cdot\text{m/s}$$

$$\lambda = \frac{h}{p} = \frac{6.6261\times10^{-34}\ \text{J/s}}{9.06\times10^{-24}\ \text{kg}\cdot\text{m/s}} = 7.3135\times10^{-11}\ \text{m} = 73.14\ \text{pm}$$

**(b)** Since the de Broglie wavelength is known to be ~300 pm, we have to perform the above solution backwards to determine the temperature:

$$p = \frac{h}{\lambda} = \frac{6.6261\times10^{-34}\ \text{J/s}}{300\times10^{-12}\,\text{m}} = 2.209\times10^{-24}\ \text{kg}\cdot\text{m/s}$$

$$v = u_{rms} = \frac{p}{m} = \frac{2.209\times10^{-24}\ \text{kg}\cdot\text{m/s}}{6.647\times10^{-27}\ \text{kg}} = 332.33\ \text{m/s}$$

Since $u_{rms} = \sqrt{3RT/M}$, solving for T yields the following:

$$T = \frac{(332.33\ \text{m/s})^2\left(4.003\times10^{-3}\ \text{kg}\right)}{3\left(8.3145\ \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}\right)} = 17.7\ \text{K}$$

**B.** The possible combinations are $1s \to np \to nd$, for example, $1s \to 3p \to 5d$. The frequencies of these transitions are calculated as follows:

$$1s \to 3p: \nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{n_i^2}-\frac{1}{n_f^2}\right) = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{1^2}-\frac{1}{3^2}\right) = 2.92\times10^{15}\ \text{Hz}$$

$$3p \to 5d: \nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{3^2}-\frac{1}{5^2}\right) = 2.34\times10^{14}\ \text{Hz}$$

The emission spectrum will have lines representing $5d \to 4p$, $5d \to 3p$, $5d \to 2p$, $4p \to 3s$, $4p \to 2s$, $4p \to 1s$, $3p \to 2s$, $3p \to 1s$, and $2p \to 1s$. The difference between the sodium atoms is that the positions of the lines will be shifted to higher frequencies by $11^2$.

# EXERCISES

## Electromagnetic Radiation

**1.** The wavelength is the distance between successive peaks. Thus, $4\times1.17\ \text{nm} = \lambda = 4.68\ \text{nm}$.

**3.** **(a)** TRUE Since frequency and wavelength are inversely related to each other, radiation of shorter wavelength has higher frequency.

**(b)** FALSE Light of wavelengths between 390 nm and 790 nm is visible to the eye.

**(c)** FALSE All electromagnetic radiation has the same speed in a vacuum.

**(d)** TRUE The wavelength of an X-ray is approximately 0.1 nm.

**5.** The light having the highest frequency also has the shortest wavelength. Therefore, choice (c) 80 nm has the highest frequency.

**7.** The speed of light is used to convert the distance into an elapsed time.

$$\text{time} = 93\times10^{6}\ \text{mi}\times\frac{5280\ \text{ft}}{1\ \text{mi}}\times\frac{12\ \text{in.}}{1\ \text{ft}}\times\frac{2.54\ \text{cm}}{1\ \text{in}}\times\frac{1\ \text{s}}{3.00\times10^{10}\ \text{cm}}\times\frac{1\ \text{min}}{60\ \text{s}} = 8.3\ \text{min}$$

## Atomic Spectra

**9.** **(a)** $\nu = 3.2881\times10^{15}\text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{5^2}\right) = 6.9050\times10^{14}\text{s}^{-1}$

**(b)** $\nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{7^2}\right) = 7.5492\times10^{14}\ \text{s}^{-1}$

$$\lambda = \frac{2.9979\times10^{8}\ \text{m/s}}{7.5492\times10^{14}\ \text{s}^{-1}} = 3.9711\times10^{-7}\ \text{m}\times\frac{10^{9}\ \text{nm}}{1\ \text{m}} = 397.11\ \text{nm}$$

**(c)** $\nu = \dfrac{3.00\times10^{8}\ \text{m}}{380\,\text{nm}\times\dfrac{1\,\text{m}}{10^{9}\,\text{nm}}} = 7.89\times10^{14}\text{s}^{-1} = 3.2881\times10^{15}\text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{n^2}\right)$

$$0.250-\frac{1}{n^2} = \frac{7.89\times10^{14}\ \text{s}^{-1}}{3.2881\times10^{15}\ \text{s}^{-1}} = 0.240 \qquad \frac{1}{\text{n}^2} = 0.250-0.240 = 0.010 \quad \text{n} = 10$$

**11.** **(a)** $E = h\nu = 6.626\times10^{-34}\ \text{J s}\times7.39\times10^{15}\ \text{s}^{-1} = 4.90\times10^{-18}\ \text{J/photon}$

**(b)** $E_m = 6.626\times10^{-34}\ \text{J s}\times1.97\times10^{14}\ \text{s}^{-1}\times\frac{6.022\times10^{23}\ \text{photons}}{\text{mol}}\times\frac{1\ \text{kJ}}{1000\ \text{J}} = 78.6\ \text{kJ/mol}$

**13.** $\Delta E = -2.179\times10^{-18}\ \text{J}\left(\frac{1}{n_\text{f}^{\,2}}-\frac{1}{n_\text{i}^{\,2}}\right) = -2.179\times10^{-18}\ \text{J}\left(\frac{1}{3^2}-\frac{1}{6^2}\right) = -1.816\times10^{-19}\ \text{J}$

$E_{\text{photon emitted}} = 1.816\times10^{-19}\ \text{J} = h\nu \qquad \nu = \frac{E}{h} = \frac{1.550\times10^{-19}\ \text{J}}{6.626\times10^{-34}\ \text{J s}} = 2.740\times10^{14}\ \text{s}^{-1}$

**15.** First we determine the frequency of the radiation, and then match it with the Balmer equation.

$$\nu = \frac{c}{\lambda} = \frac{2.9979\times10^{8}\,\text{m s}^{-1}\times\dfrac{10^{9}\,\text{nm}}{1\,\text{m}}}{389\,\text{nm}} = 7.71\times10^{14}\ \text{s}^{-1} = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{n^2}\right)$$

$$\left(\frac{1}{2^2}-\frac{1}{n^2}\right) = \frac{7.71\times10^{14}\ \text{s}^{-1}}{3.2881\times10^{15}\ \text{s}^{-1}} = 0.234 = 0.2500-\frac{1}{n^2} \qquad \frac{1}{n^2} = 0.016 \qquad n = 7.9\approx 8$$

