8-1 $E = \frac{\hbar^2 \pi^2}{2m}\left[\left(\frac{n_1}{L_x}\right)^2 + \left(\frac{n_2}{L_y}\right)^2 + \left(\frac{n_3}{L_z}\right)^2\right]$

$L_x = L$, $L_y = L_z = 2L$. Let $\frac{\hbar^2 \pi^2}{8mL^2} = E_0$. Then $E = E_0\left(4n_1^2 + n_2^2 + n_3^2\right)$. Choose the quantum numbers as follows:

| $n_1$ | $n_2$ | $n_3$ | $\frac{E}{E_0}$ | | |
|---|---|---|---|---|---|
| 1 | 1 | 1 | 6 | | ground state |
| 1 | 2 | 1 | 9 | * | first two excited states |
| 1 | 1 | 2 | 9 | * | |
| 2 | 1 | 1 | 18 | | |
| 1 | 2 | 2 | 12 | * | next excited state |
| 2 | 1 | 2 | 21 | | |
| 2 | 2 | 1 | 21 | | |
| 2 | 2 | 2 | 24 | | |
| 1 | 1 | 3 | 14 | * | next two excited states |
| 1 | 3 | 1 | 14 | * | |

Therefore the first 6 states are $\psi_{111}$, $\psi_{121}$, $\psi_{112}$, $\psi_{122}$, $\psi_{113}$, and $\psi_{131}$ with relative energies $\frac{E}{E_0} = 6$, 9, 9, 12, 14, 14. First and third excited states are doubly degenerate.

8-2 (a) $n_1 = 1$, $n_2 = 1$, $n_3 = 1$

$$E_0 = \frac{3\hbar^2\pi^2}{2mL^2} = \frac{3h^2}{8mL^2} = \frac{3\left(6.626 \times 10^{-34}\ \text{Js}\right)^2}{8\left(9.11 \times 10^{-31}\ \text{kg}\right)\left(2 \times 10^{-10}\ \text{m}\right)^2} = 4.52 \times 10^{-18}\ \text{J} = 28.2\ \text{eV}$$

(b) $n_1 = 2$, $n_2 = 1$, $n_3 = 1$ or
$n_1 = 1$, $n_2 = 2$, $n_3 = 1$ or
$n_1 = 1$, $n_2 = 1$, $n_3 = 2$

$$E_1 = \frac{6h^2}{8mL^2} = 2E_0 = 56.4\ \text{eV}$$

8-3 $n^2 = 11$

(a) $E = \left(\frac{\hbar^2\pi^2}{2mL^2}\right)n^2 = \frac{11}{2}\left(\frac{\hbar^2\pi^2}{mL^2}\right)$

(b)

| $n_1$ | $n_2$ | $n_3$ | |
|---|---|---|---|
| 1 | 1 | 3 | |
| 1 | 3 | 1 | 3-fold degenerate |
| 3 | 1 | 1 | |

(c) $\psi_{113} = A \sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{3\pi z}{L}\right)$

$$\psi_{131} = A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

$$\psi_{311} = A\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

8-4 (a) $\psi(x, y) = \psi_1(x)\psi_2(y)$. In the two-dimensional case, $\psi = A(\sin k_1 x)(\sin k_2 y)$ where $k_1 = \frac{n_1 \pi}{L}$ and $k_2 = \frac{n_2 \pi}{L}$.

(b) $$E = \frac{\hbar^2 \pi^2 \left(n_1^2 + n_2^2\right)}{2mL^2}$$

If we let $E_0 = \frac{\hbar^2 \pi^2}{mL^2}$, then the energy levels are:

| $n_1$ | $n_2$ | $\frac{E}{E_0}$ | | | |
|---|---|---|---|---|---|
| 1 | 1 | 1 | $\rightarrow$ | $\psi_{11}$ | |
| 1 | 2 | $\frac{5}{2}$ | $\rightarrow$ | $\psi_{12}$ | doubly degenerate |
| 2 | 1 | $\frac{5}{2}$ | $\rightarrow$ | $\psi_{21}$ | |
| 2 | 2 | 4 | $\rightarrow$ | $\psi_{22}$ | |

8-5 (a) $n_1 = n_2 = n_3 = 1$ and

$$E_{111} = \frac{3h^2}{8mL^2} = \frac{3\left(6.63 \times 10^{-34}\right)^2}{8\left(1.67 \times 10^{-27}\right)\left(4 \times 10^{-28}\right)} = 2.47 \times 10^{-13} \text{ J} \approx 1.54 \text{ MeV}$$

(b) States 211, 121, 112 have the same energy and $E = \frac{\left(2^2 + 1^2 + 1^2\right)h^2}{8mL^2} = 2E_{111} \approx 3.08$ MeV and states 221, 122, 212 have the energy $E = \frac{\left(2^2 + 2^2 + 1^2\right)h^2}{8mL^2} = 3E_{111} \approx 4.63$ MeV.

