41

QUANTUM MECHANICS II: ATOMIC STRUCTURE

41.1. IDENTIFY: For a particle in a cubical box, different values of n_X , n_Y , and n_Z can give the same energy.

SET UP:
$$E_{n_X, n_Y, n_Z} = \frac{(n_X^2 + n_Y^2 + n_Z^2)\pi^2\hbar^2}{2mL^2}$$
.

EXECUTE: (a) $n_X^2 + n_Y^2 + n_Z^2 = 3$. This only occurs for $n_X = 1$, $n_Y = 1$, $n_Z = 1$ so the degeneracy is 1.

(b)
$$n_X^2 + n_Y^2 + n_Z^2 = 9$$
. This occurs for $n_X = 2$, $n_Y = 2$, $n_Z = 1$, for $n_X = 1$, $n_Y = 2$, $n_Z = 2$, and for $n_X = 2$, $n_Y = 1$, $n_Z = 2$ so the degeneracy is 3.

EVALUATE: In the second case, three different states all have the same energy.

41.2. IDENTIFY: Use an electron in a cubical box to model the hydrogen atom.

SET UP:
$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2mI^2}$$
. $E_{2,1,1} = \frac{6\pi^2\hbar^2}{2mI^2}$. $\Delta E = \frac{3\pi^2\hbar^2}{2mI^2}$. $L^3 = \frac{4}{3}\pi a^3$.

$$L = \left(\frac{4\pi}{3}\right)^{1/3} a = 8.527 \times 10^{-11} \text{ m}.$$

EXECUTE:
$$\Delta E = \frac{3\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(9.109 \times 10^{-31} \text{ kg})(8.53 \times 10^{-11} \text{ m})^2} = 2.49 \times 10^{-17} \text{ J} = 155 \text{ eV}.$$
 In the Bohr model,

$$E_n = -\frac{13.6 \text{ eV}}{n^2}$$
. The energy separation between the $n = 2$ and $n = 1$ levels is

$$\Delta E_{\text{Bohr}} = (13.6 \text{ eV}) \left(\frac{1}{1^2} - \frac{1}{2^2} \right) = \frac{3}{4} (13.6 \text{ eV}) = 10.2 \text{ eV}.$$

EVALUATE: A particle in a box is not a good model for a hydrogen atom.

41.3. IDENTIFY: The energy of the photon is equal to the energy difference between the states. We can use this energy to calculate its wavelength.

SET UP:
$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2mL^2}$$
. $E_{2,2,1} = \frac{9\pi^2\hbar^2}{2mL^2}$. $\Delta E = \frac{3\pi^2\hbar^2}{mL^2}$. $\Delta E = \frac{hc}{\lambda}$.

EXECUTE:
$$\Delta E = \frac{3\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(8.00 \times 10^{-11} \text{ m})^2} = 5.653 \times 10^{-17} \text{ J. } \Delta E = \frac{hc}{\lambda} \text{ gives}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{5.653 \times 10^{-17} \text{ J}} = 3.51 \times 10^{-9} \text{ m} = 3.51 \text{ nm}.$$

EVALUATE: This wavelength is much shorter than that of visible light.

41.4. IDENTIFY: Use the probability function for a particle in a three-dimensional box to find the points where it is a maximum.

(a) SET UP:
$$n_X = 1$$
, $n_Y = 1$, $n_Z = 1$. $|\psi|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2 \frac{\pi x}{L}\right) \left(\sin^2 \frac{\pi y}{L}\right) \left(\sin^2 \frac{\pi z}{L}\right)$.

EXECUTE: $|\psi|^2$ is maximum where $\sin \frac{\pi x}{L} = \pm 1$, $\sin \frac{\pi y}{L} = \pm 1$, and $\sin \frac{\pi z}{L} = \pm 1$. $\frac{\pi x}{L} = \frac{\pi}{2}$ and $x = \frac{L}{2}$.

The next larger value is $\frac{\pi x}{L} = \frac{3\pi}{2}$ and $x = \frac{3L}{2}$, but this is outside the box. Similar results obtain for y and z,

so $|\psi|^2$ is maximum at the point x = y = z = L/2. This point is at the center of the box.

(b) SET UP:
$$n_X = 2$$
, $n_Y = 2$, $n_Z = 1$. $|\psi|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2\frac{2\pi x}{L}\right) \left(\sin^2\frac{2\pi y}{L}\right) \left(\sin^2\frac{\pi z}{L}\right)$.

EXECUTE: $|\psi|^2$ is maximum where $\sin \frac{2\pi x}{L} = \pm 1$, $\sin \frac{2\pi y}{L} = \pm 1$, and $\sin \frac{\pi z}{L} = \pm 1$. $\frac{2\pi x}{L} = \frac{\pi}{2}$ and

 $x = \frac{L}{4}$. $\frac{2\pi x}{L} = \frac{3\pi}{2}$ and $x = \frac{3L}{4}$. Similarly, $y = \frac{L}{4}$ and $\frac{3L}{4}$. As in part (a), $z = \frac{L}{2}$. $|\psi|^2$ is a maximum at

the four points $\left(\frac{L}{4}, \frac{L}{4}, \frac{L}{2}\right)$, $\left(\frac{L}{4}, \frac{3L}{4}, \frac{L}{2}\right)$, $\left(\frac{3L}{4}, \frac{L}{4}, \frac{L}{2}\right)$, and $\left(\frac{3L}{4}, \frac{3L}{4}, \frac{L}{2}\right)$.

EVALUATE: The points are located symmetrically relative to the center of the box.

41.5. IDENTIFY: A particle is in a three-dimensional box. At what planes is its probability function zero?

SET UP:
$$\left| \psi_{2,2,1} \right|^2 = \left(\frac{L}{2} \right)^3 \left(\sin^2 \frac{2\pi x}{L} \right) \left(\sin^2 \frac{2\pi y}{L} \right) \left(\sin^2 \frac{\pi z}{L} \right).$$

EXECUTE: $|\psi_{2,2,1}|^2 = 0$ for $\frac{2\pi x}{L} = 0, \pi, 2\pi, \dots$ x = 0 and x = L correspond to walls of the box. $x = \frac{L}{2}$

is the other plane where $\left|\psi_{2,2,1}\right|^2 = 0$. Similarly, $\left|\psi_{2,2,1}\right|^2 = 0$ on the plane $y = \frac{L}{2}$. The $\sin^2\frac{\pi z}{L}$ factor is

zero only on the walls of the box. Therefore, for this state $|\psi_{2,2,1}|^2 = 0$ on the following two planes other than walls of the box: $x = \frac{L}{2}$ and $y = \frac{L}{2}$.

 $|\psi_{2,1,1}|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2\frac{2\pi x}{L}\right) \left(\sin^2\frac{\pi y}{L}\right) \left(\sin^2\frac{\pi z}{L}\right)$ is zero only on one plane (x = L/2) other than the walls

 $\left|\psi_{1,1,1}\right|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2\frac{\pi x}{L}\right) \left(\sin^2\frac{\pi y}{L}\right) \left(\sin^2\frac{\pi z}{L}\right)$ is zero only on the walls of the box; for this state there are

zero additional planes. **EVALUATE:** For comparison, (2,1,1) has two nodal planes, (2,1,1) has one nodal and (1,1,1) has no nodal planes. The number of nodal planes increases as the energy of the state increases.

41.6. IDENTIFY: A proton is in a cubical box approximately the size of the nucleus.

SET UP:
$$E_{1,1,1} = \frac{3\pi^2\hbar^2}{2mL^2}$$
. $E_{2,1,1} = \frac{6\pi^2\hbar^2}{2mL^2}$. $\Delta E = \frac{3\pi^2\hbar^2}{2mL^2}$.

EXECUTE:
$$\Delta E = \frac{3\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{2(1.673 \times 10^{-27} \text{ kg})(1.00 \times 10^{-14} \text{ m})^2} = 9.85 \times 10^{-13} \text{ J} = 6.15 \text{ MeV}$$

EVALUATE: This energy difference is much greater than the energy differences involving orbital electrons.

41.7. IDENTIFY: The possible values of the angular momentum are limited by the value of n.

SET UP: For the *N* shell n = 4, $0 \le l \le n - 1$, $|m| \le l$, $m_s = \pm \frac{1}{2}$.

EXECUTE: (a) The smallest *l* is l = 0. $L = \sqrt{l(l+1)}\hbar$, so $L_{\min} = 0$.

(b) The largest *l* is n-1=3 so $L_{\text{max}} = \sqrt{3(4)}\hbar = 2\sqrt{3}\hbar = 3.65 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}.$

(c) Let the chosen direction be the z-axis. The largest m is m = l = 3.

 $L_{z,\text{max}} = m\hbar = 3\hbar = 3.16 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}.$

(d) $S_z = \pm \frac{1}{2}\hbar$. The maximum value is $S_z = \hbar/2 = 5.27 \times 10^{-35} \text{ kg} \cdot \text{m}^2/\text{s}$.

(e)
$$\frac{S_z}{L_z} = \frac{\frac{1}{2}\hbar}{3\hbar} = \frac{1}{6}$$
.

EVALUATE: The orbital and spin angular momenta are of comparable sizes.

41.8. IDENTIFY and SET UP: $L = \sqrt{l(l+1)}\hbar$. $L_z = m_l\hbar$. l = 0, 1, 2, ..., n-1. $m_l = 0, \pm 1, \pm 2, ..., \pm l$. $\cos \theta = L_z/L$.

EXECUTE: (a) Use
$$L = \sqrt{l(l+1)}\hbar$$
.

$$\underline{l=0}$$
: $L=0$, $L_z=0$.

$$l=1: L = \sqrt{2}\hbar, L_z = \hbar, 0, -\hbar.$$

$$\underline{l=2}$$
: $L=\sqrt{6}\hbar$, $L_z=2\hbar$, \hbar , 0, $-\hbar$, $-2\hbar$.

$$\underline{l=3}$$
: $L=2\sqrt{3}\hbar$, $L_z=3\hbar$, $2\hbar$, \hbar , 0 , $-\hbar$, $-2\hbar$, $-3\hbar$.

$$\underline{l=4}$$
: $L=2\sqrt{5}\hbar$, $L_z=4\hbar$, $3\hbar$, $2\hbar$, \hbar , 0 , $-\hbar$, $-2\hbar$, $-3\hbar$, $-4\hbar$.

(b) Use $\cos \theta = L_{\tau}/L$.

L = 0: θ is not defined.

$$L = \sqrt{2}\hbar$$
: 45.0°, 90.0°, 135.0°.

$$L = \sqrt{6}\hbar$$
: 35.3°, 65.9°, 90.0°, 114.1°, 144.7°.

$$\underline{L} = 2\sqrt{3}\hbar$$
: 30.0°, 54.7°, 73.2°, 90.0°, 106.8°, 125.3°, 150.0°.

$$L = 2\sqrt{5}\hbar$$
: 26.6°, 47.9°, 63.4°, 77.1°, 90.0°, 102.9°, 116.6°, 132.1°, 153.4°.

(c) The minimum angle is 26.6° and occurs for l = 4, $m_l = +4$. The maximum angle is 153.4° and occurs for l = 4, $m_l = -4$.

EVALUATE: There is no state where \vec{L} is totally aligned along the z-axis.

41.9. IDENTIFY and **SET UP:** The magnitude of the orbital angular momentum L is related to the quantum number l by Eq. (41.22): $L = \sqrt{l(l+1)}\hbar$, l = 0, 1, 2, ...

EXECUTE:
$$l(l+1) = \left(\frac{L}{\hbar}\right)^2 = \left(\frac{4.716 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}}{1.055 \times 10^{-34} \text{ J} \cdot \text{s}}\right)^2 = 20.$$

And then l(l+1) = 20 gives that l = 4.

EVALUATE: *l* must be integer.

41.10. IDENTIFY and SET UP: $L = \sqrt{l(l+1)}\hbar$. $L_z = m_l\hbar$. $m_l = 0, \pm 1, \pm 2, ..., \pm l$. $\cos\theta = L_z/L$.

EXECUTE: (a) $(m_l)_{\text{max}} = 2$, so $(L_z)_{\text{max}} = 2\hbar$.

(b)
$$L = \sqrt{l(l+1)}\hbar = \sqrt{6}\hbar = 2.45\hbar$$
. L is larger than $(L_z)_{\text{max}}$.

(c) The angle is
$$\arccos\left(\frac{L_z}{L}\right) = \arccos\left(\frac{m_l}{\sqrt{6}}\right)$$
, and the angles are, for $m_l = -2$ to $m_l = +2$ are:

EVALUATE: The minimum angle for a given l is for $m_l = l$. The angle corresponding to $m_l = l$ will always be smaller for larger l.

41.11. IDENTIFY and **SET UP:** The smallest nonzero angle for a given l occurs for $m_l = +l$. $L = \sqrt{l(l+1)}\hbar$ and $L_z = m_l\hbar$ where $m_l = 0, \pm 1, \pm 2, ..., \pm l$. $\cos\theta = L_z/L$.