**17.** The longest wavelength component has the lowest frequency (and thus, the smallest energy).

$$\nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = 4.5668\times10^{14}\ \text{s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{4.5668\times10^{14}\ \text{s}^{-1}} = 6.5646\times10^{-7}\,\text{m} = 656.46\ \text{nm}$$

$$\nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{4^2}\right) = 6.1652\times10^{14}\ \text{s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{6.1652\times10^{14}\ \text{s}^{-1}} = 4.8626\times10^{-7}\,\text{m} = 486.26\ \text{nm}$$

$$\nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{5^2}\right) = 6.9050\times10^{14}\ \text{s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{6.9050\times10^{14}\ \text{s}^{-1}} = 4.3416\times10^{-7}\,\text{m} = 434.16\ \text{nm}$$

$$\nu = 3.2881\times10^{15}\ \text{s}^{-1}\left(\frac{1}{2^2}-\frac{1}{6^2}\right) = 7.3069\times10^{14}\ \text{s}^{-1} \quad \lambda = \frac{c}{\nu} = \frac{2.9979\times10^{8}\ \text{m/s}}{7.3069\times10^{14}\ \text{s}^{-1}} = 4.1028\times10^{-7}\,\text{m} = 410.28\ \text{nm}$$

## Quantum Theory

**19.** **(a)** Here we combine $E = h\nu$ and $c = \nu\lambda$ to obtain $E = hc/\lambda$

$$E = \frac{6.626\times10^{-34}\,\text{J s}\times 2.998\times10^{8}\,\text{m/s}}{574\,\text{nm}\times\dfrac{1\,\text{m}}{10^{9}\ \text{nm}}} = 3.46\times10^{-19}\,\text{J/photon}$$

**(b)** $E_m = 3.46\times10^{-19}\ \dfrac{\text{J}}{\text{photon}}\times 6.022\times10^{23}\ \dfrac{\text{photons}}{\text{mol}} = 2.08\times10^{5}\ \text{J/mol}$

**21.** The easiest way to answer this question is to convert all of (b) through (d) into nanometers. The radiation with the smallest wavelength will have the greatest energy per photon, while the radiation with the largest wavelength has the smallest amount of energy per photon.

**(a)** $6.62 \times 10^{2}$ nm

**(b)** $2.1 \times 10^{-5}\ \text{cm} \times \dfrac{1\ \times\ 10^{7}\ \text{nm}}{1\ \text{cm}} = 2.1 \times 10^{2}\,\text{nm}$

**(c)** $3.58\ \mu\text{m} \times \dfrac{1\ \times\ 10^{3}\ \ \text{nm}}{1\ \ \mu\text{m}} = 3.58 \times 10^{3}\,\text{nm}$

**(d)** $4.1 \times 10^{-6}\,\text{m} \times \dfrac{1\ \times\ 10^{9}\ \ \text{nm}}{1\ \ \text{m}} = 4.1 \times 10^{3}\,\text{nm}$

So, $2.1 \times 10^{-5}$ nm radiation, by virtue of possessing the smallest wavelength in the set, has the greatest energy per photon. Conversely, since $4.1 \times 10^{3}$ nm has the largest wavelength, it possesses the least amount of energy per photon.

**23.** Notice that energy and wavelength are inversely related: $E = \frac{hc}{\lambda}$. Therefore radiation that is 100 times as energetic as radiation with a wavelength of 988 nm will have a wavelength one hundredth as long, namely 9.88 nm. The frequency of this radiation is found by employing the wave equation.

$\nu = \frac{c}{\lambda} = \frac{2.998\times10^{8}\text{ m/s}}{9.88\text{ nm}\times\frac{1\text{m}}{10^{9}\text{nm}}} = 3.03\times10^{16}\text{s}^{-1}$ From Figure 8-3, we can see that this is UV radiation.

## The Photoelectric Effect

**25.** **(a)** $E = h\nu = 6.63\times10^{-34}\text{ J s}\times9.96\times10^{14}\text{ s}^{-1} = 6.60\times10^{-19}\text{ J/photon}$

**(b)** Indium will display the photoelectric effect when exposed to ultraviolet light since ultraviolet light has a maximum frequency of $1\times10^{16}\text{ s}^{-1}$, which is above the threshold frequency of indium. It will not display the photoelectric effect when exposed to infrared light since the maximum frequency of infrared light is $\sim 3\times10^{14}\text{ s}^{-1}$, which is below the threshold frequency of indium.

## The Bohr Atom

**27.** **(a)** radius $= n^2a_0 = 6^2\times0.53\text{Å}\times\frac{1\text{m}}{10^{10}\text{Å}}\times\frac{10^{9}\text{ nm}}{1\text{m}} = 1.9\text{ nm}$

**(b)** $E_n = -\frac{R_H}{n^2} = -\frac{2.179\times10^{-18}\text{ J}}{6^2} = -6.053\times10^{-20}\text{ J}$

**29.** **(a)** $\nu = \frac{2.179\times10^{-18}\text{ J}}{6.626\times10^{-34}\text{ J s}}\left(\frac{1}{4^2}-\frac{1}{7^2}\right) = 1.384\times10^{14}\text{ s}^{-1}$

**(b)** $\lambda = \frac{c}{\nu} = \frac{2.998\times10^{8}\text{ m/s}}{1.384\times10^{14}\text{ s}^{-1}} = 2.166\times10^{-6}\text{ m}\times\frac{10^{9}\text{ nm}}{1\text{ m}} = 2166\text{ nm}$

**(c)** This is infrared radiation.

**31.** **(a)** According to the Bohr model, the radii of allowed orbits in a hydrogen atom are given by $r_n = (n)^2\times(5.3\times10^{-11}\text{ m})$ where n = 1, 2, 3 . . . and $a_o = 5.3\times10^{-11}$ m (0.53 Å or 53 pm) so, $r_4 = (4)^2(5.3\times10^{-11}\text{ m}) = 8.5\times10^{-10}$ m.

**(b)** Here we want to see if there is an allowed orbit at r = 4.00 Å. To answer this question we will employ the equation $r_n = n^2a_o$: 4.00 Å = $n^2$(0.53 Å) or $n$ = 2.75 Å.
Since $n$ is not a whole number, we can conclude that the electron in the hydrogen atom does not orbit at a radius of 4.00 Å (i.e., such an orbit is forbidden by selection rules).

**(c)** The energy level for the n = 8 orbit is calculated using the equation

$E_n = \dfrac{-2.179 \times 10^{-18}\text{J}}{n^2}$ $\quad E_8 = \dfrac{-2.179 \times 10^{-18}\text{J}}{8^2} = -3.405 \times 10^{-20}$ J (relative to $E_\infty = 0$ J)

**(d)** Here we need to determine if $2.500 \times 10^{-17}$ J corresponds to an allowed orbit in the hydrogen atom. Once again we will employ the equation $E_n = \dfrac{-2.179 \times 10^{-18}\text{J}}{n^2}$.

