

4-13. (a) $r_n = \frac{n^2 a_0}{Z}$ (Equation 4-18)

$$r_6 = \frac{6^2 (0.053 \text{ nm})}{1} = 1.91 \text{ nm}$$

(b) $r_6 (\text{He}^+) = \frac{6^2 (0.053 \text{ nm})}{2} = 0.95 \text{ nm}$

4-15. $\frac{1}{\lambda} = Z^2 R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$ (Equation 4-22)

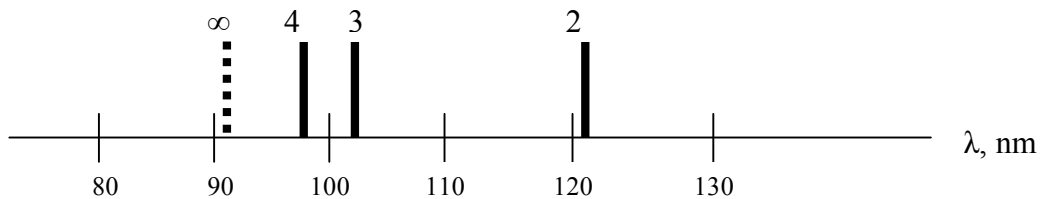
$$\frac{1}{\lambda_{ni}} = R \left(\frac{1}{1^2} - \frac{1}{n_i^2} \right) = R \left(\frac{n_i^2 - 1}{n_i^2} \right)$$

$$\lambda_{ni} = \frac{n_i^2}{R(n_i^2 - 1)} = \frac{n_i^2}{(1.0968 \times 10^7 \text{ m})(n_i^2 - 1)} = (91.17 \text{ nm}) \left(\frac{n_i^2}{n_i^2 - 1} \right)$$

$$\lambda_2 = \frac{4}{3} (91.17 \text{ nm}) = 121.57 \text{ nm} \quad \lambda_3 = \frac{9}{8} (91.17 \text{ nm}) = 102.57 \text{ nm}$$

$$\lambda_4 = \frac{16}{15} (91.17 \text{ nm}) = 97.25 \text{ nm} \quad \lambda_\infty = 91.17 \text{ nm}$$

None of these are in the visible; all are in the ultraviolet.



4-19. (a)

$$a_\mu = \frac{\hbar^2}{\mu_\mu k e^2} = \frac{\mu_e}{\mu_\mu} \frac{\hbar^2}{\mu_e k e^2} = \frac{\mu_e}{\mu_\mu} a_0 = \frac{9.11 \times 10^{-31} \text{ kg}}{1.69 \times 10^{-28} \text{ kg}} (0.0529 \text{ nm}) = 2.56 \times 10^{-4} \text{ nm}$$

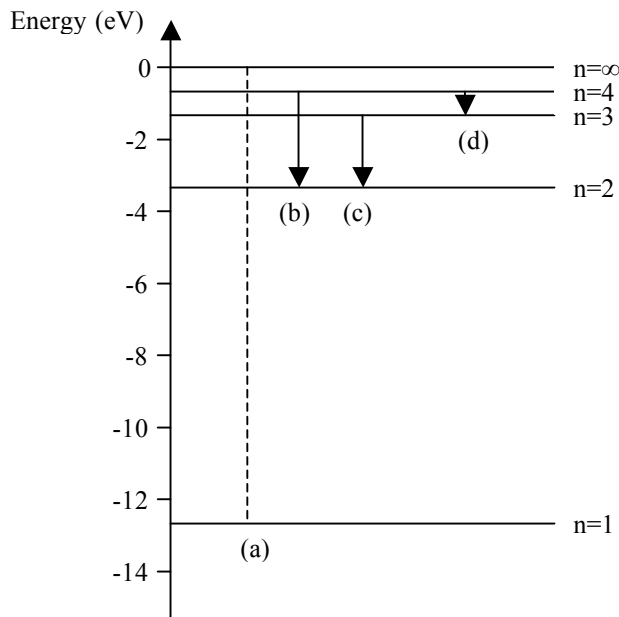
(b) $E_\mu = \frac{\mu_\mu k^2 e^4}{2\hbar^2} = \frac{\mu_\mu}{\mu_e} \frac{\mu_e k^2 e^4}{2\hbar^2} = \frac{\mu_\mu}{\mu_e} E_0 = \frac{1.69 \times 10^{-28} \text{ kg}}{9.11 \times 10^{-31} \text{ kg}} (13.6 \text{ eV}) = 2520 \text{ eV}$

