CHAPTER 12

Quantum Mechanical Model Systems

SECTION 12.1

12.1 Half the particles here have twice the momentum of the other half and therefore also have twice the wavevector of the others. The analog of the wavefunction in Eq. (12.8) is thus

\[ \psi \propto \left( \frac{1}{2} \right)^{1/2} e^{ikx} + \left( \frac{1}{2} \right)^{1/2} e^{i2kx}. \]

The probability distribution is

\[ |\psi|^2 \propto \left[ \left( \frac{1}{2} \right)^{1/2} e^{ikx} + \left( \frac{1}{2} \right)^{1/2} e^{i2kx} \right] \left[ \left( \frac{1}{2} \right)^{1/2} e^{-ikx} + \left( \frac{1}{2} \right)^{1/2} e^{-i2kx} \right] = \frac{1}{2} + \frac{1}{2} e^{-ikx} + \frac{1}{2} e^{ikx} + \frac{1}{2} = 1 + \frac{1}{2}(e^{ikx} + e^{-ikx}) = 1 + \cos kx. \]

This is an oscillatory function that oscillates between 0 and 2 with a spacing between maxima of \( \frac{2\pi}{k} \). The particles are localized to regions around these maxima (much as a standing waves of water form a regular pattern of maxima and minima), but these regions of maximum probability extend from \(-\infty\) to \(\infty\).

12.2 We wish to evaluate Eq. (12.9) using the \( w(k) \) function of Eq. (12.10):

\[ \psi(x) \propto \int_{-\infty}^{\infty} w(k) e^{-ikx} \, dk = \int_{-\infty}^{\infty} e^{-(k - k_0)^2/2\delta k^2} e^{-ikx} \, dk. \]

This integral is known. It has the form of the general definite integral
and we can identify $p^2 = 1/(\delta k)^2$, $q = ix$, $q^2 = -x^2$, and $z = k - k_0$. This gives

$$\psi(x) \propto \int_{-\infty}^{\infty} e^{-(k - k_0)^2/2(\delta k)^2} e^{-ikx} \, dk$$

$$= e^{-ik_0x} \int_{-\infty}^{\infty} e^{-(k - k_0)^2/2(\delta k)^2 - i(k - k_0)x} \, dk$$

$$= \delta k \sqrt{2\pi} e^{-ik_0x} e^{-x^2/(\delta k)^2}/2,$$

which, except for the factor $\delta k \sqrt{2\pi}$, is the function shown in the text on page 392 and plotted (as the real part) in Figure 12.2(b). (Whether one has a factor $e^{-ik_0x}$, as we have here, or a factor $e^{ik_0x}$, as in the text, is unimportant. Both have the same real part, $\cos(k_0x)$, and the imaginary part of one is the negative of that of the other.) The definite integral above is a special case of the more general definite integral we have seen before (see Problem 11.22):

$$\int_{-\infty}^{\infty} e^{-\alpha y^2} \, dy = \sqrt{\frac{\pi}{\alpha}}.$$  

We “complete the square” in the argument of the exponential:

$$\int_{-\infty}^{\infty} e^{-p^2 z^2 \pm qz} \, dz = \int_{-\infty}^{\infty} e^{-p^2 z^2 \pm qz - q^2/4p^2 + q^2/4p^2} \, dz$$

$$= e^{q^2/4p^2} \int_{-\infty}^{\infty} e^{-p^2 z^2 \pm qz - q^2/4p^2} \, dz$$

$$= e^{q^2/4p^2} \int_{-\infty}^{\infty} e^{-(pz \mp q/2p)^2} \, dz,$$

then define $y = pz \mp q/2p$ so that $dy = p \, dz$. Making these substitutions (with $\alpha = 1$) completes the derivation.
12.3  (a) If the source of particles is at \( x = -\infty \), then the \( D \) coefficient must be zero, since the term in \( \psi< \) containing \( D, e^{-ik<x} \), represents particles in the region \( x > 0 \) moving toward \( x = -\infty \). Since there is no source at \( x = \infty \) directing particles toward \( x = -\infty \) and since particles moving toward \( x = \infty \) are not reflected back at \( x = \infty \), this coefficient must be zero.

(b) The requirement \( \psi<(0) = \psi>(0) \) means \( 1 + B = C \), and the requirement that the first derivatives are equal at \( x = 0 \) means \( ik_< - ik>B = ik>C \). Solving these two simultaneous equations for \( B \) and \( C \) gives

\[
B = \frac{k_< - k_>}{k_< + k_>} \quad \text{and} \quad C = \frac{2k_<}{k_< + k_>}. \]

(c) The product \( B*B \) is

\[
B*B = \left( \frac{k_< - k_>}{k_< + k_>} \right)^2
\]

since the wavevectors \( k_< \) and \( k_> \) are both real numbers. As the total energy increases, the potential step becomes an ever-decreasing perturbation; the particle’s kinetic energy in the positive \( x \) region is almost the same as it was in the negative \( x \) region. This means \( k_> \) is approaching \( k_< \) as the energy increases, making \( B*B \) go to zero. Note as well that \( C \) approaches 1 in this high-energy limit, as it should.

12.4  (a) Here \( C \) must be zero in order to keep the wavefunction finite as \( x \to \infty \).

(b) Equality of the wavefunctions at \( x = 0 \) leads to \( 1 + B = D \), and equality of their first derivatives leads to \( ik_< - ik>B = -\kappa>D \). Simultaneous solution of these equations gives

\[
B = \frac{ik_< + \kappa_>}{ik_< - \kappa_>} \quad \text{and} \quad D = \frac{2ik_<}{ik_< - \kappa_>}. \]

(c) Here, \( B*B \) is

\[
B*B = \left( \frac{ik_< + \kappa_>}{ik_< - \kappa_>} \right)^* \left( \frac{ik_< + \kappa_>}{ik_< - \kappa_>} \right) = \frac{(-ik_< + \kappa_>)(ik_< + \kappa_>)}{(-ik_< - \kappa_>)(ik_< - \kappa_>)} = \frac{k_<^2 + \kappa_>^2}{k_<^2 + \kappa_>^2} = 1. \]
(d) The probability of barrier penetration depends on total energy $E$ through the quantity $D^*D$:

$$D^*D = \frac{4k_<^2}{k_<^2 + \kappa_>^2}. $$

Since the wavevectors $k_<$ and $\kappa_>$ depend on $E$ through

$$k_< = \frac{\sqrt{2mE}}{\hbar} \quad \text{and} \quad \kappa_> = \frac{\sqrt{2m(V - E)}}{\hbar},$$

we can write

$$D^*D = \frac{4k_<^2}{k_<^2 + \kappa_>^2} = \frac{4E}{E + (V - E)} = \frac{4E}{V}. $$

Since $E$ ranges from 0 to $V$ (because $E > V$ returns us to the energy regime of the previous problem), the probability is maximal when $E = V$.

12.5 Here, the wavefunctions can be written

$$\psi_< = C e^{-ik_<x} \quad \text{and} \quad \psi_> = e^{-ik_>x} + B e^{ik_>x}.$$ 

Note that $\psi_<$ has no term corresponding to particles moving towards $x = \infty$ (i.e., no $e^{ik_<x}$ term), since particles originate at $x = \infty$ and, while they can be reflected from the potential step at $x = 0$ and move back to $x = \infty$ in the positive $x$ region, they can only move toward $x = -\infty$ in the negative $x$ region. We find expressions for $B$ and $C$ from the requirements that the wavefunctions and their first derivatives are equal at $x = 0$:

$$1 + B = C \quad \text{and} \quad -k_> + k_>B = -k_<C.$$

Simultaneous solution of these two equations gives

$$B = k_> - k_< \quad \frac{k_>}{k_> + k_<} \quad \text{and} \quad C = \frac{2k_>}{k_> + k_<}.$$
The probability for reflection back to the source at the potential step is \( B^*B \), since \( B \) is the coefficient of the term representing particles in the positive \( x \) region moving towards \( x = \infty \). It is simply

\[
B^*B = \left( \frac{k_> - k_<}{k_> + k_<} \right)^2,
\]

and since \( k_> \) approaches \( k_< \) as \( E \) increases, \( B^*B \) approaches 0 as \( E \to \infty \).

**SECTION 12.2**

12.6 The zero-point energy of mass \( m_e \), the electron mass, in a 1-D box is

\[
E_1 = \frac{\hbar^2 \pi^2}{2m_e L^2}.
\]

Equating this to the electron’s mass-equivalent energy, \( m_e c^2 \), and solving for \( L \) gives

\[
L = \frac{h}{2\sqrt{2} m_e c} = \frac{2.43 \times 10^{-12} \text{ m}}{2\sqrt{2}} = 8.58 \times 10^{-13} \text{ m}.
\]

As an aside, we can repeat this line of reasoning for the zero-point energy of a harmonic oscillator and get another answer of the same magnitude. We write, with \( X \) representing the classical turning point of the motion,

\[
E_0 = \frac{\hbar^2}{2m_e X^2} = m_e c^2 \quad \text{or} \quad X = \frac{\hbar}{2m_e c} = 1.93 \times 10^{-13} \text{ m}.
\]

Thus, the full classical motion of the electron, from \(-X\) to \(X\), spans \( 1/2\pi \) times the Compton wavelength: \( \frac{\hbar}{m_e c} = (\hbar/m_e c)/2\pi = 3.86 \times 10^{-13} \text{ m} \).

12.7 Usually, one thinks of classical behavior as the “large quantum number limit” of a quantum-mechanical system. Here, we will find classical behavior (in the sense defined in this problem—the position uncertainty is greater than the distance between successive maxima in the probability distribution) at a surprisingly small quantum number. First, we find \( \Delta x \) for a particle in a box. The result of Problem 11.23 gives us an easy route, if we recall that \( \langle x \rangle = L/2 \):
\[(\Delta x)^2 = \langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2 = L^2 \left( \frac{1}{3} - \frac{1}{2n^2 \pi^2} \right) - \frac{L^2}{4} \quad \text{or} \quad \frac{\Delta x}{L} = \left( \frac{1}{12} - \frac{1}{2n^2 \pi^2} \right)^{1/2} \cdot \]

(As an aside, note that \(\Delta x/L\) approaches the constant limit \(1/\sqrt{12} = 0.289\) as \(n \to \infty\).) We wish to compare \(\Delta x/L\) to \(1/n\) (the spacing between maxima divided by \(L\)) and look for that \(n = n^*\) for which \(\Delta x/L > 1/n\). We make the following table:

<table>
<thead>
<tr>
<th>(n)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Delta x/L)</td>
<td>0.181</td>
<td>0.266</td>
<td>0.279</td>
<td>0.283</td>
<td>0.285</td>
<td>0.288</td>
</tr>
<tr>
<td>(1/n)</td>
<td>1</td>
<td>0.500</td>
<td>0.333</td>
<td>0.250</td>
<td>0.200</td>
<td>0.100</td>
</tr>
</tbody>
</table>

We find that \(\Delta x > L/n\) for \(n \geq 4\), which is perhaps a surprisingly small number.