EXECUTE: In this case $\theta = 26.6^{\circ}$, so $\cos 26.6^{\circ} = \frac{l}{\sqrt{l(l+1)}}$. Squaring gives $l(l+1)\cos^2(26.6^{\circ}) = l^2$.

Solving for *l* gives
$$l = \frac{\cos^2(26.6^\circ)}{1 - \cos^2(26.6^\circ)} = 4.$$

EVALUATE: For l=4 we see that the angle between the angular momentum vector and the positive z-axis ranges from 26.6° ($m_l=+l$) to $180^{\circ}-26.6^{\circ}=153.4^{\circ}$ ($m_l=-l$).

41.12. IDENTIFY and **SET UP:** $L = \sqrt{l(l+1)}\hbar$. $\cos\theta_L = L_z/L$. We know that $L_z = 2\hbar$ in this case, and $\theta_L = 63.4^\circ$. For any n, l can have the values l = 0, 1, 2, ..., n - 1.

EXECUTE: (a) First find *L*: $L = \frac{L_z}{\cos \theta_L} = \frac{2\hbar}{\cos(63.4^\circ)} = 4.467\hbar$.

Now solve for *l*: $L = \sqrt{l(l+1)}\hbar = 4.467 \hbar \rightarrow l(l+1) = (4.467)^2 \approx 20 = 4(4+1)$, so l=4.

(b) The maximum that l can be is n-1, so $n-1 \ge l_{\max}$, which means that $n \ge l_{\max} + 1$. In this case, we know that l = 4, so $n \ge 5$, so the smallest that n could be is 5.

EVALUATE: Any n > 5 is also possible.

41.13. IDENTIFY and **SET UP:** The angular momentum *L* is related to the quantum number *l* by $L = \sqrt{l(l+1)}\hbar$.

The maximum l, l_{max} , for a given n is $l_{\text{max}} = n - 1$.

EXECUTE: For n = 2, $l_{\text{max}} = 1$ and $L = \sqrt{2}\hbar = 1.414\hbar$.

For n = 20, $l_{\text{max}} = 19$ and $L = \sqrt{(19)(20)\hbar} = 19.49\hbar$.

For n = 200, $l_{\text{max}} = 199$ and $L = \sqrt{(199)(200)}\hbar = 199.5\hbar$.

EVALUATE: As n increases, the maximum L gets closer to the value $n\hbar$ postulated in the Bohr model.

41.14. IDENTIFY: l = 0, 1, 2, ..., n-1. $m_l = 0, \pm 1, \pm 2, ..., \pm l$.

SET UP: $E_n = -\frac{13.60 \text{ eV}}{n^2}$.

EXECUTE: Since n = 4, l can have the values 0, 1, 2, and 3. For each value of l, m_l can range from -l to +l. Therefore the (l, m_l) combinations are $(0, 0), (1, 0), (1, \pm 1), (2, 0), (2, \pm 1), (2, \pm 2), (3, 0), (3, \pm 1), (3, \pm 2), and (3, \pm 3), a total of 16 combinations.$

(b) Each state has the same energy because *n* is the same for all of them, so $E = -\frac{13.60 \text{ eV}}{4^2} = -0.8500 \text{ eV}$.

EVALUATE: The number of l, m_l combinations is n^2 . The energy depends only on n, so is the same for all l, m_l states for a given n.

41.15. IDENTIFY: For the 5g state, l = 4, which limits the other quantum numbers.

SET UP: $m_l = 0, \pm 1, \pm 2, \dots, \pm l$. g means l = 4. $\cos \theta = L_z/L$, with $L = \sqrt{l(l+1)}\hbar$ and $L_z = m_l\hbar$.

EXECUTE: (a) There are eighteen 5g states: $m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4$, with $m_s = \pm \frac{1}{2}$ for each.

(b) The largest θ is for the most negative m_l . $L = 2\sqrt{5}\hbar$. The most negative L_z is $L_z = -4\hbar$.

 $\cos\theta = \frac{-4\hbar}{2\sqrt{5}\hbar}$ and $\theta = 153.4^{\circ}$.

(c) The smallest θ is for the largest positive m_l , which is $m_l = +4$. $\cos \theta = \frac{4\hbar}{2\sqrt{5}\hbar}$ and $\theta = 26.6^{\circ}$.

EVALUATE: The minimum angle between \vec{L} and the z-axis is for $m_l = +l$ and for that m_l , $\cos \theta = \frac{l}{\sqrt{l(l+1)}}$.

41.16. IDENTIFY: The probability is $P = \int_0^{a/2} |\psi_{1s}|^2 4\pi r^2 dr$.

SET UP: Use the expression for the integral given in Example 41.4.

EXECUTE: **(a)** $P = \frac{4}{a^3} \left[\left(-\frac{ar^2}{2} - \frac{a^2r}{2} - \frac{a^3}{4} \right) e^{-2r/a} \right]_0^{a/2} = 1 - \frac{5e^{-1}}{2} = 0.0803.$

(b) Example 41.4 calculates the probability that the electron will be found at a distance less than a from the nucleus. The difference in the probabilities is $(1-5e^{-2})-(1-(5/2)e^{-1})=(5/2)(e^{-1}-2e^{-2})=0.243$.

EVALUATE: The probability for distances from a/2 to a is about three times the probability for distances between 0 and a/2. This agrees with Figure 41.8 in the textbook; P(r) is maximum for r = a.

41.17. IDENTIFY: Require that $\Phi(\phi) = \Phi(\phi + 2\pi)$.

SET UP:
$$e^{i(x_1+x_2)} = e^{ix_1}e^{ix_2}$$
.

EXECUTE: $\Phi(\phi + 2\pi) = e^{im_l(\phi + 2\pi)} = e^{im_l\phi}e^{im_l2\pi}$. $e^{im_l2\pi} = \cos(m_l2\pi) + i\sin(m_l2\pi)$. $e^{im_l2\pi} = 1$ if m_l is an integer.

EVALUATE: If, for example, $m_l = \frac{1}{2}$, $e^{im_l 2\pi} = e^{i\pi} = \cos(\pi) + i\sin(\pi) = -1$ and $\Phi(\phi) = -\Phi(\phi + 2\pi)$. But if $m_l = 1$, $e^{im_l 2\pi} = e^{i2\pi} = \cos(2\pi) + i\sin(2\pi) = +1$ and $\Phi(\phi) = \Phi(\phi + 2\pi)$, as required.

41.18. IDENTIFY: Apply $\Delta E = \mu_B B$.

SET UP: $\mu_{\rm B} = 5.788 \times 10^{-5} \text{ eV/T}.$

EXECUTE: (a) $\Delta E = \mu_B B = (5.79 \times 10^{-5} \text{ eV/T})(0.800 \text{ T}) = 4.63 \times 10^{-5} \text{ eV}.$

- **(b)** $m_1 = -2$ the lowest possible value of m_1 .
- (c) The energy level diagram is sketched in Figure 41.18.

$$l = 2 (d)$$
; field on $m_1 = +2$
 $l = 2 (d)$; no field $m_1 = +1$
 $m_1 = 0$
 $m_1 = -1$
 $m_1 = -2$

Figure 41.18

EVALUATE: The splitting between m_l levels is independent of the n values for the state. The splitting is much less than the energy difference between the n=3 level and the n=1 level.

41.19. IDENTIFY: Apply $\Delta U = \mu_B B$.

SET UP: For a 3*p* state, l = 1 and $m_l = 0, \pm 1$.

EXECUTE: **(a)**
$$B = \frac{U}{\mu_{\rm B}} = \frac{(2.71 \times 10^{-5} \text{ eV})}{(5.79 \times 10^{-5} \text{ eV/T})} = 0.468 \text{ T}.$$

(b) Three: $m_l = 0, \pm 1$.

EVALUATE: The $m_l = +1$ level will be highest in energy and the $m_l = -1$ level will be lowest. The $m_l = 0$ level is unaffected by the magnetic field.

41.20. IDENTIFY: The effect of the magnetic field on the energy levels is described by Eq. (41.36). In a transition m_l must change by 0 or ± 1 .

SET UP: For a 2p state, m_1 can be $0, \pm 1$. For a 1s state, m_1 must be zero.

EXECUTE: (a) There are three different transitions that are consistent with the selection rules. The initial m_l values are $0, \pm 1$; and the final m_l value is 0.

- **(b)** The transition from $m_l = 0$ to $m_l = 0$ produces the same wavelength (122 nm) that was seen without the magnetic field.
- (c) The larger wavelength (smaller energy) is produced from the $m_l = -1$ to $m_l = 0$ transition.
- (d) The shorter wavelength (greater energy) is produced from the $m_l = +1$ to $m_l = 0$ transition.

EVALUATE: The magnetic field increases the energy of the $m_l = 1$ state, decreases the energy for $m_l = -1$ and leaves the $m_l = 0$ state unchanged.

41.21. IDENTIFY and **SET UP:** The interaction energy between an external magnetic field and the orbital angular momentum of the atom is given by $U = m_l \mu_B B$. The energy depends on m_l with the most negative m_l value having the lowest energy.

EXECUTE: (a) For the 5g level, l=4 and there are 2l+1=9 different m_l states. The 5g level is split into 9 levels by the magnetic field.

(b) Each m_l level is shifted in energy an amount given by $U = m_l \mu_B B$. Adjacent levels differ in m_l by one, so $\Delta U = \mu_B B$.

$$\mu_{\rm B} = \frac{e\hbar}{2m} = \frac{(1.602 \times 10^{-19} \text{ C})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{2(9.109 \times 10^{-31} \text{ kg})} = 9.277 \times 10^{-24} \text{ A} \cdot \text{m}^2$$

 $\Delta U = \mu_{\rm B} B = (9.277 \times 10^{-24} \text{ A/m}^2)(0.600 \text{ T}) = 5.566 \times 10^{-24} \text{ J} (1 \text{ eV}/1.602 \times 10^{-19} \text{ J}) = 3.47 \times 10^{-5} \text{ eV}$

(c) The level of highest energy is for the largest m_l , which is $m_l = l = 4$; $U_4 = 4\mu_B B$. The level of lowest energy is for the smallest m_l , which is $m_l = -l = -4$; $U_{-4} = -4\mu_B B$. The separation between these two levels is $U_4 - U_{-4} = 8\mu_B B = 8(3.47 \times 10^{-5} \text{ eV}) = 2.78 \times 10^{-4} \text{ eV}$.

EVALUATE: The energy separations are proportional to the magnetic field. The energy of the n = 5 level in the absence of the external magnetic field is $(-13.6 \text{ eV})/5^2 = -0.544 \text{ eV}$, so the interaction energy with the magnetic field is much less than the binding energy of the state.

41.22. IDENTIFY: Apply the equation $\mu_z = -(2.00232) \frac{e}{2m} S_z$ with $S_z = -\frac{\hbar}{2}$.

SET UP: $\mu_{\rm B} = \frac{e\hbar}{2m} = 5.788 \times 10^{-5} \text{ eV/T}.$

EXECUTE: **(a)** $U = +(2.00232) \left(\frac{e}{2m}\right) \left(\frac{-\hbar}{2}\right) B = -\frac{2.00232}{2} \mu_{\text{B}} B.$

 $U = -\frac{2.00232}{2} (5.788 \times 10^{-5} \text{ eV/T}) (1.60 \text{ T}) = -9.27 \times 10^{-5} \text{ eV}.$

(b) Since n = 1, l = 0 so there is no orbital magnetic dipole interaction. But if $n \ne 1$ there could be orbital magnetic dipole interaction, since l < n would then allow for $l \ne 0$.

EVALUATE: The energy of the $m_s = -\frac{1}{2}$ state is lowered in the magnetic field. The energy of the $m_s = +\frac{1}{2}$ state is raised.

41.23. IDENTIFY and **SET UP:** For a classical particle $L = I\omega$. For a uniform sphere with mass m and radius R,

 $I = \frac{2}{5}mR^2$, so $L = \left(\frac{2}{5}mR^2\right)\omega$. Solve for ω and then use $v = r\omega$ to solve for v.

EXECUTE: (a) $L = \sqrt{\frac{3}{4}}\hbar$ so $\frac{2}{5}mR^2\omega = \sqrt{\frac{3}{4}}\hbar$.

 $\omega = \frac{5\sqrt{3/4}\hbar}{2mR^2} = \frac{5\sqrt{3/4}(1.055\times10^{-34} \text{ J} \cdot \text{s})}{2(9.109\times10^{-31} \text{ kg})(1.0\times10^{-17} \text{ m})^2} = 2.5\times10^{30} \text{ rad/s}.$

(b) $v = r\omega = (1.0 \times 10^{-17} \text{ m})(2.5 \times 10^{30} \text{ rad/s}) = 2.5 \times 10^{13} \text{ m/s}.$

EVALUATE: This is much greater than the speed of light c, so the model cannot be valid.

