

CHAPTER 1

THE QUANTUM WORLD

1.2 In an evacuated tube, we would expect these particles to be electrons from the metal cathode. In that case, the ratio of charge to mass would be $1.76 \times 10^{11} \text{ C} \cdot \text{kg}^{-1}$. Since this ratio for an electron is much larger than the one given for the “canal rays” in this helium-filled tube, we can reason that these particles are about 10,000 times as massive as an electron. It turns out that

He^+ has the right mass:
$$\frac{Q}{m} = \frac{1.60218 \times 10^{-19} \text{ C}}{(4.00)(1.66054 \times 10^{-27} \text{ kg})} = 2.41 \times 10^7 \text{ C} \cdot \text{kg}^{-1}$$

1.4 All of these can be determined using $\nu\lambda = c$.

(a) False. The speed of EMR is constant. (b) False. Blue light has a wavelength of 470 nm, green light a wavelength of 530 nm; the wavelength is increasing. (c) False. Since $\nu\lambda = c$ for all EMR, then

$\lambda_{IR} \nu_{IR} = \lambda_{radio} \nu_{radio}$. Therefore

$$\frac{\nu_{IR}}{\nu_{radio}} = \frac{\lambda_{radio}}{\lambda_{IR}} = \frac{1.0 \times 10^6 \text{ nm}}{1.0 \times 10^3 \text{ nm}}; \text{ this means } \nu_{IR} = 1000 \nu_{radio} \text{ not half.}$$

(d) False. Same reasoning as for (c).

1.6 radio waves < infrared radiation < visible light < ultraviolet radiation

1.8 $1 \text{ MHz} = 1 \times 10^6 \text{ Hz} = 1 \times 10^6 \text{ s}^{-1}$.

$$(a) \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{99.3 \times 10^6 \text{ s}^{-1}} = 3.0 \text{ m}$$

$$(b) \lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{1420 \times 10^6 \text{ s}^{-1}} = 0.211 \text{ m} = 211 \text{ mm}$$

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1.10 All of these can be determined using $E=h\nu$ and $\nu\lambda=c$. For example: in the first entry, energy is given, so:

$$\nu = \frac{E}{h} = \frac{2.7 \times 10^{-19} \text{ J}}{6.626 \times 10^{-34} \text{ J}\cdot\text{s}} = 4.1 \times 10^{14} \text{ sec}^{-1} = 4.1 \times 10^{14} \text{ Hz}; \text{ and}$$

$$\lambda = \frac{c}{\nu} = \frac{2.998 \times 10^8 \text{ m}\cdot\text{sec}^{-1}}{4.1 \times 10^{14} \text{ s}^{-1}} = 7.4 \times 10^{-7} \text{ m} = 740 \text{ nm}$$

Frequency	Wavelength	Energy of photon	Event
$4.1 \times 10^{14} \text{ Hz}$	740 nm	$2.7 \times 10^{-19} \text{ J}$	Traffic light
$3.00 \times 10^{14} \text{ Hz}$	999 nm	$1.99 \times 10^{-19} \text{ J}$	IR heated food
$5 \times 10^{19} \text{ Hz}$	6 pm	$3 \times 10^{-14} \text{ J}$	Cosmic ray
$1.93 \times 10^8 \text{ Hz}$	155 cm	$1.28 \times 10^{-25} \text{ J}$	Listen to radio

1.12 Given that $\Delta E \propto \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$, this quantity will be (a) 0.012 for $n = 6$ to

$n = 5$, (b) 0.049 for $n = 4$ to $n = 3$, and (c) 0.75 for $n = 2$ to $n = 1$.

Therefore (c) will have the largest energy.

1.14 (a) The Rydberg equation gives ν when $\mathfrak{R} = 3.29 \times 10^{15} \text{ s}^{-1}$, from which one can calculate λ from the relationship $c = \nu\lambda$.

$$\nu = \mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$\text{and } c = \nu\lambda = 2.997\,92 \times 10^8 \text{ m}\cdot\text{s}^{-1}$$

$$c = \mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) \lambda$$

$$2.997\,92 \times 10^8 \text{ m}\cdot\text{s}^{-1} = (3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{1} - \frac{1}{25} \right) \lambda$$

$$\lambda = 9.49 \times 10^{-8} \text{ m} = 94.9 \text{ nm}$$

(b) Lyman series

(c) This absorption lies in the ultraviolet region.