(c) Both states are threefold degenerate.

8-8 Inside the box the electron is free, and so has momentum and energy given by the de Broglie relations $|\mathbf{p}| = \hbar|\mathbf{k}|$ and $E = \hbar\omega$ with $E = \left(c^2|\mathbf{p}|^2 + m^2c^4\right)^{1/2}$ for this, the relativistic case. Here $\mathbf{k} = (k_1,\ k_2,\ k_3)$ is the wave vector whose components $k_1$, $k_2$, and $k_3$ are wavenumbers along each of three mutually perpendicular axes. In order for the wave to vanish at the walls, the box must contain an integral number of half-wavelengths in each direction. Since $\lambda_1 = \dfrac{2\pi}{k_1}$ and so on, this gives

$$L = n_1\left(\frac{\lambda_1}{2}\right) \quad \text{or} \quad k_1 = \frac{n_1\pi}{L}$$

$$L = n_2\left(\frac{\lambda_2}{2}\right) \quad \text{or} \quad k_2 = \frac{n_2\pi}{L}$$

$$L = n_3\left(\frac{\lambda_3}{2}\right) \quad \text{or} \quad k_3 = \frac{n_3\pi}{L}$$

Thus, $|\mathbf{p}|^2 = \hbar|\mathbf{k}|^2 = \hbar^2\left\{k_1^2 + k_2^2 + k_3^2\right\} = \left(\frac{\pi\hbar}{L}\right)^2\left\{n_1^2 + n_2^2 + n_3^2\right\}$ and the allowed energies are $= \left[\left(\frac{\pi\hbar c}{L}\right)^2\left\{n_1^2 + n_2^2 + n_3^2\right\} + \left(mc^2\right)^2\right]^{1/2}$. For the ground state $n_1 = n_2 = n_3 = 1$. For an electron confined to $L = 10\ \text{fm}$, we use $m = 0.511\ \text{MeV}/c^2$ and $\hbar c = 197.3\ \text{MeV fm}$ to get

$$E = \left\{3\left[\frac{(\pi)(197.3\ \text{MeV fm})}{10\ \text{fm}}\right]^2 + (0.511\ \text{MeV})^2\right\}^{1/2} = 107\ \text{MeV}.$$

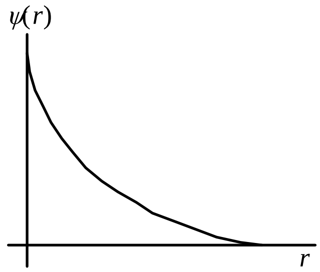
8-10 $n = 4$, $l = 3$, and $m_l = 3$.

(a) $L = \left[l(l+1)\right]^{1/2}\hbar = \left[3(3+1)\right]^{1/2}\hbar = 2\sqrt{3}\hbar = 3.65 \times 10^{-34}$ Js

(b) $L_z = m_l\hbar = 3\hbar = 3.16 \times 10^{-34}$ Js

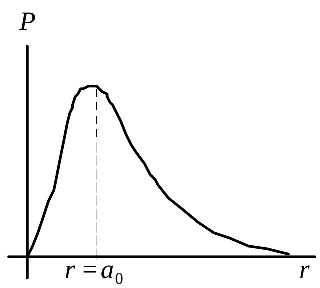
8-12 $\psi(r) = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(a)




(b) The probability of finding the electron in a volume element d$V$ is given by $|\psi|^2\, dV$. Since the wave function has spherical symmetry, the volume element d$V$ is identified here with the volume of a spherical shell of radius $r$, $dV = 4\pi r^2 dr$. The probability of finding the electron between $r$ and $r + dr$ (that is, within the spherical shell) is $P = |\psi|^2\, dV = 4\pi r^2 |\psi|^2\, dr$.

(c)




(d) $\int |\psi|^2\, dV = 4\pi \int |\psi|^2 r^2\, dr = 4\pi\left(\frac{1}{\pi}\right)\left(\frac{1}{a_0^3}\right)\int_0^\infty e^{-2r/a_0} r^2 dr = \left(\frac{4}{a_0^3}\right)\int_0^\infty e^{-2r/a_0} r^2\, dr$

Integrating by parts, or using a table of integrals, gives

$$\int |\psi|^2\, dV = \left(\frac{4}{a_0^3}\right)\left[2\left(\frac{a_0}{2}\right)^3\left(\frac{2}{a_0}\right)^3\right] = 1.$$