$2.500 \times 10^{-17}\text{ J} = \dfrac{-2.179 \times 10^{-18}\text{J}}{n^2}$ or $n^2 = \dfrac{-2.179 \times 10^{-18}\text{J}}{-2.500 \times 10^{-17}\text{J}}$ hence, $n = 0.2952$

Because n is not a whole number, $-2.500 \times 10^{-17}$ J is not an allowed energy state for the electron in a hydrogen atom.

**33.** If infrared light is produced, the quantum number of the final state must have a lower value (i.e., be of lower energy) than the quantum number of the initial state. First we compute the frequency of the transition being considered (from $\nu = c/\lambda$), and then solve for the final quantum number.

$$\nu = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{m/s}}{410 \text{ nm} \times \dfrac{1\text{m}}{10^9 \text{ nm}}} = 7.32 \times 10^{14}\text{s}^{-1}$$

$$7.32 \times 10^{14}\text{s}^{-1} = \frac{2.179 \times 10^{-18} \text{ J}}{6.626 \times 10^{-34} \text{ J s}}\left(\frac{1}{n^2} - \frac{1}{7^2}\right) = 3.289 \times 10^{15} \text{ s}^{-1}\left(\frac{1}{n^2} - \frac{1}{7^2}\right)$$

$$\left(\frac{1}{n^2} - \frac{1}{7^2}\right) = \frac{7.32 \times 10^{14} \text{ s}^{-1}}{3.289 \times 10^{15} \text{ s}^{-1}} = 0.2226 \qquad \frac{1}{n^2} = 0.2226 + \frac{1}{7^2} = 0.2429 \qquad n = 2$$

**35.** **(a)** Line A is for the transition n = 3 → n = 1, while Line B is for the transition n = 4 → n = 1

**(b)** This transition corresponds to the n = 3 to n = 1 transition. Hence, ΔE = hc/λ

$\Delta E = (6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^8\text{ m s}^{-1}) \div (103 \times 10^{-9}\text{ m}) = 1.92\underline{9} \times 10^{-18}$ J

$\Delta E = -Z^2R_H/n_1^2 - -Z^2R_H/n_2^2$

$1.92\underline{9} \times 10^{-18}\text{ J} = -Z^2(2.179 \times 10^{-18})/(3)^2 + Z^2(2.179 \times 10^{-18})/(1)^2$

$Z^2 = 0.996$ and $Z = 0.998$ Thus, this is the spectrum for the hydrogen atom.

**37.** **(a)** Line A is for the transition n = 5 → n = 2, while Line B is for the transition n = 6 → n = 2

**(b)** This transition corresponds to the n = 5 to n = 2 transition. Hence, ΔE = hc/λ.

$\Delta E = (6.626 \times 10^{-34}\text{ J s}) \times (2.998 \times 10^8\text{ m s}^{-1}) \div (27.1 \times 10^{-9}\text{ m}) = 7.33 \times 10^{-18}$ J

$\Delta E = -Z^2R_H/n_1^2 - -Z^2R_H/n_2^2$

$4.57\underline{7} \times 10^{-19}\text{ J} = -Z^2(2.179 \times 10^{-18})/(5)^2 + Z^2(2.179 \times 10^{-18})/(2)^2$

$Z^2 = 16.0\underline{2}$ and $Z = 4.00$ Thus, this is the spectrum for the $Be^{3+}$ cation.

## Wave–Particle Duality

**39.** The de Broglie equation is $\lambda = h / mv$. This means that, for a given wavelength to be produced, a lighter particle would have to be moving faster. Thus, electrons would have to move faster than protons to display matter waves of the same wavelength.

**41.**

$$\lambda = \frac{h}{mv} = \frac{6.626\times10^{-34}\,\text{J s}}{\left(145\ \text{g}\times\frac{1\,\text{kg}}{1000\,\text{g}}\right)\left(168\,\text{km/h}\times\frac{1\text{h}}{3600\,\text{s}}\times\frac{1000\,\text{m}}{1\,\text{km}}\right)} = 9.79\times10^{-35}\,\text{m}$$

The diameter of a nucleus approximates $10^{-15}$ m, which is far larger than the baseball's wavelength.

## The Heisenberg Uncertainty Principle

**43.** The Bohr model is a determinant model for the hydrogen atom. It implies that the position of the electron is exactly known at any time in the future, once its position is known at the present. The distance of the electron from the nucleus also is exactly known, as is its energy. And finally, the velocity of the electron in its orbit is exactly known. All of these exactly known quantities—position, distance from nucleus, energy, and velocity—can't, according to the Heisenberg uncertainty principle, be known with great precision simultaneously.

**45.**

$$\Delta v = \left(\frac{1}{100}\right)(0.1)\left(2.998\ \times\ 10^{8}\ \frac{\text{m}}{\text{s}}\right) = 2.\underline{998} \times 10^{5}\ \text{m/s} \quad m = 1.673 \times 10^{-27}\ \text{kg}$$

$$\Delta p = m\Delta v = (1.673 \times 10^{-27}\ \text{kg})(2.998 \times 10^{5}\ \text{m/s}) = 5.\underline{0} \times 10^{-22}\ \text{kg m s}^{-1}$$

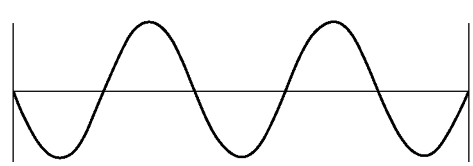
$$\Delta x = \frac{h}{4\pi\,\Delta p} = \frac{6.626\times10^{-34}\ \text{J s}}{(4\pi)(5._{0}\times10^{-22}\ \frac{\text{kg m}}{\text{s}})} = \sim1 \times 10^{-13}\ \text{m}\ \ (\sim100 \text{ times the diameter of a nucleus})$$

**47.** Electron mass = $9.109 \times 10^{-31}$ kg, $\lambda = 0.53$ Å ( 1 Å = $1 \times 10^{-10}$ m), hence $\lambda = 0.53 \times 10^{-10}$ m

$$\lambda = \frac{h}{mv} \text{ or } v = \frac{h}{m\lambda} = \frac{6.626\times10^{-34}\ \text{J s}}{(9.109\times10^{-31}\ \text{kg})(0.53\times10^{-10}\ \text{m})} = 1.4 \times 10^{7}\ \text{m s}^{-1}$$

## Wave Mechanics

**49.** A sketch of this situation is presented at right. We see that 2.50 waves span the space of the 42 cm. Thus, the length of each wave is obtained by equating: $2.50\lambda = 42$ cm, giving $\lambda \simeq 17$ cm.



