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 ψ_{111}, ψ_{121}, ψ_{112}, ψ_{122}, ψ_{113}, and ψ_{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) $n_1=1$, $n_2=1$, $n_3=1$

$$E_0=\frac{3\hbar^2\pi^2}{2mL^2}=\frac{3h^2}{8mL^2}=\frac{3\left(6.626\times10^{-34}\text{ Js}\right)^2}{8\left(9.11\times10^{-31}\text{ kg}\right)\left(2\times10^{-10}\text{ m}\right)^2}=4.52\times10^{-18}\text{ J}=28.2\text{ eV}$$

(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	$\rightarrow$	ψ_{11}	
1	2	$\frac{5}{2}$	$\rightarrow$	ψ_{12}	doubly degenerate
2	1	$\frac{5}{2}$	$\rightarrow$	ψ_{21}	
2	2	4	$\rightarrow$	ψ_{22}	

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

$$E_{111} = \frac{3h^2}{8mL^2} = \frac{3\left(6.63\times10^{-34}\right)^2}{8\left(1.67\times10^{-27}\right)\left(4\times10^{-28}\right)} = 2.47\times10^{-13}\ \text{J} \approx 1.54\ \text{MeV}$$

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

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

(c) Both states are threefold degenerate.

8-6 There is no force on a free particle, so that $U(r)$ is a constant which, for simplicity, we take to be zero. Substituting $\Psi(\mathbf{r}, t) = \psi_1(x)\psi_2(y)\psi_3(z)\phi(t)$ into Schrödinger's equation with $U(r) = 0$ gives $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi(\mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r}, t)$. Upon dividing through by $\psi_1(x)\psi_2(y)\psi_3(z)\phi(t)$ we obtain $-\frac{\hbar^2}{2m}\left[\frac{\psi_1''(x)}{\psi_1(x)} + \frac{\psi_2''(y)}{\psi_2(y)} + \frac{\psi_3''(z)}{\psi_3(z)}\right] = \frac{i\hbar\phi'(t)}{\phi(t)}$. Each term in this equation is a function of one variable only. Since the variables *x, y, z, t* are all independent, each term, by itself, must be constant, an observation leads to the four separate equations

$$-\frac{\hbar^2}{2m}\left(\frac{\psi_1''(x)}{\psi_1(x)}\right)=E_1$$
$$-\frac{\hbar^2}{2m}\left(\frac{\psi_2''(x)}{\psi_2(x)}\right)=E_2$$
$$-\frac{\hbar^2}{2m}\left(\frac{\psi_3''(x)}{\psi_3(x)}\right)=E_3$$
$$i\hbar\left[\frac{\phi'(t)}{\phi(t)}\right]=E$$

This is subject to the condition that $E_1+E_2+E_3=E$. The equation for ψ_1 can be rearranged as $\frac{d^2\psi_1}{dx^2}=\left(-\frac{2mE_1}{\hbar^2}\right)\psi_1(x)$, whereupon it is evident the solutions are sinusoidal $\psi_1(x)=\alpha_1\sin(k_1x)+\beta_1\cos(k_1x)$ with $k_1^2=\frac{2mE_1}{\hbar^2}$. However, the mixing coefficients α_1 and β_1 are indeterminate from this analysis. Similarly, we find

$$\psi_2(y)=\alpha_2\sin(k_2y)+\beta_2\cos(k_2y)$$
$$\psi_3(z)=\alpha_3\sin(k_3z)+\beta_3\cos(k_3z)$$

with $k_2^2=\frac{2mE_2}{\hbar^2}$ and $k_3^2=\frac{2mE_3}{\hbar^2}$. The equation for ϕ can be integrated once to get $\phi(t)=\gamma e^{-i\omega t}$ with $\omega=\frac{E}{\hbar}$ and γ another indeterminate coefficient. Since the energy operator is $[E]=i\hbar\frac{\partial}{\partial t}$ and $i\hbar\left(\frac{\partial}{\partial t}\right)\phi=E\phi$ energy is sharp at the value *E* in this state. Also, since $[p_x^2]=-\hbar^2\left(\frac{\partial^2}{\partial x^2}\right)$ and $-\hbar^2\left(\frac{\partial^2}{\partial x^2}\right)\psi_1=(\hbar k_1)^2\psi_1$ the magnitude of momentum in the *x* direction is sharp at the value $\hbar k_1$. Similarly, the magnitude of momentum in the *y* and *z* directions are sharp at the values $\hbar k_2$ and $\hbar k_3$, respectively. (The sign of momentum also will be sharp here if the mixing coefficients are chosen in the ratios $\frac{\alpha_1}{\beta_1}=i$, and so on).

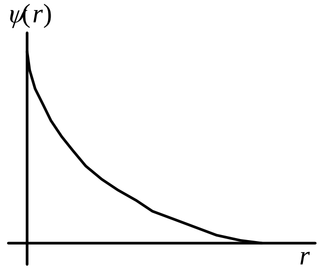
8-10 $n=4$, $l=3$, and $m_l=3$.

(a) $L=[l(l+1)]^{1/2}\hbar=[3(3+1)]^{1/2}\hbar=2\sqrt{3}\hbar=3.65\times10^{-34}$ Js

(b) $L_z=m_l\hbar=3\hbar=3.16\times10^{-34}$ Js

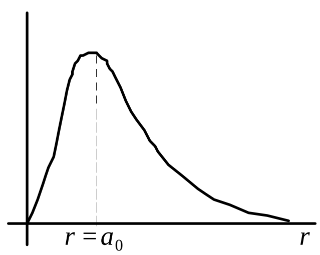
8-12 $\psi(r) = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(a)



(b) The probability of finding the electron in a volume element dV is given by $|\psi|^2 dV$. Since the wave function has spherical symmetry, the volume element dV 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, $l = 2$

$$L = [l(l+1)]^{1/2}\hbar = (6)^{1/2}\left(1.055 \times 10^{-34}\ \text{Js}\right) = 2.58 \times 10^{-34}\ \text{Js}$$

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

$$L = [l(l+1)]^{1/2}\hbar = (12)^{1/2}\left(1.055 \times 10^{-34}\ \text{Js}\right) = 3.65 \times 10^{-34}\ \text{Js}$$

8-18 The state is 6*g*

(a) $n = 6$

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

(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	$\hbar$	$2\hbar$	$3\hbar$	$4\hbar$
θ	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 $A = \frac{1}{2(6)^{1/2}a_0^{5/2}}$

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

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