

## QUANTUM MECHANICS II: ATOMIC STRUCTURE

**VP41.1.1. IDENTIFY:** This problem involves a particle in a three-dimensional cubical box.

**SET UP:** Eq. (41.15) gives the wave function of the particle, and the square of the wave function is the probability density.

**EXECUTE: (a)** We want to find where the probability distribution function is zero.

$$|\psi_{2,1,3}|^2 = |C|^2 \sin^2 \frac{2\pi x}{L} \sin^2 \frac{\pi y}{L} \sin^2 \frac{3\pi z}{L} = 0.$$

$$2\pi x/L = \pi : x = L/2$$

$$\pi y/L = \pi : y = L \text{ (none inside the box)}$$

$$3\pi z/L = m\pi : z = mL/3 = L/3 \text{ and } 2L/3.$$

**(b)** We want the probability that the particle will be found within the range  $0 \leq x \leq L/3$ . Use results from Example 41.1.  $C = (2/L)^{3/2}$ . The probability is given by

$$P = |C|^2 \int_0^{L/3} \sin^2 \frac{2\pi x}{L} dx \int_0^L \sin^2 \frac{\pi y}{L} dy \int_0^L \sin^2 \frac{3\pi z}{L} dz.$$

The  $y$  and  $z$  integrals are each equal to  $L/2$ , and the  $x$  integral is  $L/6 - (L/8\pi)\sin 4\pi/3 = 0.201L$ . The probability is  $P = [(2/L)^{3/2}]^2(0.201L)(L/2)(L/2) = 0.402$ .

**EVALUATE:** The probability of finding the particle between  $x = 0$  and  $x = L/3$  is about 40%, so the probability of finding it between  $x = L/3$  and  $L$  is about 60%.

**VP41.1.2. IDENTIFY:** This problem involves a particle in a three-dimensional cubical box.

**SET UP:** Eq. (41.15) gives the wave function of the particle, and the square of the wave function is the probability density. We want the probability of finding the particle in the region  $L/4 \leq x \leq 3L/4$ .

**EXECUTE: (a)** The state is (1,1,1). We integrate using results from Example 41.1.  $C = (2/L)^{3/2}$ .

$$P = |C|^2 \int_{L/4}^{3L/4} \sin^2 \frac{\pi x}{L} dx \int_0^L \sin^2 \frac{\pi y}{L} dy \int_0^L \sin^2 \frac{\pi z}{L} dz.$$

The second two integrals are each equal to  $L/2$ , and the first one is  $L(1/4 + 1/2\pi)$ . Therefore,  $P = [(2/L)^{3/2}]^2(L/2)^2[L(1/4 + 1/2\pi)] = 1/2 + 1/\pi = 0.818$ .

**(b)** The state is (2,1,2). The only difference from part (a) is the  $x$  integral, which is

$$\int_{L/4}^{3L/4} \sin^2 \frac{2\pi x}{L} dx = L/4.$$

Therefore  $P = (2/L)^3(L/2)^2(L/4) = 0.500$ .

**(c)** The state is (3,2,3). Only the  $x$  integral is different from parts (a) and (b).

$$\int_{L/4}^{3L/4} \sin^2 \frac{3\pi x}{L} dx = \frac{L}{4} - \frac{L}{6\pi} = L\left(\frac{1}{4} - \frac{1}{6\pi}\right).$$

$P = (2/L)^3(L/2)^2L(1/4 - 1/6\pi) = 0.394$ .

**(d)** The state is (4,1,1). Use the same procedure. In this case, the  $x$  integral gives  $L/4$ , so the probability is  $P = (2/L)^3(L/2)^2(L/4) = 0.500$ .

**EVALUATE:** Note that the probability is 0.500 whenever  $n_x$  is an even integer. Also note that even though the region contains half the volume of the cube, the probability of finding a particle there is not necessarily 0.500.

**VP41.1.3. IDENTIFY:** This problem involves a particle in a three-dimensional cubical box.

**SET UP:** Eq. (41.15) gives the wave function of the particle, and the square of the wave function is the probability density. We want the probability of finding the particle in the region  $0 \leq x \leq L/4$ ,  $0 \leq y \leq L/4$ . Use the same approach as in the previous two problems.