- 1.16** Because the line is in the visible part of the spectrum, it belongs to the Balmer series for which the ending n is 2. We can use the following equation to solve for the starting value of n :

$$\nu = \frac{c}{\lambda} = \frac{2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{434 \times 10^{-9} \text{ m}} = 6.91 \times 10^{14} \text{ s}^{-1}$$

$$\nu = (3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right)$$

$$6.91 \times 10^{14} \text{ s}^{-1} = (3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{2^2} - \frac{1}{n_1^2} \right)$$

$$0.210 = 0.250 - \frac{1}{n_1^2}$$

$$\frac{1}{n_1^2} = 0.04$$

$$n_1^2 = \frac{1}{0.04}$$

$$n_1 = 5$$

This transition is from the $n = 5$ to the $n = 2$ level.

- 1.18** Here we are searching for a transition of He^+ whose frequency matches that of the $n = 2$ to $n = 1$ transition of H. The frequency of the H transition is:

$$\nu_{\text{H}} = \mathfrak{R} \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \left(\frac{3}{4} \right) \mathfrak{R}$$

A transition of the He^+ ion with the same frequency is the $n = 2$ to $n = 4$ transition:

$$\nu_{\text{He}^+} = (Z^2) \mathfrak{R} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) = (2^2) \mathfrak{R} \left(\frac{3}{16} \right) = \left(\frac{3}{4} \right) \mathfrak{R}$$

- 1.20** (a) false. UV photons have higher energy than infrared photons. (b) false. The kinetic energy of the electron is directly proportional to the

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energy (and hence frequency) of the radiation in excess of the amount of energy required to eject the electron from the metal surface. (c) true.

1.22 Electron diffraction (b) best supports the idea that particles have wave properties. Diffraction was thought to be purely a wave property; however electrons also exhibit diffraction when reflected from a crystal.

1.24 From $c = \nu\lambda$ and $E = h\nu$, $E = hc\lambda^{-1}$.

$$\begin{aligned} E \text{ (for one atom)} &= \frac{(6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})(2.997\ 92 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{470 \times 10^{-9} \text{ m}} \\ &= 4.23 \times 10^{-19} \text{ J}\cdot\text{atom}^{-1} \end{aligned}$$

$$\begin{aligned} E \text{ (for 1.00 mol)} &= (6.022 \times 10^{23} \text{ atoms}\cdot\text{mol}^{-1})(4.23 \times 10^{-19} \text{ J}\cdot\text{atom}^{-1}) \\ &= 2.5 \times 10^5 \text{ J}\cdot\text{mol}^{-1} \text{ or } 250 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

1.26 (a) $E = h\nu$

$$\begin{aligned} &= (6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})(1.2 \times 10^{17} \text{ s}^{-1}) \\ &= 8.0 \times 10^{-17} \text{ J} \end{aligned}$$

(b) The energy per mole will be 6.022×10^{23} times the energy of one atom .

$$\begin{aligned} E &= (2.00 \text{ mol})(6.022 \times 10^{23} \text{ atoms}\cdot\text{mol}^{-1}) \\ &\quad \times (6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})(1.2 \times 10^{17} \text{ s}^{-1}) \\ &= 9.6 \times 10^7 \text{ J or } 96 \times 10^4 \text{ kJ} \end{aligned}$$

(c)
$$\begin{aligned} E &= \left(\frac{2.00 \text{ g Cu}}{63.54 \text{ g}\cdot\text{mol}^{-1}} \right) \\ &\quad \times (6.022 \times 10^{23} \text{ atoms}\cdot\text{mol}^{-1})(8.0 \times 10^{-17} \text{ J}\cdot\text{atom}^{-1}) \\ &= 1.5 \times 10^6 \text{ J or } 1.5 \times 10^3 \text{ kJ} \end{aligned}$$

1.28 $40 \text{ W} = 40 \text{ J}\cdot\text{sec}^{-1}$, so in 2 seconds 80 J will be emitted.