12.8 We write

\[P(x) \, dx = \frac{dt}{\tau_{1/2}} = \frac{dx}{\tau_{1/2}(dx/dt)} ,\]

and with \(x(t) = X \cos \omega t\), \(dx/dt = -X \omega \sin \omega t\). Since \(\tau_{1/2} = \pi/\omega\), we have

\[P(x) \, dx = \frac{dt}{\tau_{1/2}} = \frac{dx}{\tau_{1/2}(dx/dt)} = \frac{dx}{X \omega \pi \sin \omega t} = \frac{dx}{\pi X \sin \omega t} .\]

(We can neglect the minus sign in \(dx/dt\), since probabilities must be positive.) Now we write \(\cos \omega t = x/X\), and since \(\sin^2 \omega t + \cos^2 \omega t = 1\), we have \(\sin \omega t = (X^2 - x^2)^{1/2}/X\) so that

\[P(x) \, dx = \frac{dx}{\pi X \sin \omega t} = \frac{dx}{\pi \left( X^2 - x^2 \right)^{1/2}} \]

as we wished to show. The normalization integral follows from

\[\int_{-X}^{X} P(x) \, dx = \frac{1}{\pi} \int_{-X}^{X} \frac{dx}{\left( X^2 - x^2 \right)^{1/2}} .\]

Let \(x = yX\) so that \(dx = X \, dy\). Then the integral above becomes
\[
\frac{1}{\pi} \int_{-X}^{X} \frac{dx}{\left(X^2 - x^2\right)^{1/2}} = \frac{1}{\pi} \int_{-1}^{1} \frac{X \, dy}{\left(X^2 - y^2\right)^{1/2}} = \frac{1}{\pi} \int_{-1}^{1} \frac{dy}{\left(1 - y^2\right)^{1/2}} = \frac{\pi}{\pi} = 1 \, .
\]

12.9 At the classical turning point of a harmonic oscillator, \( x = X_v \) where \( X_v \) is the classical turning point for state \( v \). Moreover, the energy of state \( v \) is \( E_v = kX_v^2/2 \) for force constant \( k \). Thus, the Schrödinger equation becomes

\[
-\frac{\hbar^2}{2\mu} \frac{d^2\psi_v}{dx^2} + \left(\frac{kx^2}{2} - E_v\right)\psi_v = -\frac{\hbar^2}{2\mu} \frac{d^2\psi_v}{dx^2} + \left(\frac{kx^2}{2} - \frac{kX_v^2}{2}\right)\psi_v = 0 \, .
\]

If \( x = X_v \), the terms in parentheses cancel each other, and we are left with \( d^2\psi_v/dx^2 = 0 \). The wavefunction has an inflection point at the classical turning point, as Figure 12.8 (and Figure 11.2 for the ground state) indicate. This must be a general result, since the definition of a classical turning point is that point at which the total energy equals the potential energy and the terms in parentheses in the Schrödinger equation as written above are always (potential energy – total energy).

12.10 The coordinate \( q \) used to express the harmonic oscillator wavefunctions in Eq. (12.19) is shown on page 406 in the text to equal \( \sqrt{2v + 1} x/X_v \) so that \( q_1 = \sqrt{3} x/X_1 \) and \( q_2 = \sqrt{5} x/X_2 \). The Hermite polynomials for these two states are in Table 12.1: \( H_1(q) = 2q \) and \( H_2(q) = 4q^2 - 2 \). The normalization constants given by Eq. (12.20) are for the wavefunction written in terms of the dimensionless variable \( q \). We want the normalization constants for the wavefunction written in terms of the real distance variable \( x \), and thus we use the expressions listed in the Summary to Chapter 12 on page 440. (See also the comments at the end of Example 12.4 on page 406.) We have

\[
N_1 = \left(\sqrt{\frac{k}{\pi \hbar \omega}} \frac{1}{2}\right)^{1/2} \quad \text{and} \quad N_2 = \left(\sqrt{\frac{k}{8 \pi \hbar \omega}} \frac{1}{8}\right)^{1/2} \, .
\]

Since \( q \) can also be written as \( \sqrt{k/\hbar \omega} x \), we have \( \sqrt{k/\hbar \omega} = \sqrt{2v + 1}/X_v \). This makes the normalization constants equal to

\[
N_1 = \left(\frac{1}{2 \sqrt{\pi X_1}} \sqrt{3}\right)^{1/2} \quad \text{and} \quad N_2 = \left(\frac{1}{8 \sqrt{\pi X_2}} \sqrt{5}\right)^{1/2} \, .
\]
Thus, the entire wavefunctions are

\[ \psi_1 = \left( \frac{1}{2\sqrt{\pi}} x_1 \right)^{1/2} \left( \frac{\sqrt{3} x}{x_1} \right) e^{-3x^2/2x_1^2} \]

\[ \psi_2 = \left( \frac{1}{8\sqrt{\pi}} x_2 \right)^{1/2} \left( \frac{5x^2}{x_2^2} - 2 \right) e^{-5x^2/2x_2^2} . \]

12.11 As we used in the previous problem, there is a simple relationship between the classical turning point of any harmonic oscillator state and its parameters \( m \) and \( k \). For the ground state, the relationship is

\[ X_0 = \sqrt{\frac{\hbar \omega}{k}}. \]

Since \( \omega = \sqrt{k/m} \), this can also be written as

\[ X_0 = \sqrt{\frac{\hbar \omega}{k}} = \sqrt{\frac{\hbar \sqrt{k}}{k \sqrt{m}}} = \sqrt{\frac{\hbar \sqrt{k}}{\sqrt{mk}}}. \]

Using the values for \( k \) and \( m \) quoted in the problem, we find \( X_0 = 0.123 \) Å for \( \text{H}_2 \) and \( X_0 = 4.98 \times 10^{-2} \) Å for \( \text{I}_2 \). Thus, \( X_0/R_e = 0.166 \) for \( \text{H}_2 \) and \( X_0/R_e = 1.87 \times 10^{-2} \) for \( \text{I}_2 \). Hydrogen vibrates over a total distance (classically) that is about 33% of its bond length while \( \text{I}_2 \) vibrates over a much smaller 4% or so.

12.12 There is a clear symmetry we can exploit here. We want the ground-state wavefunction to have its maximum at \( x = 0 \). If the potential was a particle-in-a-box extending over \(-L/2 \leq x \leq L/2\), we know the ground-state wavefunction would be symmetric about and maximal at \( x = 0 \). Likewise, a harmonic potential centered at \( x = 0 \) has a ground-state wavefunction symmetric about and maximal at \( x = 0 \). Thus, since what we have here is half of each type of potential, we want a continuous wavefunction that is the particle-in-a-box wavefunction for \(-L/2 \leq x \leq 0\) and a harmonic oscillator wavefunction for \( x \geq 0 \). Our usual coordinate system for a particle-in-a-box extends from 0 to \( L \); since the potential we are imagining here has been shifted towards smaller \( x \) by \( L/2 \), the ground-state wavefunction has the sine function of Eq. (12.11) replaced by cosine:

\[ \psi(x \leq 0) = \sqrt{\frac{2}{L}} \cos \frac{\pi x}{L} \]
The harmonic oscillator ground-state wavefunction is
\[
\psi(x \geq 0) = \frac{1}{\sqrt{\pi X_0}} e^{-x^2/2X_0} = \left( \frac{k}{\pi \hbar \omega} \right)^{1/4} e^{-k^2 x^2/2 \hbar \omega}.
\]

For these to join smoothly at \(x = 0\), they must equal each other and have equal first derivatives. Equal derivatives is assured: both wavefunctions have maxima (and thus zero first derivatives) at \(x = 0\). Continuity of the wavefunctions (along with \(\omega = \sqrt{k/m}\)) gives us the relationship among \(m, L,\) and \(k\) that we seek:
\[
\left( \frac{2^L}{L} \right)^{1/2} = \left( \frac{k}{\pi \hbar \omega} \right)^{1/4} = \left( \frac{\sqrt{mE}}{\pi \hbar} \right)^{1/4} \quad \text{or} \quad L = 2 \sqrt{\frac{\pi \hbar}{\sqrt{mk}}}.
\]

12.13 Here, we can exploit the eigenvalue expressions for the creation and annihilation operators given on page 405 in the text:
\[
\begin{align*}
(q - \frac{d}{dq})\psi_v &= [2(v + 1)]^{1/2}\psi_{v + 1}, \quad v = 0, 1, 2, \ldots \\
(q + \frac{d}{dq})\psi_v &= (2v)^{1/2}\psi_{v - 1}, \quad v = 1, 2, 3, \ldots
\end{align*}
\]

We write the matrix element \(q_{nm}\) and expand it as follows:
\[
q_{nm} = \int \psi_n \hat{q} \psi_m dq = \frac{1}{2} \int \psi_n \left[ (q - \frac{d}{dq}) + (q + \frac{d}{dq}) \right] \psi_m dq
\]
\[
= \frac{1}{2} \left[ \int \psi_n (q - \frac{d}{dq}) \psi_m dq + \int \psi_n (q + \frac{d}{dq}) \psi_m dq \right]
\]
\[
= \frac{1}{2} \left[ \sqrt{2(m + 1)} \int \psi_n \psi_{m + 1} dq + \sqrt{2m} \int \psi_n \psi_{m - 1} dq \right].
\]

Since the wavefunctions are orthonormal, the first integral in the last line above vanishes unless \(n = m + 1\) (in which case it equals 1), and the second integral vanishes unless \(n = m - 1\) (in which case it, too, equals 1). Thus, if \(n = m + 1\), \(q_{nm} = q_{n,n - 1} = \sqrt{2(m + 1)}/2 = \sqrt{2n}/2\), and if \(n = m - 1\), \(q_{nm} = q_{n,n + 1} = \sqrt{2m}/2 = \sqrt{2(n + 1)/2}\). See also Problem 13.15 for another representation of these integrals.
12.14 The matrix representation of the square if the $\widehat{q}$ operator is the square of the matrix representation of the $\widehat{q}$ operator alone:

$$q_{nm}^2 = \sum_{i=1}^{\infty} q_{ni}q_{im}.$$

The previous problem gives the pattern of nonzero values for $q_{nm}$, and armed with this pattern and the equation above, we can deduce that the pattern of nonzero values for $q_{nm}^2$ must be

$$q^2 = \begin{pmatrix} 0 & q_{01} & 0 & \cdots \\ q_{10} & 0 & q_{12} & \cdots \\ 0 & q_{21} & 0 & \cdots \\ \vdots & \vdots & \vdots & \ddots \end{pmatrix}^2.$$ 

In particular, we see that $q_{00}^2$ is nonzero and equals

$$q_{00}^2 = q_{00}q_{10} = \frac{\sqrt{2}}{2} \cdot \frac{\sqrt{2}}{2} = 1/2.$$

Problem 11.34 found $\langle x^2 \rangle = X^2/2$ where $X$ is the classical turning point. Our result here, $q_{00}^2 = \langle q^2 \rangle_{00} = 1/2$, is the dimensionless variant of $\langle x^2 \rangle$ for the ground state for which $q = x/X$. Thus, $\langle q^2 \rangle_{00} = \langle x^2 \rangle_{00}/X^2 = 1/2$.