**51.**

$$50.\text{ pm}\times\frac{1\text{ m}}{1\times10^{12}\text{ pm}}=5.0\times10^{-11}\text{ m}$$

$$E=\frac{n^2h^2}{8mL^2}$$

Where n=energy level, h=Planck's constant, m= mass, L=length of box

$$\Delta E = E_{\text{excited state}} - E_{\text{ground state}}$$

$$\Delta E=\left[\frac{4^2(6.626\times10^{-34}\text{ Js})^2}{8(9.109\times10^{-31}\text{ kg})(5.0\times10^{-11}\text{ m})^2}\right]-\left[\frac{1^2(6.626\times10^{-34}\text{ Js})^2}{8(9.109\times10^{-31}\text{ kg})(5.0\times10^{-11}\text{ m})^2}\right]$$

$$\Delta E=3.856\times10^{-16}\text{ J}-2.410\times10^{-17}\text{ J}$$

$$\Delta E=3.615\times10^{-16}\text{ J}$$

$$\lambda=\frac{hc}{\Delta E}=\frac{(6.626\times10^{-34}\text{ Js})(3.00\times10^{8}\text{ ms}^{-1})}{3.615\times10^{-16}\text{ J}}$$

$$\lambda=5.499\times10^{-10}\text{ m}\times\frac{10^9\text{ nm}}{1\text{ m}}=0.5499\text{ nm}=0.55\text{ nm}$$

**53.**

$$20.0\text{ nm}\times\frac{1\text{ m}}{10^9\text{ nm}}=2.00\times10^{-8}\text{ m= length of the box}$$

$$\Delta E=\frac{hc}{\lambda}=\frac{(6.626\times10^{-34}\text{ Js})(3.00\times10^{8}\text{ ms}^{-1})}{8.60\times10^{-5}\text{ m}}$$

$$\Delta E=2.311\times10^{-21}\text{ J}$$

$$\Delta E = E_{\text{excitedstate}} - E_{\text{ground state}}$$

$$E=\frac{n^2h^2}{8mL^2}$$

Where n=energy level, h=Planck's constant, m= mass, L=length of box

$$2.311\times10^{-21}\text{ J}=\left[\frac{n^2(6.626\times10^{-34}\text{ Js})^2}{8(9.109\times10^{-31}\text{ kg})(2.00\times10^{-8}\text{ m})^2}\right]-\left[\frac{1^2(6.626\times10^{-34}\text{ Js})^2}{8(9.109\times10^{-31}\text{ kg})(2.00\times10^{-8}\text{ m})^2}\right]$$

$$2.311\times10^{-21}\text{ J}=1.506\times10^{-22}n^2-1.506\times10^{-22}$$

$$n^2=16.35$$

$$n=4.0$$

**55.** The differences between Bohr orbits and wave mechanical orbitals are given below.

**(a)** The first difference is that of shape. Bohr orbits, as originally proposed, are circular (later, Sommerfeld proposed elliptical orbits). Orbitals, on the other hand, can be spherical, or shaped like two tear drops or two squashed spheres, or shaped like four tear drops meeting at their points.

**(b)** Bohr orbits are planar pathways, while orbitals are three-dimensional regions of space in which there is a high probability of finding electrons.

**(c)** The electron in a Bohr orbit has a definite trajectory. Its position and velocity are known at all times. The electron in an orbital, however, does not have a well-known position or velocity. In fact, there is a small but definite probability that the electron may be found outside the boundaries generally drawn for the orbital. Orbits and orbitals are similar in that the radius of a Bohr orbit is comparable to the average distance of the electron from the nucleus in the corresponding wave mechanical orbital.

## Quantum Numbers and Electron Orbitals

**57.** Answer (a) is incorrect because the values of $m_s$ may be either $+\frac{1}{2}$ or $-\frac{1}{2}$. Answers (b) and (d) are incorrect because the value of $\ell$ may be any integer $\geq |m_\ell|$, and less than $n$. Thus, answer (c) is the only one that is correct.

**59.** **(a)** $n = 5$ $\ell = 1$ $m_\ell = 0$ designates a $5p$ orbital. ($\ell = 1$ for all $p$ orbitals.)

**(b)** $n = 4$ $\ell = 2$ $m_\ell = -2$ designates a $4d$ orbital. ($\ell = 2$ for all $d$ orbitals.)

**(c)** $n = 2$ $\ell = 0$ $m_\ell = 0$ designates a $2s$ orbital. ($\ell = 0$ for all $s$ orbitals.)

**61.**

**(a)** 1 electron (All quantum numbers are allowed and each electron has a unique set of four quantum numbers)

**(b)** 2 electrons ($m_s$ = + ½ and – ½ )

**(c)** 10 electrons ($m_\ell$ = -2,-1,0,1,2 and $m_s$ = + ½ and – ½ for each $m_\ell$ orbital)

**(d)** 32 electrons ($\ell$=0,1,2,3 so there are one s, three p, five d, and seven f orbitals in n=4 energy level. Each orbital has 2 electrons.)

**(e)** 5 electrons (There are five electrons in the 4d orbital that are spin up.)

## The Shapes of Orbitals and Radial Probabilities

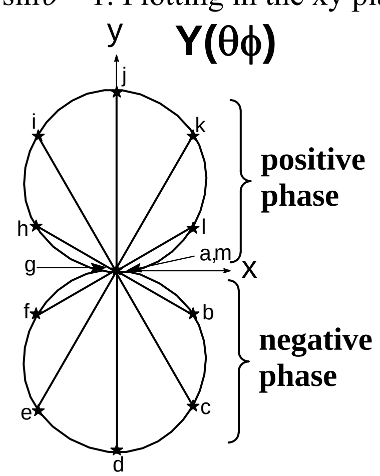
**63.** The wave function for the 2s orbital of a hydrogen atom is:

$$\psi_{2s} = \frac{1}{4}\left(\frac{1}{2\pi a_o^{3}}\right)^{1/2}\left(2 - \frac{r}{a_o}\right) e^{-\frac{r}{2a_o}}$$

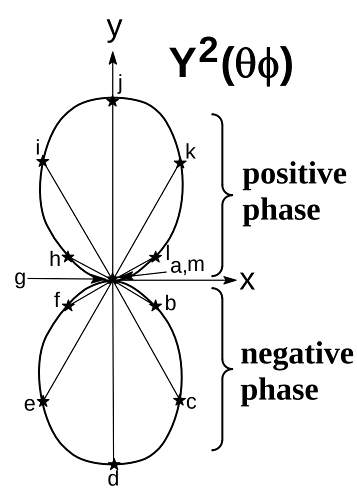
Where $r = 2a_o$, the $\left(2 - \frac{r}{a_o}\right)$ term becomes zero, thereby making $\psi_{2s} = 0$. At this point, the wave function has a radial node (i.e., the electron density is zero). The finite value of r is 2 $a_o$ at the node, which is equal to 2 × 53 pm or 106 pm. Thus at 106 pm, there is a nodal surface with zero electron density.

**65.** The angular part of the $2p_y$ wave function is $Y(\theta\phi)_{py} = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$. The two lobes of the $2p_y$ orbital lie in the xy plane and perpendicular to this plane is the xz plane. For all points in the xz plane $\phi = 0$, and since the sine of 0° is zero, this means that the entire x z plane is a node. Thus, the probability of finding a $2p_y$ electron in the xz plane is zero.