For blue light ($\lambda = 470 \text{ nm} = 470 \times 10^{-9} \text{ m}$) the energy per photon is:

$$\begin{aligned} E &= hc\lambda^{-1} \\ &= (6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(2.99792 \times 10^8 \text{ m}\cdot\text{s}^{-1})(470 \times 10^{-9} \text{ m})^{-1} \\ &= 4.2 \times 10^{-19} \text{ J}\cdot\text{photons}^{-1} \end{aligned}$$

$$\begin{aligned} \text{number of photons} &= (80. \text{ J})(4.7 \times 10^{-19} \text{ J}\cdot\text{photon}^{-1})^{-1} \\ &= 1.7 \times 10^{20} \text{ photons} \end{aligned}$$

$$\begin{aligned} \text{moles of photons} &= (1.7 \times 10^{20} \text{ photons})(6.022 \times 10^{23} \text{ mol}\cdot\text{photons}^{-1})^{-1} \\ &= 2.8 \times 10^{-4} \text{ mol photons} \end{aligned}$$

1.30 From Wien's law: $T\lambda_{\text{max}} = 2.88 \times 10^{-3} \text{ K}\cdot\text{m}$.

$$\begin{aligned} \lambda_{\text{max}} &= \frac{2.88 \times 10^{-3} \text{ K}\cdot\text{m}}{2.3 \times 10^4 \text{ K}} \\ \lambda_{\text{max}} &= 1.3 \times 10^{-7} \text{ m} = 130 \text{ nm}. \end{aligned}$$

1.32 From Wien's law: $T\lambda_{\text{max}} = 2.88 \times 10^{-3} \text{ K}\cdot\text{m}$.

$$\begin{aligned} (T)(572 \times 10^{-9} \text{ m}) &= 2.88 \times 10^{-3} \text{ K}\cdot\text{m} \\ T &\approx 5.03 \times 10^3 \text{ K} \end{aligned}$$

1.34 The wavelength of radiation needed will be the sum of the energy of the work function plus the kinetic energy of the ejected electron.

$$\begin{aligned} E_{\text{work function}} &= (4.37 \text{ eV})(1.6022 \times 10^{-19} \text{ J}\cdot\text{eV}^{-1}) = 7.00 \times 10^{-19} \text{ J} \\ E_{\text{kinetic}} &= \frac{1}{2} mv^2 \\ &= \frac{1}{2} (9.10939 \times 10^{-31} \text{ kg})(1.5 \times 10^6 \text{ m}\cdot\text{s}^{-1})^2 \\ &= 1.02 \times 10^{-18} \text{ J} \\ E_{\text{total}} &= E_{\text{work function}} + E_{\text{kinetic}} \\ &= 7.00 \times 10^{-19} \text{ J} + 1.02 \times 10^{-18} \text{ J} \\ &= 1.72 \times 10^{-18} \text{ J} \end{aligned}$$

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To obtain the wavelength of radiation we use the relationships between E , frequency, wavelength, and the speed of light:

From $E = h\nu$ and $c = \nu\lambda$ we can write

$$\begin{aligned}\lambda &= \frac{hc}{E} \\ &= \frac{(6.626 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{1.72 \times 10^{-18} \text{ J}} \\ &= 1.16 \times 10^{-7} \text{ m or } 116 \text{ nm}\end{aligned}$$

1.36 (a) Mass of one hydrogen atom:

$$1.008 \text{ g}\cdot\text{mol}^{-1} \left(\frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) \left(\frac{1 \times 10^{-3} \text{ kg}}{1 \text{ g}} \right) = 1.674 \times 10^{-27} \text{ kg}$$

Using the de Broglie relationship, we get

$$\begin{aligned}\lambda &= h(mv)^{-1} \\ &= (6.626 \text{ } 08 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1}) [(1.675 \times 10^{-27} \text{ kg})(10. \text{ m}\cdot\text{s}^{-1})]^{-1} \\ &= 4.0 \times 10^{-8} \text{ m} = 40. \text{ nm}.\end{aligned}$$

(b) Since $\lambda \propto \text{speed}$, decreasing the speed should cause the wavelength to decrease.

1.38 Let $x = \text{wavelength}$; then $\nu = x \text{ m}\cdot\text{s}^{-1}$. Now use the de Broglie relationship:

$$\begin{aligned}\lambda &= x = h(m_e \nu)^{-1} \\ &= (6.626 \text{ } 08 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1}) [(9.1094 \times 10^{-31} \text{ kg})(x \text{ m}\cdot\text{s}^{-1})]^{-1} \\ x^2 &= 7.27 \times 10^{-4} \text{ m}^2 \\ x &= 2.70 \times 10^{-2} \text{ m} = 2.70 \text{ cm}.\end{aligned}$$