12.15 Differentiating the generating function gives

$$\frac{dH_v}{dq} = \frac{d}{dq} \left[ (-1)^v q^2 e^{\frac{dv}{2}} e^{-q^2} \right] = (-1)^v \left( 2qe^{\frac{dv}{2}} e^{-q^2} \frac{dv}{dq} + 1 \right) = 2qH_v - H_v + 1.$$

Differentiating this gives
\[
\frac{d^2 H_v}{dq^2} = \frac{d(2qH_v - H_{v+1})}{dq} = 2H_v + 2q\frac{dH_v}{dq} - \frac{dH_v}{dq} = 2H_v + 2q(2qH_v - H_{v+1}) - 2qH_v + 1 + H_v + 2 = (2 + 4q^2)H_v - 4qH_v + 1 + H_v + 2.
\]

If we substitute these expressions for the first and second derivatives of \(H_v\) into Hermite’s differential equation, we find

\[
\frac{d^2 H_v}{dq^2} - 2q\frac{dH_v}{dq} + 2vH_v = (2 + 2v)H_v + H_v + 2 - 2qH_v + 1 = 0.
\]

To arrive at the recurrence relation shown in the text, define \(w = v + 1\), so that \(v = w - 1\). This gives

\[
[2 + 2(w - 1)]H_{w-1} + H_w + 1 - 2qH_w = 2wH_{w-1} + H_w + 1 - 2qH_w = 0.
\]

Changing the symbol that indexes the Hermite polynomial in this equation from \(w\) to \(v\) lets us write the recurrence relation as it is shown in the text, \(H_v + 1 = 2qH_v - 2vH_v - 1\). Finally, if we substitute this expression into our original expression for the first derivative of \(H_v\), we find

\[
\frac{dH_v}{dq} = 2qH_v - H_v + 1 = 2qH_v - 2qH_v + 2vH_v - 1 = 2vH_v - 1.
\]

12.16 If we expand the Lennard-Jones potential function in a Taylor’s series with the aim of finding its effective force constant, \(k\) we see that we need the second derivative of \(V\), since \(k = (d^2V/dx^2)_x = x_e\). We can write \(V\) as

\[
V(x) = D\left(1 - 2x_e^6x^{-6} + x_e^{12}x^{-12}\right)
\]

so that the first derivative is

\[
\frac{dV(x)}{dx} = D\left(12x_e^6x^{-7} - 12x_e^{12}x^{-13}\right)
\]

and the second derivative is

\[
\frac{d^2V(x)}{dx^2} = D\left(72x_e^5x^{-8} - 144x_e^{11}x^{-14}\right)
\]

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\[
\frac{d^2V(x)}{dx^2} = D \left(-12 \cdot 7 e^{-8} + 12 \cdot 13 e^{-14}\right).
\]

Evaluating this at \(x = x_e\) gives the answer we seek:

\[
k = \left(\frac{d^2V(x)}{dx^2}\right)_{x = x_e} = D \left(-12 \cdot 7 e^{-8} + 12 \cdot 13 e^{-14}\right) = \frac{72D}{x_e^2}.
\]

**SECTION 12.3**

12.17 A particle moving freely in 3-D space has the same Hamiltonian whether the space is confined to a finite region (the 3-D particle-in-a-box potential) or extends to infinity. The Hamiltonian is given by Eq. (12.21):

\[
\hat{H} = -\frac{\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m} \nabla^2.
\]

Since the three directions in space \(x, y,\) and \(z\) are equivalent and independent of each other, the most general 3-D free particle wavefunction has the form

\[
\psi(x,y,z) = Ae^{i(k_x x + k_y y + k_z z)} + Be^{-i(k_x x + k_y y + k_z z)} = Ae^{i\mathbf{k} \cdot \mathbf{r}} + Be^{-i\mathbf{k} \cdot \mathbf{r}}
\]

where \(k_x, k_y,\) and \(k_z\) are the wavevectors for motion along the \(x, y,\) and \(z\) directions, respectively, and where \(\mathbf{k}\) is the vector with components \(k_x, k_y,\) and \(k_z,\) \(\mathbf{r}\) is the vector with components \(x, y,\) and \(z,\) and \(\mathbf{k} \cdot \mathbf{r}\) represents the vector dot product of \(\mathbf{k}\) and \(\mathbf{r}.\) The three quantum numbers needed to describe the state of the system (including its energy) are the wavevector components since

\[
k_x = \frac{p_x}{\hbar}, \quad k_y = \frac{p_y}{\hbar}, \quad k_z = \frac{p_z}{\hbar}, \quad \text{and} \quad E = \frac{\hbar^2}{2m} \left(\frac{k_x^2}{2} + \frac{k_y^2}{2} + \frac{k_z^2}{2}\right).
\]

Each wavevector can vary continuously from \(-\infty\) to \(\infty\) (although \(\pm \infty\) implies an infinite velocity, which relativity does not allow).

12.18 The 2-D particle-in-a-box quantum numbers are \(n_x\) and \(n_y,\) and each can range from 1 to \(\infty\) in integral steps. Since the box is a square (all sides of length \(L\)), the total energy expression is
\[ E = E_x + E_y = \frac{\hbar^2 \pi^2}{2mL^2} \left( n_x^2 + n_y^2 \right). \]

To find all the states with energy \( E \leq 9 \frac{\hbar^2 \pi^2}{ml^2} \), we can define the dimensionless energy \( \varepsilon = E / (\frac{\hbar^2 \pi^2}{ml^2}) = \frac{n_x^2 + n_y^2}{2} \), which we can tabulate:

<table>
<thead>
<tr>
<th>( n_x )</th>
<th>( n_y )</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>5/2</td>
<td>5</td>
<td>17/2</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5/2</td>
<td>4</td>
<td>13/2</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>13/2</td>
<td>9</td>
<td>25/2</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>17/2</td>
<td>10</td>
<td>25/2</td>
<td>32</td>
<td></td>
</tr>
</tbody>
</table>

Entries in italics have \( \varepsilon > 9 \) and thus correspond to states we are not interested in here. This shows us that the state with \( \varepsilon = 1 \) (or \( E = \frac{\hbar^2 \pi^2}{ml^2} \)) is nondegenerate, as are those with \( \varepsilon = 4 \) (\( E = 4 \frac{\hbar^2 \pi^2}{ml^2} \)) and those with \( \varepsilon = 9 \) (\( E = 9 \frac{\hbar^2 \pi^2}{ml^2} \)). The states with \( \varepsilon = 5/2 \) (\( E = 5 \frac{\hbar^2 \pi^2}{2ml^2} \)), with \( \varepsilon = 13/2 \) (\( E = 13 \frac{\hbar^2 \pi^2}{2ml^2} \)), and with \( \varepsilon = 17/2 \) (\( E = 17 \frac{\hbar^2 \pi^2}{2ml^2} \)) are doubly degenerate. To locate the most probable position of the particle in any one state, we look at the square of the wavefunction. If we define the \( x \) and \( y \) coordinates so that the edges of the box extend over the ranges \( 0 \leq x, y \leq L \), the square of the wavefunction is

\[
\psi^2(x, y) = \psi^2_{n_x}(x) \psi^2_{n_y}(y) = \left( \frac{2}{L} \right)^{1/2} \sin^2 \frac{n_x \pi x}{L} \sin^2 \frac{n_y \pi y}{L} = \frac{2}{L} \sin^2 \left( \frac{n_x \pi x}{L} \right) \sin^2 \left( \frac{n_y \pi y}{L} \right).
\]

Wherever this function is a maximum for any \((n_x, n_y)\) choice locates the most probable position or positions. An easy way to see this probability is as density plot (an analog of a contour plot) that plots \( \psi^2 \) in two dimensions as a gradation in shade that is proportional to the value of \( \psi^2 \). Such plots are shown at the top of the next page for the states \((n_x, n_y) = (1, 1), (3, 1), (1, 3), \) and \((2, 2)\), drawn so that the darkest shade locates the maximum or maxima in \( \psi^2 \).
The probability peaks in the center of the box (at $x = y = L/2$) for the $(1, 1)$ state. The states $(1, 3)$ and $(3, 1)$ are related by simple symmetry: rotate the picture of one by $90^\circ$ to get the picture of the other. State $(1, 3)$ peaks at $x = L/2$ and $y = L/6, L/2,$ and $5L/6,$ while state $(3, 1)$ peaks at $Y = L/2$ and $x = L/6, L/2,$ and $5L/6.$ State $(2, 2)$ peaks at the four positions $(x, y) = (L/4, L/4),$ $(3L/4, L/4),$ $(L/4, 3L/4),$ and $(3L/4, 3L/4).

12.19 For an isotropic 3-D harmonic oscillator, $\omega = \sqrt{k/m}$ is the only parameter needed to characterize the energy of the system. There are three independent quantum numbers that specify a particular state and energy of such a system: $v_x, v_y,$ and $v_z,$ and each can range from 0 to $\infty$. The energy expression is

$$E = E_x + E_y + E_z$$

$$= \hbar \omega \left[ (v_x + \frac{1}{2}) + (v_y + \frac{1}{2}) + (v_z + \frac{1}{2}) \right]$$

$$= \hbar \omega \left[ v_x + v_y + v_z + \frac{3}{2} \right].$$
and we can use it to tabulate $\epsilon = E/\hbar \omega$ for various combinations of quantum numbers:

<table>
<thead>
<tr>
<th>$v_x$</th>
<th>$v_y$</th>
<th>$v_z$</th>
<th>$\epsilon$</th>
<th>$v_x$</th>
<th>$v_y$</th>
<th>$v_z$</th>
<th>$\epsilon$</th>
<th>$v_x$</th>
<th>$v_y$</th>
<th>$v_z$</th>
<th>$\epsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3/2</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>7/2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>9/2</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>5/2</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>7/2</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>9/2</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>5/2</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>7/2</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>9/2</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>1</td>
<td>5/2</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>7/2</td>
<td>0</td>
<td>2</td>
<td>1</td>
<td>9/2</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>7/2</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>7/2</td>
<td>1</td>
<td>2</td>
<td>0</td>
<td>9/2</td>
</tr>
</tbody>
</table>

We see that the lowest energy state is nondegenerate, at $E = 3\hbar \omega/2$, the next highest state is three-fold degenerate at $E = 5\hbar \omega/2$, the next is six-fold degenerate at $E = 7\hbar \omega/2$, and the fourth state is ten-fold degenerate at $E = 9\hbar \omega/2$.

12.20 We first convert the C–C bond energy, 200 kJ mol$^{-1}$, to joule per molecule units:

$$\frac{200 \text{ kJ mol}^{-1}}{6.022 \times 10^{23} \text{ molecules mol}^{-1}} = 3.32 \times 10^{-19} \text{ J molecule}^{-1}.$$

Now we seek a quantum number $n$ that, when substituted in the energy expression in Example 12.5 with $m =$ mass of one He atom $= 6.65 \times 10^{-27}$ kg and $r_m =$ radial distance the He can move inside the C$_{60}$ cage $= 0.45$ Å $= 4.5 \times 10^{-11}$ m, equals or exceed this energy. Thus, we solve the following expression for $n$:

$$E_n = 3.32 \times 10^{-19} \text{ J} = \frac{\hbar^2 \pi^2}{2mr_m^2} n^2 = (4.08 \times 10^{-21} \text{ J})n^2,$$

and find $n = 9.02$, so that, since $n$ must be an integer, any state with $n \geq 9$ or so gives the He atom sufficient energy to escape the C$_{60}$ cage. (Of course, the 200 kJ mol$^{-1}$ bond energy is not a very accurately known number here, and since our answer $n = 9.02$ is so close to 9, it may well be that the state with $n = 9$ is not really sufficiently energetic. On the other hand, the model itself is quite crude, and we should expect the motion of a He atom inside C$_{60}$ to be more complex than what we have indicated here. As mentioned in Example 12.5, there are other states for this system in which the He atom has angular momentum about the center of the cage. These should also be considered.)
SECTION 12.4

12.21 We start with the Cartesian representation of $\hat{L}_z$ given by Eq. (12.31):

$$\hat{L}_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)$$

and follow the steps outlined in the problem to transform to plane polar coordinates. Using the relations $r = (x^2 + y^2)^{1/2}$ and $\theta = \tan^{-1}(y/x)$, we can derive

$$\frac{\partial r}{\partial x} = \frac{x}{(x^2 + y^2)^{1/2}} = \frac{x}{r}, \quad \frac{\partial r}{\partial y} = \frac{y}{(x^2 + y^2)^{1/2}} = \frac{y}{r}, \quad \frac{\partial \theta}{\partial x} = -\frac{y}{x^2 + y^2} = -\frac{y}{r^2}, \quad \frac{\partial \theta}{\partial y} = \frac{1}{x^2 + y^2} = \frac{x}{r^2}.$$

We use these expressions to build the operator through the chain rule:

$$x \frac{\partial}{\partial y} = x \left[ \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial y} \frac{\partial}{\partial \theta} \right] = x \left( \frac{y}{r} \frac{\partial}{\partial r} + \frac{x}{r^2} \frac{\partial}{\partial \theta} \right),$$

$$y \frac{\partial}{\partial x} = y \left[ \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \theta}{\partial x} \frac{\partial}{\partial \theta} \right] = y \left( \frac{x}{r} \frac{\partial}{\partial r} - \frac{y}{r^2} \frac{\partial}{\partial \theta} \right),$$

so that

$$x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} = x \left( \frac{y}{r} \frac{\partial}{\partial r} + \frac{x}{r^2} \frac{\partial}{\partial \theta} \right) - y \left( \frac{x}{r} \frac{\partial}{\partial r} - \frac{y}{r^2} \frac{\partial}{\partial \theta} \right) = \frac{xy}{r} \frac{\partial}{\partial r} + \frac{x^2}{r^2} \frac{\partial}{\partial \theta} - \frac{xy}{r} \frac{\partial}{\partial r} + \frac{y^2}{r^2} \frac{\partial}{\partial \theta} = \frac{x^2 + y^2}{r^2} \frac{\partial}{\partial \theta} = \frac{\partial}{\partial \theta}.$$

This proves that $\hat{L}_z$ in plane polar coordinates equals $(\hbar/i)(\partial/\partial \theta)$. 