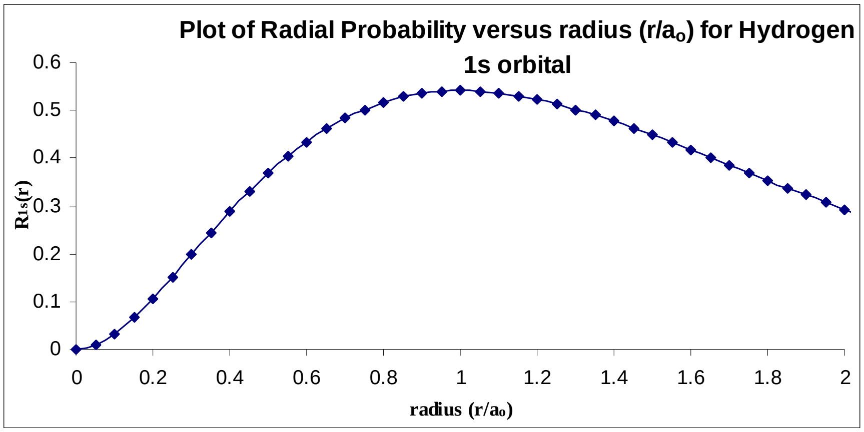
**67.** The $2p_y$ orbital $Y(\theta\phi) = \sqrt{\frac{3}{4\pi}}\sin\theta\sin\phi$, however, in the xy plane $\theta = 90°$ and $\sin\theta = 1$. Plotting in the xy plane requires that we vary only $\phi$.




| Point | Angle(°) | $Y(\theta\phi)$ | $Y^2(\theta\phi)$ |
|---|---|---|---|
| a | 0 | 0.0000 | 0.0000 |
| b | 30 | 0.2443 | 0.0597 |
| c | 60 | 0.4231 | 0.1790 |
| d | 90 | 0.4886 | 0.2387 |
| e | 120 | 0.4231 | 0.1790 |
| f | 150 | 0.2443 | 0.0597 |
| g | 180 | 0.0000 | 0.0000 |
| h | 210 | -0.2443 | 0.0597 |
| I | 240 | -0.4231 | 0.1790 |
| j | 270 | -0.4886 | 0.2387 |
| k | 300 | -0.4231 | 0.1790 |
| l | 330 | -0.2443 | 0.0597 |
| m | 360 | 0.000 | 0.000 |



**69.** A plot of radial probability distribution versus $r/a_o$ for a $H_{1s}$ orbital shows a maximum at 1.0 (that is, $r = a_o$ or r = 53 pm). The plot is shown below:




**71.** **(a)** To answer this question, we must keep two simple rules in mind.
1. Value of $\ell$ is the number of angular nodes.
2. Total number of nodes = n -1.

From this we see that this is a p-orbital (1 angular node → $\ell$ = 1) and because there are a total of 2 nodes, n = 3. This must be a 3p orbital.

**(b)** From this we see that this is a d-orbital (2 angular nodes → $\ell$ = 2) and because there are a total of 2 nodes, n = 3. This must be a 3d orbital.

**(c)** From this we see that this is an f-orbital (3 angular nodes → $\ell$ = 2) and because there are a total of 5 nodes, n = 6. This must be a 6f orbital.

**73.** The orbital is in the xy plane and has two angular nodes (d-orbital) and 2 spherical nodes (total nodes = 4, hence n = 5). Since the orbital points between the x-axis and y-axis, this is a $5d_{xyz}$ orbital. The second view of the same orbital is just a 90° rotation about the x-axis.

## Electron Configurations

**75.** **(a)** N is the third element in the $p$-block of the second period. It has three $2p$ electrons.

**(b)** Rb is the first element in the $s$-block of the *fifth* period. It has two $4s$ electrons.

**(c)** As is in the $p$-block of the fourth period. The $3d$ subshell is filled with ten electrons, but no $4d$ electrons have been added.

**(d)** Au is in the $d$-block of the sixth period; the $4f$ subshell is filled. Au has fourteen $4f$ electrons.

**(e)** Pb is the second element in the $p$-block of the sixth period; it has two $6p$ electrons. Since these two electrons are placed in separate $6p$ orbitals, they are unpaired. There are two unpaired electrons.

**(f)** Group 14 of the periodic table is the group with the elements C, Si, Ge, Sn, and Pb. This group currently has five named elements.

**(g)** The sixth period begins with the element Cs $(Z = 55)$ and ends with the element Rn $(Z = 86)$. This period is 32 elements long.

**77.** Configuration (b) is correct for phosphorus. The reasons why the other configurations are incorrect are given below.

**(a)** The two electrons in the $3s$ subshell must have opposed spins, or different values of $m_s$.

**(c)** The three $3p$ orbitals must each contain one electron, before a pair of electrons is placed in any one of these orbitals.

**(d)** The three unpaired electrons in the $3p$ subshell must all have the same spin, either all spin up or all spin down.

**79.** We write the correct electron configuration first in each case.

**(a)** P: $[\text{Ne}]3s^2 3p^3$ There are 3 unpaired electrons in each P atom.

**(b)** Br: $[\text{Ar}]3d^{10} 4s^2 4p^5$ There are ten 3*d* electrons in an atom of Br.

**(c)** Ge: $[\text{Ar}]3d^{10} 4s^2 4p^2$ There are two 4*p* electrons in an atom of Ge.

**(d)** Ba: $[\text{Xe}]6s^2$ There are two 6*s* electrons in an atom of Ba.

**(e)** Au: $[\text{Xe}]4f^{14}5d^{10}6s^1$ (exception) There are fourteen 4*f* electrons in an atom of Au.

**81.** Since the periodic table is based on electron structure, two elements in the same group (Pb and element 114) should have similar electron configurations.

**(a)** Pb: [Xe] $4f^{14}5d^{10}6s^2 6p^2$ **(b)** 114: [Rn] $5f^{14}6d^{10}7s^2 7p^2$

**83.** **(a)** This is an excited state; the 2s orbital should fill before any electrons enter the 2p orbital.

**(b)** This is an excited state; the electrons in the 2p orbitals should have the same spin (Hund's rule).

**(c)** This is the ground state configuration of N.

**(d)** This is an excited state; there should be one set of electrons paired up in the 2p orbital (Hund's rule is violated).