1.40 Use the de Broglie relationship, $\lambda = h\nu^{-1} = h(mv)^{-1}$.
(162 km · h⁻¹)(1000 m/km)(1 h/3600 s) = 45 m · s⁻¹

$$\begin{aligned}\lambda &= h(mv)^{-1} \\ &= (6.626 \text{ } 08 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1}) [(1645 \text{ kg})(45 \text{ m}\cdot\text{s}^{-1})]^{-1} \\ &= 8.95 \times 10^{-39} \text{ m}\end{aligned}$$

1.42 The mass of one He atom is given by the molar mass of He divided by Avogadro's constant:

$$\begin{aligned}\text{mass of He atom} &= \frac{4.00 \text{ g} \cdot \text{mol}^{-1}}{6.022 \times 10^{23} \text{ atoms} \cdot \text{mol}^{-1}} \\ &= 6.64 \times 10^{-24} \text{ g or } 6.64 \times 10^{-27} \text{ kg}\end{aligned}$$

From the de Broglie relationship, $p = h\lambda^{-1}$ or $h = mv\lambda$, we can calculate wavelength.

$$\begin{aligned}\lambda &= h(mv)^{-1} \\ &= \frac{6.626 \text{ 08} \times 10^{-34} \text{ J} \cdot \text{s}}{(6.64 \times 10^{-27} \text{ kg})(1230 \text{ m} \cdot \text{s}^{-1})} \\ &= \frac{6.626 \text{ 08} \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(6.64 \times 10^{-27} \text{ kg})(1230 \text{ m} \cdot \text{s}^{-1})} \\ &= 8.11 \times 10^{-11} \text{ m}\end{aligned}$$

1.44 The uncertainty principle states that $\Delta p \Delta x = \frac{1}{2} \hbar$; so, for a hydrogen,

$$\Delta p = m_H \Delta v, \text{ then } m_H \Delta v \Delta x = \frac{1}{2} \hbar \text{ and } \Delta x = \frac{1}{2} \frac{\hbar}{m_H \Delta v}; \text{ if we assume that}$$

the uncertainty in the velocity of the hydrogen atom is

$\Delta v = 5.0 \text{ m} \cdot \text{s}^{-1}$, knowing that the mass of a hydrogen atom is

$$m_H = 1.0079 \text{ g} \cdot \text{mol}^{-1} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.6737 \times 10^{-27} \text{ kg},$$

and remembering that $1 \text{ J} = 1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}$, gives

$$\begin{aligned}\hbar &= (1.054 \text{ 457} \times 10^{-34} \text{ J} \cdot \text{s}) \left(\frac{1 \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-2}}{\text{J}} \right) \\ &= 1.054 \text{ 457} \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}\end{aligned}$$

Then,

$$\Delta x = \frac{1}{2} \left(\frac{1.054 \text{ 457} \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(1.67 \text{ 3 7} \times 10^{-27} \text{ kg})(5.0 \text{ m} \cdot \text{s}^{-1})} \right)$$

$$\Delta x = 6.3 \times 10^{-9} \text{ m} = 6.3 \text{ nm}.$$

1.46 The uncertainty principle states that $m\Delta v\Delta x = \frac{1}{2}\hbar$; so, $\Delta v = \frac{1}{2} \frac{\hbar}{m\Delta x}$.

(a) For an electron confined in a nanoparticle of diameter 2.00×10^2 nm:

$$\begin{aligned}\Delta v &= \frac{1}{2} \frac{\hbar}{m_e \Delta x} = \frac{1}{2} \left(\frac{1.054\,457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(9.1094 \times 10^{-31} \text{ kg})(2.00 \times 10^{-7} \text{ m})} \right) \\ &= 289 \text{ m} \cdot \text{s}^{-1}\end{aligned}$$

(b) For a Li^+ ion confined to the same nanoparticle:

$$\begin{aligned}m_{\text{Li}^+} &= 6.94 \text{ g} \cdot \text{mol}^{-1} \times \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 1.15 \times 10^{-26} \text{ kg} \\ \Delta v &= \frac{1}{2} \frac{\hbar}{m_e \Delta x} = \frac{1}{2} \left(\frac{1.054\,457 \times 10^{-34} \text{ kg} \cdot \text{m}^2 \cdot \text{s}^{-1}}{(1.15 \times 10^{-26} \text{ kg})(2.00 \times 10^{-7} \text{ m})} \right) \\ &= 0.0229 \text{ m} \cdot \text{s}^{-1}\end{aligned}$$

(c) The Li^+ ion has a smaller deviation in its speed, therefore it can be defined more accurately.