- (c) The shortest wavelength in the Lyman series is the series limit ($n_i = \infty$, $n_f = 1$). The photon energy is equal in magnitude to the ground state energy $-E_\mu$.

$$\lambda_\infty = \frac{hc}{E_\mu} = \frac{1240 \text{ eV} \cdot \text{nm}}{2520 \text{ eV}} = 0.492 \text{ nm}$$

(The reduced masses have been used in this solution.)

4-21.



(a) Lyman limit, (b) H_β line, (c) H_α line, (d) longest wavelength line of Paschen series

- 4-24. (a) The reduced mass correction to the Rydberg constant is important in this case.

$$R = R_\infty \left(\frac{1}{1 + m/M} \right) = R_\infty \left(\frac{1}{2} \right) = 5.4869 \times 10^6 \text{ m}^{-1} \quad (\text{from Equation 4-26})$$

$$E_n = -hcR/n^2 \quad (\text{from Equations 4-23 and 4-24})$$

$$E_1 = -(1240 \text{ eV} \cdot \text{nm}) (5.4869 \times 10^6 \text{ m}^{-1}) (10^{-9} \text{ m/nm}) / (1)^2 = -6.804 \text{ eV}$$

$$\text{Similarly, } E_2 = -1.701 \text{ eV} \text{ and } E_3 = -0.756 \text{ eV}$$

- (b) Lyman α is the $n = 2 \rightarrow n = 1$ transition.

$$\frac{hc}{\lambda} = E_2 - E_1 \quad \rightarrow \quad \lambda_\alpha = \frac{hc}{E_2 - E_1} = \frac{1240eV \cdot nm}{-1.701eV - (-6.804eV)} = 243nm$$

Lyman β is the $n = 3 \rightarrow n = 1$ transition.

$$\lambda_\beta = \frac{hc}{E_3 - E_1} = \frac{1240eV \cdot nm}{-0.756eV - (-6.804eV)} = 205nm$$

4-25. (a) The radii of the Bohr orbits are given by (see Equation 4-18)

$$r = n^2 a_0 / Z \text{ where } a_0 = 0.0529nm \text{ and } Z = 1 \text{ for hydrogen.}$$

$$\text{For } n = 600, r = (600)^2 (0.0529nm) = 1.90 \times 10^4 nm = 19.0\mu m$$

This is about the size of a tiny grain of sand.

(b) The electron's speed in a Bohr orbit is given by

$$v^2 = ke^2 / mr \text{ with } Z = 1$$

Substituting r for the $n = 600$ orbit from (a), then taking the square root,

$$v^2 = (8.99 \times 10^9 N \cdot m^2) (1.609 \times 10^{-19} C)^2 / (9.11 \times 10^{-31} kg) (19.0 \times 10^{-6} m)$$

$$v^2 = 1.33 \times 10^7 m^2 / s^2 \quad \rightarrow \quad v = 3.65 \times 10^3 m / s$$

For comparison, in the $n = 1$ orbit, v is about $2 \times 10^6 m / s$

$$4-26. (a) \quad \frac{1}{\lambda} = R(Z-1)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$\lambda_3 = \left[(1.097 \times 10^7 m^{-1}) (42-1)^2 \left(\frac{1}{1^2} - \frac{1}{3^2} \right) \right]^{-1} = 6.10 \times 10^{-11} m = 0.0610nm$$

$$\lambda_4 = \left[(1.097 \times 10^7 m^{-1}) (42-1)^2 \left(\frac{1}{1^2} - \frac{1}{4^2} \right) \right]^{-1} = 5.78 \times 10^{-11} m = 0.0578nm$$

$$(b) \quad \lambda_{limit} = \left[(1.097 \times 10^7 m^{-1}) (42-1)^2 \left(\frac{1}{1^2} - 0 \right) \right]^{-1} = 5.42 \times 10^{-11} m = 0.0542nm$$

$$4-27. \quad \frac{1}{\lambda} = R(Z-1)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = R(Z-1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right) \text{ for } K_\alpha$$

$$Z-1 = \left[\frac{1}{\lambda R \left(1 - \frac{1}{4} \right)} \right]^{1/2} = \left[\frac{1}{(0.0794 \text{ nm})(1.097 \times 10^{-2} / \text{nm})(3/4)} \right]^{1/2}$$

$$Z = 1 + 39.1 \approx 40 \text{ Zirconium}$$

$$4-29. \quad r_n = \frac{n^2 a_0}{Z} \quad (\text{Equation 4-18})$$

The $n=1$ electrons “see” a nuclear charge of approximately $Z-1$, or 78 for Au.

