

4-11 $\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$. For the Balmer series, $n_f = 2$; $n_i = 3, 4, 5, \dots$. The first three lines in the series have wavelengths given by $\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{n^2}\right)$ where $R = 1.097\ 37 \times 10^7 \text{ m}^{-1}$.

$$\text{1st line: } \frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{9}\right) = \left(\frac{5}{36}\right)R; \lambda = \frac{36}{5R} = 656.112 \text{ nm}$$

$$\text{2nd line: } \frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{16}\right) = \left(\frac{3}{16}\right)R; \lambda = \frac{16}{3R} = 486.009 \text{ nm}$$

$$\text{3rd line: } \frac{1}{\lambda} = R\left(\frac{1}{4} - \frac{1}{25}\right) = \left(\frac{21}{100}\right)R; \lambda = \frac{100}{21R} = 433.937 \text{ nm}$$

4-12 $\frac{1}{\lambda} = R\left(\frac{1-1}{n^2}\right)$ where $n = 2, 3, 4, \dots$ and $R = 1.097\ 373\ 2 \times 10^7 \text{ m}^{-1}$;

$$\text{For } n = 2: \lambda = R^{-1}\left(1 - \frac{1}{2^2}\right)^{-1} = 1.215\ 02 \times 10^{-7} \text{ m} = 121.502 \text{ nm (UV)}$$

$$\text{For } n = 3: \lambda = R^{-1}\left(1 - \frac{1}{3^2}\right)^{-1} = 1.025\ 17 \times 10^{-7} \text{ m} = 102.517 \text{ nm (UV)}$$

$$\text{For } n = 4: \lambda = R^{-1}\left(1 - \frac{1}{4^2}\right)^{-1} = 1.972\ 018 \times 10^{-7} \text{ m} = 97.201\ 8 \text{ nm (UV)}$$

4-14 (a) $r_n = \frac{n^2 \hbar^2}{m_e k e^2}$; where $n = 1, 2, 3, \dots$

$$r_n = n^2 \frac{(1.055 \times 10^{-34} \text{ Js})^2}{(9.11 \times 10^{-31} \text{ kg})(9.0 \times 10^9 \text{ Nm}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2} = (0.052\ 9 \text{ nm})n^2$$

$$\text{For } n = 1: r_n = 0.052\ 9 \text{ nm}$$

$$\text{For } n = 2: r_n = 0.212\ 1 \text{ nm}$$

$$\text{For } n = 3: r_n = 0.477\ 2 \text{ nm}$$

(b) From Equation 4.26, $v = \left(\frac{ke^2}{m_e r}\right)^{1/2}$

$$v_1 = \left[\frac{(8.99 \times 10^9 \text{ Nm}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{(9.11 \times 10^{-31} \text{ kg})(0.052\ 9 \times 10^{-9} \text{ m})}\right]^{1/2} = 2.19 \times 10^6 \text{ m/s}$$

$$v_2 = 1.09 \times 10^6 \text{ m/s}$$

$$v_3 = 7.28 \times 10^5 \text{ m/s}$$

(c) As $c = 3.0 \times 10^8 \text{ m/s}$, $v \ll c$ and no relativistic correction is necessary.

4-15 (a) The energy levels of a hydrogen-like ion whose charge number is 2 is given by

$$E_n = (-13.6 \text{ eV})\frac{Z^2}{n^2} = \frac{-54.4 \text{ eV}}{n^2} \text{ for } Z = 2. (\text{He}^+)$$

_____ 0

$$E_3 = -6.04 \text{ eV}$$

$$E_2 = -13.6 \text{ eV}$$

So

$$E_1 = -54.4 \text{ eV}$$

$$E_2 = -13.6 \text{ eV}$$

$$E_3 = -6.04 \text{ eV, etc.}$$

$$E_1 = -54.4 \text{ eV}$$

- (b) For He^+ , $Z=2$ so we see that the ionization energy (the energy required to take the electron from the state $n=1$ to the state $n=\infty$) is

$$E = (-13.6 \text{ eV}) \frac{2^2}{1^2} = \frac{-54.4 \text{ eV}}{n^2} \text{ for } Z=2. (\text{He}^+)$$

4-17 $r = \frac{n^2 \hbar^2}{Z m_e k e^2} = \left(\frac{n^2}{Z} \right) \left(\frac{\hbar^2}{m_e k e^2} \right); n=1$

$$r = \frac{1}{Z} \left[\frac{(1.055 \times 10^{-34} \text{ Js})^2}{(9.11 \times 10^{-31} \text{ kg})(9 \times 10^9 \text{ Nm}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2} \right] = \frac{5.30 \times 10^{-11} \text{ m}}{Z}$$