**EXECUTE:** (a) The state is (1,1,1). We integrate using results from Example 41.1.  $C = (2/L)^{3/2}$ .

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

The  $z$  integral is equal to  $L/2$ . The  $y$  and  $z$  integrals are each equal to  $L(1/8 - 1/4\pi)$ . Therefore

$$P = (2/L)^3(L)[L(1/8 - 1/4\pi)]^2 = 8.25 \times 10^{-3}.$$

(b) The state is (2,1,2). Use the previous results and those of example 41.1. Doing so, we find that the  $x$  integral is  $L/8$ , the  $y$  integral is  $L(1/8 - 1/4\pi)$ , and the  $z$  integral is  $L/2$ . The probability is

$$P = (2/L)^3(L/8)[L(1/8 - 1/4\pi)](L/2) = 0.0227.$$

(c) The state is (3,2,3). The  $x$  integral is  $L(1/8 + 1/12\pi)$ , the  $y$  integral is  $L/8$ , the  $z$  integral is  $L/2$ , so  $P = (2/L)^3[L(1/8 + 1/12\pi)](L/8)(L/2) = 0.0758$ .

(d) The state is (4,1,1).  $x$  integral is  $L/8$ ,  $y$  integral is  $L(1/8 - 1/4\pi)$ ,  $z$  integral is  $L/2$ , so  $P = 0.0227$ .

**EVALUATE:** Note that  $P_{4,1,1}$  is the same as  $P_{2,1,2}$ . Also note that even though the region contains 6.25% of the volume of the cube, the probability of finding a particle there is not necessarily 0.0625.

**VP41.1.4. IDENTIFY:** This problem involves a particle in a three-dimensional cubical box.

**SET UP:** Eq. (41.15) gives the wave function of the particle, and the square of the wave function is the probability density.

**EXECUTE:** (a) We want  $V_{\text{inside}}/V_{\text{box}}$ .  $V_{\text{box}} = L^3$  and  $V_{\text{inside}} = (L/2)^3 = L^3/8$ . Dividing the volumes gives  $V_{\text{inside}}/V_{\text{box}} = (L^3/8)/L^3 = 1/8 = 0.125$ .

(b) We want the probability that the particle is in this region. We use the wave functions in Eq. (41.15), square them and integrate to get the probability as in the previous problems. All the integrals are of the same form as the  $x$  integral in problem VP41.1.2(a), so each integral gives the factor  $L(1/4 + 1/2\pi)$ . The probability is  $P = (2/L)^3[L(1/4 + 1/2\pi)]^3 = 0.548$ .

**EVALUATE:** Note that the probability of finding the particle in the given volume is not necessarily the same as the percent that volume is of the total volume of the box. We have seen the same thing in previous problems.

**VP41.4.1. IDENTIFY:** We are looking at the possible states of the hydrogen atom with  $n = 3$ .

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

**EXECUTE:** (a)  $l = 0, 1, \dots, 5$  and  $m_l = 0, \pm 1, \pm 2, \dots, \pm 5$ . The possible states are:

$l = 0, m_l = 0$ : 1 state

$l = 1, m_l = 0, \pm 1$ : 3 states

$l = 2, m_l = 0, \pm 1, \pm 2$ : 5 states

$l = 3, m_l = 0, \pm 1, \pm 2, \pm 3$ : 7 states

$l = 4, m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4$ : 9 states

$l = 5, m_l = 0, \pm 1, \pm 2, \pm 3, \pm 4, \pm 5$ : 11 states

The total is 36 states.

(b)  $l_{\text{max}} = 5$ , so  $L_{\text{max}} = \sqrt{5(5+1)}\hbar = \sqrt{30}\hbar$ .

(c)  $L_z = m_l\hbar$ , so the maximum  $L_z$  is  $5\hbar$ .

**EVALUATE:** As  $n$  increases, the number of possible states increases rapidly.

**VP41.4.2. IDENTIFY:** We are looking at the possible states of the hydrogen atom with  $n = 6$ .

**SET UP:**  $l = 0, 1, 2, \dots, n-1$  and  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ .  $L = \sqrt{l(l+1)}\hbar$ .  $L_z = m_l\hbar$ .

**EXECUTE:** (a) Using the restrictions on  $l$  and  $m_l$  gives

$$l = 0, m_l = 0$$

$$l = 1, m_l = 0, \pm 1$$

$$l = 2, m_l = 0, \pm 1, \pm 2$$

So the  $(l, m_l)$  states are  $(0, 0)$ ,  $(1, -1)$ ,  $(1, 0)$ ,  $(1, 1)$ ,  $(2, -2)$ ,  $(2, -1)$ ,  $(2, 0)$ ,  $(2, 1)$ ,  $(2, 2)$ .