$$r_1 = 0.0529 \text{ nm} / 78 = 6.8 \times 10^{-4} \text{ nm} (10^{-9} \text{ m} / \text{nm}) (10^{15} \text{ fm} / \text{m}) = 680 \text{ fm}, \text{ or about 100}$$

times

the radius of the Au nucleus.

$$4-36. \quad \Delta E = \frac{hc}{\lambda} = \frac{1240 \text{ eV} \cdot \text{nm}}{790 \text{ nm}} = 1.610 \text{ eV}. \text{ The first decrease in current will occur when}$$

the voltage reaches 1.61 V.

$$4-43. \quad \lambda = \left[R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \right]^{-1} \quad \Delta \lambda = \frac{d\lambda}{d\mu} \Delta \mu = (-R^{-2}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} \frac{dR}{d\mu} \Delta \mu$$

$$\text{Because } R \propto \mu, \quad dR/d\mu = R/\mu. \quad \Delta \lambda \approx (-R^{-2}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)^{-1} (R/\mu) \Delta \mu = -\lambda (\Delta \mu / \mu)$$

$$\mu_H = \frac{m_e m_p}{m_e + m_p} \quad \mu_D = \frac{m_e m_d}{m_e + m_d}$$

$$\frac{\Delta \mu}{\mu} = \frac{\mu_D - \mu_H}{\mu_H} = \frac{\mu_D}{\mu_H} - 1 = \frac{m_e m_d / (m_e + m_d)}{m_e m_p / (m_e + m_p)} - 1 = \frac{m_d / (m_e + m_d)}{m_p / (m_e + m_p)} - 1 = \frac{m_e (m_d - m_p)}{m_p (m_e + m_d)}$$

If we approximate $m_d = 2m_p$ and $m_e \ll m_d$, then $\frac{\Delta \mu}{\mu} \approx \frac{m_e}{2m_p}$ and

$$\Delta\lambda = -\lambda(\Delta\mu/\mu) = -(656.3\text{nm})\frac{0.511\text{MeV}}{2(938.28\text{MeV})} = -0.179\text{nm}$$

4-45. (a) $E_n = -E_0 Z^2 / n^2$ (Equation 4-20)

For Li^{++} , $Z = 3$ and $E_n = -13.6\text{eV}(9)/n^2 = -122.4/n^2\text{eV}$

The first three Li^{++} levels that have the same (nearly) energy as H are:

$$n = 3, E_3 = -13.6\text{eV} \quad n = 6, E_6 = -3.4\text{eV} \quad n = 9, E_9 = -1.51\text{eV}$$

Lyman α corresponds to the $n = 6 \rightarrow n = 3$ Li^{++} transitions. Lyman β corresponds

to the $n = 9 \rightarrow n = 3$ Li^{++} transition.

(b) $R(H) = R_\infty (1/(1 + 0.511\text{MeV}/938.8\text{MeV})) = 1.096776 \times 10^7 \text{m}^{-1}$

$$R(\text{Li}) = R_\infty (1/(1 + 0.511\text{MeV}/6535\text{MeV})) = 1.097287 \times 10^7 \text{m}^{-1}$$

For Lyman α :

$$\frac{1}{\lambda} = R(H) \left(1 - \frac{1}{2^2}\right) = 1.096776 \times 10^7 \text{m}^{-1} (10^{-9} \text{m/nm})(3/4) \rightarrow 121.568\text{nm}$$