- (a) For He^+ , $Z=2$, $r = \frac{5.30 \times 10^{-11} \text{ m}}{2} = 2.65 \times 10^{-11} \text{ m} = 0.0265 \text{ nm}$
- (b) For Li^{2+} , $Z=3$, $r = \frac{5.30 \times 10^{-11} \text{ m}}{3} = 1.77 \times 10^{-11} \text{ m} = 0.0177 \text{ nm}$
- (c) For Be^{3+} , $Z=4$, $r = \frac{5.30 \times 10^{-11} \text{ m}}{4} = 1.32 \times 10^{-11} \text{ m} = 0.0132 \text{ nm}$

4-18 (a) $\Delta E = (13.6 \text{ eV}) \left(\frac{1}{1^2} - \frac{1}{3^2} \right) = 12.1 \text{ eV}$

(b) Either $\Delta E = 12.1 \text{ eV}$ or $\Delta E = (13.6 \text{ eV}) \left(\frac{1}{1} - \frac{1}{2^2} \right) = 10.2 \text{ eV}$ and

$$\Delta E = (13.6 \text{ eV}) \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = 1.89 \text{ eV.}$$

4-19 (a) $\Delta E = (-13.6 \text{ eV}) \left(\frac{1}{n_i^2} - \frac{1}{n_f^2} \right) = (-13.6 \text{ eV}) \left(\frac{1}{9} - \frac{1}{4} \right) = 1.89 \text{ eV}$

(b) $E = \frac{hc}{\lambda} \Rightarrow \lambda = \frac{hc}{E} = (4.14 \times 10^{-15} \text{ eV s}) \frac{3 \times 10^8 \text{ m/s}}{1.89 \text{ eV}} = 658 \text{ nm}$

(c) $c = \lambda f \Rightarrow f = \frac{c}{\lambda} = \frac{3 \times 10^8 \text{ m/s}}{657 \times 10^{-9} \text{ m}} = 4.56 \times 10^{14} \text{ Hz}$

$$4-20 \quad \Delta E = (-13.6 \text{ eV}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

$$(a) \quad \Delta E = (-13.6 \text{ eV}) \left(\frac{1}{25} - \frac{1}{16} \right) = 0.306 \text{ eV}$$

$$(b) \quad \Delta E = (-13.6 \text{ eV}) \left(\frac{1}{36} - \frac{1}{25} \right) = 0.166 \text{ eV}$$

4-22 $E = K + U = \frac{mv^2}{2} - \frac{ke^2}{r}$. But $\frac{mv^2}{2} = \left(\frac{1}{2}\right) \frac{ke^2}{r}$. Thus $E = \left(\frac{1}{2}\right) \left(\frac{-ke^2}{r}\right) = \frac{U}{2}$, so $U = 2E = 2(-13.6 \text{ eV}) = -27.2 \text{ eV}$ and $K = E - U = -13.6 \text{ eV} - (-27.2 \text{ eV}) = 13.6 \text{ eV}$.

$$4-23 \quad (a) \quad r_1 = (0.0529 \text{ nm})n^2 = 0.0529 \text{ nm} \text{ (when } n = 1)$$

$$(b) \quad m_e v = m_e \left(\frac{ke^2}{m_e r} \right)^{1/2}$$

$$m_e = \left[\frac{(9.1 \times 10^{-31} \text{ kg})(9 \times 10^9 \text{ Nm}^2/\text{C}^2)}{5.29 \times 10^{-11} \text{ m}} \right]^{1/2} \times (1.6 \times 10^{-19} \text{ C})$$

$$M_e v = 1.99 \times 10^{-24} \text{ kg m/s}$$

$$(c) \quad L = m_e v r = (1.99 \times 10^{-24} \text{ kg m/s})(5.29 \times 10^{-11} \text{ m}), L = 1.05 \times 10^{-34} (\text{kg m}^2/\text{s}) = \hbar$$

$$(d) \quad K = |E| = 13.6 \text{ eV}$$

$$(e) \quad U = -2K = -27.2 \text{ eV}$$

$$(f) \quad E = K + U = -13.6 \text{ eV}$$

$$4-25 \quad (a) \quad \Delta E = hf = (13.6 \text{ eV}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \text{ or } f = (13.6 \text{ eV}) \left(\frac{\frac{1}{9} - \frac{1}{16}}{4.14 \times 10^{-15} \text{ eV s}} \right) = 1.60 \times 10^{14} \text{ Hz}$$

$$(b) \quad T = \frac{2\pi r_n}{v} \text{ so } f_{\text{rev}} = \frac{1}{T} = \frac{v}{2\pi r_n}. \text{ Using } v = \left(\frac{ke^2}{m_e r_n} \right)^{1/2}, f_{\text{rev}} = \left(\frac{ke^2}{m_e r_n} \right)^{1/2}.$$
 For $n = 3$,