(b) Using  $\cos\theta_L = L_z/L$ , we see that the angle between the orbital angular momentum and the *negative*  $z$ -axis will be a minimum when  $\theta_L$  is closest to  $\pi$ , so the cosine should be closest to  $-1$ .

$$\cos\theta_L = L_z/L = \frac{m_l\hbar}{\sqrt{l(l+1)}\hbar} = \frac{m_l}{\sqrt{l(l+1)}}.$$

So for  $m_l = -2$  and  $l = 2$ , we get  $\cos\theta_L = -2/\sqrt{6}$ , which gives  $\theta_L = 144.7^\circ$ . Therefore the angle with the  $-z$ -axis is  $180^\circ - 144.7^\circ = 35.3^\circ$ . This is for the state  $l = 2, m_l = -2$ .

**EVALUATE:** The greatest angle that the angular momentum makes with the  $+z$ -axis is  $144.7^\circ$ .

**VP41.4.3. IDENTIFY:** We are looking at transition energy in the hydrogen atom.

**SET UP:**  $E_n = -(13.60 \text{ eV})/n^2$ . The energy of a shell depends on  $n$ . The photon energy is equal to the energy lost by an electron due to its transition to a lower energy level.

**EXECUTE:** (a)  $n = 3 \rightarrow n = 2$ .  $\Delta E = (13.6 \text{ eV})(1/2^2 - 1/3^2) = 1.89 \text{ eV}$ .

(b)  $n = 4 \rightarrow n = 2$ .  $\Delta E = (13.6 \text{ eV})(1/2^2 - 1/4^2) = 2.55 \text{ eV}$ .

(c)  $n = 2 \rightarrow n = 1$ .  $\Delta E = (13.6 \text{ eV})(1/1^2 - 1/2^2) = 10.2 \text{ eV}$ .

**EVALUATE:** Note that the energy difference between adjacent shells is not the same but depends on the value of  $n$ .

**VP41.4.4. IDENTIFY:** We are investigating the properties of the hydrogen wave function.

**SET UP:** The probability density is the square of the wave function. We want the probability that the electron will be found within each given region using the given wave function.

$$P = \int |\psi|^2 dV = \int \frac{1}{\pi a^3} e^{-2r/a} 4\pi r^2 dr = -\frac{4}{a^3} \left( \frac{ar^2}{2} + \frac{a^2 r}{2} + \frac{a^3}{4} \right) e^{-2r/a}.$$

**EXECUTE:** (a)  $0 \leq r \leq 2a$ . Evaluating the expression above for the limits of the integral gives

$$P = -\frac{4}{a^3} \left[ \left( 2a^3 + a^3 + \frac{a^3}{4} \right) e^{-4} - \frac{a^3}{4} \right] = -\left( \frac{13}{e^4} - 1 \right) = 0.762.$$

(b)  $a \leq r \leq 3a$ . Evaluating as in part (a) for the new limits gives  $P = 0.615$ .

(c)  $r \geq 4a$ . In this case, the upper limit is infinity. Evaluating as before gives  $P = 0.0138$ .

**EVALUATE:** Our results are consistent with Figure 41.8 in the textbook for a  $1s$  electron in hydrogen. From the graph for a  $1s$  electron, we see that the probability distribution for  $P(r)$  is a maximum at  $r = a$ . The range in part (a) includes that value, so the probability for that range is greater than for the others that do not include it.

**VP41.8.1. IDENTIFY:** This problem involves the Zeeman effect in which an external magnetic field affects the energy levels.

**SET UP:** The following conditions hold:

$$U = -\mu_z B, \mu_z = -(2.00232) \frac{e}{2m} S_z, S_z = \pm \frac{\hbar}{2}.$$

**EXECUTE:** (a) We want the energy difference. Combining these conditions gives

$$\Delta U = (2.00232) \frac{eB}{2m} \Delta S_z = (2.00232) \frac{eB}{2m} \left[ \frac{\hbar}{2} - \left( -\frac{\hbar}{2} \right) \right] = (2.00232) \mu_B B.$$

Using  $B = 3.14 \text{ T}$  and  $\mu_B = 5.788 \times 10^{-5} \text{ eV/T}$  gives  $\Delta U = 3.64 \times 10^{-4} \text{ eV}$ .