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12.22 We note first that the four first derivatives among the two coordinate systems’ variables that we derived in the previous problem can also be written

\[
\begin{align*}
\frac{\partial r}{\partial x}\bigg|_y &= \frac{x}{r} = \cos \theta \\
\frac{\partial r}{\partial y}\bigg|_x &= \frac{y}{r} = \sin \theta \\
\frac{\partial \theta}{\partial x}\bigg|_y &= \frac{-y}{r^2} = -\frac{\sin \theta}{r} \\
\frac{\partial \theta}{\partial y}\bigg|_x &= \frac{x}{r^2} = \frac{\cos \theta}{r}.
\end{align*}
\]

Using these expressions in the chain rule lets us write

\[
\begin{align*}
\frac{\partial F}{\partial x}\bigg|_y &= \cos \theta \left( \frac{\partial F}{\partial r}\bigg|_\theta \right) - \frac{\sin \theta}{r} \left( \frac{\partial F}{\partial \theta}\bigg|_r \right) \\
\frac{\partial F}{\partial y}\bigg|_x &= \sin \theta \left( \frac{\partial F}{\partial r}\bigg|_\theta \right) + \frac{\cos \theta}{r} \left( \frac{\partial F}{\partial \theta}\bigg|_r \right).
\end{align*}
\]

We substitute from these six expressions as called for into the general expressions for the second derivatives:

\[
\begin{align*}
\frac{\partial^2 F}{\partial x^2} &= \left( \frac{\partial r}{\partial x}\bigg|_y \right) \left[ \frac{\partial }{\partial r}\left( \frac{\partial F}{\partial x}\bigg|_y \right) \right] + \left( \frac{\partial \theta}{\partial x}\bigg|_y \right) \left[ \frac{\partial }{\partial \theta}\left( \frac{\partial F}{\partial x}\bigg|_y \right) \right] \\
&= \cos \theta \left[ \frac{\partial }{\partial r}\left( \cos \theta \frac{\partial }{\partial r} - \frac{\sin \theta}{r} \frac{\partial }{\partial \theta} \right) \right] - \frac{\sin \theta}{r} \left[ \frac{\partial }{\partial \theta}\left( \cos \theta \frac{\partial }{\partial r} - \frac{\sin \theta}{r} \frac{\partial }{\partial \theta} \right) \right] \\
\frac{\partial^2 F}{\partial y^2} &= \left( \frac{\partial r}{\partial y}\bigg|_x \right) \left[ \frac{\partial }{\partial r}\left( \frac{\partial F}{\partial y}\bigg|_x \right) \right] + \left( \frac{\partial \theta}{\partial y}\bigg|_x \right) \left[ \frac{\partial }{\partial \theta}\left( \frac{\partial F}{\partial y}\bigg|_x \right) \right] \\
&= \sin \theta \left[ \frac{\partial }{\partial r}\left( \sin \theta \frac{\partial }{\partial r} + \frac{\cos \theta}{r} \frac{\partial }{\partial \theta} \right) \right] + \frac{\cos \theta}{r} \left[ \frac{\partial }{\partial \theta}\left( \sin \theta \frac{\partial }{\partial r} + \frac{\cos \theta}{r} \frac{\partial }{\partial \theta} \right) \right]
\end{align*}
\]

and expand each expression:
\[ \frac{\partial^2 F}{\partial x^2} = \cos^2 \theta \frac{\partial^2 F}{\partial r^2} + \frac{\sin^2 \theta}{r^2} \frac{\partial^2 F}{\partial r \partial \theta} - \frac{2 \cos \theta \sin \theta}{r} \frac{\partial^2 F}{\partial r \partial \theta} \]

\[ + \frac{\sin^2 \theta}{r^2} \frac{\partial^2 F}{\partial \theta^2} + \frac{2 \cos \theta \sin \theta}{r^2} \frac{\partial F}{\partial \theta} \]

\[ \frac{\partial^2 F}{\partial y^2} = \sin^2 \theta \frac{\partial^2 F}{\partial r^2} + \frac{\cos^2 \theta}{r^2} \frac{\partial F}{\partial r} + \frac{2 \cos \theta \sin \theta}{r^2} \frac{\partial^2 F}{\partial r \partial \theta} \]

\[ + \frac{\cos^2 \theta}{r^2} \frac{\partial^2 F}{\partial \theta^2} - \frac{2 \cos \theta \sin \theta}{r^2} \frac{\partial \theta}{\partial \theta} \cdot \]

Adding these and recalling that \( \sin^2 \theta + \cos^2 \theta = 1 \) gives us

\[ \nabla^2 = \frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} \]

\[ = \frac{\partial^2 F}{\partial r^2} + \frac{1}{r} \frac{\partial F}{\partial r} + \frac{1}{r^2} \frac{\partial^2 F}{\partial \theta^2} \]

\[ = \frac{1}{r} \frac{\partial}{\partial r} \left( \frac{1}{r} \frac{\partial F}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 F}{\partial \theta^2} \cdot \]

12.23 We start with the expressions for the components of the angular momentum operator written in spherical polar coordinates as given in Eq. (12.32):

\[ \hat{L}_x = \frac{\hbar}{i} \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \]

\[ \hat{L}_y = \frac{\hbar}{i} \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \]

\[ \hat{L}_z = \frac{\hbar}{i} \left( \frac{\partial}{\partial \phi} \right) \cdot \]

then we square each operator:

\[ \hat{L}_x \hat{L}_x = -\hbar^2 \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \]
\[ \hat{L}_x \hat{L}_y = -\hbar^2 \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \]
\[ \hat{L}_z \hat{L}_z = -\hbar^2 \left( \frac{\partial}{\partial \phi} \right)^2 \]

and expand the products:

\[ \hat{L}_x \hat{L}_x = -\hbar^2 \left[ -\cos \phi \sin \phi \left( \cot^2 \theta + \csc^2 \theta \right) \frac{\partial^2}{\partial \phi^2} + \cos^2 \phi \cot^2 \theta \frac{\partial^2}{\partial \phi^2} \right. \]
\[ \left. + 2 \cos \phi \sin \phi \cot \theta \frac{\partial^2}{\partial \theta \partial \phi} + \sin^2 \phi \frac{\partial^2}{\partial \theta^2} + \cos^2 \phi \cot \theta \frac{\partial}{\partial \theta} \right] \]

\[ \hat{L}_y \hat{L}_y = -\hbar^2 \left[ \cos \phi \sin \phi \left( \cot^2 \theta + \csc^2 \theta \right) \frac{\partial}{\partial \phi} \right. \]
\[ \left. + \sin^2 \phi \cot^2 \theta \frac{\partial^2}{\partial \phi^2} + \cos^2 \phi \cot \theta \frac{\partial}{\partial \phi} \right] \]

\[ \hat{L}_z \hat{L}_z = -\hbar^2 \left( \frac{\partial^2}{\partial \phi^2} \right) \]

We add these to form the operator we seek, \( \hat{L}^2 = \hat{L}_x \hat{L}_x + \hat{L}_y \hat{L}_y + \hat{L}_z \hat{L}_z \). Fortunately, several terms cancel, and the identity \( \sin^2 \phi + \cos^2 \phi = 1 \) simplifies several others:

\[ \hat{L}^2 = -\hbar^2 \left[ (\cot^2 \theta + 1) \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} \right] \]
\[ = -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \]
\[ = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \phi} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] . \]

To express \( \hat{L}^2 \) in Cartesian coordinates, we use Eq. (12.31) for each component operator:
\[ \hat{L}_x = \frac{\hbar}{i} \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \]

\[ \hat{L}_y = \frac{\hbar}{i} \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) \]

\[ \hat{L}_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right), \]

then we square and expand each component. Since all three operators are so similar, once we square and expand one in detail, we can immediately write the other two by analogy:

\[ \hat{L}_x \hat{L}_x = \hbar^2 \left( y \frac{\partial^2}{\partial z^2} - z \frac{\partial^2}{\partial y^2} \right) \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \]

\[ = \hbar^2 \left( y^2 \frac{\partial^2}{\partial z^2} - xy \frac{\partial^2}{\partial y^2} + z^2 \frac{\partial^2}{\partial y^2} - y \frac{\partial}{\partial y} + z \frac{\partial}{\partial z} \right) \]

Thus, the squares of the other two components are

\[ \hat{L}_y \hat{L}_y = \hbar^2 \left( z^2 \frac{\partial^2}{\partial x^2} - z \frac{\partial^2}{\partial x \partial z} + x^2 \frac{\partial^2}{\partial z^2} - x \frac{\partial}{\partial x} \right) \]

and

\[ \hat{L}_z \hat{L}_z = \hbar^2 \left( x^2 \frac{\partial^2}{\partial y^2} - xy \frac{\partial^2}{\partial y \partial x} + y^2 \frac{\partial^2}{\partial x^2} - x \frac{\partial}{\partial x} - y \frac{\partial}{\partial y} \right). \]

We add these three expressions to form the operator for the square of the total angular momentum, \( \hat{L}^2 = \hat{L}_x \hat{L}_x + \hat{L}_y \hat{L}_y + \hat{L}_z \hat{L}_z \), shown at the top of the next page. Note that this version of the operator is considerably more complicated than the version written in spherical polar coordinates earlier in this problem. Consequently, the Cartesian representation is rarely used.
\[
\hat{L}^2 = -\hbar^2 \left[ y^2 \frac{\partial^2}{\partial z^2} - 2yz \frac{\partial^2}{\partial z \partial y} + z^2 \frac{\partial^2}{\partial y^2} - y \frac{\partial}{\partial y} - z \frac{\partial}{\partial z} \\
+ z^2 \frac{\partial^2}{\partial x^2} - 2zx \frac{\partial^2}{\partial x \partial z} + x^2 \frac{\partial^2}{\partial z^2} - z \frac{\partial}{\partial z} - x \frac{\partial}{\partial x} \\
+ x^2 \frac{\partial^2}{\partial y^2} - 2xy \frac{\partial^2}{\partial y \partial x} + y^2 \frac{\partial^2}{\partial x^2} - x \frac{\partial}{\partial x} - y \frac{\partial}{\partial y} \right]
\]

12.24 The expression in part (a), \([\hat{L}_x, \hat{L}_y] = i \hbar \hat{L}_z\), is easiest to prove using Cartesian coordinates:

\[
[\hat{L}_x, \hat{L}_y] = \hat{L}_x \hat{L}_y - \hat{L}_y \hat{L}_x \\
= \hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) - \hbar \left( z \frac{\partial}{\partial x} - x \frac{\partial}{\partial z} \right) - \hbar \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)
\]

The expression in part (b), \([\hat{L}_x^2, \hat{L}_x] = 0\), is easiest to prove using spherical polar coordinates, and the calculus is perhaps a bit easier and more transparent if we write the operator \(\hat{L}_x^2\) in the following expanded way, which we first encountered in the previous problem:

\[
\hat{L}_x^2 = -\hbar^2 \left[ \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]

\[
= -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]
\]
This lets us write \( \hat{L}^2 \hat{L}_z \) as

\[
\hat{L}^2 \hat{L}_z = -\hbar^2 \left[ \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \left( \frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \\
= -\frac{\hbar^3}{i} \left( \frac{\partial^3}{\partial \theta^2 \partial \phi} + \cot \theta \frac{\partial^2}{\partial \theta \partial \phi} + \frac{1}{\sin^2 \theta} \frac{\partial^3}{\partial \phi^3} \right)
\]

and \( \hat{L}_z \hat{L}^2 \) as

\[
\hat{L}_z \hat{L}^2 = \left( \frac{\hbar}{i} \frac{\partial}{\partial \phi} \right) \left[ -\hbar^2 \left( \frac{\partial^2}{\partial \theta^2} + \cot \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \right] \\
= -\frac{\hbar^3}{i} \left( \frac{\partial^3}{\partial \theta^2 \partial \phi} + \cot \theta \frac{\partial^2}{\partial \theta \partial \phi} + \frac{1}{\sin^2 \theta} \frac{\partial^3}{\partial \phi^3} \right).
\]

Subtracting these to form the commutator clearly gives zero.