$$r_3 = (3)^2 a_0 \text{ and}$$

$$f_{\text{rev}} = \frac{(8.99 \times 10^9 \text{ Nm}^2/\text{C}^2)(1.60 \times 10^{-19} \text{ C})^2}{\frac{[(9.11 \times 10^{-31} \text{ kg})(9)(5.29 \times 10^{-11} \text{ m})]^{1/2}}{(2)(3.14)(9)(5.29 \times 10^{-11} \text{ m})}}$$

$$f_{\text{rev}} = 2.44 \times 10^{14} \text{ Hz } (n = 3)$$

$$f_{\text{rev}} = 1.03 \times 10^{14} \text{ Hz } (n = 4)$$

Thus the photon frequency is about halfway between the two frequencies of the revolution.

$$(b) \quad R = \frac{2^2}{36 \, 545.6 \times 10^{-8} \text{ cm}} = 109 \, 720 \text{ cm}^{-1}$$

4-26 Lyman series has $n_f = 1$, λ_{\max} has $n_i = 2$; λ_{\min} has $n_i = \infty$

$$\frac{1}{\lambda_{\max}} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = R \left(\frac{1-1}{2^2} \right) = \frac{3R}{4}$$

$$\lambda_{\max} = \frac{4}{3R} = \frac{4}{(3)(1.097 \times 10^7 \text{ m}^{-1})} = 121.5 \text{ nm}$$

$$\lambda_{\min} = \frac{1}{R} = 91.16 \text{ nm}$$

As shown on the inside front cover, the visible spectrum begins at about 350 nm, so the Lyman series is in the UV.

$$4-35 \quad \mu = \frac{m_e M}{m_e + M} = \frac{m_e}{2} \text{ since } m_e = M. \text{ In general, } r_n = \frac{n^2 \hbar^2}{Z \mu k e^2}, \text{ so for positronium } Z = 1,$$

$$\mu = \frac{m_e}{2} \text{ and } r_{\text{positronium}} = \left(\frac{\hbar^2 n^2}{1} \right) \left(\frac{m_e}{2} \right) k e^2 = 2 a_0 n^2 = 2 r_{\text{hydrogen}}. \text{ Similarly,}$$

$$E_{\text{positronium}} = \frac{E_{\text{hydrogen}}}{2} = \frac{-6.80 \text{ eV}}{n^2}.$$

4-31 (a) $(m_e v r) = n\hbar ; v = \frac{n\hbar}{m_e r},$

$$f_e = \frac{v}{2\pi r} = \frac{\frac{n\hbar}{m_e r}}{2\pi r} = \frac{n\hbar}{2\pi m_e r^2} = \frac{n\hbar}{2\pi m_e n^4 (a_0)^2} = \frac{\hbar}{2m_e (a_0)^2 n^3} = \left(\frac{m_e k^2 Z^2 e^4}{2\pi \hbar^3} \right) \left(\frac{1}{n^3} \right)$$

using $a_0 = \frac{\hbar^2}{m_e k e^2}.$

(b) $\Delta E = h\nu_{\text{photon}} = \left(\frac{kZ^2 e^2}{2a_0 h} \right) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$

$$f_{\text{photon}} = \left(\frac{kZ^2 e^2}{2a_0 h} \right) \left(\frac{n_i^2 - n_f^2}{n_i^2 n_f^2} \right) = \left(\frac{kZ^2 e^2}{2a_0 h} \right) \left[\frac{(n_i - n_f)(n_i + n_f)}{n_f^2 n_i^2} \right]$$

$$= \left(\frac{m_e k^2 Z^2 e^4}{2\pi \hbar^3} \right) \left(\frac{n_i + n_f}{2n_f^2 n_i^2} \right) (n_i - n_f)$$

For $n_i - n_f = 1, f_{\text{photon}} = \left(\frac{m_e k^2 Z^2 e^4}{2\pi \hbar^3} \right) \left(\frac{n_i + n_f}{2n_f^2 n_i^2} \right).$ For $n_i = 2, n_f = 1, n_i = 3, n_f = 2,$

etc., $\frac{1}{n_i^3} < \frac{n_i + n_f}{2n_f^2 n_i^2} < \frac{1}{n_f^3}.$

(c) Frequency of emitted radiation is *in between* the initial orbital frequency and the final. As $n_i \rightarrow \infty$ the initial and final orbital frequencies squeeze closer together making the frequency of emitted radiation equal to the orbital frequency. This result agrees with Bohr's correspondence principle.