(b) We want to know which state has greater energy.

$$U = -\mu_z B = -(-2.00232) \frac{e}{2m} S_z B = +(2.00232) \frac{eB}{2m} S_z, \text{ so } S_z = +\frac{\hbar}{2} \text{ has greater energy.}$$

**EVALUATE:** The *magnitude* of the energy is the same for either of the  $S_z$  states.

**VP41.8.2. IDENTIFY:** We are looking at the effect of an external magnetic field on an atom.

**SET UP:** The energy of the radiation must be equal to the energy difference between the two spin states of the outermost electron. The following conditions hold:

$$U = -\mu_z B, \mu_z = -(2.00232) \frac{e}{2m} S_z, S_z = \pm \frac{\hbar}{2}$$

**EXECUTE:** As we saw in problem VP41.8.1(a).

$$\Delta U = (2.00232) \frac{eB}{2m} \Delta S_z = (2.00232) \frac{eB}{2m} \left[ \frac{\hbar}{2} - \left( -\frac{\hbar}{2} \right) \right] = (2.00232) \mu_B B.$$

The radiation energy  $hf$  must therefore be  $hf = (2.00232) \mu_B B$ . Using  $B = 2.36 \text{ T}$  and solving for  $f$  gives  $f = 6.61 \times 10^{10} \text{ Hz}$ . The wavelength is  $\lambda = c/f = 4.53 \text{ mm}$ .

**EVALUATE:** The energy difference between the two spin states is very small, so the wavelength is much longer than that of visible light.

**VP41.8.3. IDENTIFY:** This problem deals with the effect of a magnetic field on the energy levels of an atom.

**SET UP:** We know the energy of a photon and from the two previous problems we know the energy difference due to the magnetic field.

$$\Delta U = (2.00232) \mu_B B, E = hc/\lambda$$

**EXECUTE:** (a) We want the energy difference between the two  $4p$  levels.

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = \frac{hc(\lambda_2 - \lambda_1)}{\lambda_1 \lambda_2}.$$

Using the given wavelengths gives  $\Delta E = 7.16 \times 10^{-3} \text{ eV}$ .

(b) We want the magnetic field. We use the energy difference from part (a) and solve for  $B$ .

$$\Delta U = (2.00232) \mu_B B$$

$$B = 61.8 \text{ T}.$$

**EVALUATE:** This is a *very* strong magnetic field.

**VP41.8.4. IDENTIFY:** This problem involves the effect of spin and angular momentum on the energy of the hydrogen atom.

**SET UP:** Eq. (41.41) gives the energy levels, where  $j = |l \pm 1/2|$ .

**EXECUTE:** (a) Use Eq. (41.41) to calculate the energy levels.

$$E_{3,3/2} = -\frac{13.60 \text{ eV}}{3^2} \left[ 1 + \frac{\alpha^2}{3^2} \left( \frac{3}{3/2 + 1/2} - \frac{3}{4} \right) \right] = -1.511 \text{ eV} \left( 1 + \frac{\alpha^2}{12} \right).$$

$$E_{3,1/2} = -1.511 \text{ eV} \left( 1 + \frac{\alpha^2}{4} \right)$$

$$(b) E_{3,3/2} - E_{3,1/2} = -1.511 \text{ eV} \left[ \left( 1 + \frac{\alpha^2}{12} \right) - \left( 1 + \frac{\alpha^2}{4} \right) \right] = (-1.511 \alpha^2) \left( \frac{1}{12} - \frac{1}{4} \right) = 1.34 \times 10^{-5} \text{ eV}.$$

The difference is positive, so the  $j = 3/2$  state has higher energy.

(c) We want the difference in wavelengths. Use the answer from part (b) and the approach of Example 41.8.

As in that example, the difference in the wavelengths is

$$\Delta \lambda = -\frac{\lambda}{E_{\text{photon}}} \Delta E_{\text{photon}}.$$

The *difference* in the energy between the  $j = 3/2$  and  $j = 1/2$  levels of the  $n = 3$  shell is *very small* compared to the energy of that shell. Therefore the energy of the photon is essentially  $E_3 - E_2$ .

$$E_{\text{photon}} = E_3 - E_2 = -\frac{13.60 \text{ eV}}{3^2} - \left( -\frac{13.60 \text{ eV}}{2^2} \right) = 1.8890 \text{ eV}.$$

The wavelength of this photon is

$$\lambda = hc/E_{\text{photon}} = hc/(1.8890 \text{ eV}) = 6.565 \times 10^{-7} \text{ m}.$$

The difference in the wavelengths is therefore

$$\Delta\lambda = -\frac{\lambda}{E_{\text{photon}}} \Delta E_{\text{photon}} = -\frac{4.136 \times 10^{-15} \text{ eV} \cdot \text{s}}{1.8890 \text{ eV}} (1.34 \times 10^{-5} \text{ eV}) = -4.66 \times 10^{-12} \text{ m} = -4.66 \times 10^{-3} \text{ nm}.$$

$\lambda_1 - \lambda_2$  is negative, so  $\lambda_2 > \lambda_1$  with  $\lambda_2$  being for the  $j = 1/2$  initial state.