41.24. IDENTIFY: The transition energy ΔE of the atom is related to the wavelength λ of the photon by

 $\Delta E = \frac{hc}{\lambda}$. For an electron in a magnetic field the spin magnetic interaction energy is $\pm \mu_B B$. Therefore the effective magnetic field is given by $\Delta E = 2\mu_B B$ when ΔE is produced by the hyperfine interaction.

SET UP: $\mu_{\rm B} = 5.788 \times 10^{-5} \,\text{eV/T}.$

EXECUTE: **(a)** $\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{(5.9 \times 10^{-6} \text{ eV})} = 21 \text{ cm},$

 $f = \frac{c}{\lambda} = \frac{(3.00 \times 10^8 \text{ m/s})}{0.21 \text{ m}} = 1.4 \times 10^9 \text{ Hz}$, a short radio wave.

(b) The effective field is $B \cong \Delta E/2\mu_{\rm B} = 5.1 \times 10^{-2}$ T, far smaller than that found in Example 41.7 for spin-orbit coupling.

EVALUATE: The level splitting due to the hyperfine interaction is much smaller than the level splittings due to the spin-orbit interaction.

41.25. IDENTIFY and **SET UP:** The interaction energy is $U = -\vec{\mu} \cdot \vec{B}$, with μ_z given by

$$\mu_z = -(2.00232) \left(\frac{e}{2m}\right) S_z.$$

EXECUTE: $U = -\vec{\mu} \cdot \vec{B} = +\mu_z B$, since the magnetic field is in the negative z-direction.

$$\mu_z = -(2.00232) \left(\frac{e}{2m}\right) S_z$$
, so $U = -(2.00232) \left(\frac{e}{2m}\right) S_z B$.

$$S_z = m_s \hbar$$
, so $U = -2.00232 \left(\frac{e\hbar}{2m}\right) m_s B$.

$$\frac{e\hbar}{2m} = \mu_{\rm B} = 5.788 \times 10^{-5} \text{ eV/T}.$$

$$U = -2.00232 \mu_{\rm B} m_s B$$
.

The $m_s = +\frac{1}{2}$ level has lower energy.

$$\Delta U = U(m_s = -\frac{1}{2}) - U(m_s = +\frac{1}{2}) = -2.00232 \ \mu_B B(-\frac{1}{2} - (+\frac{1}{2})) = +2.00232 \ \mu_B B.$$

$$\Delta U = +2.00232(5.788 \times 10^{-5} \text{ eV/T})(1.45 \text{ T}) = 1.68 \times 10^{-4} \text{ eV}.$$

EVALUATE: The interaction energy with the electron spin is the same order of magnitude as the interaction energy with the orbital angular momentum for states with $m_l \neq 0$. But a 1s state has

l = 0 and $m_l = 0$, so there is no orbital magnetic interaction.

41.26. IDENTIFY and **SET UP:** *j* can have the values l+1/2 and l-1/2. The energy levels due to spin-orbit

coupling are
$$E_{n,j} = -\frac{13.60 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right].$$

EXECUTE: (a) If j takes the values 7/2 and 9/2 it must be that l - 1/2 = 7/2 and l = 8/2 = 4. The letter that labels this l is g.

(b) Use the equation
$$E_{n,j} = -\frac{13.60 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]$$
 to calculate the energy for each value of j and

then take the difference in these energies. The effect of spin-orbit coupling is very small, so we don't do all of the arithmetic until the end since we are subtracting the two energies.

$$E_{5,9/2} = -\frac{13.60 \text{ eV}}{5^2} \left[1 + \frac{(7.2974 \times 10^{-3})^2}{5^2} \left(\frac{5}{\frac{9}{2} + \frac{1}{2}} - \frac{3}{4} \right) \right] = -\frac{13.60 \text{ eV}}{5^2} (1 + 5.325 \times 10^{-7}).$$

$$E_{5,7/2} = -\frac{13.60 \text{ eV}}{5^2} \left| 1 + \frac{(7.2974 \times 10^{-3})^2}{5^2} \left(\frac{5}{\frac{7}{2} + \frac{1}{2}} - \frac{3}{4} \right) \right| = -\frac{13.60 \text{ eV}}{5^2} (1 + 10.650 \times 10^{-7}).$$

$$\Delta E = E_{5,9/2} - E_{5,7/2} = \frac{13.60 \text{ eV}}{5^2} (10.650 \times 10^{-7} - 5.325 \times 10^{-7}) = 2.90 \times 10^{-7} \text{ eV}.$$

EVALUATE: The very small energy difference in (b) is due to spin-orbit coupling. Without spin-orbit coupling, the energy of an n = 5 electron would be $(13.60 \text{ eV})/5^2 = 0.544 \text{ eV}$. The effect due to spin-orbit coupling is obviously *much* smaller than this.

41.27. IDENTIFY: The ten lowest energy levels for electrons are in the n = 1 and n = 2 shells.

SET UP:
$$l = 0, 1, 2, ..., n-1$$
. $m_l = 0, \pm 1, \pm 2, ..., \pm l$. $m_s = \pm \frac{1}{2}$

EXECUTE:
$$n = 1, l = 0, m_l = 0, m_s = \pm \frac{1}{2}$$
: 2 states. $n = 2, l = 0, m_l = 0, m_s = \pm \frac{1}{2}$: 2 states.

$$n = 2, l = 1, m_l = 0, \pm 1, m_s = \pm \frac{1}{2}$$
: 6 states.

EVALUATE: The ground state electron configuration for neon is $1s^2 2s^2 2p^6$. The electron configuration specifies the *n* and *l* quantum numbers for each electron.

41.28. IDENTIFY: Fill the subshells in the order of increasing energy. An *s* subshell holds 2 electrons, a *p* subshell holds 6, and a *d* subshell holds 10 electrons.

SET UP: Germanium has 32 electrons.

EXECUTE: The electron configuration is
$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^2$$
.

EVALUATE: The electron configuration is that of zinc (Z = 30) plus two electrons in the 4p subshell.

41.29. IDENTIFY: Write out the electron configuration for ground-state beryllium.

SET UP: Beryllium has 4 electrons.

EXECUTE: (a)
$$1s^2 2s^2$$
.

(b) $1s^2 2s^2 2p^6 3s^2$. Z = 12 and the element is magnesium.

(c)
$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$$
. $Z = 20$ and the element is calcium.

EVALUATE: Beryllium, calcium, and magnesium are all in the same column of the periodic table.

41.30. IDENTIFY: Write out the electron configuration for ground-state carbon.

SET UP: Carbon has 6 electrons.

EXECUTE: (a)
$$1s^2 2s^2 2p^2$$
.

(b) The element of next larger Z with a similar electron configuration has configuration $1s^2 2s^2 2p^6 3s^2 3p^2$. Z = 14 and the element is silicon.

EVALUATE: Carbon and silicon are in the same column of the periodic table.

41.31. IDENTIFY and **SET UP:** The energy of an atomic level is given in terms of n and Z_{eff} by

$$E_n = -\left(\frac{Z_{\text{eff}}^2}{n^2}\right)$$
 (13.6 eV). The ionization energy for a level with energy $-E_n$ is $+E_n$.

EXECUTE:
$$n = 5$$
 and $Z_{eff} = 2.771$ gives $E_5 = -\frac{(2.771)^2}{5^2}(13.6 \text{ eV}) = -4.18 \text{ eV}.$

The ionization energy is 4.18 eV.

EVALUATE: The energy of an atomic state is proportional to Z_{eff}^2 .

41.32. IDENTIFY and **SET UP:** Apply $E_n = -\left(\frac{Z_{\text{eff}}^2}{n^2}\right)$ (13.6 eV).

EXECUTE: For the 4s state, E = -4.339 eV and $Z_{\text{eff}} = 4\sqrt{(-4.339)/(-13.6)} = 2.26$. Similarly,

 $Z_{\text{eff}} = 1.79$ for the 4p state and 1.05 for the 4d state.

EVALUATE: The electrons in the states with higher *l* tend to be farther away from the filled subshells and the screening is more complete.

41.33. IDENTIFY and SET UP: Use the exclusion principle to determine the ground-state electron configuration, as in Table 41.3. Estimate the energy by estimating Z_{eff} , taking into account the electron screening of the

EXECUTE: (a) Z = 7 for nitrogen so a nitrogen atom has 7 electrons. N^{2+} has 5 electrons: $1s^2 2s^2 2p$.

(b) $Z_{\text{eff}} = 7 - 4 = 3$ for the 2*p* level.

$$E_n = -\left(\frac{Z_{\text{eff}}^2}{n^2}\right) (13.6 \text{ eV}) = -\frac{3^2}{2^2} (13.6 \text{ eV}) = -30.6 \text{ eV}.$$

(c) Z = 15 for phosphorus so a phosphorus atom has 15 electrons.

$$P^{2+}$$
 has 13 electrons: $1s^2 2s^2 2p^6 3s^2 3p$.

(d)
$$Z_{\text{eff}} = 15 - 12 = 3$$
 for the $3p$ level.

$$E_n = -\left(\frac{Z_{\text{eff}}^2}{n^2}\right) (13.6 \text{ eV}) = -\frac{3^2}{3^2} (13.6 \text{ eV}) = -13.6 \text{ eV}.$$

EVALUATE: In these ions there is one electron outside filled subshells, so it is a reasonable approximation to assume full screening by these inner-subshell electrons.

41.34. IDENTIFY and **SET UP:** Apply
$$E_n = \frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV}).$$

EXECUTE: (a)
$$E_2 = -\frac{13.6 \text{ eV}}{4} Z_{\text{eff}}^2$$
, so $Z_{\text{eff}} = 1.26$.

(b) Similarly,
$$Z_{\text{eff}} = 2.26$$
.

EVALUATE: (c) Z_{eff} becomes larger going down a column in the periodic table. Screening is less complete as n of the outermost electron increases.

41.35. IDENTIFY and **SET UP:** Estimate Z_{eff} by considering electron screening and use Eq. (41.45) to calculate the energy. Z_{eff} is calculated as in Example 41.9.

EXECUTE: (a) The element Be has nuclear charge Z = 4. The ion Be⁺ has 3 electrons. The outermost electron sees the nuclear charge screened by the other two electrons so $Z_{\text{eff}} = 4 - 2 = 2$.

$$E_n = -\left(\frac{Z_{\text{eff}}^2}{n^2}\right) (13.6 \text{ eV}) \text{ so } E_2 = -\frac{2^2}{2^2} (13.6 \text{ eV}) = -13.6 \text{ eV}.$$

(b) The outermost electron in Ca⁺ sees a
$$Z_{\text{eff}} = 2$$
. $E_4 = -\frac{2^2}{4^2}(13.6 \text{ eV}) = -3.4 \text{ eV}$

EVALUATE: For the electron in the highest *l*-state it is reasonable to assume full screening by the other electrons, as in Example 41.9. The highest *l*-states of Be⁺, Mg⁺, Ca⁺, etc. all have a $Z_{\text{eff}} = 2$. But the energies are different because for each ion the outermost sublevel has a different *n* quantum number.

41.36. IDENTIFY and **SET UP:** Apply Eq. (41.48) and solve for Z.

EXECUTE:
$$E_{K\alpha} \cong (Z-1)^2 (10.2 \text{ eV})$$
. $Z \approx 1 + \sqrt{\frac{7.46 \times 10^3 \text{ eV}}{10.2 \text{ eV}}} = 28.0$, which corresponds to the element

Nickel (Ni).

EVALUATE: We use Z-1 rather than Z in the expression for the transition energy, in order to account for screening by the other K-shell electron.

41.37. IDENTIFY and SET UP: Apply $E_{K\alpha} \cong (Z-1)^2 (10.2 \text{ eV})$. E = hf and $c = f\lambda$.

EXECUTE: (a)
$$Z = 20$$
: $f = (2.48 \times 10^{15} \text{ Hz})(20 - 1)^2 = 8.95 \times 10^{17} \text{ Hz}$.

$$E = hf = (4.14 \times 10^{-15} \text{ eV} \cdot \text{s})(8.95 \times 10^{17} \text{ Hz}) = 3.71 \text{ keV}. \quad \lambda = \frac{c}{f} = \frac{3.00 \times 10^8 \text{ m/s}}{8.95 \times 10^{17} \text{ Hz}} = 3.35 \times 10^{-10} \text{ m}.$$

(b)
$$Z = 27$$
: $f = 1.68 \times 10^{18}$ Hz. $E = 6.96$ keV. $\lambda = 1.79 \times 10^{-10}$ m.

(c)
$$Z = 48$$
: $f = 5.48 \times 10^{18}$ Hz, $E = 22.7$ keV, $\lambda = 5.47 \times 10^{-11}$ m.

EVALUATE: f and E increase and λ decreases as Z increases.

41.38. IDENTIFY: The energies of the x rays will be equal to the energy differences between the shells. From its energy, we can calculate the wavelength of the x ray.

SET UP: $\Delta E = \frac{hc}{\lambda}$. A K_{α} x ray is produced in a $L \to K$ transition and a K_{β} x ray is produced in a $M \to K$ transition.