For part (c), we substitute the definition \( \hat{L}_+ = \hat{L}_x + i\hat{L}_y \) into the expanded commutator of interest:

\[
[\hat{L}_z, \hat{L}_+ \hat{L}^2] = [\hat{L}_z (\hat{L}_x + i\hat{L}_y)] - (\hat{L}_x + i\hat{L}_y) [\hat{L}_z] \\
= \hat{L}_z \hat{L}_x - \hat{L}_x \hat{L}_z + i(\hat{L}_z \hat{L}_y - \hat{L}_y \hat{L}_z) \\
= [\hat{L}_z, \hat{L}_x] + i[\hat{L}_z, \hat{L}_y] \\
= i \hbar \hat{L}_y + i(-i \hbar \hat{L}_x) \\
= \hbar (\hat{L}_x + i\hat{L}_y) = \hbar \hat{L}_+.
\]

For part (d), we again substitute the definition \( \hat{L}_+ = \hat{L}_x + i\hat{L}_y \) in the commutator of interest here and write

\[
[\hat{L}_+, \hat{L}^2] = [(\hat{L}_x + i\hat{L}_y), \hat{L}^2] = [\hat{L}_x, \hat{L}^2] + i[\hat{L}_y, \hat{L}^2].
\]

(Note how commutator algebra is distributive. This lets us jump directly and confidently from the second to the third step above.) Since \( \hat{L}^2 \) commutes with \textit{every} angular momentum component operator, both of the final two commuta-
tors equal zero, as, therefore, does the operator \([\hat{L}_+, \hat{L}_-^2]\). Thus, these two operators commute.

To see if \(\hat{L}_+\) and \(\hat{L}_-\) commute, we write

\[
[\hat{L}_+, \hat{L}_-] = [(\hat{L}_x + i\hat{L}_y), (\hat{L}_x - i\hat{L}_y)] \\
= (\hat{L}_x + i\hat{L}_y)(\hat{L}_x - i\hat{L}_y) - (\hat{L}_x - i\hat{L}_y)(\hat{L}_x + i\hat{L}_y) \\
= \hat{L}_x^2 - i\hat{L}_x\hat{L}_y + i\hat{L}_y\hat{L}_x + \hat{L}_y^2 - i\hat{L}_x\hat{L}_y - i\hat{L}_y\hat{L}_x + i\hat{L}_y\hat{L}_x - \hat{L}_y^2 \\
= 2i(\hat{L}_y\hat{L}_x - \hat{L}_x\hat{L}_y) = 2i[\hat{L}_y, \hat{L}_x] \\
= 2i(-\hat{\eta}\hat{L}_z) = 2\hat{\eta}\hat{L}_z.
\]

Since the final result is not identically zero, these operators do not commute.

12.25 Let \(\psi_m\) be an eigenfunction such that \(\hat{L}_z\psi_m = m\hat{\eta}\psi_m\). Then we argue as follows:

\[
\hat{L}_z(\hat{L}_-\psi_m) = \hat{L}_z\hat{L}_-\psi_m \\
= (\hat{L}_z\hat{L}_- - \hat{L}_-\hat{L}_z)\psi_m \\
= ([\hat{L}_z, \hat{L}_-] + \hat{L}_-\hat{L}_z)\psi_m \\
= (-\hat{\eta}\hat{L}_- + \hat{L}_-\hat{L}_z)\psi_m \\
= \hat{L}_-\hat{L}_z\psi_m - \hat{\eta}\hat{L}_-\psi_m \\
= \hat{L}_-(m\hat{\eta})\psi_m - \hat{\eta}\hat{L}_-\psi_m \\
= (m - 1)\hat{\eta}(\hat{L}_-\psi_m).
\]

Thus, the function \(\hat{L}_-\psi_m\) has an eigenvalue for the \(\hat{L}_z\) operator that is one \(\hat{\eta}\) unit lower than \(\psi_m\) itself.

12.26 If \(l = 1\) and \(m = 1\), the eigenfunction \(\psi_{1m} = \psi_{1,1}\) must satisfy the following equation:

\[
(\hat{L}_-^2 - \hat{L}_z^2)\psi_{1,1} = \hat{L}_-^2\psi_{1,1} - \hat{L}_z^2\psi_{1,1} = 2\hat{\eta}^2\psi_{1,1} - \hat{\eta}^2\psi_{1,1} = \hat{\eta}^2\psi_{1,1}
\]

so that \(\sqrt{\hat{L}_x^2 + \hat{L}_y^2} = \hat{\eta}\). This, along with \(\hat{L}_z = \hat{\eta}\) and \(|\mathbf{L}| = \sqrt{2}\hat{\eta}\), lets us construct the diagram at the top of the next page for the classical vector \(\mathbf{L}\). The \(\mathbf{L}\)
vector lies somewhere on the surface of the shaded cone in this figure; the Uncertainty Principle does not allow us to say exactly where.

For the general case of \( l = m \), we note that the length of \( \mathbf{L} \) is \( \sqrt{l(l+1)} \mathbf{\hat{z}} \) and the length of its \( z \) component is \( m \mathbf{\hat{z}} = l \mathbf{\hat{z}} \). Thus, we can make the following diagram of the general classical vector geometry:

We see that \( \cos \theta = l/\sqrt{l(l+1)} \), and thus as \( l \to \infty \), \( \cos \theta \to 1 \), or \( \theta \to 0 \).

12.27 To write \( \hat{L}_z \) in spherical polar coordinates, we substitute the spherical polar forms of \( \hat{L}_x \) and \( \hat{L}_y \) into the definition of \( \hat{L}_z \). Since we will need \( \hat{L}_\pm \) later on in this problem, we can derive both at once. We also take advantage of the identity \( e^{i\phi} = \cos \phi + i \sin \phi \) and find
\[ \hat{L}_x = \hat{L}_x \pm i \hat{L}_y \]
\[ = \frac{\hbar}{i} \left[ \left( -\sin \phi \frac{\partial}{\partial \theta} - \cot \theta \cos \phi \frac{\partial}{\partial \phi} \right) \pm i \left( \cos \phi \frac{\partial}{\partial \theta} - \cot \theta \sin \phi \frac{\partial}{\partial \phi} \right) \right] \]
\[ = \frac{\hbar}{i} \left[ \left( \pm i \cos \phi - \sin \phi \right) \frac{\partial}{\partial \theta} - \cot \theta (\cos \phi \pm i \sin \phi) \frac{\partial}{\partial \phi} \right] \]
\[ = \frac{\hbar}{i} \left[ i \frac{e^{\pm i \phi}}{e} \frac{\partial}{\partial \theta} - \cot \theta \frac{e^{\pm i \phi}}{e} \frac{\partial}{\partial \phi} \right] \]
\[ = \frac{\hbar}{i} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right]. \]

Next, we take \( l = m, \Theta_{l,l}(\theta) = \sin^l \theta, \) and \( \Phi_l(\phi) = e^{il \phi} = e^{il \phi} \) and operate on \( \Theta \Phi \) with \( \hat{L}_+ \). Since \( \hat{L}_+ \) raises the \( z \) component one \( \hbar \) unit, but for \( m = l \), this component is already as large as it can be, the operator should yield zero:
\[ \hat{L}_+ \Theta_{l,l}(\theta) \Phi_l(\phi) = \hat{L}_+ \left[ \sin^l \theta \right] e^{il \phi} \]
\[ = \frac{\hbar}{i} \left[ \frac{\partial}{\partial \theta} + i \cot \theta \frac{\partial}{\partial \phi} \right] \left[ \sin^l \theta \right] e^{il \phi} \]
\[ = \frac{\hbar}{i} \left[ i e^{il \phi} \cos \theta \sin^{l-1} \theta - l e^{il \phi} \cot \theta \sin^l \theta \right] \]
\[ = \frac{\hbar}{i} \left[ i e^{il \phi} \cos \theta \sin^{l-1} \theta - l e^{il \phi} \cos \theta \sin^l \theta \right] \]
\[ = \frac{\hbar}{i} \left[ i e^{il \phi} \cos \theta \sin^{l-1} \theta - l e^{il \phi} \cos \theta \sin^l \theta \right] \]
\[ = 0. \]

Finally, we set \( l = 2 \) and operate on \( (\sin^2 \theta) \Phi_{2}(\phi) = (\sin^2 \theta)e^{2i \phi} \) with \( \hat{L}_- \):
\[ \hat{L}_- \Theta_{2,2}(\theta) \Phi_2(\phi) = \hat{L}_- \left[ \sin^2 \theta \right] e^{2i \phi} \]
\[ = \frac{\hbar}{i} e^{-i \phi} \left( i \cot \theta \frac{\partial}{\partial \phi} - \frac{\partial}{\partial \theta} \right) \left[ \sin^2 \theta \right] e^{2i \phi} \]
\[ = \frac{\hbar}{i} e^{-i \phi} \left( -2 e^{2i \phi} \cot \theta \sin^2 \theta - 2 e^{2i \phi} \cos \theta \sin \theta \right) \]
\[ = \frac{\hbar}{i} e^{-i \phi} \left( -2 e^{2i \phi} \cos \theta \sin \theta - 2 e^{2i \phi} \cos \theta \sin \theta \right) \]
\[ = \frac{\hbar}{i} e^{-i \phi} \left( -2 e^{2i \phi} \cos \theta \sin \theta - 2 e^{2i \phi} \cos \theta \sin \theta \right) \]
\[ = -4 \frac{\hbar}{i} e^{i \phi} \cos \theta \sin \theta. \]
Since we have not included normalization constants in our wavefunctions, this result is only proportional to $\psi_{2,1}$, but we can see that it has the correct functional dependence on $\theta$ and $\phi$ for this wavefunction: for $m = 1$, we should find a factor $e^{im\phi}$, and we do; for $l = 2$ and $m = 1$, we should find the factors $(\cos \theta \sin \theta)$ that represent the $\theta$ dependence of the $Y_{2,1}(\theta, \phi)$ spherical harmonic function (see Table 12.2), and we do.