**EVALUATE:** As a check, you could also calculate the energy differences using Eq. (41.41) and calculate the wavelength differences from those results. But the algebra gets a bit tedious.

- 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:**  $E_{1,1,1} = \frac{3\pi^2 \hbar^2}{2mL^2}$ ,  $E_{2,1,1} = \frac{6\pi^2 \hbar^2}{2mL^2}$ ,  $\Delta E = \frac{3\pi^2 \hbar^2}{2mL^2}$ ,  $L^3 = \frac{4}{3}\pi a^3$ .

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

**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:**  $\Delta E = \frac{3\pi^2 (1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(8.00 \times 10^{-11} \text{ m})^2} = 5.653 \times 10^{-17} \text{ J}$ .  $\Delta E = \frac{hc}{\lambda}$  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  $\left(\frac{L}{4}, \frac{L}{4}, \frac{L}{2}\right)$ ,  $\left(\frac{3L}{4}, \frac{L}{4}, \frac{L}{2}\right)$ ,  $\left(\frac{L}{4}, \frac{3L}{4}, \frac{L}{2}\right)$ , 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:** This problem is about an electron in a three-dimensional cubical box.

**SET UP:** The energy levels are given by Eq. (41.16). In the ground state, all three quantum numbers are equal to 1. In the second excited state, two are equal to 2 and one is equal to 1. Therefore the energy

levels are  $E_1 = \frac{3\pi^2\hbar^2}{2mL^2}$  and  $E_2 = \frac{9\pi^2\hbar^2}{2mL^2}$ . The photon energy is  $E = hc/\lambda$ . We want  $L$ .

**EXECUTE:** The energy of the photon is equal to the energy difference between the two states.

$$\Delta E = (9 - 3) \frac{\pi^2\hbar^2}{2mL^2} = \frac{hc}{\lambda}. L = \sqrt{\frac{3h\lambda}{4mc}} = \sqrt{\frac{3h(8.00 \text{ nm})}{4mc}} = 0.121 \text{ nm}.$$

**EVALUATE:** The diameter of a Bohr-model hydrogen atom is about 0.11 nm, so this box is around that size.

- 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:** This problem is about an electron in a three-dimensional cubical box.

**SET UP:** The probability density is the square of the wave function, and Eq. (41.15) gives the wave function. We want the planes for which the probability density is zero, which is where the wave function is zero.

**EXECUTE:** x-axis:  $n_x = 3$ , so  $3\pi x/L = \pi, 2\pi$ . This gives  $x = L/3, x = 2L/3$ .

y-axis:  $n_y = 2$ , so  $2\pi y/L = \pi$ . This gives  $y = L/2$ .

z-axis:  $n_z = 1$ , so  $\pi z/L = \pi$ . This gives  $z = L$ , so there are no  $z$ -planes within the box.

**EVALUATE:** For the  $z$ -axis the probability is zero only at the walls of the box.

- 41.8. IDENTIFY:** We are comparing the quantum mechanical description of the hydrogen atom with the Bohr model.

**SET UP:** Quantum model:  $L = \sqrt{l(l+1)}\hbar$ , Bohr model:  $L = n\hbar$ .

**EXECUTE:** (a)  $n = 3$ . Quantum model: The largest  $l$  is  $n - 1 = 2$ .

$$L = \sqrt{l(l+1)}\hbar = \sqrt{2(2+1)}\hbar = 2.45\hbar.$$

Bohr model:  $L = n\hbar = 3\hbar$ .

$$\text{Percent difference} = (3.00 - 2.45)/3.00 = 18\%.$$

(b)  $n = 30$ .  $l = n - 1 = 29$ . Quantum model:  $L = \sqrt{l(l+1)}\hbar = \sqrt{29(29+1)}\hbar = 29.5\hbar$ .

Bohr model:  $L = n\hbar = 30\hbar$ .

$$\text{Percent difference} = (30 - 29.5)/30 = 1.7\%.$$

**EVALUATE:** For higher states, the results for quantum mechanical and Bohr models get closer together.

- 41.9. IDENTIFY:** The possible values of the angular momentum are limited by the value of  $n$ .

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

**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  $L_{\max} = \sqrt{3(4)}\hbar = 2\sqrt{3}\hbar = 3.65 \times 10^{-34} \text{ kg} \cdot \text{m}^2/\text{s}$ .

