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.

8-3 $n^2=11$

(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) $$\psi_{113}=A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{3\pi z}{L}\right)$$
$$\psi_{131}=A\sin\left(\frac{\pi x}{L}\right)\sin\left(\frac{3\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$
$$\psi_{311}=A\sin\left(\frac{3\pi x}{L}\right)\sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi z}{L}\right)$$

8-6 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

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

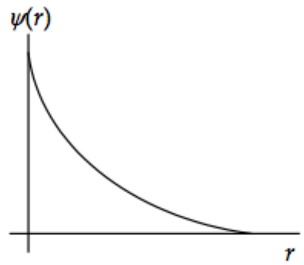
This is subject to the condition that $E_1+E_2+E_3=E$. The equation for ψ_1 can be rearranged as $\frac{d^2\psi_1}{dx^2}=\left(-\frac{2mE_1}{\hbar^2}\right)\psi_1(x)$, whereupon it is evident the solutions are sinusoidal $\psi_1(x)=\alpha_1\sin(k_1x)+\beta_1\cos(k_1x)$ with $k_1^2=\frac{2mE_1}{\hbar^2}$.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

$$
\begin{aligned}
\psi_2(y)&=\alpha_2\sin(k_2y)+\beta_2\cos(k_2y)\\
\psi_3(z)&=\alpha_3\sin(k_3z)+\beta_3\cos(k_3z)
\end{aligned}
$$

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 $\left[p_x^2\right]=-\hbar^2\left(\frac{\partial^2}{\partial x^2}\right)$ 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).

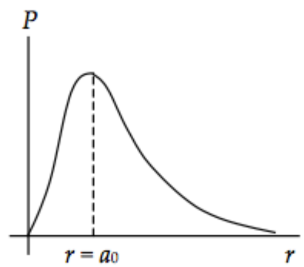
8-12 $\psi(r) = \left(\frac{1}{\pi}\right)^{1/2}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}$

(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 $r_2 = \frac{3a_0}{2}$

$$\begin{aligned} P &= \left(\frac{4}{a_0^3}\right)\int_{r_1}^{r_2} r^2 e^{-2r/a_0} dr \qquad \text{let } z = \frac{2r}{a_0} \\ &= \frac{1}{2}\int_1^3 z^2 e^{-z} dz \\ &= -\frac{1}{2}\left(z^2 + 2z + 2\right)e^{-z}\Big|_1^3 \quad \text{(integrating by parts)} \\ &= -\frac{17}{2}e^{-3} + \frac{5}{2}e^{-1} = 0.496 \end{aligned}$$

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 $E_3 = \frac{-Z^2}{3^2}(13.6\ \text{eV})$

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

8-16 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.

8-18 The state is 6g

(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°