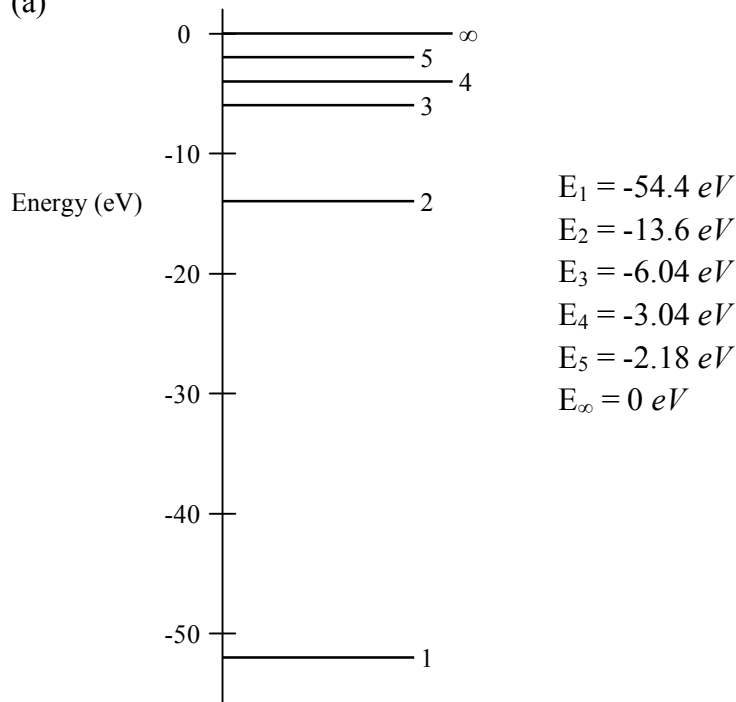
For Li^{++} equivalent:

$$\frac{1}{\lambda} = R(\text{Li}) \left(\frac{1}{3^2} - \frac{1}{6^2}\right) Z^2 = 1.097287 \times 10^7 \text{m}^{-1} (10^{-9} \text{m/nm}) \left(\frac{1}{9} - \frac{1}{36}\right) (3)^2$$

$$\lambda = 121.512\text{nm} \quad \Delta\lambda = 0.056\text{nm}$$

4-50. For He: $E_n = -13.6\text{eV} Z^2 / n^2 = -54.4\text{eV} / n^2$ (Equation 4-20)

(a)



(b) Ionization energy is 54.5eV.

(c) H Lyman α : $\lambda = hc / \Delta E = 1240eV \cdot nm / (13.6eV - 3.4eV) = 121.6nm$

H Lyman β : $\lambda = hc / \Delta E = 1240eV \cdot nm / (13.6eV - 1.41eV) = 102.6nm$

He⁺ Balmer α : $\lambda = hc / \Delta E = 1240eV \cdot nm / (13.6eV - 6.04eV) = 164.0nm$

He⁺ Balmer β : $\lambda = hc / \Delta E = 1240eV \cdot nm / (13.6eV - 3.40eV) = 121.6nm$

$\Delta\alpha = 42.4nm$ $\Delta\beta = 19.0nm$

(The reduced mass correction factor does not change the energies calculated above

to three significant figures.)

(d) $E_n = -13.6eV Z^2 / n^2$ because for He⁺, $Z = 2$, then $Z^2 = 2^2$. Every time n is an even number a 2^2 can be factored out of n^2 and cancelled with the $Z^2 = 2^2$ in the numerator; e.g., for He⁺,

$$E_2 = -13.6eV \cdot 2^2 / 2^2 = -13.6eV \quad (\text{H ground state})$$

$$E_4 = -13.6eV \cdot 2^2 / 4^2 = -13.6eV / 2^2 \quad (\text{H } -1^{\text{st}} \text{ excited state})$$

$$E_6 = -13.6eV \cdot 2^2 / 6^2 = -13.6eV / 3^2 \quad (\text{H } -2^{\text{nd}} \text{ excited state})$$

⋮

etc.

Thus, all of the H energy level values are to be found within the He⁺ energy levels, so

He⁺ will have within its spectrum lines that match (nearly) a line in the H spectrum.