12.28 With the help of Table 12.2, which lists the spherical harmonic functions we need and shows us that the $\phi$ part of each term in the Theorem’s sum vanishes, since $\phi$ appears in the spherical harmonic functions as $e^{im\phi}$ and this term times its complex conjugate gives simply 1, we write Unsöld’s Theorem for the particular case of $l = 1$ as

$$\sum_{m = -1}^{1} |Y_{1m}(\theta, \phi)|^2 = |Y_{1, -1}|^2 + |Y_{1, 0}|^2 + |Y_{1, 1}|^2$$

$$= \frac{1}{2\pi} \left[ \frac{3}{4} \sin^2 \theta + \frac{3}{2} \cos^2 \theta + \frac{3}{4} \sin^2 \theta \right]$$

$$= \frac{3}{4\pi} \left( \sin^2 \theta + \cos^2 \theta \right) = \frac{3}{4\pi} = \text{constant.}$$

For $l = 2$, we follow the same argument, using two trigonometric identities to simplify our result, $\sin^2 \theta = 1 - \cos^2 \theta$ and $\sin^4 \theta - \cos^4 \theta = \sin^2 \theta - \cos^2 \theta$:

$$\sum_{m = -2}^{2} |Y_{2m}(\theta, \phi)|^2 = |Y_{2, -2}|^2 + |Y_{2, -1}|^2 + |Y_{2, 0}|^2 + |Y_{2, 1}|^2 + |Y_{2, 2}|^2$$

$$= \frac{1}{2\pi} \left[ \frac{2}{16} \sin^4 \theta + \frac{15}{16} \sin^2 \theta \cos^2 \theta \right] + \frac{5}{8} (3\cos^2 \theta - 1)^2$$

$$= \frac{5}{16\pi} \left[ 9\cos^4 \theta - 6\cos^2 \theta + 3\sin^4 \theta + 12\cos^2 \theta \sin^2 \theta + 1 \right]$$

$$= \frac{5}{16\pi} \left[ 9\cos^4 \theta - 6\cos^2 \theta + 3\sin^4 \theta + 12\cos^2 \theta (1 - \cos^2 \theta) + 1 \right]$$

$$= \frac{5}{16\pi} \left[ 6\cos^2 \theta + 3(\sin^2 \theta - \cos^2 \theta) + 1 \right]$$

$$= \frac{5}{16\pi} \left( 3\sin^2 \theta + 3\cos^2 \theta + 1 \right) = \frac{5}{4\pi} = \text{constant.}$$
One can show that, in general, the constant is \((2l + 1)/4\pi\).

12.29 We follow the logic used in Example 12.7 here, using the energy expression in Eq. (12.42) with \(R = a_0\), the Bohr radius of Eq. (12.45) with \(\mu = m_e\). We find

\[
E = \frac{l(l+1) \hbar^2}{2m_e a_0^2} = \frac{e^4 m_e}{2m_e \left(\frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2}\right)^2} \frac{2(4\pi \varepsilon_0)^2 \hbar^2}{e^2} = l(l+1) \times (2.18 \times 10^{-18} \text{ J}) = l(l+1) \times (13.6 \text{ eV}) .
\]

Note that the energy constant \(e^4 m_e / 2(4\pi \varepsilon_0)^2 \hbar^2 = e^2 / 2(4\pi \varepsilon_0) a_0 = -E_1\), which is the negative of the usual H atom ground state energy (see Eq. (12.46b)), appears here.

12.30 Equating the attractive force between the proton and electron to the centrifugal force of an orbiting electron in the Bohr model gives us

\[
\frac{e^2}{4\pi \varepsilon_0 a^2} = m_e \omega^2 .
\]

The Bohr quantization condition, \(m_e a^2 \omega = n \hbar\), gives us an expression for the orbiting frequency \(\omega\):

\[
\omega = \frac{n \hbar}{m_e a^2} ,
\]

that, when substituted in the first equality, gives

\[
\frac{e^2}{4\pi \varepsilon_0 a^2} = m_e \left(\frac{n \hbar}{m_e a^2}\right)^2 , \quad \text{or} \quad a = n^2 \frac{4\pi \varepsilon_0 \hbar^2}{m_e e^2} = n^2 a_0 .
\]

If \(E = -T = -m_e a^2 \omega^2 / 2\), we can use the expressions above for \(\omega\) to write an expression for \(a^2 \omega^2\) that, when substituted in the energy expression, gives something we can arrange in the form of Eq. (12.52):
\[
E = \frac{-m_e a^2 \omega^2}{2} = -m_e \frac{n^2 I^2}{2m_e^2 a^2} = -\frac{n^2 I^2}{2m_e a^2} = -\frac{e^2 n^2 I^2}{2(4\pi\varepsilon_0)^2 n^2} = -\frac{e^2}{2(4\pi\varepsilon_0) a_0}\frac{1}{n^2},
\]

where, in the last step, we have collected those constants that define the Bohr radius, \(a_0 = (4\pi\varepsilon_0)^{1/2} / m_e e^2\).

12.31 If we scale a \(1.2 \times 10^{-15}\) m proton radius up to 1 mm (a magnification factor of \(8.33 \times 10^{11}\)), and if we define the proton distance from the center of mass to be \(r_p\) and the electron distance \(r_e\), then we can write two expressions relating \(r_p\) and \(r_e\). The first is that they add to give our measure of a 1s H atom radius, which we are taking to be \(\langle r \rangle\) so that \(r_p + r_e = \langle r \rangle\). The second is the definition of center of mass: \(m_p r_p = m_e r_e\). The 1s state value for \(\langle r \rangle\) is \(3a_0/2 = 7.94 \times 10^{-11}\) m, which, when scaled by our magnification factor, becomes about 66 m. Solving the two expressions for \(r_p\) and \(r_e\) gives

\[
\begin{align*}
    r_p &= \frac{m_e}{m_p + m_e} \langle r \rangle, \\
    r_e &= \frac{m_p}{m_p + m_e} \langle r \rangle.
\end{align*}
\]

The magnified numerical values are \(r_p = 36\) mm and \(r_e = 66\) m. (All current theories and experiments on electrons, by the way, indicate that the electron has no radius; it is a true point.) In terms familiar to American readers, if we place the center of mass on the goal line of an American football field, the proton is about 1.4 in. into the end zone and the electron is on the opponent’s 28 yard line.

12.32 From the general expression \(\Delta E = h c / \lambda\) for the emission wavelength \(\lambda\) accompanying an energy change \(\Delta E\), we can write

\[
\lambda =\frac{hc}{\Delta E} = \frac{hc}{E_n - E_m} = \frac{hc}{E_1 - E_1} \frac{1}{n^2} = \frac{hc n^2 m^2}{E_1 (m^2 - n^2)} = \frac{hc}{-E_1 n^2 - m^2}.
\]

With \(E_1 = -e^2 / 2(4\pi\varepsilon_0) a_0\), we identify the constant in the general expression, Eq. (11.3): \(91.127\) nm = \(2(4\pi\varepsilon_0) a_0 hc / e^2\). Setting \(m = 2\) gives the constant in Eq. (11.2), the Balmer formula.
12.33 The differences in size and ionization energy for the three isotopic forms of hydrogen are due to the different reduced masses \( \mu \) of each isotope. The reduced mass enters the Bohr radius expression and the ground-state energy expression (the negative of which is the ionization potential):

\[
a_0 = \frac{4\pi\varepsilon_0 \hbar^2}{\mu e^2} \quad \text{and} \quad \text{IP} = -E_1 = \frac{e^2}{2(4\pi\varepsilon_0)a_0}.
\]

Using the full number of significant figures in the mass of the electron along with the accurate nuclear masses given in the problem and the conversion factor between atomic mass units and kg, we can calculate reduced masses:

\[
\mu_H = \frac{m_em_H}{m_e + m_H} = 9.104 \, 434 \times 10^{-31} \text{ kg}
\]
\[
\mu_D = \frac{m_em_D}{m_e + m_D} = 9.106 \, 909 \times 10^{-31} \text{ kg}
\]
\[
\mu_T = \frac{m_em_T}{m_e + m_T} = 9.107 \, 733 \times 10^{-31} \text{ kg}.
\]

From these, the following radii and ionization potentials follow:

\[
a_0(H) = \frac{4\pi\varepsilon_0 \hbar^2}{e^2\mu_H} = 5.294 \, 653 \times 10^{-11} \text{ m}
\]
\[
\text{IP}_H = \frac{e^2}{2(4\pi\varepsilon_0)a_0(H)} = 2.178 \, 688 \times 10^{-18} \text{ J}
\]
\[
a_0(D) = \frac{4\pi\varepsilon_0 \hbar^2}{e^2\mu_D} = 5.293 \, 214 \times 10^{-11} \text{ m}
\]
\[
\text{IP}_D = \frac{e^2}{2(4\pi\varepsilon_0)a_0(D)} = 2.179 \, 281 \times 10^{-18} \text{ J}
\]
\[ a_0(T) = \frac{4\pi\epsilon_0 \hbar^2}{e^2\mu_T} = 5.292 \, 735 \times 10^{-11} \, \text{m} \]

\[ \text{IP}_T = \frac{\frac{e^2}{2(4\pi\epsilon_0)a_0(T)}}{e^2 \mu_T} = 2.179 \, 478 \times 10^{-18} \, \text{J} . \]

The size differences are inconsequential and unobservable, but the ionization energy differences are experimentally observable.

12.34 The general rules that guide us here are: the total number of nodes = \( n - 1 \) and the total number of spherical nodes = \( n - l - 1 \). For wavefunction (a), “spherically symmetric” tells us \( l = 0 \) (an s state), and “three spherical nodes” tells us \( 3 = n - 0 - 1 \) or \( n = 4 \). It also follows that \( m = 0 \). For wavefunction (b), the three planar nodes (and thus no spherical nodes) again tell us \( 3 = n - 1 \) or \( n = 4 \). Since there are no spherical nodes, \( 0 = n - l - 1 = 4 - l - 1 \) or \( l = 3 \) (an f state). This is the 4f\(_{xyz}\) wavefunction shown in Figure 12.16(e), and we cannot uniquely identify \( m \). Wavefunction (c) has one spherical and one planar node so that \( 2 = n - 1 \) or \( n = 3 \). The one spherical node tells us \( 1 = n - l - 1 = 3 - l - 1 \) or \( l = 1 \) (a p state). Since the nodal plane is the \( xy \) plane, the wavefunction is cylindrically symmetric about the \( z \) axis. This is the 3p\(_z\) wavefunction (\( m = 0 \)). Wavefunction (d) has two spherical nodes and two nonspherical (conical) nodes: \( 4 = n - 1 \) or \( n = 5 \) and \( 2 = n - l - 1 = 5 - l - 1 \) or \( l = 2 \) (a d state). Again, \( m = 0 \) because conical nodes are cylindrically symmetric about \( z \). This is the 5d\(_{z^2}\) wavefunction. For (e), the symmetry tells us \( m = 0 \), and the single nodal plane (which must be the \( xy \) plane) tells us \( l = 1 \) so that \( n = 2 \). This is the 2p\(_z\) wavefunction of in Figure 12.14(d).

12.35 From Table 12.4, we see that the angular portion of the 2p\(_z\) wavefunction is simply \( \cos \theta \). For the 3d\(_{z^2}\) wavefunction, it is \( 3 \cos^2 \theta - 1 \). Polar plots of \( r = \cos \theta \) and \( r = 3 \cos^2 \theta - 1 \) are shown below.
These plots show the symmetry and rough spatial extent of the electron probability density plots shown in Figures 12.14(d) and 12.15(a).

12.36 For the 1s state, \( \langle r \rangle = \frac{3a_0}{2} = 7.94 \times 10^{-11} \text{ m} \), while \( a_0 = 5.29 \times 10^{-11} \text{ m} \). The radius \( r^* \) that encloses 90% of the electron probability in this state is given implicitly by the equation

\[
0.90 = \int_0^{2\pi} d\phi \int_0^\pi \sin \theta \; d\theta \int_0^{r^*} r^2 \psi_{1s}^2 \, dr = \frac{4}{a_0^3} \int_0^{r^*} e^{-2r/a_0} r^2 \, dr .
\]

If we let \( x = r/a_0 \), this integral becomes

\[
0.90 = 4 \int_0^{x^*} e^{-2x} x^2 \, dx .
\]
which cannot be evaluated in closed form. Numerical integration gives \( x^* = 2.661 \), or \( r^* = 2.661a_0 = 1.41 \times 10^{-10} \) m, a larger measure of the 1s atomic “size” than either \( a_0 \) or \( \langle r \rangle \). It is interesting to look at a graph of probability versus \( r \) for this state just to see how rapidly the probability is approaching 1:

![Graph of probability versus r](image)

At the \( \langle r \rangle \) value, which is 1.5 on the scale of this figure, the probability is only 0.6 or so.