1.48 (a) The highest energy photon is the one that corresponds to the ionization energy of the atom, the energy required to produce the condition in which the electron and nucleus are “infinitely” separated. This energy corresponds to the transition from the highest energy level for which $n = 1$ to the highest energy level for which $n = \infty$.

$$\begin{aligned}E &= h\mathfrak{R} \left(\frac{1}{n_{\text{lower}}^2} - \frac{1}{n_{\text{upper}}^2} \right) \\ &= (6.626\,08 \times 10^{-34} \text{ J} \cdot \text{s}) \times (3.29 \times 10^{15} \text{ s}^{-1}) \left(\frac{1}{1^2} - \frac{1}{\infty^2} \right) \\ &= 2.18 \times 10^{-18} \text{ J}\end{aligned}$$

(b) The wavelength is obtained from

$$c = v\lambda \text{ and } E = hv, \text{ or } E = hc\lambda^{-1}, \text{ or } \lambda = hcE^{-1}.$$

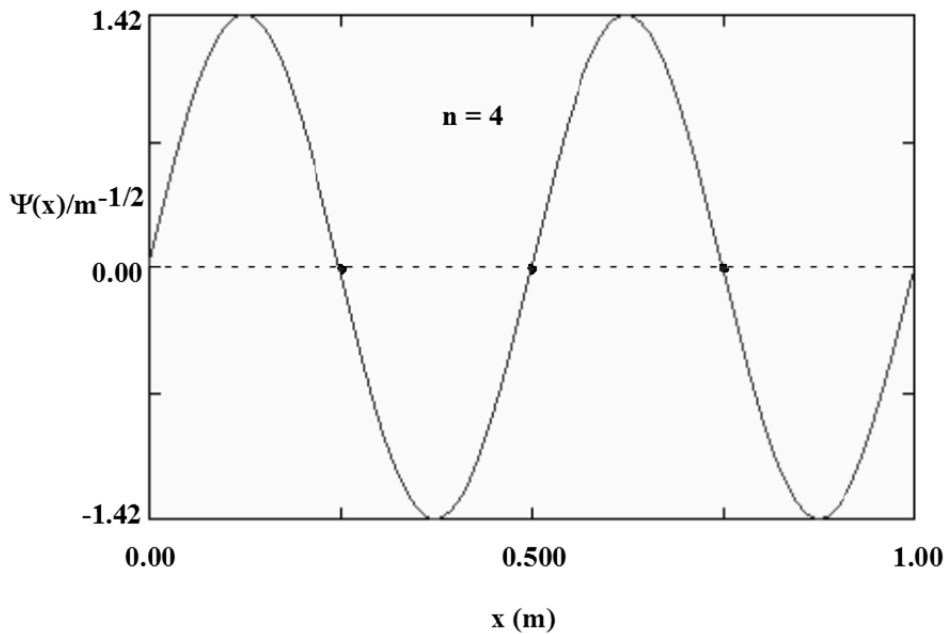
$$\lambda = \frac{(6.626\ 08 \times 10^{-34}\ \text{J} \cdot \text{s})(2.997\ 92 \times 10^8\ \text{m} \cdot \text{s}^{-1})}{2.18 \times 10^{-18}\ \text{J}}$$

$$= 9.11 \times 10^{-8}\ \text{m} = 91.1\ \text{nm}$$

(c) ultraviolet

1.50 Yes, degeneracies are allowed. The lowest energy states which are degenerate in energy are the $n_1 = 1, n_2 = 2$ state and the $n_1 = 2, n_2 = 2$ state.

1.52 When $n = 4$, three nodes are seen (marked with a \bullet):



1.54 The observed line is the third lowest energy line.

The frequency of the given line is:

$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^8\ \text{m s}^{-1}}{5910 \times 10^{-9}\ \text{m}} = 5.073 \times 10^{13}\ \text{s}^{-1}$$

This frequency is closest to the frequency resulting from the $n = 9$ to $n = 6$ transition:

$$\nu = \mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = 3.29 \times 10^{15}\ \text{Hz} \left(\frac{1}{6^2} - \frac{1}{9^2} \right) = 5.08 \times 10^{13}\ \text{Hz}$$

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1.56 (a) $\lambda = 0.20 \text{ nm}$; $E = h\nu$ or $E = hc\lambda^{-1}$

$$E = \frac{(6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})(2.997\ 92 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{0.20 \times 10^{-9} \text{ m}}$$

$$= 9.9 \times 10^{-16} \text{ J}$$

This radiation is in the x-ray region of the electromagnetic spectrum. For comparison, the K_α radiation from Cu is 0.154 439 0 nm and that from Mo is 0.0709 nm. X-rays produced from these two metals are those most commonly employed for determining structures of molecules in single crystals.