EXECUTE: K_{α} : $\Delta E = E_L - E_K = -12,000 \text{ eV} - (-69,500 \text{ eV}) = +57,500 \text{ eV}.$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{57,500 \text{ eV}} = 0.0216 \text{ nm}.$$

$$K_B$$
: $\Delta E = E_M - E_K = -2200 \text{ eV} - (-69,500 \text{ eV}) = +67,300 \text{ eV}.$

$$\lambda = \frac{hc}{\Delta E} = \frac{(4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{67,300 \text{ eV}} = 0.0184 \text{ nm}.$$

EVALUATE: These wavelengths are much shorter than the wavelengths in the visible spectrum of hydrogen.

41.39. IDENTIFY: The electrons cannot all be in the same state in a cubical box.

SET UP and **EXECUTE:** The ground state can hold 2 electrons, the first excited state can hold 6 electrons, and the second excited state can hold 6. Therefore, two electrons will be in the second excited state, which has energy $3E_{1,1,1}$.

EVALUATE: The second excited state is the third state, which has energy $3E_{1,1,1}$, as shown in Figure 41.4.

41.40. IDENTIFY: For a rectangular box having sides of lengths L_X , L_Y , and L_Z , the possible energy levels of an

electron in the box are
$$E_{n_X, n_Y, n_Z} = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2} + \frac{n_Z^2}{L_Z^2}\right) \frac{\pi^2 \hbar^2}{2m}$$
, where n_X , n_Y , and $n_Z = 1, 2, 3, ...$

SET UP: For this box, we know that $L_X = 0.600$ nm and $L_Y = L_Z = 2L_X = 1.20$ nm. Using $L_Y = L_Z = 2L_X$, the energy levels can be written as

$$E_{n_X,n_Y,n_Z} = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{4L_Y^2} + \frac{n_Z^2}{4L_Z^2}\right) \frac{\pi^2 \hbar^2}{2m} = \left(4n_X^2 + n_Y^2 + n_Z^2\right) \frac{\pi^2 \hbar^2}{8mL_X^2} = \left(4n_X^2 + n_Y^2 + n_Z^2\right) E_0.$$

EXECUTE: First calculate
$$E_0$$
:
$$E_0 = \frac{\pi^2 \hbar^2}{8mL_X^2} = \frac{\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{8(9.109 \times 10^{-31} \text{ kg})(0.600 \times 10^{-9} \text{ m})^2} = 4.1846 \times 10^{-20} \text{ J} = 0.2612 \text{ eV}.$$
First (lowest) state: $n_1 = n_2 = n_3 = 1$, so the state is $(1, 1, 1)$ and the energy is E_1 .

<u>First (lowest) state</u>: $n_X = n_Y = n_Z = 1$, so the state is (1, 1, 1) and the energy is $E_{1,1,1}$. Using the information we have gives $E_{1,1,1} = [4(1^2) + 1^2 + 1^2]E_0 = 6E_0 = 6(0.2612 \text{ eV}) = 1.57 \text{ eV}$.

The degeneracy in just the quantum numbers is just 1 because there is only one set of quantum numbers that will give this energy. But the electron has 2 spin states, so the degeneracy is 2.

Second state: The quantum numbers are $n_X = 1$, $n_Y = 2$, $n_Z = 1$ and $n_X = 1$, $n_Y = 1$, $n_Z = 2$. Both sets give the same energy, so the degeneracy is 4 (including spin). The states are (1, 2, 1) and

(1, 1, 2). The energy is $E_{1,2,1} = E_{1,1,2} = [4(1^2) + 1^2 + 2^2]E_0 = 9E_0 = 9(0.2612 \text{ eV}) = 2.35 \text{ eV}.$

Third state: The state is (1, 2, 2), and it has degeneracy 2 (including spin). The energy is

$$\overline{E_{1,2,2}} = [4(1^2) + 2^2 + 2^2]E_0 = 12E_0 = 12(0.2612 \text{ eV}) = 3.13 \text{ eV}.$$

Fourth state: The possibilities are (1, 3, 1) and (1, 1, 3), so the degeneracy is 4 (including spin). The energy is $E_{1,3,1} = E_{1,1,3} = [4(1^2) + 3^2 + 1^2]E_0 = 14E_0 = 14(0.2612 \text{ eV}) = 3.66 \text{ eV}.$

EVALUATE: These energy states are all higher than the n = 3 state of hydrogen, which is 1.51 eV.

- 41.41. IDENTIFY: Calculate the probability of finding a particle in a given region within a cubical box.
 - (a) SET UP and EXECUTE: The box has volume L^3 . The specified cubical space has volume $(L/4)^3$. Its

fraction of the total volume is $\frac{1}{64} = 0.0156$.

(b) SET UP and **EXECUTE:** $P = \left(\frac{2}{I}\right)^3 \left[\int_0^{L/4} \sin^2 \frac{\pi x}{I} dx\right] \left[\int_0^{L/4} \sin^2 \frac{\pi y}{I} dy\right] \left[\int_0^{L/4} \sin^2 \frac{\pi z}{I} dz\right].$

From Example 41.1, each of the three integrals equals $\frac{L}{8} - \frac{L}{4\pi} = \frac{1}{2} \left(\frac{L}{2}\right) \left(\frac{1}{2} - \frac{1}{\pi}\right)$.

$$P = \left(\frac{2}{L}\right)^3 \left(\frac{L}{2}\right)^3 \left(\frac{1}{2}\right)^3 \left(\frac{1}{2} - \frac{1}{\pi}\right)^3 = 7.50 \times 10^{-4}.$$

EVALUATE: Note that this is the cube of the probability of finding the particle anywhere between x = 0 and x = L/4. This probability is much less that the fraction of the total volume that this space represents. In this quantum state the probability distribution function is much larger near the center of the box than near its walls.

(c) SET UP and EXECUTE:
$$|\psi_{2,1,1}|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2 \frac{2\pi x}{L}\right) \left(\sin^2 \frac{\pi y}{L}\right) \left(\sin^2 \frac{\pi z}{L}\right).$$

$$P = \left(\frac{2}{L}\right)^3 \left[\int_0^{L/4} \sin^2 \frac{2\pi x}{L} dx\right] \left[\int_0^{L/4} \sin^2 \frac{\pi y}{L} dy\right] \left[\int_0^{L/4} \sin^2 \frac{\pi z}{L} dz\right].$$

$$\left[\int_0^{L/4} \sin^2 \frac{\pi y}{L} dy\right] = \left[\int_0^{L/4} \sin^2 \frac{\pi z}{L} dz\right] = \frac{L}{2} \left(\frac{1}{2}\right) \left(\frac{1}{2} - \frac{1}{\pi}\right). \int_0^{L/4} \sin^2 \frac{2\pi x}{L} dx = \frac{L}{8}$$

$$P = \left(\frac{2}{L}\right)^3 \left(\frac{L}{2}\right)^2 \left(\frac{1}{2}\right)^2 \left(\frac{1}{2} - \frac{1}{\pi}\right)^2 \left(\frac{L}{8}\right) = 2.06 \times 10^{-3}.$$

EVALUATE: This is about a factor of three larger than the probability when the particle is in the ground state. **41.42. IDENTIFY:** For a rectangular box having sides of lengths L_X , L_Y , and L_Z , the possible energy levels of an

electron in the box are $E_{n_X, n_Y, n_Z} = \left(\frac{n_X^2}{I_{xy}^2} + \frac{n_Y^2}{I_{xy}^2} + \frac{n_Z^2}{I_{xy}^2}\right) \frac{\pi^2 \hbar^2}{2m}$, where n_X , n_Y , and $n_Z = 1, 2, 3, ...$

SET UP: For this box, we know that $L_X = L_Z$. We also know that the two lowest energy levels are 2.24 eV and 3.47 eV and both of these levels have degeneracy 2 including electron spin. Using $L_X = L_Z$, the energy

levels can be written as
$$E_{n_X,n_Y,n_Z} = \left(\frac{n_X^2 + n_Z^2}{L_Y^2} + \frac{n_Y^2}{L_Y^2}\right) \frac{\pi^2 \hbar^2}{2m}$$
.

EXECUTE: (a) Looking at the possibilities for the quantum numbers, we see that the two lowest levels having degeneracy 2 are (1, 1, 1) and (1, 2, 1). Therefore $E_{1,1,1} = 2.24$ eV and $E_{1,2,1} = 3.47$ eV. (We cannot have $E_{1,1,2}$ because it is degenerate with $E_{2,1,1}$ so this state would have degeneracy 4 including spin.)

(b) Using the numbers we know gives
$$E_{1,1,1} = \left(\frac{1^2+1^2}{L_X^2} + \frac{1^2}{L_Y^2}\right) \frac{\pi^2 \hbar^2}{2m}$$
 and $E_{1,2,1} = \left(\frac{1^2+1^2}{L_X^2} + \frac{2^2}{L_Y^2}\right) \frac{\pi^2 \hbar^2}{2m}$.

Subtracting these two equations gives $\frac{3}{L_Y^2} \left(\frac{\pi^2 \hbar^2}{2m} \right) = 3.47 \text{ eV} - 2.24 \text{ eV} = 1.23 \text{ eV}.$

Solving for L_Y gives $L_Y = \sqrt{\frac{3\pi^2\hbar^2}{2m(1.23 \text{ eV})}} = 9.58 \times 10^{-10} \text{ m} = 0.958 \text{ nm}$. Now use this result to solve for L_X

and
$$L_Z$$
. Using the $E_{1,1,1}$ equation gives $\frac{2}{L_X^2} = (2.24 \text{ eV}) \left(\frac{2\text{m}}{\pi^2 \hbar^2}\right) - \frac{1}{L_Y^2}$. Using $L_Y = 0.958 \text{ nm}$, gives

 $L_X = L_Z = 0.641$ nm.

(c) The next higher energy state is (1, 1, 2) and (2, 1, 1), which has degeneracy 4 (including spin). The

energy is
$$E_{1,1,2} = \left(\frac{1+2^2}{L_X^2} + \frac{1}{L_Y^2}\right) \left(\frac{\pi^2 \hbar^2}{2m}\right) = \left[\frac{5}{(0.641 \text{ nm})^2} + \frac{1}{(0.958 \text{ nm})^2}\right] \left(\frac{\pi^2 \hbar^2}{2m}\right) = 5.00 \text{ eV} = E_{2,1,1}.$$

EVALUATE: The longest side of this box is about 9 times the diameter of the Bohr hydrogen atom, and the shorter sides are each about 6 times that diameter.

41.43. IDENTIFY: Calculate the probability of finding a particle in certain regions of a three-dimensional box.

SET UP:
$$|\psi_{1,1,1}|^2 = \left(\frac{L}{2}\right)^3 \left(\sin^2\frac{\pi x}{L}\right) \left(\sin^2\frac{\pi y}{L}\right) \left(\sin^2\frac{\pi z}{L}\right)$$
.

EXECUTE: (a)
$$P = \left(\frac{2}{L}\right)^3 \left[\int_0^{L/2} \sin^2 \frac{\pi x}{L} dx\right] \left[\int_0^L \sin^2 \frac{\pi y}{L} dy\right] \left[\int_0^L \sin^2 \frac{\pi z}{L} dz\right].$$

$$\left[\int_{0}^{L} \sin^{2} \frac{\pi y}{L} dy \right] = \left[\int_{0}^{L} \sin^{2} \frac{\pi z}{L} dz \right] = \frac{L}{2}. \quad \int_{0}^{L/2} \sin^{2} \frac{\pi x}{L} dx = \left[\frac{x}{2} - \frac{L}{4\pi} \sin \frac{2\pi x}{L} \right]_{0}^{L/2} = \left(\frac{L}{2} \right) \left(\frac{1}{2} \right).$$

$$P = \left(\frac{2}{L} \right)^{3} \left(\frac{L}{2} \right)^{3} \left(\frac{1}{2} \right) = \frac{1}{2} = 0.500.$$

$$(b) \quad P = \left(\frac{2}{L} \right)^{3} \left[\int_{L/4}^{L/2} \sin^{2} \frac{\pi x}{L} dx \right] \left[\int_{0}^{L} \sin^{2} \frac{\pi y}{L} dy \right] \left[\int_{0}^{L} \sin^{2} \frac{\pi z}{L} dz \right].$$

$$\left[\int_{0}^{L} \sin^{2} \frac{\pi y}{L} dy \right] = \left[\int_{0}^{L} \sin^{2} \frac{\pi z}{L} dz \right] = \frac{L}{2}. \quad \int_{L/4}^{L/2} \sin^{2} \frac{\pi x}{L} dx = \left[\frac{x}{2} - \frac{L}{4\pi} \sin \frac{2\pi x}{L} \right]_{L/4}^{L/2} = \left(\frac{L}{2} \right) \left(\frac{1}{4} + \frac{1}{2\pi} \right).$$

$$P = \left(\frac{2}{L} \right)^{3} \left(\frac{L}{2} \right)^{3} \left(\frac{1}{4} + \frac{1}{2\pi} \right) = \frac{1}{4} + \frac{1}{2\pi} = 0.409.$$

EVALUATE: In Example 41.1 for this state the probability for finding the particle between x = 0 and x = L/4 is 0.091. The sum of this result and our result in part (b) is 0.091 + 0.409 = 0.500. This in turn equals the probability of finding the particle in half the box, as calculated in part (a).