12.37 From Example 12.8, the radial distribution function, rdf, is defined as \( 4\pi r^2 R_{nl}^2 \) where \( R_{nl} \) is the radial part of the wavefunction for the state with quantum numbers \( n \) and \( l \). These radial factors are listed in Table 12.3, and thus we can write

\[
\text{rdf}_{1s} = 4\pi r^2 \frac{4}{a_0^3} e^{-2r/a_0} = \frac{16\pi}{a_0^3} r^2 e^{-2r/a_0} \\
\text{rdf}_{2p_z} = 4\pi r^2 \frac{1}{24a_0^3} \frac{r^2}{a_0^2} e^{-r/a_0} = \frac{\pi}{6a_0^5} r^3 e^{-r/a_0}.
\]

We find the maxima in these functions by differentiation:

\[
\frac{drdf_{1s}}{dr} = \frac{16\pi}{a_0^3} \left( 2r e^{-2r/a_0} - r^2 \frac{2}{a_0} e^{-2r/a_0} \right)
\]

\[
\frac{drdf_{2p_z}}{dr} = \frac{\pi}{6a_0^5} \left( 3r^2 e^{-r/a_0} - r^3 \frac{e^{-r/a_0}}{a_0^3} \right).
\]
When these derivatives equal zero, we are at the maximum. For 1s, this happens when \((2r - 2r^2/a_0) = 0\) or when \(r = a_0\). For 2p_z, we want \(3r^2 - r^3/a_0 = 0\) or \(r = 3a_0\). Finally, we find the 2s radial distribution function:

\[
\text{rdf}_{2s} = 4\pi r^2 \left[ \frac{1}{8a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0} \right] = \frac{\pi r^2}{2a_0^3} \left( 2 - \frac{r}{a_0} \right)^2 e^{-r/a_0}. 
\]

This function is zero at \(r = 0\) and \(\infty\) (neither of which counts as a node) and at \(r = 2a_0\), which is the node location. The graph in Example 12.8 on page 432 in the text shows this node as well as the maximum in the 1s rdf at \(r = a_0\).

12.38 The general expression for the ionization potential of a one-electron atom of nuclear charge \(Z\) is \(\text{IP}(Z) = -Z^2E_1\) where \(E_1\) is the H atom ground-state energy. For \(U^{91+}\), \(Z = 92\) and \(\text{IP} = 8464E_1 = 115\,093\) eV. The general expression for \(<\hat{r}>\) is

\[
<\hat{r}> = \frac{a_0}{2Z} \left[ 3n^2 - l(l + 1) \right].
\]

If \(Z = 92\), \(n = 1\), and \(l = 0\), we find \(<\hat{r}> = 3a_0/184 = 0.0163\) \(a_0 = 8.63 \times 10^{-3}\) Å. If we consider only \(l = 0\) states, for some \(n = n^*\) the \(U^{91+}\) size will exceed the H atom 1s size, given by \(<\hat{r}> = 3a_0/2\). Thus, we write

\[
\frac{3a_0}{2} = \frac{3a_0}{2.92} n^*^2 \quad \text{or} \quad n^*^2 = 92
\]

so that (since \(n^*\) must be integral) \(n^* \geq 10\). We can make a plot of \(<\hat{r}>_1s = 3a_0/2Z\) versus \(\text{IP}(Z) = -Z^2E_1\) for \(Z = 1\) through 92 if we solve each expression for \(Z\) and equate the results. We find \(<\hat{r}> = (3a_0/2) \times (-E_1/\text{IP})^{1/2}\), which is graphed below in a log–log plot.
12.39 The Earth’s speed \( v \) in its orbit around the sun is

\[
v = \frac{2\pi r}{\tau} = \frac{2\pi (1.5 \times 10^{11} \text{ m})}{10\pi \times 10^6 \text{ s}} \cong 3 \times 10^4 \text{ m s}^{-1}
\]

so that its angular momentum is

\[
L = mvr = (6 \times 10^{24} \text{ kg}) \times (3 \times 10^4 \text{ m s}^{-1}) \times (1.5 \times 10^{11} \text{ m}) \\
\cong 2.4 \times 10^{40} \text{ kg m}^2 \text{ s}^{-1} \cong 2.6 \times 10^{74} \hat{\mathcal{J}}.
\]

The huge number \( 2.6 \times 10^{74} \) represents an angular momentum quantum number \( l \). (The correct quantum expression \( L = \sqrt{l(l + 1)} \hat{\mathcal{J}} \) reduces to \( L = l \hat{\mathcal{J}} \) in the large \( l \) limit.) An H atom must have \( n \) at least this large in order to have such an angular momentum. Thus, if we take \( n = l = 2.6 \times 10^{74} \) and substitute into the general expression for \( \langle \hat{r} \rangle \), we find

\[
\langle \hat{r} \rangle = \frac{a_0}{2} \left[ 3n^2 - l(l + 1) \right] = \frac{a_0}{2} \left( 3n^2 - n^2 - n \right) \cong a_0 n^2
\]

or \( \langle \hat{r} \rangle \cong 6.6 \times 10^{148} a_0 = 3.5 \times 10^{138} \) m. This huge number, larger than the radius of the known Universe, indicates that while \( n \) can increase without limit in the simplest theory of atomic hydrogen, states with very large \( n \) do not have physical significance.

12.40 The \( \hat{L}_z \) operator is \( (\hat{\mathcal{J}}/i)(\partial/\partial \phi) \), and the \( 2p_x \) and \( 2p_y \) hybrid functions depend on \( \phi \) as shown in the text on page 434: \( 2p_x \propto \cos \phi \) and \( 2p_y \propto \sin \phi \). Since we
know \( \partial \cos \phi / \partial \phi = \sin \phi \) and \( \partial \sin \phi / \partial \phi = -\cos \phi \), these hybrid functions are not eigenfunctions of \( \hat{L}_z \). In fact, the \( \hat{L}_z \) operator turns one function into something at least proportional to the other.

12.41 Table 12.5 lists the general form of the hybrid H-atom wavefunctions, and for the 3p\(_x\) and 3p\(_y\) functions, we find

\[ 3p_x = \frac{1}{\sqrt{2}} \left( \Psi_{311} + \Psi_{31-1} \right) \quad \text{and} \quad 3p_y = -i \frac{1}{\sqrt{2}} \left( \Psi_{311} - \Psi_{31-1} \right). \]

Table 12.4 in turn gives the hydrogenic wavefunctions \( \Psi_{31\pm1} \) as

\[ \Psi_{31\pm1} = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-r/3a_0} \left( \frac{6r}{a_0^2} - \frac{r^2}{a_0^2} \right) \sin \theta e^{\pm i\phi}. \]

Substitution and simplification (using \( 2 \cos \phi = e^{i\phi} + e^{-i\phi} \) and \( 2i \sin \phi = e^{i\phi} - e^{-i\phi} \)) gives

\[ 3p_x = \frac{\sqrt{2}}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} \left( \frac{6r}{a_0} - \frac{r^2}{a_0^2} \right) \cos \phi \sin \theta e^{-r/3a_0} \]
\[ 3p_y = \frac{\sqrt{2}}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} \left( \frac{6r}{a_0} - \frac{r^2}{a_0^2} \right) \sin \phi \sin \theta e^{-r/3a_0}. \]

The one radial node in each of these hybrids occurs when \( 6r/a_0 - r^2/a_0^2 = 0 \), or at \( r = 6a_0 \). The 3p\(_x\) hybrid has a nodal plane wherever \( \cos \phi = 0 \), which is the y-z plane with \( x = 0 \), exactly like the 2p\(_x\) hybrid, and the 3p\(_y\) hybrid has a nodal plane wherever \( \sin \phi = 0 \), which is the x-z plane with \( y = 0 \), exactly like the 2p\(_y\) hybrid.

12.42 We follow the logic of the previous problem again here, starting with the general forms of the hybrids in Table 12.5:
\[ 3d_{xz} = \frac{1}{\sqrt{2}} \left( \Psi_{321} + \Psi_{32-1} \right) \]
\[ 3d_{yz} = -\frac{i}{\sqrt{2}} \left( \Psi_{321} - \Psi_{32-1} \right) \]
\[ 3d_{xy} = -\frac{i}{\sqrt{2}} \left( \Psi_{322} - \Psi_{32-2} \right) . \]

The hydrogenic wavefunctions we need are in Table 12.4:
\[ \Psi_{32\pm1} = \frac{1}{81 \sqrt{\pi} a_0^{3/2}} e^{-r/3a_0} \frac{r^2}{a_0^2} \sin \theta \cos \theta e^{\pm i \phi} \]
\[ \Psi_{32\pm2} = \frac{1}{162 \sqrt{\pi} a_0^{3/2}} e^{-r/3a_0} \frac{r^2}{a_0^2} \sin^2 \theta e^{\pm 2i \phi} . \]

Substitution and simplification again gives the hybrids:
\[ 3d_{xz} = \frac{\sqrt{2}}{81 \sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \cos \phi \cos \theta \sin \theta \]
\[ 3d_{yz} = \frac{\sqrt{2}}{81 \sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \sin \phi \cos \theta \sin \theta \]
\[ 3d_{xy} = \frac{\sqrt{2}}{81 \sqrt{\pi} a_0^{3/2}} \frac{r^2}{a_0^2} e^{-r/3a_0} \cos \phi \sin \phi \sin^2 \theta . \]

Using the relationships between Cartesian and spherical polar coordinates
\[ x = r \sin \theta \cos \phi , \ y = r \sin \theta \sin \phi , \ \text{and} \ z = r \cos \theta , \]
we can see that the 3d_{xz} hybrid contains \( xz/r^2 = \cos \phi \cos \theta \sin \theta \), the 3d_{yz} hybrid contains \( yz/r^2 = \sin \phi \cos \theta \sin \theta \), and the 3d_{xy} hybrid contains \( xy/r^2 = \cos \phi \sin \phi \sin^2 \theta \). Thus, 3d_{xz} is zero wherever \( xz = 0 \) and similarly for the other two hybrids.

**SECTION 12.5**
12.43 Equation (12.53b) gives us the eigenvalues for the \( \hat{S}_z \) operator: \( \hat{S}_z \alpha = (\hbar/2) \alpha \) and \( \hat{S}_z \beta = -(\hbar/2) \beta \). The eigenvalue expressions for the square of \( \hat{S}_z \) are therefore

\[
\begin{align*}
\hat{S}_z^2 \alpha &= \hat{S}_z \hat{S}_z \alpha = \hat{S}_z \left( \frac{\hbar}{2} \alpha \right) = \frac{\hbar}{2} \hat{S}_z \alpha = \frac{\hbar^2}{4} \alpha \\
\hat{S}_z^2 \beta &= \hat{S}_z \hat{S}_z \beta = \hat{S}_z \left( -\frac{\hbar}{2} \beta \right) = -\frac{\hbar}{2} \hat{S}_z \beta = \frac{\hbar^2}{4} \beta .
\end{align*}
\]

Since the expectation value of an operator that gives an exact eigenvalue is just the eigenvalue, we can write, for either the \( \alpha \) or \( \beta \) spin state, \( \langle \hat{S}_z^2 \rangle = \frac{\hbar^2}{4} \).

Thus, \( \langle \hat{S}_z^2 \rangle = 3 \langle \hat{S}_z^2 \rangle = 3 \frac{\hbar^2}{4} = (1/2)(1/2 + 1) \frac{\hbar^2}{4} \), in accord with Eq. (12.53a).