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

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

(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.

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

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

$$l=0: L=0, L_z=0.$$

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

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

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

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

(b) Use  $\cos \theta = L_z/L$ .

$$L=0: \theta \text{ is not defined.}$$

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

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

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

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

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

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

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

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

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

**EVALUATE:**  $l$  must be integer.

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

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

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

**(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:

144.7°, 114.1°, 90.0°, 65.9°, 35.3°.

**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  $l$ .

- 41.13. 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  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ .  $\cos\theta = L_z/L$ .

**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  $26.6^\circ$  ( $m_l = +l$ ) to  $180^\circ - 26.6^\circ = 153.4^\circ$  ( $m_l = -l$ ).

- 41.14. 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  $l = 0, 1, 2, \dots, n-1$ .

**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  $n-1 \geq l_{\max}$ , which means that  $n \geq l_{\max} + 1$ . In this case, we know that  $l = 4$ , so  $n \geq 5$ , so the smallest that  $n$  could be is 5.

**EVALUATE:** Any  $n > 5$  is also possible.

- 41.15. IDENTIFY:** This problem deals with a hydrogen atom in the seventh excited level. For the seventh excited level,  $n = 8$ .

**SET UP and EXECUTE: (a)** We want the energy.  $E_n = -(13.6 \text{ eV})/n^2 = -(13.6 \text{ eV})/8^2 = -0.213 \text{ eV}$ .

**(b)** We want  $L_{\max}$ .  $L = \sqrt{l(l+1)}\hbar$  and  $l_{\max} = n-1 = 7$ .  $L_{\max} = \sqrt{7(7+1)}\hbar = 7.48\hbar$ .

**(c)** We want the largest possible angle.  $\cos\theta_L = L_z/L$ .  $L_z = m_l\hbar$ , and  $m_l = 0, \pm 1, \dots, \pm l$ . The angle will be greatest when  $L_z$  is most negative, which in this case is when  $m_l = -7$ , so  $l = 7$ . Therefore  $\cos\theta_L = -7/7.48$ , which gives  $\theta_L = 159^\circ$ .

**EVALUATE:** There are many other possible values for  $\theta_L$  but the value we found is the largest this angle can be.



**41.16. IDENTIFY:**  $l = 0, 1, 2, \dots, n-1$ .  $m_l = 0, \pm 1, \pm 2, \dots, \pm l$ .

**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  $n$ .

**41.17. 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  $\theta$  is for the most negative  $m_l$ .  $L = 2\sqrt{5}\hbar$ . The most negative  $L_z$  is  $L_z = -4\hbar$ .

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

**(c)** The smallest  $\theta$  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  $m_l$ ,

$$\cos \theta = \frac{l}{\sqrt{l(l+1)}}.$$

**41.18. 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  $r = a$ .

**41.19. 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,  $m_l = \frac{1}{2}$ ,  $e^{im_l2\pi} = e^{i\pi} = \cos(\pi) + i\sin(\pi) = -1$  and  $\Phi(\phi) = -\Phi(\phi + 2\pi)$ . But if  $m_l = 1$ ,  $e^{im_l2\pi} = e^{i2\pi} = \cos(2\pi) + i\sin(2\pi) = +1$  and  $\Phi(\phi) = \Phi(\phi + 2\pi)$ , as required.

**41.20. IDENTIFY:** This problem is about the probability distribution for hydrogen.

**SET UP:** Refer to the graphs in Figure 41.8 in the textbook,  $a = 5.29 \times 10^{-11} \text{ m}$ .

**EXECUTE:** (a)  $r/a = (0.476 \text{ nm})/a = 9.00$ . From the bottom graph in Figure 41.8 we see that the  $3d$  curve peaks at approximately  $r/a = 9.00$  and has only one peak, so this must be the state.

(b) Using the same graph as in (a), we see that the  $4f$  graph peaks at  $r/a \approx 16$ , so  $r \approx 16a = 0.85 \text{ nm}$ .

**EVALUATE:** Note that the  $4f$  state peaks after the  $3d$  state, but *before* the second peak of the  $4d$  state.

**41.21. IDENTIFY:** Apply  $\Delta U = \mu_B B$ .

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

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

(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.

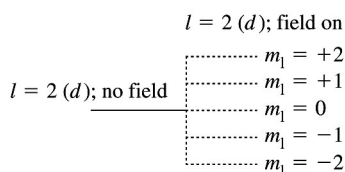
**41.22. IDENTIFY:** Apply  $\Delta E = \mu_B B$ .