41.44. IDENTIFY and **SET UP:** Evaluate $\partial^2 \psi / \partial x^2$, $\partial^2 \psi / \partial y^2$, and $\partial^2 \psi / \partial z^2$ for the proposed ψ and put into Eq. (41.5). Use that ψ_{n_x} , ψ_{n_y} , and ψ_{n_z} are each solutions to Eq. (40.44).

EXECUTE: **(a)**
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = E\psi.$$

$$\psi_{n_x}$$
, ψ_{n_y} , ψ_{n_z} are each solutions of Eq. (40.44), so $-\frac{\hbar^2}{2m}\frac{d^2\psi_{n_x}}{dx^2} + \frac{1}{2}k'x^2\psi_{n_x} = E_{n_x}\psi_{n_x}$.

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{n_y}}{dy^2} + \frac{1}{2}k'y^2\psi_{n_y} = E_{n_y}\psi_{n_y}.$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{n_z}}{dz^2} + \frac{1}{2}k'z^2\psi_{n_z} = E_{n_z}\psi_{n_z}.$$

$$\psi = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z), U = \frac{1}{2}k'x^2 + \frac{1}{2}k'y^2 + \frac{1}{2}k'z^2.$$

$$\frac{\partial^2 \psi}{\partial x^2} = \left(\frac{d^2 \psi_{n_x}}{dx^2}\right) \psi_{n_y} \psi_{n_z}, \quad \frac{\partial^2 \psi}{\partial y^2} = \left(\frac{d^2 \psi_{n_y}}{dy^2}\right) \psi_{n_x} \psi_{n_z}, \quad \frac{\partial^2 \psi}{\partial z^2} = \left(\frac{d^2 \psi_{n_z}}{dz^2}\right) \psi_{n_x} \psi_{n_y}.$$

So
$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = \left(-\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_x}}{dx^2} + \frac{1}{2} k' x^2 \psi_{n_x} \right) \psi_{n_y} \psi_{n_z}$$

$$+ \left(-\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_y}}{dy^2} + \frac{1}{2} k' y^2 \psi_{n_y} \right) \psi_{n_x} \psi_{n_z} + \left(-\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_z}}{dz^2} + \frac{1}{2} k' z^2 \psi_{n_z} \right) \psi_{n_x} \psi_{n_y}$$

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = (E_{n_x} + E_{n_y} + E_{n_z})\psi.$$

Therefore, we have shown that this ψ is a solution to Eq. (41.5), with energy

$$E_{n_x n_y n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \left(n_x + n_y + n_z + \frac{3}{2}\right)\hbar\omega.$$

(b) and **(c)** The ground state has $n_x = n_y = n_z = 0$, so the energy is $E_{000} = \frac{3}{2}\hbar\omega$. There is only one set of n_x , n_y , and n_z that give this energy.

First-excited state:

$$n_x = 1$$
, $n_y = n_z = 0$ or $n_y = 1$, $n_x = n_z = 0$ or $n_z = 1$, $n_x = n_y = 0$ and $E_{100} = E_{010} = E_{001} = \frac{5}{2}\hbar\omega$.

There are three different sets of n_x , n_y , n_z quantum numbers that give this energy, so there are three different quantum states that have this same energy.

EVALUATE: For the three-dimensional isotropic harmonic oscillator, the wave function is a product of one-dimensional harmonic oscillator wavefunctions for each dimension. The energy is a sum of energies for three one-dimensional oscillators. All the excited states are degenerate, with more than one state having the same energy.

41.45. IDENTIFY: Find solutions to Eq. (41.5).

SET UP: $\omega_1 = \sqrt{k_1'/m}$, $\omega_2 = \sqrt{k_2'/m}$. Let $\psi_{n_2}(x)$ be a solution of Eq. (40.44) with

 $E_{n_x} = (n_x + \frac{1}{2}) \hbar \omega_1, \psi_{n_y}(y)$ be a similar solution, and let $\psi_{n_z}(z)$ be a solution of Eq. (40.44) but with z as the independent variable instead of x, and energy $E_{n_z} = (n_z + \frac{1}{2}) \hbar \omega_2$

EXECUTE: (a) As in Problem 41.44, look for a solution of the form $\psi(x, y, z) = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$.

Then, $-\frac{\hbar^2}{2m}\frac{\partial^2 \psi}{\partial x^2} = (E_{n_x} - \frac{1}{2}k_1'x^2)\psi$ with similar relations for $\frac{\partial^2 \psi}{\partial y^2}$ and $\frac{\partial^2 \psi}{\partial z^2}$. Adding,

$$-\frac{\hbar^{2}}{2m} \left(\frac{\partial^{2} \psi}{\partial x^{2}} + \frac{\partial^{2} \psi}{\partial y^{2}} + \frac{\partial^{2} \psi}{\partial z^{2}} \right) = (E_{n_{x}} + E_{n_{y}} + E_{n_{z}} - \frac{1}{2}k'_{1}x^{2} - \frac{1}{2}k'_{1}y^{2} - \frac{1}{2}k'_{2}z^{2})\psi$$
$$= (E_{n_{y}} + E_{n_{y}} + E_{n_{y}} - U)\psi = (E - U)\psi$$

where the energy E is $E = E_{n_x} + E_{n_y} + E_{n_z} = \hbar \left[(n_x + n_y + 1)\omega_1^2 + (n_z + \frac{1}{2})\omega_2^2 \right]$, with n_x , n_y , and n_z all nonnegative integers.

- **(b)** The ground level corresponds to $n_x = n_y = n_z = 0$, and $E = \hbar(\omega_1^2 + \frac{1}{2}\omega_2^2)$. The first excited level corresponds to $n_x = n_y = 0$ and $n_z = 1$, since $\omega_1^2 > \omega_2^2$, and $E = \hbar(\omega_1^2 + \frac{3}{2}\omega_2^2)$.
- **(c)** There is only one set of quantum numbers for both the ground state and the first excited state. **EVALUATE:** For the isotropic oscillator of Problem 41.44 there are three states for the first excited level but only one for the anisotropic oscillator.
- **41.46. IDENTIFY:** The probability is a maximum where $|\psi|^2$ is a maximum, and this is where $\frac{\partial}{\partial x}|\psi|^2 = 0$. The probability is zero where $|\psi|^2$ is zero.

SET UP: $|\psi^2| = A^2 x^2 e^{-2(\alpha x^2 + \beta y^2 + \gamma z^2)}$. To save some algebra, let $u = x^2$, so that $|\psi|^2 = u e^{-2\alpha u} f(y, z)$.

EXECUTE: (a) $\frac{\partial}{\partial u} |\psi|^2 = (1 - 2\alpha u) |\psi|^2$; the maximum occurs at $u_0 = \frac{1}{2\alpha}$, $x_0 = \pm \frac{1}{\sqrt{2\alpha}}$.

(b) ψ vanishes at x = 0, so the probability of finding the particle in the x = 0 plane is zero. The wave function also vanishes for $x = \pm \infty$.

EVALUATE: $|\psi|^2$ is a maximum at $y_0 = z_0 = 0$.

41.47. IDENTIFY and **SET UP:** To calculate the total number of states for the n^{th} principal quantum number shell we must add up all the possibilities. The spin states multiply everything by 2. The maximum l value is (n-1), and each l value has (2l+1) different m_l values.

EXECUTE: (a) The total number of states is

$$N = 2\sum_{l=0}^{n-1} (2l+1) = 2\sum_{l=0}^{n-1} 1 + 4\sum_{l=0}^{n-1} l = 2n + \frac{4(n-1)(n)}{2} = 2n + 2n^2 - 2n = 2n^2.$$

(b) The n = 5 shell (*O*-shell) has 50 states.

EVALUATE: The n = 1 shell has 2 states, the n = 2 shell has 8 states, etc.

41.48. IDENTIFY: The orbital angular momentum is limited by the shell the electron is in.

SET UP: For an electron in the *n* shell, its orbital angular momentum quantum number *l* is limited by $0 \le l < n-1$, and its orbital angular momentum is given by $L = \sqrt{l(l+1)}\hbar$. The *z*-component of its angular momentum is $L_z = m_l \hbar$, where $m_l = 0, \pm 1, \ldots, \pm l$, and its spin angular momentum is $S = \sqrt{3/4}\hbar$ for all electrons. Its energy in the n^{th} shell is $E_n = -(13.6 \text{ eV})/n^2$.

EXECUTE: (a) $L = \sqrt{l(l+1)}\hbar = \sqrt{20}\hbar = \sqrt{4(4+1)}\hbar$ $\Rightarrow l = 4$. Thus the smallest that *n* can be is 5, so $E_n = -(13.6 \text{ eV})/n^2 = -(13.6 \text{ eV})/5^2 = -0.5400 \text{ eV}$.

- **(b)** For l=4, $m_l=\pm 4,\pm 3,\pm 2,\pm 1,0$. Since $L_z=m_l\hbar$, the largest L_z can be is $4\hbar$ and the smallest it can be is $-4\hbar$.
- (c) $S = \sqrt{3/4}\hbar = \frac{\sqrt{3}}{2}\hbar$ for all electrons.
- (d) In this case, n = 3, so l = 2, 1, 0. Therefore the maximum that L can be is $L_{\text{max}} = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$. The minimum L can be is zero when l = 0.

EVALUATE: At the quantum level, electrons in atoms can have only certain allowed values of their angular momentum.

49.49. (a) IDENTIFY and SET UP: The energy is given by $E_n = K_n + U_n = -\frac{1}{\epsilon_0^2} \frac{me^4}{8n^2h^2}$ from Chapter 39, which is

identical to the Bohr energy levels for hydrogen from this chapter. The potential energy is given by

$$U(r) = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r}$$
, with $q_1 = +Ze$ and $q_2 = -e$.

EXECUTE: $E_{1s} = -\frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{2\hbar^2}$; $U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}$.

$$E_{1s} = U(r) \text{ gives } -\frac{1}{(4\pi\epsilon_0)^2} \frac{me^4}{2\hbar^2} = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r}.$$

$$r = \frac{(4\pi\varepsilon_0)2\hbar^2}{me^2} = 2a.$$

EVALUATE: The turning point is twice the Bohr radius.

(b) IDENTIFY and **SET UP:** For the 1s state the probability that the electron is in the classically forbidden

region is $P(r > 2a) = \int_{2a}^{\infty} |\psi_{1s}|^2 dV = 4\pi \int_{2a}^{\infty} |\psi_{1s}|^2 r^2 dr$. The normalized wave function of the 1s state of

hydrogen is given in Example 41.4: $\psi_{1s}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$. Evaluate the integral; the integrand is the same as in Example 41.4.

EXECUTE:
$$P(r > 2a) = 4\pi \left(\frac{1}{\pi a^3}\right) \int_{2a}^{\infty} r^2 e^{-2r/a} dr$$
.

Use the integral formula $\int r^2 e^{-\alpha r} dr = -e^{-\alpha r} \left(\frac{r^2}{\alpha} + \frac{2r}{\alpha^2} + \frac{2}{\alpha^3} \right)$, with $\alpha = 2/a$.

$$P(r > 2a) = -\frac{4}{a^3} \left[e^{-2r/a} \left(\frac{ar^2}{2} + \frac{a^2r}{2} + \frac{a^3}{4} \right) \right]_{2a}^{\infty} = +\frac{4}{a^3} e^{-4} (2a^3 + a^3 + a^3/4).$$

$$P(r > 2a) = 4e^{-4}(13/4) = 13e^{-4} = 0.238$$

EVALUATE: These is a 23.8% probability of the electron being found in the classically forbidden region, where classically its kinetic energy would be negative.

49.50. IDENTIFY: At the r where P(r) has its maximum value, $\frac{d(r^2|\psi|^2)}{dr} = 0$.

SET UP: From Example 41.4, $r^2 |\psi|^2 = Cr^2 e^{-2r/a}$.

EXECUTE: $\frac{d(r^2|\psi|^2)}{dr} = Ce^{-2r/a}(2r - (2r^2/a))$. This is zero for r = a. Therefore, P(r) has its maximum

value at r = a, the distance of the electron from the nucleus in the Bohr model.

EVALUATE: Our result agrees with Figure 41.8 in the textbook.

41.51. IDENTIFY: At the value of r where P(r) is a maximum, $\frac{dP}{dr} = 0$.

SET UP: $P(r) = \left(\frac{1}{24a^5}\right) r^4 e^{-r/a}$.