**GENERAL PROBLEMS**

12.44 For scenario (a), the H\(_2\)O bending angle, we note first that the H–O–H bending angle \( \theta \) varies between 0\(^\circ\) (the two H atoms overlap) and 180\(^\circ\) (the molecule is linear). Moreover, we know that water has an equilibrium (lowest energy) structure with \( \theta \approx 105^\circ \). As \( \theta \to 0^\circ \), the potential energy should rise rapidly as the two H atoms bump into and repel each other; the \( \theta = 0^\circ \) limit should not be reachable. As \( \theta \to 180^\circ \), the potential should reach a maximum, since, by symmetry, the linear configuration divides configurations that are bent to one side or the other of linear. This leads to the qualitative sketch shown below.
We can graph the potential for scenario (b) exactly: it is the Coulombic repulsive potential energy between two identical charges, $V(r_{12}) = \frac{e^2}{4\pi\varepsilon_0}r_{12}$, with the zero of energy taken at $r_{12} = \infty$. It looks like this:

![Graph of potential energy](image)

The methyl cyanide, CH$_3$CN, to methyl isocyanide, CH$_3$NC, isomerization in part (c) is characterized by an isomerization angle $\theta$ that we can take to be $0^\circ$ in the cyanide configuration and $180^\circ$ in the isocyanide configuration. Since the cyanide configuration is the more stable of the two, $V(\theta)$ must have an absolute minimum at $\theta = 0^\circ$. But since the isocyanide is also stable, there must be a secondary minimum in $V(\theta)$ at $180^\circ$ that is higher in energy than the absolute minimum. For all angles in between, the energy must rise smoothly to a maximum and then fall again, leading to the following qualitative diagram:

![Graph of isomerization angle](image)

As the O–H group is rotated around the C–O bond, the alcoholic H alternately eclipses and staggers hydrogens on the methyl group. Thus, every $120^\circ$, there
is a maximum in \( V(\theta) \) at each eclipse, and 60° past each maximum, half way between successive maxima, we encounter a minimum representing each staggered conformation. All the maxima have the same height, all the minima have the same height, and \( \theta \) ranges from 0° to 360°. These are the characteristics of a function we can write as \( V(\theta) = V_0 [1 + \cos(3\theta)] \) where the constant \( V_0 \) measures the potential difference between the minima and maxima. This function is shown below.

Note that there is no sound theoretical argument that says the cosine (or sine—our choice is arbitrary) function accurately represents the true \( V(\theta) \). Any function with the right number of wiggles of uniform height could perhaps do as well or better, but the cosine is the simplest function with a chance at being correct, and experiments have shown that it can do a good job of reproducing some of the phenomena associated with this sort of internal motion.

12.45 If the new variables are \( x' = (x + y)/\sqrt{2} \) and \( y' = (y - x)/\sqrt{2} \), we can solve these equations for the original variables: \( x = (x' - y')/\sqrt{2} \) and \( y = (x' + y')/\sqrt{2} \), and substitute these expressions into the potential energy function \( V(x, y) \):

\[
V(x, y) = k_0 (5x^2 + 5y^2 + 6xy) \\
= k_0 \left[ \frac{5}{2} (x' - y')^2 + \frac{5}{2} (x' + y')^2 + \frac{6}{2} (x' - y')(x' + y') \right] \\
= k_0 (8x'^2 + 2y'^2) \\
= \frac{1}{2} (16k_0) x'^2 + \frac{1}{2} (4k_0) y'^2 .
\]
Not only does this variable change remove the cross term that precluded a separation of variables solution, the final form of $V$ shows at a glance that the potential is simply a sum of harmonic oscillator potentials in the two independent variables $x'$ and $y'$. Written this way, we can easily identify the force constants $k_{x'}$ and $k_{y'}$ for these two directions:

$$k_{x'} = 16k_0 \quad \text{and} \quad k_{y'} = 4k_0.$$ 

The energy expression for a mass $m$ bound to this 2-D potential is therefore

$$E = \frac{\hbar}{2} \omega_{x'} \left(\varphi_{x'} + \frac{1}{2}\right) + \frac{\hbar}{2} \omega_{y'} \left(\varphi_{y'} + \frac{1}{2}\right), \quad \omega_{x'} = 4\sqrt{\frac{k_0}{m}} \quad \text{and} \quad \omega_{y'} = 2\sqrt{\frac{k_0}{m}}.$$ 

12.46 Classically, the electron and positron in positronium move toward each other, moving symmetrically about a center of mass that, since $e^-$ and $e^+$ have the same mass, is always half way between them. For states of zero orbital angular momentum, these two particles move along a line. The only difference between the Ps atom quantum mechanical problem and the ordinary H atom problem is the reduced mass: for H, $\mu_H = m_em_p/(m_e + m_p) \equiv m_e$, but for Ps, $\mu_{Ps} = m_em_e/(m_e + m_e) = m_e/2 = \mu_H/2$. Since the ionization energy of H is the negative of the ground-state energy: $IP = -E_1$, and since $E_1 \propto \mu$ (see Eq. (12.46a)), the Ps ionization energy is half that of H. Since the Bohr radius is proportional to $1/\mu$ (see Eq. (12.45)), the Ps Bohr radius is twice that of H. The energy level expression for Ps is identical to that for H with the exception of the change in the energy constant:

$$E_n(H) = -\frac{2.179 \times 10^{-18} \text{ J}}{n^2}, \quad E_n(Ps) = -\frac{2.179 \times 10^{-18} \text{ J}}{2n^2} = -\frac{1.090 \times 10^{-18} \text{ J}}{n^2}.$$ 

For H, the longest wavelength a ground-state atom can absorb is that which takes the atom from $n = 1$ to $n = 2$. It is 121.5 nm, the longest wavelength of the Lyman series mentioned on page 351 and shown in Figure 11.1 in the text. The same calculation holds for Ps:

$$\lambda = \frac{hc}{\Delta E} = \frac{hc}{E_2(Ps) - E_1(Ps)} = \frac{hc}{-\frac{1.090 \times 10^{-18} \text{ J}}{2^2} \left(-\frac{1.090 \times 10^{-18} \text{ J}}{1^2}\right)} = 243 \text{ nm},$$
exactly twice the H atom $n = 2 \rightarrow 1$ wavelength. In a classical picture of the Ps ground state, the positron–electron motion is along a line connecting both particles through the center of mass. The classical turning point of this motion for Ps is $4a_0$, found by writing $E_1(\text{Ps}) = \text{the total energy} = V(r = \text{classical turning point}) = -e^2/(4\pi \varepsilon_0)r$ and solving for $r$. The time $\tau$ it takes the electron (say) to go from its turning point, in to $r = 0$, out to the opposite turning point, then back to $r = 0$ and on to the original turning point must be four times the time to move from the first turning point to $r = 0$. (This time is the same for the positron to make its mirror-image motion.) It can be shown that this total time is four times as long as the time for the electron in the Bohr model of H to make one Bohr orbit around the proton, which for Ps is a total time $\tau \approx 6 \times 10^{-16}$ s. Thus, in $0.1 \text{ ns} = 10^{-10}$ s, the Ps mean lifetime, the electron and positron make about 170 000 “classical orbits” around their mutual center of mass.

12.47 The density of states for a particle in a 1-D box is worked out as Example 20.1 on page 754 in the text. We can follow the logic shown there to derive the density of states for a particle-on-a-ring, introduced in Example 12.6 on page 419 in the text. The energy expression is $E = m^2 \vec{p}^2/(2MR^2)$ for a particle of mass $M$ with quantum number $m = 0, \pm 1, \pm 2, \ldots$. One difference between this system and the particle-in-a-box is that every state here except $m = 0$ is doubly degenerate. It introduces little error to derive the general expression assuming all states are doubly degenerate, and thus we write the density of states $\rho(E)$ as

$$\rho(E) = 2 \frac{dm}{dE} = 2 \left( \frac{dE}{dm} \right)^{-1} = 2 \left( \frac{m^2 \vec{p}^2}{MR^2} \right)^{-1} = 2 \left[ \left( \frac{2MR^2}{\vec{p}^2} \right)^{1/2} \frac{\vec{p}^2}{MR^2} \right]^{-1} = \frac{R}{\vec{p}} \sqrt{\frac{2M}{E}}.$$

12.48 If $V(r) = (\text{constant})r^n$, the general form of the Virial Theorem becomes

$$2 \langle \hat{T} \rangle = \langle r \frac{\partial V}{\partial r} \rangle = \langle \text{(constant)}rmr^{n-1} \rangle = n \langle V \rangle.$$

Since $E = \langle \hat{T} \rangle + \langle \hat{V} \rangle$, we can write

$$E = \langle \hat{T} \rangle + \langle \hat{V} \rangle = \frac{n}{2} \langle \hat{V} \rangle + \langle \hat{V} \rangle = \frac{n+2}{2} \langle \hat{V} \rangle = \langle \hat{T} \rangle + \frac{2}{n} \langle \hat{T} \rangle = \frac{n+2}{n} \langle \hat{T} \rangle.$$

If $n = 2$ (harmonic), we see that $\langle \hat{T} \rangle = -\langle \hat{V} \rangle$. For $n = -1$ (Coulombic), $\langle \hat{T} \rangle = -\langle \hat{V} \rangle/2$. 

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If we equate the total energy of a state of the H atom, $E_n$, to the effective potential energy (the sum of the centrifugal potential and the Coulombic potential), we can write

$$E_n = -\frac{e^2}{2(4\pi\varepsilon_0)a_0} \frac{1}{n^2} - \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{(4\pi\varepsilon_0)r}, \quad a_0 = \frac{(4\pi\varepsilon_0)\hbar^2}{\mu e^2}.$$ 

With the definition suggested in the problem, $\rho = r/a_0$, this can be written

$$0 = \frac{e^2}{(4\pi\varepsilon_0)r} - \frac{e^2}{2(4\pi\varepsilon_0)a_0} \frac{1}{n^2} - \frac{l(l+1)\hbar^2}{2\mu r^2} - \frac{e^2}{(4\pi\varepsilon_0)r^2}$$

$$= \frac{e^2}{(4\pi\varepsilon_0)r} - \frac{e^2}{2(4\pi\varepsilon_0)a_0} \frac{1}{n^2} - \frac{l(l+1)a_0 e^2}{2(4\pi\varepsilon_0)r^2}$$

$$= \frac{1}{r} - \frac{1}{2n^2} - \frac{l(l+1)a_0}{r^2} = \frac{1}{\rho} - \frac{1}{2n^2} - \frac{l(l+1)}{2\rho^2}$$

or $2n^2\rho - \rho^2 - l(l+1)n^2 = 0$. A quadratic solution for $\rho$ gives

$$\rho = n^2 \pm n\sqrt{n^2 - l(l+1)}.$$ 

The two solutions represent the two classical turning points. Note that for $l = 0$ (i.e., s states), the expression simplifies to $\rho = 2n^2$ and $\rho = 0$, which simply means that $r = 0$ can be reached in s states. In units of $a_0$, the outer classical turning points (the values for $\rho$ with the + sign chosen) are 32 for 4s, 30.967 for 4p, 28.649 for 4d, and 24 for 4f. These can be compared to the $<r>$ values for the same states: 24, 23, 21, and 18, respectively, using the expression for $<r>$ given on page 431 in the text.

If we take $p = \hbar j/R$, so that $T = \hbar^2/2m_e R$ and thus $F_{\text{out}} = -dT/dR = \hbar^2/m_e R^3$, we can write the force balance equation

$$F_{\text{out}} + F_{\text{in}} = \frac{\hbar^2}{m_e R^3} - \frac{e^2}{(4\pi\varepsilon_0)R^2} = 0.$$ 

Solving this expression for $R$ gives $R = \hbar^2/(4\pi\varepsilon_0)m_e e^2 = a_0$, the usual Bohr radius. The Virial Theorem says $E = -T = -\hbar^2/2m_e a_0 = E_1$, the exact H atom ground-state energy. Thus, this simple model gives the same energy and size parameter as the Bohr theory, which, in turn, gives the same energy and size as the complete quantum mechanical theory.