**85.** **(a)** Hg: $[\text{Xe}]6s^2 4f^{14} 5d^{10}$ **(d)** Sn: $[\text{Kr}]5s^2 4d^{10} 5p^2$

**(b)** Ca: $[Ar]4s^2$

**(c)** Po: $[Xe]6s^2 4f^{14} 5d^{10} 6p^4$

**(e)** Ta: $[Xe]6s^2 4f^{14} 5d^3$

**(f)** I: $[Kr]5s^2 4d^{10} 5p^5$

**87.** **(a)** rutherfordium; **(b)** carbon; **(c)** vanadium; **(d)** tellurium; **(e)** not an element

# INTEGRATIVE AND ADVANCED EXERCISES

**91.** **(a)** We first must determine the wavelength of light that has an energy of 435 kJ/mol and compare that wavelength with those known for visible light.

$$E = \frac{435 \frac{\text{kJ}}{\text{mol}} \times \frac{1000\text{ J}}{1\text{ kJ}}}{6.022 \times 10^{23} \text{ photons/mol}} = 7.22 \times 10^{-19} \text{ J/photon} = h\nu$$

$$\nu = \frac{E}{h} = \frac{7.22 \times 10^{-19}\text{ J}}{6.626 \times 10^{-34}\text{ J} \cdot \text{s}} = 1.09 \times 10^{15}\text{ s}^{-1} \qquad \lambda = \frac{c}{\nu} = \frac{2.9979 \times 10^8\text{ m s}^{-1}}{1.09 \times 10^{15}\text{ s}^{-1}} \times \frac{10^9\text{ nm}}{1\text{ m}} = 275\text{ nm}$$

Because the shortest wavelength of visible light is 390 nm, the photoelectric effect for mercury cannot be obtained with visible light.

**(b)** We first determine the energy per photon for light with 215 nm wavelength.

$$E = h\nu = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{ J} \cdot \text{s} \times 2.9979 \times 10^8\text{ m s}^{-1}}{215\text{ nm} \times \frac{1\text{ m}}{10^9\text{ nm}}} = 9.24 \times 10^{-19}\text{ J/photon}$$

Excess energy, over and above the threshold energy, is imparted to the electron as kinetic energy. Electron kinetic energy $= 9.24 \times 10^{-19}\text{ J} - 7.22 \times 10^{-19}\text{ J} = 2.02 \times 10^{-19}\text{ J} = \frac{mv^2}{2}$

**(c)** We solve for the velocity $v = \sqrt{\frac{2 \times 2.02 \times 10^{-19}\text{ J}}{9.109 \times 10^{-31}\text{kg}}} = 6.66 \times 10^5\text{ m s}^{-1}$

**92.** We first determine the energy of an individual photon.

$$E = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34}\text{ J s} \times 2.998 \times 10^8\text{ m/s}}{1525\text{ nm} \times \frac{1\text{ m}}{10^9\text{nm}}} = 1.303 \times 10^{-19}\text{ J}$$

$$\frac{\text{no. photons}}{\text{sec}} = \frac{95\text{ J}}{\text{s}} \times \frac{1\text{ photon}}{1.303 \times 10^{-19}\text{ J}} \times \frac{14\text{ photons produced}}{100\text{ photons theoretically possible}} = 1.0 \times 10^{20}\ \frac{\text{photons}}{\text{sec}}$$

**93.** A watt = joule/second, so joules = watts × seconds  J = 75 watts × 5.0 seconds = 37$\underline{5}$ Joules
E = (number of photons) hν and ν = c/λ, so E =(number of photons)hc/λ and

$$\lambda = (\text{number of photons})\frac{hc}{E} = \frac{(9.91\times10^{20}\text{ photons})(6.626\times10^{-34}\text{ J sec})(3.00\times10^{8}\, m/\text{sec})}{37\underline{5}\text{ watts}}$$

$\lambda = 5.3\times10^{-7}\, m$ or 530 nm  The light will be green in color.

**96.** First we determine the frequency of the radiation. Then rearrange the Rydberg equation (generalized from the Balmer equation) and solve for the parenthesized expression.

$$v = \frac{c}{\lambda} = \frac{2.9979\times10^{8}\text{ m s}^{-1}\times\dfrac{10^{9}\text{ nm}}{1\text{ m}}}{1876\text{ nm}} = 1.598\times10^{14}\text{ s}^{-1} = 3.2881\times10^{15}\text{ s}^{-1}\left(\frac{1}{m^2}-\frac{1}{n^2}\right)$$

$$\left(\frac{1}{m^2}-\frac{1}{n^2}\right) = \frac{1.598\times10^{14}\text{ s}^{-1}}{3.2881\times10^{15}\text{ s}^{-1}} = 0.0486$$

We know that $m < n$, and both numbers are integers. Furthermore, we know that $m \neq 2$ (the Balmer series) which is in the visible region, and $m \neq 1$ which is in the ultraviolet region, since the wavelength 1876 nm is in the infrared region. Let us try $m = 3$ and $n = 4$.

$\dfrac{1}{3^2}-\dfrac{1}{4^2} = 0.04861$  These are the values we want.

**101.** First we must determine the energy per photon of the radiation, and then calculate the number of photons needed, (i.e., the number of ozone molecules (with the ideal gas law)). (Parts per million $O_3$ are assumed to be by volume.) The product of these two numbers is total energy in joules.

$$E_1 = hv = \frac{hc}{\lambda} = \frac{6.626\times10^{-34}\text{ J}\cdot\text{s}\times2.9979\times10^{8}\text{ m s}^{-1}}{254\text{ nm}\times\dfrac{1\text{ m}}{10^{9}\text{ nm}}} = 7.82\times10^{-19}\text{ J/photon}$$

$$\text{no. photons} = \frac{\left(748\text{ mmHg}\times\dfrac{1\text{ atm}}{760\text{ mmHg}}\right)\times\left(1.00\text{ L}\times\dfrac{0.25\text{ L}\quad O_3}{10^{6}\text{ L air}}\right)}{\dfrac{0.08206\text{ L atm}}{\text{mol K}}\times(22+273)\text{ K}}\times\frac{6.022\times10^{23}\text{ molecules}}{1\text{ mol }O_3}$$

$$\times\frac{1\text{ photon}}{1\text{ molecule }O_3} = 6.1\times10^{15}\text{ photons}$$

energy needed = $7.82\times10^{-19}\text{ J/photon}\times6.1\times10^{15}\text{ photons} = 4.8\times10^{-3}\text{ J}$ or 4.8 mJ

**102.** First we compute the energy per photon, and then the number of photons received per second.

$$E = hv = 6.626\times10^{-34}\text{J}\cdot\text{s}\times8.4\times10^{9}\text{ s}^{-1} = 5.6\times10^{-24}\text{ J/photon}$$

$$\frac{\text{photons}}{\text{second}} = \frac{4\times10^{-21}\text{ J/s}}{5.6\times10^{-24}\text{ J/photon}} = 7\times10^{2}\text{photons/s}$$

**105.** First, we must calculate the energy of the 300 nm photon. Then, using the amount of energy required to break a Cl–Cl bond energy and the energy of the photon, we can determine how much excess energy there is after bond breakage.