(b) From the de Broglie relationship $p = h\lambda^{-1}$, we can write $h\lambda^{-1} = mv$, or $v = hm^{-1}\lambda^{-1}$. For an electron, $m_e = 9.109\ 39 \times 10^{-28} \text{ g}$. (Convert units to kg and m.)

$$v = \frac{(6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})}{(9.109\ 39 \times 10^{-31} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= \frac{(6.626\ 08 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1})}{(9.109\ 39 \times 10^{-31} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= 3.6 \times 10^6 \text{ m}\cdot\text{s}^{-1}$$

(c) Solve similarly to (b). For a neutron, $m_n = 1.674\ 93 \times 10^{-24} \text{ g}$.

(Convert units to kg and m.)

$$v = \frac{(6.626\ 08 \times 10^{-34} \text{ J}\cdot\text{s})}{(1.674\ 93 \times 10^{-27} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= \frac{(6.626\ 08 \times 10^{-34} \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-1})}{(1.67493 \times 10^{-27} \text{ kg})(200 \times 10^{-12} \text{ m})}$$

$$= 2.0 \times 10^3 \text{ m}\cdot\text{s}^{-1}$$

1.58 (a) We would expect to see the excited electron in the hydrogen atom fall from the $n_1 = 5$ level to each of levels below it: $n_2 = 4, 3, 2,$ and 1; therefore, we would expect to see four lines in its atomic spectrum.

(b) the range of wavelengths should span from $n_1 = 5$, $n_2 = 4$ to

$n_1 = 5$, $n_2 = 1$. Thus:

$$\nu_{5,4} = \mathfrak{R} \left(\frac{1}{n_2^2} - \frac{1}{n_1^2} \right) = 3.29 \times 10^{15} \text{ Hz} \left(\frac{1}{4^2} - \frac{1}{5^2} \right) = 7.40 \times 10^{13} \text{ Hz}$$

$$\lambda_{5,4} = \frac{c}{\nu_{5,4}} = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{7.40 \times 10^{13} \text{ m}^{-1}} = 4.05 \times 10^{-6} \text{ m} = 4050 \text{ nm}.$$

Likewise, for the $n_1 = 5$, $n_2 = 1$ transition, we get

$$\nu_{5,1} = 3.16 \times 10^{15} \text{ Hz and } \lambda_{5,1} = 9.49 \times 10^{-8} \text{ m} = 94.9 \text{ nm}.$$

The wavelengths expected should range from 94.9 nm to 4050 nm.

1.60 If each droplet observed had contained an even number of electrons, the technicians would have reported the charge of an electron to be twice as large as it really is.

1.62 The approach to showing that this is true involves integrating the probability function over all space. The probability function is given by the square of the wave function, so that for the particle in the box we have

$$\psi = \left(\frac{2}{L} \right)^{\frac{1}{2}} \sin \left(\frac{n\pi x}{L} \right)$$

and the probability function will be given by

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

Because x can range from 0 to L (the length of the box), we can write the integration as

$$\int_0^x \psi^2 dx = \int_0^x \left(\frac{2}{L} \right) \sin^2 \left(\frac{n\pi x}{L} \right) dx$$

for the entire box, we write

probability of finding the particle somewhere in the box =

$$\int_0^L \left(\frac{2}{L} \right) \sin^2 \left(\frac{n\pi x}{L} \right) dx$$

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$$probability = \left(\frac{2}{L}\right) \int_0^x \sin^2\left(\frac{n\pi x}{L}\right) dx$$

$$\begin{aligned} \int_0^{\frac{L}{2}} \Psi^2 &= \frac{2}{L} \int_0^{\frac{L}{2}} \left(\sin \frac{n\pi x}{L}\right)^2 dx \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos \frac{n\pi x}{L} \cdot \sin \frac{n\pi x}{L} + \frac{x}{2} \right) \right]_0^L \\ &= \frac{2}{L} \left[\left(\frac{-1}{2n\pi} \cdot \cos n\pi \cdot \sin n\pi + \frac{L}{2} \right) - 0 \right] \end{aligned}$$

if n is an integer, $\sin n\pi$ will always be zero and

$$probability = \frac{2}{L} \left[\frac{L}{2} \right] = 1$$

1.64 (a) 4.8×10^{-10} esu; (b) 14 electrons

1.66 (a) $\lambda = \frac{c}{\nu} = \frac{2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{7.83 \times 10^{14} \text{ s}^{-1}} = 3.83 \times 10^{-7} \text{ m} = 383 \text{ nm}$