(e) $P = 4\pi \int_{r_1}^{r_2} |\psi|^2 r^2\, dr$ where $r_1 = \frac{a_0}{2}$ and $r_2 = \frac{3a_0}{2}$

$$P=\left(\frac{4}{a_0^3}\right)\int_{r_1}^{r_2} r^2 e^{-2r/a_0}\,dr \qquad \text{let } z=\frac{2r}{a_0}$$

$$=\frac{1}{2}\int_1^3 z^2 e^{-z}\,dz$$

$$=-\frac{1}{2}\left(z^2+2z+2\right)e^{-z}\Big|_1^3 \qquad \text{(integrating by parts)}$$

$$=-\frac{17}{2}e^{-3}+\frac{5}{2}e^{-1}=0.496$$

8-13 $Z=2$ for $He^+$

(a) For $n=3$, $l$ can have the values of 0, 1, 2

$$l=0 \rightarrow m_l=0$$
$$l=1 \rightarrow m_l=-1,\ 0,\ +1$$
$$l=2 \rightarrow m_l=-2,\ -1,\ 0,\ +1,\ +2$$

(b) All states have energy $E_3=\frac{-Z^2}{3^2}(13.6\text{ eV})$

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

8-14 $Z=3$ for $Li^{2+}$

(a) $n=1\rightarrow l=0\rightarrow m_l=0$
$n=2\rightarrow l=0\rightarrow m_l=0$
and $l=1\rightarrow m_l=-1,\ 0,\ +1$

(b) For $n=1$, $E_1=-\left(\frac{3^2}{1^2}\right)(13.6)=-122.4\text{ eV}$

For $n=2$, $E_2=-\left(\frac{3^2}{2^2}\right)(13.6)=-30.6\text{ eV}$

8-16 For a *d* state, $l=2$. Thus, $m_l$ can take on values –2, –1, 0, 1, 2. Since $L_z=m_l\hbar$, $L_z$ can be $\pm 2\hbar$, $\pm\hbar$, and zero.

8-17 (a) For a *d* state, $l=2$

$$L=\left[l(l+1)\right]^{1/2}\hbar=(6)^{1/2}\left(1.055\times10^{-34}\text{ Js}\right)=2.58\times10^{-34}\text{ Js}$$

(b) For an *f* state, $l=3$

$$L=\left[l(l+1)\right]^{1/2}\hbar=(12)^{1/2}\left(1.055\times10^{-34}\text{ Js}\right)=3.65\times10^{-34}\text{ Js}$$

8-18 The state is 6*g*

(a) $n=6$

(b) $E_n = -\frac{13.6 \text{ eV}}{n^2}$ $E_6 = \frac{-13.6}{6^2} \text{ eV} = -0.378 \text{ eV}$

(c) For a *g*-state, $l = 4$

$$L = [l(l+1)]^{1/2}\hbar = (4 \times 5)^{1/2}\hbar = \sqrt{20}\hbar = 4.47\hbar$$

(d) $m_l$ can be –4, –3, –2, –1, 0, 1, 2, 3, or 4

$L_z = m_l\hbar$; $\cos\theta = \frac{L_z}{L} = \frac{m_l}{[l(l+1)]^{1/2}}\hbar = \frac{m_l}{\sqrt{20}}$

| $m_l$ | –4 | –3 | –2 | –1 | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|---|---|---|---|
| $L_z$ | $-4\hbar$ | $-3\hbar$ | $-2\hbar$ | $-\hbar$ | 0 | $\hbar$ | $2\hbar$ | $3\hbar$ | $4\hbar$ |
| $\theta$ | 153.4° | 132.1° | 116.6° | 102.9° | 90° | 77.1° | 63.4° | 47.9° | 26.6° |

8-21 (a) $\psi_{2s}(r) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}\left(2 - \frac{r}{a_0}\right)e^{-r/2a_0}$. At $r = a_0 = 0.529 \times 10^{-10}$ m we find

$$\psi_{2s}(a_0) = \frac{1}{4(2\pi)^{1/2}}\left(\frac{1}{a_0}\right)^{3/2}(2-1)e^{-1/2} = (0.380)\left(\frac{1}{a_0}\right)^{3/2}$$

$$= (0.380)\left[\frac{1}{0.529 \times 10^{-10} \text{ m}}\right]^{3/2} = 9.88 \times 10^{14} \text{ m}^{-3/2}$$

(b) $|\psi_{2s}(a_0)|^2 = \left(9.88 \times 10^{14} \text{ m}^{-3/2}\right)^2 = 9.75 \times 10^{29} \text{ m}^{-3}$

(c) Using the result to part (b), we get $P_{2s}(a_0) = 4\pi a_0^2 |\psi_{2s}(a_0)|^2 = 3.43 \times 10^{10} \text{ m}^{-1}$.

8-22 $R_{2p}(r) = Are^{-r/2a_0}$ where $A = \frac{1}{2(6)^{1/2} a_0^{5/2}}$

$$P(r) = r^2 R_{2p}^2(r) = A^2 r^4 e^{-r/a_0}$$

$$\langle r \rangle = \int_0^\infty rP(r)dr = A^2 \int_0^\infty r^5 e^{-r/a_0} dr = A^2 a_0^6 5! = 5a_0 = 2.645 \text{ Å}$$