Energy of a single photon at 300 nm is:

$$E = h\nu = hc/\lambda$$

$$E = \frac{(6.6261\times10^{-34}\ \text{J}\cdot\text{s})(2.998\times10^{8}\ \text{m}\cdot\text{s}^{-1})}{(300\times10^{-9}\ \text{m})} = 6.6215\times10^{-19}\ \text{J}$$

The bond energy of a single Cl–Cl bond is determined as follows:

$$\text{Cl}-\text{Cl B.E.} = \frac{242.6\times10^{3}\ \text{J}}{\text{mol Cl}_2}\times\frac{1\ \text{mol Cl}_2}{6.022\times10^{23}\ \text{molec.}}\times\frac{1\ \text{molec.}}{1\ \text{Cl}-\text{Cl bond}} = 4.028\times10^{-19}\ \text{J/Cl}-\text{Cl bond}$$

Therefore, the excess energy after splitting a Cl–Cl bond is (6.6215 – 4.028)×10-19 J = 2.59×10-19 J. Statistically, this energy is split evenly between the two Cl atoms and imparts a kinetic energy of 1.29×10-19 J to each.

The velocity of each atom is determined as follows:

$$\text{mass of Cl} = \frac{35.45\ \text{g Cl}}{1\ \text{mol Cl}}\times\frac{1\ \text{mol Cl}}{6.022\times10^{23}\ \text{molec.}} = 5.887\times10^{-23}\ \text{kg/Cl atom}$$

$$e_k = \frac{1}{2}mu^2$$

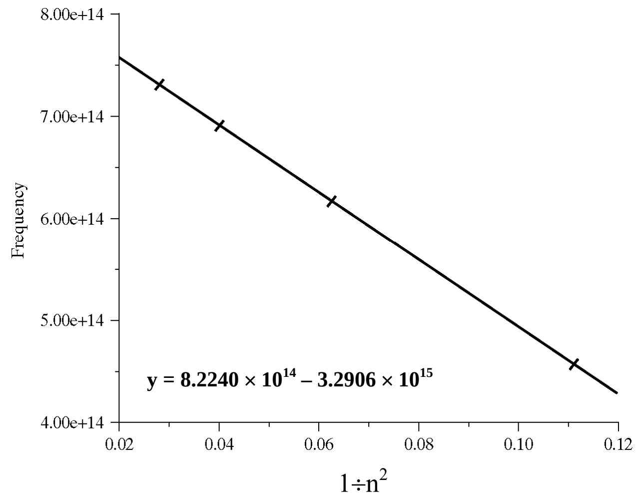
$$u = \sqrt{\frac{2e_k}{m}} = \sqrt{\frac{2(1.29\times10^{-19}\ \text{J})}{5.887\times10^{-23}\ \text{kg}}} = 66.2\ \text{m/s}$$

# FEATURE PROBLEMS

**114.** The equation of a straight line is $y = mx + b$, where $m$ is the slope of the line and $b$ is its y-intercept. The Balmer equation is $\nu = 3.2881\times10^{15}\ \text{Hz}\left(\frac{1}{2^2}-\frac{1}{n^2}\right) = \frac{c}{\lambda}$. In this equation, one plots $\nu$ on the vertical axis, and $1/n^2$ on the horizontal axis. The slope is $b = -3.2881\times10^{15}$ Hz and the intercept is $3.2881\times10^{15}\ \text{Hz}\div2^2 = 8.2203\times10^{14}\ \text{Hz}$.

The plot of the data for Figure 8-10 follows.

| | | | | |
|---|---|---|---|---|
| $\lambda$ | 656.3 nm | 486.1 nm | 434.0 nm | 410.1 nm |
| $\nu$ | $4.568\times10^{14}$ Hz | $6.167\times10^{14}$ Hz | $6.908\times10^{14}$ Hz | $7.310\times10^{14}$ Hz |
| $n$ | 3 | 4 | 5 | 6 |




We see that the slope ($-3.2906 \times 10^{15}$) and the y-intercept ($8.2240 \times 10^{14}$) are almost exactly what we had predicted from the Balmer equation.

**116.** **(a)** First we calculate the range of energies for the incident photons used in the absorption experiment. Remember: $E_{\text{photon}} = h\nu$ & $\nu = c/\lambda$. At one end of the range, $\lambda$ = 100 nm.

Therefore, $\nu = 2.998 \times 10^{8}\ \text{m s}^{-1} \div (1.00 \times 10^{-7}\ \text{m}) = 2.998 \times 10^{15}\ \text{s}^{-1}$.

So $E_{\text{photon}} = 6.626 \times 10^{-34}\ \text{J s}(2.998 \times 10^{15}\ \text{s}^{-1}) = 1.98 \times 10^{-18}$ J.

At the other end of the range, $\lambda$ = 1000 nm.

Therefore, $\nu = 2.998 \times 10^{8}\ \text{m s}^{-1} \div 1.00 \times 10^{-6}\ \text{m} = 2.998 \times 10^{14}\ \text{s}^{-1}$.

So $E_{\text{photon}} = 6.626 \times 10^{-34}\ \text{J s}(2.998 \times 10^{14}\ \text{s}^{-1}) = 1.98 \times 10^{-19}$ J.

Next, we will calculate what excitations are possible using photons with energies between $1.98 \times 10^{-18}$ J and $1.98 \times 10^{-19}$ J and the electron initially residing in the $n = 1$ level. These "orbit transitions" can be found with the equation

$\Delta E = E_f - E_i = -2.179 \times 10^{-18}\left(\frac{1}{(1)^2} - \frac{1}{(n_f)^2}\right)$. For the lowest energy photon

$$1.98 \times 10^{-19}\ \text{J} = -2.179 \times 10^{-18}\left(\frac{1}{(1)^2} - \frac{1}{(n_f)^2}\right) \quad \text{or} \quad 0.0904 = 1 - \frac{1}{(n_f)^2}$$

From this $-0.9096 = -\frac{1}{(n_f)^2}$ and $n_f = 1.05$

Thus, the lowest energy photon is not capable of promoting the electron above the $n = 1$ level. For the highest energy level:

$$1.98 \times 10^{-18}\ \text{J} = -2.179 \times 10^{-18}\left(\frac{1}{(1)^2} - \frac{1}{(n_f)^2}\right) \quad \text{or} \quad 0.9114 = 1 - \frac{1}{(n_f)^2}$$

From this $-0.0886 = -\frac{1}{(n_f)^2}$ and $n_f = 3.35$ Thus, the highest energy photon can promote a ground state electron to both the $n = 2$ and $n = 3$ levels. This means that we would see two lines in the absorption spectrum, one corresponding to the $n = 1 \rightarrow n = 2$ transition and the other to the $n = 1 \rightarrow n = 3$ transition.