**SET UP:**  $\mu_B = 5.788 \times 10^{-5} \text{ eV/T}$ .

**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)  $m_l = -2$  the lowest possible value of  $m_l$ .

(c) The energy level diagram is sketched in Figure 41.22.



**Figure 41.22**

**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.

**41.23. 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  $\Delta U = \mu_B B$ .

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

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

(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.

**41.24. 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  $\pm 1$ .

**SET UP:** For a  $2p$  state,  $m_l$  can be 0,  $\pm 1$ . For a  $1s$  state,  $m_l$  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.

**41.25. 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  $\omega$  and then use  $v = r\omega$  to solve for  $v$ .

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

$$\omega = \frac{5\sqrt{3/4}\hbar}{2mR^2} = \frac{5\sqrt{3/4}(1.055 \times 10^{-34} \text{ J} \cdot \text{s})}{2(9.109 \times 10^{-31} \text{ kg})(1.0 \times 10^{-17} \text{ m})^2} = 2.5 \times 10^{30} \text{ rad/s}.$$

**(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.

**41.26. IDENTIFY:** The transition energy  $\Delta E$  of the atom is related to the wavelength  $\lambda$  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  $\Delta E$  is produced by the hyperfine interaction.

**SET UP:**  $\mu_B = 5.788 \times 10^{-5} \text{ eV/T}$ .

**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  $B \equiv \Delta E/2\mu_B = 5.1 \times 10^{-2} \text{ T}$ , 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.

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

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

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

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

$$U = -2.00232 \mu_B m_s B.$$

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.

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

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

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

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

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

**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.

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

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

**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.

**41.30. 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.

**41.31. 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.

**41.32. 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.

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

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

**EXECUTE:**  $n = 5$  and  $Z_{\text{eff}} = 2.771$  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  $Z_{\text{eff}}^2$ .

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

**EXECUTE:** For the  $4s$  state,  $E = -4.339 \text{ eV}$  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.

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

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

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

$\text{P}^{2+}$  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.

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

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

**EVALUATE:**  $f$  and  $E$  increase and  $\lambda$  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  $K_\alpha$  x ray is produced in a  $L \rightarrow K$  transition and a  $K_\beta$  x ray is produced in a  $M \rightarrow K$  transition.

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

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

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

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

**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 in the textbook.

**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  $n_Z = 1, 2, 3, \dots$

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

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

**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:  $n_X = n_Y = n_Z = 1$ , 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  $E_{1,2,2} = [4(1^2) + 2^2 + 2^2]E_0 = 12E_0 = 12(0.2612 \text{ eV}) = 3.13 \text{ eV}$ .

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

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

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

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

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

**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  $E_{n_X, n_Y, n_Z} = \left( \frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2} + \frac{n_Z^2}{L_Z^2} \right) \frac{\pi^2 \hbar^2}{2m}$ , where  $n_X, n_Y$ , and  $n_Z = 1, 2, 3, \dots$

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

**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  $E_{1,1,1} = 2.24 \text{ eV}$  and  $E_{1,2,1} = 3.47 \text{ eV}$ . (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  $\frac{2}{L_X^2} = (2.24 \text{ eV})\left(\frac{2m}{\pi^2\hbar^2}\right) - \frac{1}{L_Y^2}$ . Using  $L_Y = 0.958 \text{ nm}$ , gives

$$L_X = L_Z = 0.641 \text{ nm}.$$

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

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

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

**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  $\psi$  and put into Eq. (41.5). Use that  $\psi_{n_x}$ ,  $\psi_{n_y}$ , and  $\psi_{n_z}$  are each solutions to Eq. (40.44).

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

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

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

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

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



$$\begin{aligned}\frac{\partial^2 \psi}{\partial x^2} &= \left( \frac{d^2 \psi_{n_x}}{dx^2} \right) \psi_{n_y} \psi_{n_z}, \quad \frac{\partial^2 \psi}{\partial y^2} = \left( \frac{d^2 \psi_{n_y}}{dy^2} \right) \psi_{n_x} \psi_{n_z}, \quad \frac{\partial^2 \psi}{\partial z^2} = \left( \frac{d^2 \psi_{n_z}}{dz^2} \right) \psi_{n_x} \psi_{n_y} \\ \text{So, } -\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi &= \left( -\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_x}}{dx^2} + \frac{1}{2} k' x^2 \psi_{n_x} \right) \psi_{n_y} \psi_{n_z} \\ &+ \left( -\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_y}}{dy^2} + \frac{1}{2} k' y^2 \psi_{n_y} \right) \psi_{n_x} \psi_{n_z} + \left( -\frac{\hbar^2}{2m} \frac{d^2 \psi_{n_z}}{dz^2} + \frac{1}{2} k' z^2 \psi_{n_z} \right) \psi_{n_x} \psi_{n_y} \\ &- \frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) + U\psi = (E_{n_x} + E_{n_y} + E_{n_z})\psi.\end{aligned}$$