EXECUTE: $\frac{dP}{dr} = \left(\frac{1}{24a^5}\right) \left(4r^3 - \frac{r^4}{a}\right) e^{-r/a}$. $\frac{dP}{dr} = 0$ when $4r^3 - \frac{r^4}{a} = 0$; r = 4a. In the Bohr model,

 $r_n = n^2 a$ so $r_2 = 4a$, which agrees with the location of the maximum in P(r).

EVALUATE: Our result agrees with Figure 41.8. The figure shows that P(r) for the 2p state has a single maximum and no zeros except at r = 0 and $r \to \infty$.

41.52. IDENTIFY and **SET UP:** Apply $E_n = \frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV})$ and the concept of screening. For a level with quantum number n the ionization energy is $-E_n$.

EXECUTE: (a) For large values of n, the inner electrons will completely shield the nucleus, so $Z_{\text{eff}} = 1$ and the ionization energy would be $\frac{13.60 \text{ eV}}{n^2}$.

(b) The ionization energy is $\frac{13.60 \text{ eV}}{300^2} = 1.51 \times 10^{-4} \text{ eV}$, and the Bohr radius is

 $r_{300} = (300)^2 a_0 = (300)^2 (0.529 \times 10^{-10} \text{ m}) = 4.76 \times 10^{-6} \text{ m} = 4.76 \ \mu\text{m}.$

(c) Similarly for n = 600. The ionization energy is $\frac{13.60 \text{ eV}}{(600)^2} = 3.78 \times 10^{-5} \text{ eV}$, and the Bohr radius is

 $r_{600} = (600)^2 (0.529 \times 10^{-10} \text{ m}) = 1.90 \times 10^{-5} \text{ m} = 19.0 \ \mu\text{m}.$

EVALUATE: For a Rydberg atom with large n, the Bohr radius of the electron's orbit is extremely large compared to hydrogen, and the ionization energy is much less than it is for hydrogen.

- **41.53.** IDENTIFY: Use Figure 41.6 in the textbook to relate θ_L to L_z and L: $\cos \theta_L = \frac{L_z}{L}$ so $\theta_L = \arccos\left(\frac{L_z}{L}\right)$.
 - (a) SET UP: The smallest angle $(\theta_L)_{\min}$ is for the state with the largest L and the largest L_z . This is the state with l = n 1 and $m_l = l = n 1$.

EXECUTE: $L_z = m_l \hbar = (n-1)\hbar$.

 $L = \sqrt{l(l+1)}\hbar = \sqrt{(n-1)n}\hbar.$

$$(\theta_L)_{\min} = \arccos\left(\frac{(n-1)\hbar}{\sqrt{(n-1)n}\hbar}\right) = \arccos\left(\frac{(n-1)}{\sqrt{(n-1)n}}\right) = \arccos\left(\sqrt{\frac{n-1}{n}}\right) = \arccos(\sqrt{1-1/n}).$$

EVALUATE: Note that $(\theta_L)_{\min}$ approaches 0° as $n \to \infty$.

(b) SET UP: The largest angle $(\theta_L)_{\text{max}}$ is for l = n - 1 and $m_l = -l = -(n - 1)$.

EXECUTE: A similar calculation to part (a) yields $(\theta_L)_{\text{max}} = \arccos(-\sqrt{1-1/n})$

EVALUATE: Note that $(\theta_L)_{\text{max}}$ approaches 180° as $n \to \infty$.

41.54. IDENTIFY: The presence of an external magnetic field shifts the energy levels up or down, depending upon the value of m_l .

SET UP: The selection rules tell us that for allowed transitions, $\Delta l = 1$ and $\Delta m_l = 0$ or ± 1 .

EXECUTE: (a) $E = hc/\lambda = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(475.082 \text{ nm}) = 2.612 \text{ eV}.$

(b) For allowed transitions, $\Delta l = 1$ and $\Delta m_l = 0$ or ± 1 . For the 3d state, n = 3, l = 2, and m_l can have the values 2, 1, 0, -1, -2. In the 2p state, n = 2, l = 1, and m_l can be 1, 0, -1. Therefore the 9 allowed transitions from the 3d state in the presence of a magnetic field are:

$$\begin{split} l &= 2, \, m_l = 2 \to l = 1, \, m_l = 1 \\ l &= 2, \, m_l = 1 \to l = 1, \, m_l = 0 \\ l &= 2, \, m_l = 1 \to l = 1, \, m_l = 1 \\ l &= 2, \, m_l = 0 \to l = 1, \, m_l = 0 \\ l &= 2, \, m_l = 0 \to l = 1, \, m_l = 1 \end{split}$$

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

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

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

$$l = 2, m_1 = -2 \rightarrow l = 1, m_1 = -1$$

(c)
$$\Delta E = \mu_B B = (5.788 \times 10^{-5} \text{ eV/T})(3.500 \text{ T}) = 0.000203 \text{ eV}.$$

So the energies of the new states are -8.50000 eV + 0 and $-8.50000 \text{ eV} \pm 0.000203 \text{ eV}$, giving energies of: -8.50020 eV, -8.50000 eV, and -8.49980 eV.

(d) The energy differences of the allowed transitions are equal to the energy differences if no magnetic field were present (2.61176 eV, from part (a)), and that value $\pm \Delta E$ (0.000203 eV, from part (c)). Therefore we get the following:

For E = 2.61176 eV: $\lambda = 475.082 \text{ nm}$ (which was given).

For E = 2.61176 eV + 0.000203 eV = 2.611963 eV:

$$\lambda = hc/E = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(2.611963 \text{ eV}) = 475.045 \text{ nm}.$$

For E = 2.61176 eV - 0.000203 eV = 2.61156 eV:

$$\lambda = hc/E = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})/(2.61156 \text{ eV}) = 475.119 \text{ nm}.$$

EVALUATE: Even a strong magnetic field produces small changes in the energy levels, and hence in the wavelengths of the emitted light.

41.55. IDENTIFY: The presence of an external magnetic field shifts the energy levels up or down, depending upon the value of m_l .

SET UP: The energy difference due to the magnetic field is $\Delta E = \mu_B B$ and the energy of a photon is $E = hc/\lambda$.

EXECUTE: For the p state, $m_l = 0$ or ± 1 , and for the s state $m_l = 0$. Between any two adjacent lines,

 $\Delta E = \mu_{\rm B} B$. Since the change in the wavelength $(\Delta \lambda)$ is very small, the energy change (ΔE) is also very

small, so we can use differentials. $E = hc/\lambda$. $|dE| = \frac{hc}{\lambda^2} d\lambda$ and $\Delta E = \frac{hc\Delta\lambda}{\lambda^2}$. Since $\Delta E = \mu_B B$, we get

$$\mu_B B = \frac{hc\Delta\lambda}{\lambda^2}$$
 and $B = \frac{hc\Delta\lambda}{\mu_B\lambda^2}$.

$$B = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})(0.0462 \text{ nm})/(5.788 \times 10^{-5} \text{ eV/T})(575.050 \text{ nm})^2 = 3.00 \text{ T}$$

EVALUATE: Even a strong magnetic field produces small changes in the energy levels, and hence in the wavelengths of the emitted light.

41.56. IDENTIFY: Apply constant acceleration equations to relate F_z to the motion of an atom.

SET UP: According to the equation $\mu_z = -(2.00232) \left(\frac{e}{2m}\right) S_z$, the magnitude of μ_z is

 $|\mu_z| = 9.28 \times 10^{-24} \text{ A} \cdot \text{m}^2$. The atomic mass of silver is 0.1079 kg/mol.

EXECUTE: The time required to transit the horizontal 50 cm region is $t = \frac{\Delta x}{v_x} = \frac{0.500 \text{ m}}{375 \text{ m/s}} = 1.333 \text{ ms}$. The

force required to deflect each spin component by 0.50 mm is

$$F_z = ma_z = \pm m \frac{2\Delta z}{t^2} = \pm \left(\frac{0.1079 \text{ kg/mol}}{6.022 \times 10^{23} \text{ atoms/mol}}\right) \frac{2(0.50 \times 10^{-3} \text{ m})}{(1.333 \times 10^{-3} \text{ s})^2} = \pm 1.008 \times 10^{-22} \text{ N. Thus, the required}$$

magnetic-field gradient is
$$\left| \frac{dB_z}{dz} \right| = \left| \frac{F_z}{\mu_z} \right| = \frac{1.008 \times 10^{-22} \text{ N}}{9.28 \times 10^{-24} \text{ J/T}} = 10.9 \text{ T/m}, \text{ which rounds to } 11 \text{ T/m}.$$

EVALUATE: The two spin components are deflected in opposite directions.

41.57. IDENTIFY: The ratio according to the Boltzmann distribution is given by $\frac{n_1}{n_0} = e^{-(E_1 - E_0)/kT}$ (from

Chapter 39), where 1 is the higher energy state and 0 is the lower energy state.

SET UP: The interaction energy with the magnetic field is $U = -\mu_z B = 2.00232 \left(\frac{e\hbar}{2m}\right) m_s B$ (Example 41.6.).

The energy of the $m_s = +\frac{1}{2}$ level is increased and the energy of the $m_s = -\frac{1}{2}$ level is decreased.

$$\frac{n_{1/2}}{n_{-1/2}} = e^{-(U_{1/2} - U_{-1/2})/kT}.$$

Execute:
$$U_{1/2} - U_{-1/2} = 2.00232 \left(\frac{e\hbar}{2m}\right) B \left[\frac{1}{2} - \left(-\frac{1}{2}\right)\right] = 2.00232 \left(\frac{e\hbar}{2m}\right) B = 2.00232 \mu_{\rm B} B.$$

$$\frac{n_{1/2}}{n_{-1/2}} = e^{-(2.00232)\mu_{\rm B}B/kT}.$$

(a)
$$B = 5.00 \times 10^{-5} \text{ T.}$$

$$\frac{n_{1/2}}{n_{-1/2}} = e^{-2.00232(9.274 \times 10^{-24} \text{ A/m}^2)(5.00 \times 10^{-5} \text{ T})/[(1.381 \times 10^{-23} \text{ J/K})(300 \text{ K})]}$$

$$\frac{n_{1/2}}{n_{-1/2}} = e^{-2.24 \times 10^{-7}} = 0.99999978 = 1 - 2.2 \times 10^{-7}.$$

(b)
$$B = 0.500 \text{ T}, \frac{n_{1/2}}{n_{-1/2}} = e^{-2.24 \times 10^{-3}} = 0.9978.$$

(c)
$$B = 5.00 \text{ T}, \frac{n_{1/2}}{n_{-1/2}} = e^{-2.24 \times 10^{-2}} = 0.978.$$

EVALUATE: For small fields the energy separation between the two spin states is much less than kT for T = 300 K and the states are equally populated. For B = 5.00 T the energy spacing is large enough for there to be a small excess of atoms in the lower state.

41.58. IDENTIFY: The magnetic field at the center of a current loop of radius r is $B = \frac{\mu_0 I}{2r}$. $I = e\left(\frac{v}{2\pi r}\right)$.

SET UP: Use $L = mvr = \sqrt{l(l+1)}\hbar$. The Bohr radius is n^2a_0 .

EXECUTE: $v = \frac{\sqrt{l(l+1)}\hbar}{m(n^2a_0)} = \frac{\sqrt{2}(6.63\times10^{-34} \text{ J} \cdot \text{s})}{2\pi(9.11\times10^{-31} \text{ kg})(4)(5.29\times10^{-11} \text{ m})} = 7.74\times10^5 \text{ m/s}.$ The magnetic field

generated by the "moving" proton at the electron's position is

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{4\pi} \frac{ev}{r^2} = (10^{-7} \text{ T} \cdot \text{m/A}) \frac{(1.60 \times 10^{-19} \text{ C})(7.74 \times 10^5 \text{ m/s})}{(4)^2 (5.29 \times 10^{-11} \text{ m})^2} = 0.277 \text{ T}.$$

EVALUATE: The effective magnetic field calculated in Example 41.7 for 3*p* electrons in sodium is much larger than the value we calculated for 2*p* electrons in hydrogen.

41.59. IDENTIFY and **SET UP:** m_s can take on four different values: $m_s = -\frac{3}{2}$, $-\frac{1}{2}$, $+\frac{1}{2}$, $+\frac{3}{2}$. Each nlm_l state can have four electrons, each with one of the four different m_s values. Apply the exclusion principle to determine the electron configurations.

EXECUTE: (a) For a filled n = 1 shell, the electron configuration would be $1s^4$; four electrons and Z = 4. For a filled n = 2 shell, the electron configuration would be $1s^42s^42p^{12}$; twenty electrons and Z = 20.

- (b) Sodium has Z = 11; eleven electrons. The ground-state electron configuration would be $1s^4 2s^4 2p^3$. **EVALUATE**: The chemical properties of each element would be very different.
- **41.60.** IDENTIFY: Apply $U = -\mu_z B$, where B is the effective magnetic field. $\Delta E = \frac{hc}{\lambda}$.