(b) $\nu = \frac{c}{\lambda} = \frac{2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1}}{452 \times 10^{-9} \text{ m}} = 6.63 \times 10^{14} \text{ s}^{-1}$

1.68 Use $\Delta E = hc\lambda^{-1}$ to determine the change in energy for each wavelength; this will be the change in energy per barium atom. To get the change in energy per mole simply multiply by Avogadro's number. So, for 487 nm:

$$\begin{aligned} \Delta E_{487} &= \frac{(6.62608 \times 10^{-34} \text{ J} \cdot \text{s})(2.99792 \times 10^8 \text{ m} \cdot \text{s}^{-1})}{487 \times 10^{-9} \text{ m}} \\ &= 4.08 \times 10^{-19} \text{ J} \cdot \text{Ba atom}^{-1} \end{aligned}$$

On a per mole basis this becomes:

$$\begin{aligned} \Delta E_{487} &= (6.022 \times 10^{23} \text{ Ba atoms} \cdot \text{mol}^{-1})(4.08 \times 10^{-19} \text{ J} \cdot \text{Ba atom}^{-1}) \\ &= 2.46 \times 10^5 \text{ J} \cdot \text{mol}^{-1} \text{ or } 246 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Similarly, we obtain the following values for the other wavelengths:

$$\Delta E_{524} = 228 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta E_{543} = 220 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta E_{553} = 216 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta E_{578} = 207 \text{ kJ} \cdot \text{mol}^{-1}.$$

1.70 The allowed energies of a particle of mass m in a one-dimensional

box of length L are determined using $E_n = \frac{n^2 h^2}{8mL^2}$.

(a) if $L = 139 \text{ pm} = 1.39 \times 10^{-10} \text{ m}$ for a C–C bond, and

$m_e = 9.109 \times 10^{-31} \text{ kg}$, then

$$\Delta E = \frac{(6.626 \text{ 08} \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(1.39 \times 10^{-10} \text{ m})^2} (2^2 - 1^2)$$

$$= 9.35 \times 10^{-18} \text{ J}$$

(b) This energy corresponds to a wavelength of $2.13 \times 10^{-8} \text{ m}$ or 21.3 nm. This falls within the X-ray region.

(c) If the chain is extended to be 10 carbons long, then

$L = 1251 \text{ pm} = 1.251 \times 10^{-9} \text{ m}$ (the length of 9 C–C bonds). For the

$n = 5$ to $n = 6$ transition, we get:

$$\Delta E = \frac{(6.626 \text{ 08} \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(1.251 \times 10^{-9} \text{ m})^2} (6^2 - 5^2)$$

$$= 4.25 \times 10^{-19} \text{ J}$$

(d) This energy corresponds to a wavelength of $4.69 \times 10^{-7} \text{ m}$ or 469 nm. This falls within the visible region.

(e) A wavelength of 696 nm corresponds to an energy of

$2.85 \times 10^{-19} \text{ J}$ being required for the promotion of an electron from

the $n = 6$ to $n = 7$ level. Rearranging the equation from part (a) to

solve for L we get

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$$L^2 = \frac{h^2}{8m_e\Delta E}(n_2^2 - n_1^2) = \frac{(6.626\ 08 \times 10^{-34}\ \text{J}\cdot\text{s})^2}{8(9.109 \times 10^{-31}\ \text{kg})(2.85 \times 10^{-19}\ \text{J})}(7^2 - 6^2)$$
$$= 2.75 \times 10^{-18}\ \text{m}^2$$

This will give $L = 1.658 \times 10^{-9}\ \text{m} = 1658\ \text{pm}$. Since each C – C bond is 139 pm long, this length corresponds to the chain of carbon atoms having twelve C – C bonds, therefore being thirteen carbons in total length.