Energy for the $n = 1 \rightarrow n = 2$ transition $= -2.179 \times 10^{-18}\left(\frac{1}{(1)^2} - \frac{1}{(2)^2}\right) = 1.634 \times 10^{-18}$ J

$\nu = \frac{1.634 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 2.466 \times 10^{15}\ \text{s}^{-1}$ $\quad \lambda = \frac{2.998 \times 10^{8}\ \text{m s}^{-1}}{2.466 \times 10^{15}\ \text{s}^{-1}} = 1.215 \times 10^{-7}$ m

$\lambda = 121.5$ nm

Thus, we should see a line at 121.5 nm in the absorption spectrum.

Energy for the $n = 1 \rightarrow n = 3$ transition $= -2.179 \times 10^{-18}\left(\frac{1}{(1)^2} - \frac{1}{(3)^2}\right) = 1.937 \times 10^{-18}$ J

$\nu = \frac{1.937 \times 10^{-18}\ \text{J}}{6.626 \times 10^{-34}\ \text{J s}} = 2.923 \times 10^{15}\ \text{s}^{-1}$ $\quad \lambda = \frac{2.998 \times 10^{8}\ \text{m s}^{-1}}{2.923 \times 10^{15}\ \text{s}^{-1}} = 1.025 \times 10^{-7}$ m

$\lambda = 102.5$ nm

Consequently, the second line should appear at 102.6 nm in the absorption spectrum.

**(b)** An excitation energy of 1230 kJ $\text{mol}^{-1}$ to 1240 kJ $\text{mol}^{-1}$ works out to $2 \times 10^{-18}$ J per photon. This amount of energy is sufficient to raise the electron to the $n = 4$ level. Consequently, six lines will be observed in the emission spectrum. The calculation for each emission line is summarized below:

$E_{4\rightarrow1} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{1^2} - \frac{1}{4^2}\right) = 3.083\times10^{15}\ \text{s}^{-1}$ $\quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{3.083\times10^{15}\ \text{s}^{-1}} = 9.724 \times 10^{-8}$ m

$\lambda = 97.2$ nm

$E_{4\rightarrow2} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{2^2} - \frac{1}{4^2}\right) = 6.167\times 10^{14}\ \text{s}^{-1}$ $\quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{6.167\times10^{14}\ \text{s}^{-1}} = 4.861 \times 10^{-7}$ m

$\lambda = 486.1$ nm

$E_{4\rightarrow3} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{3^2} - \frac{1}{4^2}\right) = 1.599\times 10^{14}\ \text{s}^{-1}$ $\quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{1.599\times10^{14}\ \text{s}^{-1}} = 1.875 \times 10^{-6}$ m

$\lambda = 1875$ nm

$$E_{3\to1} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{1^2}-\frac{1}{3^2}\right) = 2.924\times 10^{15}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{2.924\times10^{15}\,\text{s}^{-1}} = 1.025\times10^{-7}\ \text{m}$$

$\lambda$ = 102.5 nm

$$E_{3\to2} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{2^2}-\frac{1}{3^2}\right) = 4.568\times 10^{14}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{4.568\times10^{14}\,\text{s}^{-1}} = 6.563\times10^{-7}\ \text{m}$$

$\lambda$ = 656.3 nm

$$E_{2\to1} = \frac{2.179\times10^{-18}\ \text{J}}{6.626\times10^{-34}\ \text{J s}}\left(\frac{1}{1^2}-\frac{1}{2^2}\right) = 2.467\times 10^{15}\,\text{s}^{-1} \quad \lambda = \frac{2.998\times10^{8}\ \frac{\text{m}}{\text{s}}}{2.467\times10^{15}\,\text{s}^{-1}} = 1.215\times10^{-7}\ \text{m}$$

$\lambda$ = 121.5 nm

**(c)** The number of lines observed in the two spectra is not the same. The absorption spectrum has two lines, while the emission spectrum has six lines. Notice that the 102.5 nm and 1021.5 nm lines are present in both spectra. This is not surprising since the energy difference between each level is the same whether it is probed by emission or absorption spectroscopy.

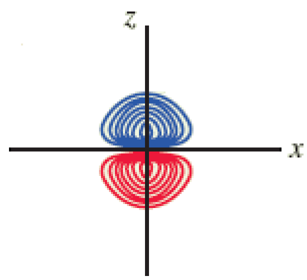
## SELF-ASSESSMENT EXERCISES

**122.** Atomic orbitals of multi-electron atoms resemble those of the H atom in having both angular and radial nodes. They differ in that subshell energy levels are not degenerate and their radial wave functions no longer conform to the expressions in Table 8.1.

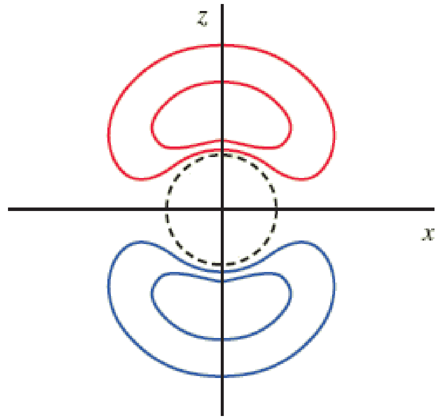
**123.** Effective nuclear charge is the amount of positive charge from the nucleus that the valence shell of the electrons actually experiences. This amount is less than the actual nuclear charge, because electrons in other shells shield the full effect.

**124.** The $p_x$, $p_y$ and $p_z$ orbitals are triply degenerate (the are the same energy), and they have the same shape. Their difference lies in their orientation with respect to the arbitrarily assigned x, y, and z axes of the atom, as shown in Figure 8-28 of the textbook.

**125.** The difference between the 2p and 3p orbitals is that the 2p orbital has only one node (n = 2-1) which is angular, whereas the 3p orbital has two nodes, angular and radial. See the figures below, which are extracted from the text.



$2p_z$



$3p_z$

**126.** The answer is (a). If the speed is the same for all particles, the lightest particle will have the longest wavelength.

**127.** **(a)** Velocity of the electromagnetic radiation is fixed at the speed of light in a vacuum.
**(b)** Wavelength is inversely proportional to frequency, because $\nu = c/\lambda$.
**(c)** Energy is directly proportional to frequency, because $E=h\nu$.

**128.** Sir James Jeans's obtuse metaphor for the photoelectric effect points to the fact that it is a quantum-mechanical phenomenon. The photoelectric effect is a single photon-to-electron phenomenon; that is, a single photon that meets the minimum energy requirement can cause the ejection of an electron from the atom. If the photon is particularly energetic, the excess energy will not eject a second electron. Hence, you can't kill two birds with one stone. Furthermore, the atom cannot accumulate the energy from multiple photon hits to eject an electron: only one hit of sufficient energy equals one and only one ejection. Therefore, you can't kill a bird with multiple stones.