4-52. (a) $E_n = -\frac{ke^2}{2r_n} = -\frac{ke^2}{2n^2r_o}$ $E_{n-1} = -\frac{ke^2}{2(n-1)^2r_o}$

$$hf = E_n - E_{n-1} = -\frac{ke^2}{2n^2r_o} - \left(-\frac{ke^2}{2(n-1)^2r_o} \right)$$

$$f = \frac{ke^2}{2hr_o} \left[\frac{1}{(n-1)^2} - \frac{1}{n^2} \right] = \frac{ke^2}{2hr_o} \frac{n^2 - (n^2 - 2n + 1)}{n^2(n-1)^2}$$

$$= \frac{ke^2}{2hr_o} \frac{2n-1}{n^2(n-1)^2} \approx \frac{ke^2}{r_o hn^3} \quad \text{for } n \gg 1$$

$$(b) \quad f_{rev} = \frac{v}{2\pi r} \quad \rightarrow \quad f_{rev}^2 = \frac{v^2}{4\pi^2 r^2} = \frac{1}{4\pi^2 mr} \frac{mv^2}{r} = \frac{1}{4\pi^2 mr} \frac{ke^2}{r^2} = \frac{ke^2}{4\pi^2 mr_o^3 n^6}$$

(c) The correspondence principle implies that the frequencies of radiation and revolution

are equal.

$$f^2 = \left(\frac{ke^2}{r_o hn^3} \right)^2 = \frac{ke^2}{4\pi^2 mr_o^3 n^6} = f_{rev}^2 \quad r_o = \frac{ke^2}{4\pi^2 mn^6} \left(\frac{hn^3}{ke^2} \right)^2 = \frac{h^2}{4\pi^2 mke^2} = \frac{\hbar^2}{mke^2}$$

which is the same as a_o in Equation 4-19.

$$4-53. \quad \frac{kZe^2}{r} = \frac{mv^2}{r} \quad \rightarrow \quad \frac{kZe^2}{r^2} = \frac{(\gamma mv)^2}{mr} \quad (\text{from Equation 4-12})$$

$$\gamma v = \left(\frac{kZe^2}{mr} \right)^{1/2} = \frac{v}{\sqrt{1-\beta^2}}$$

$$\frac{c^2 \beta^2}{1-\beta^2} = \left(\frac{kZe^2}{mr} \right) \quad \text{Therefore, } \beta^2 \left[c^2 + \left(\frac{kZe^2}{mr} \right) \right] = \left(\frac{kZe^2}{mr} \right)$$

$$\beta^2 \approx \frac{1}{c^2} \left(\frac{kZe^2}{ma_o} \right) \quad \rightarrow \quad \beta = 0.0075Z^{1/2} \quad \rightarrow \quad v = 0.0075cZ^{1/2} = 2.25 \times 10^6 \text{ m/s} \times Z^{1/2}$$

$$E = KE - kZe^2 / r = mc^2 (\gamma - 1) - \frac{kZe^2}{r} = mc^2 \left[\frac{1}{\sqrt{1-\beta^2}} - 1 \right] - \frac{kZe^2}{r}$$

And substituting $\beta = 0.0075$ and $r = a_o$

$$E = 511 \times 10^3 \text{ eV} \left[\frac{1}{\sqrt{1-(0.0075)^2}} - 1 \right] - 28.8Z \text{ eV}$$

$$= 14.4 \text{ eV} - 28.8Z \text{ eV} = -14.4Z \text{ eV}$$

4-57. Refer to Figure 4-16. All possible transitions starting at $n = 5$ occur.

$n = 5$ to $n = 4, 3, 2, 1$

$n = 4$ to $n = 3, 2, 1$

$n = 3$ to $n = 2, 1$

$n = 2$ to $n = 1$

Thus, there are 10 different photon energies emitted.

(Problem 4-57 continued)

n_i	n_f	fraction	no. of photons
5	4	$1/4$	125
5	3	$1/4$	125
5	2	$1/4$	125
5	1	$1/4$	125
4	3	$1/4 \times 1/3$	42
4	2	$1/4 \times 1/3$	42
4	1	$1/4 \times 1/3$	42
3	2	$1/2 [1/4 + 1/4(1/3)]$	83
3	1	$1/2 [1/4 + 1/4(1/3)]$	83
2	1	$[(1/2(1/4 + 1/4)(1/3)) + 1/4(1/3) + 1/4]$	250

Total = 1,042

Note that the number of electrons arriving at the $n = 1$ level ($125+42+83+250$) is 500, as it should be.