SET UP:
$$\mu_{\rm B} = \frac{e\hbar}{2m} = \frac{eh}{4\pi m}$$

EXECUTE: The effective field is that which gives rise to the observed difference in the energy level transition, $B = \frac{\Delta E}{\mu_{\rm B}} = \frac{hc}{\mu_{\rm B}} \left(\frac{\lambda_{\rm l} - \lambda_{\rm 2}}{\lambda_{\rm l} \lambda_{\rm 2}} \right) = \frac{4\pi mc}{e} \left(\frac{\lambda_{\rm l} - \lambda_{\rm 2}}{\lambda_{\rm l} \lambda_{\rm 2}} \right)$. Substitution of numerical values gives $B = 7.28 \times 10^{-3} \, \text{T}$.

EVALUATE: The effective magnetic field we have calculated is much smaller than that calculated for sodium in Example 41.7.

41.61. (a) **IDENTIFY** and **SET UP:** The energy of the photon equals the transition energy of the atom:

 $\Delta E = hc/\lambda$. The energies of the states are given by $E_n = -\frac{13.60 \text{ eV}}{n^2}$.

EXECUTE:
$$E_n = -\frac{13.60 \text{ eV}}{n^2}$$
 so $E_2 = -\frac{13.60 \text{ eV}}{4}$ and $E_1 = -\frac{13.60 \text{ eV}}{1}$. Thus $\Delta E = E_2 - E_1$ gives

 $\Delta E = 13.60 \text{ eV} (-\frac{1}{4} + 1) = \frac{3}{4} (13.60 \text{ eV}) = 10.20 \text{ eV} = (10.20 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV}) = 1.634 \times 10^{-18} \text{ J}.$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.634 \times 10^{-18} \text{ J}} = 1.22 \times 10^{-7} \text{ m} = 122 \text{ nm}.$$

(b) IDENTIFY and **SET UP:** Calculate the change in ΔE due to the orbital magnetic interaction energy, $U = m_l \mu_B B$, and relate this to the shift $\Delta \lambda$ in the photon wavelength.

EXECUTE: The shift of a level due to the energy of interaction with the magnetic field in the z-direction is $U = m_l \mu_B B$. The ground state has $m_l = 0$ so is unaffected by the magnetic field. The n = 2 initial state has

 $m_l = -1$ so its energy is shifted downward an amount $U = m_l \mu_B B = (-1)(9.274 \times 10^{-24} \text{ A/m}^2)(2.20 \text{ T}) = (-2.040 \times 10^{-23} \text{ J})(1 \text{ eV}/1.602 \times 10^{-19} \text{ J}) = 1.273 \times 10^{-4} \text{ eV}.$

Note that the shift in energy due to the magnetic field is a very small fraction of the 10.2 eV transition energy. Problem 39.76c shows that in this situation $|\Delta \lambda/\lambda| = |\Delta E/E|$. This gives

$$|\Delta \lambda| = \lambda |\Delta E/E| = 122 \text{ nm} \left(\frac{1.273 \times 10^{-4} \text{ eV}}{10.2 \text{ eV}} \right) = 1.52 \times 10^{-3} \text{ nm} = 1.52 \text{ pm}.$$

EVALUATE: The upper level in the transition is lowered in energy so the transition energy is decreased. A smaller ΔE means a larger λ ; the magnetic field increases the wavelength. The fractional shift in wavelength, $\Delta \lambda / \lambda$ is small, only 1.2×10^{-5} .

41.62. IDENTIFY: The interaction energy for an electron in a magnetic field is $U = -\mu_z B$, where μ_z is given by

$$\mu_z = -(2.00232) \left(\frac{e}{2m}\right) S_z.$$

SET UP: $\Delta S_{\tau} = \hbar$.

EXECUTE: (a) $\Delta E = (2.00232) \frac{e}{2m} B \Delta S_z \approx \frac{e\hbar}{m} B = \frac{hc}{\lambda} \Rightarrow B = \frac{2\pi mc}{\lambda e}$.

(b)
$$B = \frac{2\pi (9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})}{(0.0420 \text{ m})(1.60 \times 10^{-19} \text{ C})} = 0.255 \text{ T}.$$

EVALUATE: As shown in Figure 41.18 in the textbook, the lower state in the transition has $m_s = -\frac{1}{2}$ and the upper state has $m_s = +\frac{1}{2}$.

41.63. IDENTIFY: Estimate the atomic transition energy and use Eq. (39.5) to relate this to the photon wavelength. **(a) SET UP:** For vanadium, Z = 23.

EXECUTE: Minimum wavelength (corresponds to largest transition energy):

The highest occupied shell is the N shell (n = 4). The highest energy transition is $N \to K$, with transition

energy $\Delta E = E_N - E_K$. Since the shell energies scale like $1/n^2$ neglect E_N relative to E_K , so

 $\Delta E = E_K = (Z - 1)^2 (13.6 \text{ eV}) = (23 - 1)^2 (13.6 \text{ eV}) = 6.582 \times 10^3 \text{ eV} = 1.055 \times 10^{-15} \text{ J}$. The energy of the emitted photon equals this transition energy, so the photon's wavelength is given by $\Delta E = hc/\lambda$ so $\lambda = hc/\Delta E$.

$$\lambda = \frac{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})}{1.055 \times 10^{-15} \text{ J}} = 1.88 \times 10^{-10} \text{ m} = 0.188 \text{ nm}.$$

<u>Maximum wavelength</u> (corresponds to smallest transition energy, so for the K_{α} transition):

The frequency of the photon emitted in this transition is given by Moseley's law (Eq. 41.47).

$$f = (2.48 \times 10^{15} \text{ Hz})(Z - 1)^2 = (2.48 \times 10^{15} \text{ Hz})(23 - 1)^2 = 1.200 \times 10^{18} \text{ Hz}.$$

$$\lambda = \frac{c}{f} = \frac{2.998 \times 10^8 \text{ m/s}}{1.200 \times 10^{18} \text{ Hz}} = 2.50 \times 10^{-10} \text{ m} = 0.250 \text{ nm}.$$

(b) SET UP: For rhenium, Z = 45. Apply the analysis of part (a), just with this different value of Z.

EXECUTE: Minimum wavelength:

$$\Delta E = E_K = (Z - 1)^2 (13.6 \text{ eV}) = (45 - 1)^2 (13.6 \text{ eV}) = 2.633 \times 10^4 \text{ eV} = 4.218 \times 10^{-15} \text{ J}.$$

$$\lambda = hc/\Delta E = \frac{(6.626 \times 10^{-34} \,\mathrm{J \cdot s})(2.998 \times 10^8 \,\mathrm{m/s})}{4.218 \times 10^{-15} \,\mathrm{J}} = 4.71 \times 10^{-11} \,\mathrm{m} = 0.0471 \,\mathrm{nm}.$$

Maximum wavelength:

$$f = (2.48 \times 10^{15} \text{ Hz})(Z - 1)^2 = (2.48 \times 10^{15} \text{ Hz})(45 - 1)^2 = 4.801 \times 10^{18} \text{ Hz}.$$

$$\lambda = \frac{c}{f} = \frac{2.998 \times 10^8 \text{ m/s}}{4.801 \times 10^{18} \text{ Hz}} = 6.24 \times 10^{-11} \text{ m} = 0.0624 \text{ nm}.$$

EVALUATE: Our calculated wavelengths have values corresponding to x rays. The transition energies increase when *Z* increases and the photon wavelengths decrease.

41.64. IDENTIFY: The photons have different energy due to spin-orbit coupling, which sifts the energy levels very slightly.

SET UP: Without spin-orbit coupling, the energy levels are given by $E_n = -\frac{13.60 \text{ eV}}{n^2}$. If we include this

coupling, they are
$$E_{n,j} = -\frac{13.60 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right]$$
. The energy of a photon due a transition

involving energy change ΔE is $\Delta E = \frac{hc}{\lambda}$. Follow the ideas presented in Example 41.8, in which it was

shown that $\Delta \lambda = -\frac{\lambda}{E_{\text{photon}}} \Delta E_{\text{photon}}$ since the energy shifts due to spin-orbit coupling are extremely small.

EXECUTE: For a transition from n = 3 to n = 2, without including fine structure, we use $E_n = -\frac{13.60 \text{ eV}}{2}$

to find the energy difference ΔE , whis is equal to the energy of the photon. This gives

$$E_{\text{photon}} = \Delta E = (-13.6 \text{ eV})(1/3^2 - 1/2^2) = 1.889 \text{ eV}.$$

The wavelength of this photon is
$$\lambda = hc/E_{\text{photon}} = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s}) (2.998 \times 10^8 \text{ m/s})/(1.889 \text{ eV}) = 6.56 \times 10^{-7} \text{ m} = 656 \text{ nm}.$$

 $\Delta E_{\rm photon}$ is the energy difference between thre $E_{3,3/2}$ and the $E_{3,1/2}$ states. We calculate the energies of these

states using
$$E_{n,j} = -\frac{13.60 \text{ eV}}{n^2} \left[1 + \frac{\alpha^2}{n^2} \left(\frac{n}{j + \frac{1}{2}} - \frac{3}{4} \right) \right].$$

$$E_{3,3/2} = -\frac{13.60 \text{ eV}}{3^2} \left[1 + \frac{(0.007297)^2}{3^2} \left(\frac{3}{\frac{3}{2} + \frac{1}{2}} - \frac{3}{4} \right) \right] = -\frac{13.60 \text{ eV}}{9} (1 + 4.437 \times 10^{-6}).$$

$$E_{3,1/2} = -\frac{13.60 \text{ eV}}{3^2} \left[1 + \frac{(0.007297)^2}{3^2} \left(\frac{3}{\frac{1}{2} + \frac{1}{2}} - \frac{3}{4} \right) \right] = -\frac{13.60 \text{ eV}}{9} (1 + 13.312 \times 10^{-6}).$$

$$\Delta E_{\text{photon}} = E_{3,3/2} - E_{3,1/2} = [(13.60 \text{ eV})/9](13.312 \times 10^{-6} - 4.437 \times 10^{-6}) = 1.341 \times 10^{-5} \text{ eV}.$$

We now use $\Delta \lambda = -\frac{\lambda}{E_{\text{photon}}} \Delta E_{\text{photon}}$ to find the difference in the wavelengths.

$$\Delta \lambda = -\frac{656 \text{ nm}}{1.889 \text{ eV}} (1.341 \times 10^{-5} \text{ eV}) = -4.66 \times 10^{-3} \text{ nm} = -0.00466 \text{ nm}.$$

The photon for the transition from the $j = \frac{1}{2}$ state has the longer wavelength because the transition energy

EVALUATE: The wavelength difference is only 0.00466 nm compared to a wavelength of 656 nm without spin-orbit coupling, so this is a very small effect.

41.65. IDENTIFY: The inner electrons shield much of the nuclear charge from the outer electrons, and this shielding affects the energy levels compared to the hydrogen levels. The atom behaves like hydrogen with an effective charge in the nucleus.

SET UP: The ionization energies are $E_n = \frac{Z_{\text{eff}}^2}{2}$ (13.6 eV).

EXECUTE: (a) Make the conversions requested using the following conversion factor.

$$E(eV/atom) = E(kJ/mol) \left(\frac{1 \text{ mol}}{6.02214 \times 10^{23} \text{ atoms}}\right) \left(\frac{1000 \text{ J}}{1 \text{ kJ}}\right) \left(\frac{1 \text{ eV}}{1.602 \times 10^{-19} \text{ J}}\right) = 0.010364 E(kJ/mol).$$

<u>Li</u>: E = (0.010364)(520.2 kJ/mol) = 5.391 eV

$$\overline{\text{Na}}$$
: $E = (0.010364)(495.8 \text{ kJ/mol}) = 5.139 \text{ eV}$

$$\underline{K}$$
: $E = (0.010364)(418.8 \text{ kJ/mol}) = 4.341 \text{ eV}$

Rb:
$$E = (0.010364)(403.0 \text{ kJ/mol}) = 4.177 \text{ eV}$$

$$\overline{\text{Cs}}$$
: $E = (0.010364)(375.7 \text{ kJ/mol}) = 3.894 \text{ eV}$

Fr:
$$E = (0.010364)(380 \text{ kJ/mol}) = 3.9 \text{ eV}.$$

(b) From the periodic chart in the Appendix, we get the following information.

$$\underline{\text{Li}}$$
: $Z = 3$, $n = 2$

Na:
$$Z = 11$$
, $n = 3$

$$\underline{\mathbf{K}}$$
: $Z = 19$, $n = 4$

Rb:
$$Z = 37$$
, $n = 5$

Cs:
$$Z = 55$$
, $n = 6$
Fr: $Z = 87$, $n = 7$.

(c) Use
$$E_n = \frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV})$$
 and the values of *n* in part (b) to calculate Z_{eff} . For example, for Li we have

5.391 eV =
$$\frac{Z_{\text{eff}}^2}{2^2}$$
 (13.6 eV) \rightarrow $Z_{\text{eff}} = 1.26$, and for Na we have

5.139 eV =
$$\frac{Z_{\text{eff}}^2}{3^2}$$
(13.6 eV) \rightarrow Z_{eff} = 1.84. Doing this for the other atoms gives

$$\underline{\text{Li}}$$
: $Z_{\text{eff}} = 1.26$

Na:
$$Z_{\text{eff}} = 1.84$$

$$\underline{\mathbf{K}}$$
: $Z_{\text{eff}} = 2.26$

Rb:
$$Z_{\text{eff}} = 2.77$$

Cs:
$$Z_{\text{eff}} = 3.21$$

Fr:
$$Z_{\text{eff}} = 3.8$$
.

EVALUATE: (d) We can see that Z_{eff} increases as Z increases. The outer (valence) electron has increasing probability density within the inner shells as Z increases, and therefore it "sees" more of the nuclear charge.

41.66. IDENTIFY and **SET UP:** The energy levels of a particle in a cubical box of length L are

$$E_{n_x, n_y, n_z} = \frac{(n_X^2 + n_Y^2 + n_Z^2)\pi^2\hbar^2}{2mL^2}.$$
 The longest wavelength absorbed is for the smallest energy transition,

which is between the ground state (1, 1, 1) and the next higher state (2, 1, 1). The energy absorbed by the photon is $\Delta E = \frac{hc}{2}$.

EXECUTE: (a) The lowest energy transition is $\Delta E = \left[(2^2 + 1^2 + 1^2) - (1^2 + 1^2 + 1^2) \right] \frac{\pi^2 \hbar^2}{2mL^2}$, and this is equal

to the energy of the photon $\Delta E = \frac{hc}{\lambda}$. So $\frac{hc}{624 \text{ nm}} = \frac{3\pi^2 \hbar^2}{2mL^2} = \frac{3h^2}{8mL^2}$, which gives $L = \sqrt{\frac{3h(624 \text{ nm})}{8mc}}$.

$$L = \sqrt{\frac{3(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(624 \text{ nm})}{8(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})}} = 7.53 \times 10^{-10} \text{ m} = 0.753 \text{ nm}.$$

(b) The final state is now n. Call the wavelength in part (a) λ_1 and the one in part (b) λ_2 . From part (a) we

have $\frac{hc}{\lambda_1} = \frac{3\pi^2\hbar^2}{2mL^2}$ and for part (b) we have $\frac{hc}{\lambda_2} = (n^2 - 3)\frac{\pi^2\hbar^2}{2mL^2}$. Diving these two equations gives

$$\frac{hc/\lambda_2}{hc/\lambda_1} = \frac{\lambda_1}{\lambda_2} = \frac{624}{234} = \frac{n^2 - 3}{3}.$$
 Solving for *n* gives $n^2 = 3 + 3(624/234) = 3 + 8 = 11.$

There are 3 possibilities: (1, 1, 3), (1, 3, 1), and (3, 1, 1), so the degeneracy is 6 including spin.

EVALUATE: The dimensions of this box are around 7 times the diameter of the Bohr hydrogen atom, which is reasonable.

41.67. IDENTIFY and **SET UP:** The energy due to the interaction of the electron with the magnetic field is $U = -\mu_z B$. In a transition from the $m_s = -\frac{1}{2}$ state to the $m_s = \frac{1}{2}$ state, $\Delta U = 2\mu_z B$. This energy difference is the energy of the absorbed photon. The energy of the photon is E = hf, and $f\lambda = c$. For an electron, $S_z = \hbar/2$.

EXECUTE: (a) First find the frequency for each wavelength in the table with the problem. For example for the first column, $f = c/\lambda = (2.998 \times 10^8 \text{ m/s})/(0.0214 \text{ m}) = 1.40 \times 10^{10} \text{ Hz}$. Doing this for all the

wavelengths gives the values in the following table. Figure 41.67 (next page) shows the graph of f versus B for this data. The slope of the best-fit straight line is 2.84×10^{10} Hz/T.

<i>B</i> (T)	0.51	0.74	1.03	1.52	2.02	2.48	2.97
$f(10^{10} \text{Hz})$	1.401	2.097	2.802	4.199	5.604	7.005	8.398

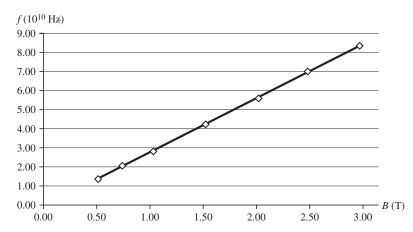


Figure 41.67

(b) The photon energy is E = hf, and that is the energy difference between the two levels. So $E = \Delta U = 2\mu_z B = hf$, which gives $f = \left(\frac{2\mu_z}{h}\right)B$. The graph of f versus B should be a straight line having slope equal to $2\mu_z/h$. Therefore the magnitude of the spin magnetic moment is

 $\mu_z = \frac{1}{2} h(\text{slope}) = \frac{1}{2} (6.626 \times 10^{-34} \text{ J} \cdot \text{s}) (2.84 \times 10^{10} \text{ Hz/T}) = 9.41 \times 10^{-24} \text{ J/T}.$

(c) Using $\gamma = \frac{|\mu_z|}{|S_z|} = \frac{|\mu_z|}{\hbar/2}$ gives $\gamma = \frac{2(9.41 \times 10^{-24} \text{ J/T})}{1.055 \times 10^{-34} \text{ J} \cdot \text{s}} = 1.784 \times 10^{11} \text{ Hz/T}$, which rounds to

1.78×10¹¹ Hz/T. This gives $\frac{\gamma}{e/2m} = \frac{2\gamma m}{e} = \frac{2(1.784 \times 10^{11} \text{ Hz/T})(9.11 \times 10^{-31} \text{ kg})}{1.602 \times 10^{-19} \text{ C}} = 2.03.$

EVALUATE: Our result of 2.03 for the gyromagnetic ratio for electron spin is in good agreement with the currently accepted value of 2.00232.

41.68. IDENTIFY and **SET UP:** The potential $U(x) = \frac{1}{2}k'x^2$ is that of a simple harmonic oscillator. Treated quantum mechanically (see Section 40.5) each *energy* state has energy $E_n = \hbar\omega(n + \frac{1}{2})$. Since electrons obey the exclusion principle, this allows us to put *two* electrons (one for each $m_s = \pm \frac{1}{2}$) for every value of n—each quantum state is then defined by the ordered pair of quantum numbers (n, m_s) .

EXECUTE: By placing two electrons in each energy level the lowest energy is

$$2\left(\sum_{n=0}^{N-1} E_n\right) = 2\left(\sum_{n=0}^{N-1} \hbar \omega (n + \frac{1}{2})\right) = 2\hbar \omega \left[\sum_{n=0}^{N-1} n + \sum_{n=0}^{N-1} \frac{1}{2}\right] = 2\hbar \omega \left[\frac{(N-1)(N)}{2} + \frac{N}{2}\right] =$$

 $\hbar\omega[N^2 - N + N] = \hbar\omega N^2 = \hbar N^2 \sqrt{\frac{k}{m}}$. Here we realize that the first value of n is zero and the last value of n is N-1, giving us a total of N energy levels filled.

EVALUATE: The minimum energy for one electron moving in this potential is $\frac{1}{2}\hbar\omega$, with $\omega=\sqrt{\frac{k'}{m}}$. For 2N electrons the minimum energy is larger than $(2N)(\frac{1}{2}\hbar\omega)$, because only two electrons can be put into each energy state. For example, for N=2 (4 electrons), there are two electrons in the $E=\frac{1}{2}\hbar\omega$ energy state and two in the $\frac{3}{2}\hbar\omega$ state, for a total energy of $2(\frac{1}{2}\hbar\omega)+2(\frac{3}{2}\hbar\omega)=4\hbar\omega$, which is in agreement with our general result.

41.69. IDENTIFY and **SET UP:** Apply Newton's second law and Bohr's quantization to one of the electrons. **EXECUTE:** (a) Apply Coulomb's law to the orbiting electron and set it equal to the centripetal force. There is an attractive force with charge +2e a distance r away and a repulsive force a distance 2r away. So,

 $\frac{(+2e)(-e)}{4\pi\varepsilon_0 r^2} + \frac{(-e)(-e)}{4\pi\varepsilon_0 (2r)^2} = \frac{-mv^2}{r}$. But, from the quantization of angular momentum in the first Bohr orbit,

$$L = mvr = \hbar \Rightarrow v = \frac{\hbar}{mr}. \text{ So } \frac{-2e^2}{4\pi\varepsilon_0 r^2} + \frac{e^2}{4\pi\varepsilon_0 (2r)^2} = \frac{-mv^2}{r} = \frac{-m\left(\frac{\hbar}{mr}\right)^2}{r} = -\frac{\hbar^2}{mr^3} \Rightarrow \frac{-7}{4}\frac{e^2}{r^2} = -\frac{4\pi\varepsilon_0 \hbar^2}{mr^3}.$$

$$r = \frac{4}{7} \left(\frac{4\pi \varepsilon_0 \hbar^2}{me^2} \right) = \frac{4}{7} a_0 = \frac{4}{7} (0.529 \times 10^{-10} \text{ m}) = 3.02 \times 10^{-11} \text{ m}. \text{ And}$$

$$v = \frac{\hbar}{mr} = \frac{7}{4} \frac{\hbar}{ma_0} = \frac{7}{4} \frac{(1.054 \times 10^{-34} \text{ J} \cdot \text{s})}{(9.11 \times 10^{-31} \text{ kg})(0.529 \times 10^{-10} \text{ m})} = 3.83 \times 10^6 \text{ m/s}.$$

(b)
$$K = 2(\frac{1}{2}mv^2) = 9.11 \times 10^{-31} \text{ kg} (3.83 \times 10^6 \text{ m/s})^2 = 1.34 \times 10^{-17} \text{ J} = 83.5 \text{ eV}.$$

(c)
$$U = 2\left(\frac{-2e^2}{4\pi\varepsilon_0 r}\right) + \frac{e^2}{4\pi\varepsilon_0(2r)} = \frac{-4e^2}{4\pi\varepsilon_0 r} + \frac{e^2}{4\pi\varepsilon_0(2r)} = \frac{-7}{2}\left(\frac{e^2}{4\pi\varepsilon_0 r}\right) = -2.67 \times 10^{-17} \text{ J} = -166.9 \text{ eV}.$$

(d) $E_{\infty} = -[-166.9 \text{ eV} + 83.5 \text{ eV}] = 83.4 \text{ eV}$, which is only off by about 5% from the real value of 79.0 eV.

EVALUATE: The ground state energy of helium in this model is K + U = -83.4 eV. The ground state energy of He⁺ is 4(-13.6 eV) = -54.4 eV. Therefore, the energy required to remove one electron from helium in this model is -(-83.4 eV + 54.4 eV) = 29.0 eV. The experimental value for this quantity is 24.6 eV.

41.70. IDENTIFY and **SET UP:** For the Bohr hydrogen model, $r = a_0 n^2$.

EXECUTE: Using $r = a_0 n^2$ gives 1×10^{-6} m = 5.29×10^{-11} m, so $n = 137 \approx 140$, which makes choice (a) the correct one.

EVALUATE: The energy of an electron in this state would be only $E_{140} = (-13.6 \text{ eV})/137^2 = -7.25 \times 10^{-4} \text{ eV}$, which is very small compared to ground-state hydrogen.

41.71. IDENTIFY and **SET UP:** Particle density is the number particles divided by the volume they occupy. The distance between particles is 10 times their size, which is 20 μ m.

EXECUTE: Think of each atom as being in a cubical box that is 20 μ m on each side. The particle density is $(1 \text{ atom})/(20 \text{ }\mu\text{m})^3 = (1 \text{ atom})/(20 \times 10^{-4} \text{ cm})^3 = 1.25 \times 10^8 \text{ atoms/cm}^3 \approx 10^8 \text{ atoms/cm}^3$, choice (b).

EVALUATE: For rubidium, with 85 nucleons, the mass density ρ of these atoms would be $\rho = (85)(1.67 \times 10^{-24} \text{ g})(10^8 \text{ atoms/cm}^3) = 1.4 \times 10^{-14} \text{ g/cm}^3$. Ordinary rubidium has a density of 1.53 g/cm³, so these Rydberg atoms are much farther apart than rubidium atoms under normal conditions.

41.72. IDENTIFY and SET UP: $L = \sqrt{l(l+1)}\hbar$. For this state, n = 100 and l = 2.

EXECUTE: $L = \sqrt{l(l+1)}\hbar = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$. So choice (b) is correct.

EVALUATE: This is not the largest that L could be since l could be 99 for n = 100.

41.73. IDENTIFY and SET UP: $m_l = \pm l, \pm (l-1), ..., 0.$ $m_s = \pm \frac{1}{2}$ for each m_l value.

EXECUTE: If l = 2, $m_l = -2$, -1, 0, +1, +2; and $m_s = \pm \frac{1}{2}$ for each of these states, so there are 10 possible states, which is choice (d).

EVALUATE: In the n = 100 state, there are 100 possible values of l, so there are many more additional states for these values of l.