Therefore, we have shown that this  $\psi$  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  $\psi_{n_x}(x)$  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,

$$\begin{aligned}-\frac{\hbar^2}{2m} \left( \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) &= (E_{n_x} + E_{n_y} + E_{n_z} - \frac{1}{2} k'_1 x^2 - \frac{1}{2} k'_1 y^2 - \frac{1}{2} k'_2 z^2) \psi \\ &= (E_{n_x} + E_{n_y} + E_{n_z} - U) \psi = (E - U) \psi\end{aligned}$$

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:** This problem deals with a particle in a three-dimensional noncubical box.

**SET UP:** The energy levels are shown in Eq. (41.17) in textbook.

**EXECUTE: (a)** We want energy difference between the first excited energy level and the ground state.

For this box,  $L_Y = 2L_X$  and  $L_Z = L_Y/3 = 2L_X/3$ . In terms of  $L_X$ , the energies are

$$E_{n_X, n_Y, n_Z} = \left( \frac{n_X^2}{L_X^2} + \frac{n_Y^2}{4L_X^2} + \frac{9n_Z^2}{4L_X^2} \right) \frac{\pi^2 \hbar^2}{2m}.$$

For the ground state, all the quantum numbers are equal to 1. For the first excited state, the smallest energy above the ground state is when  $n_X = n_Z = 1$  and  $n_Y = 2$ . The energy difference between this state and ground is  $\Delta E = E_{1,2,1} - E_{1,1,1}$ . Using the above energy equation gives

$$\Delta E = \left[ \left( \frac{1^2}{1} + \frac{2^2}{4} + \frac{9}{4} \right) - \left( \frac{1^2}{1} + \frac{1^2}{4} + \frac{9}{4} \right) \right] \frac{\pi^2 \hbar^2}{2mL_X^2} = \frac{3\pi^2 \hbar^2}{8mL_X^2}.$$

We could also express the result in terms of  $L_Y$  as  $\Delta E = \frac{3\pi^2 \hbar^2}{2mL_Y^2}$ .

**(b)** This state is *not* degenerate because no other set of quantum numbers gives the same energy.

**(c)** We want to know where the probability distribution is greatest for the ground state.

Along the  $x$ -axis:  $\sin \pi x/L_X$  is greatest when  $\pi x/L_X = \pi/2$ , which is when  $x = L_X/2$ .

Along the  $y$ -axis:  $\sin \pi y/L_Y = \sin \pi y/2L_X$  is greatest when  $\pi y/2L_X = \pi/2$ , so  $y = L_X$ .

Along the  $z$ -axis:  $\sin \pi z/L_Z = \sin \pi z/(2L_X/3)$  is greatest when  $3\pi z/2L_X = \pi/2$ , so  $z = L_X/3$ .

**EVALUATE:** The energy degeneracy is removed for a noncubical box because, due to the different dimensions, the quantum numbers all have different coefficients.

**41.47. IDENTIFY and SET UP:** To calculate the total number of states for the  $n^{\text{th}}$  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:** We are modeling nuclei in the sun as a particle in a three-dimensional cubical box.

**SET UP and EXECUTE: (a)** Assume the sun is all hydrogen with one electron each. The number  $N$  of electrons is  $N = m_{\text{sun}}/m_{\text{proton}} = (2.0 \times 10^{30} \text{ kg})/(1.7 \times 10^{-27} \text{ kg}) = 1.2 \times 10^{57}$  electrons.

**(b)** The volume  $V$  each electron occupies is  $V_{\text{sun}}/N = (4/3 \pi R^3)/N = 4/3 \pi (7000 \text{ km})^3/(1.2 \times 10^{57}) = 1.2 \times 10^{-36} \text{ m}^3$ .

**(c)** We want the volume per carbon atom. Each carbon atom has 6 electrons, so it occupies the space of 6 electrons. Hence its volume is  $7.2 \times 10^{-36} \text{ m}^3$ .

**(d)** If the volume is a cube with side of length  $L$ , then  $L^3 = 7.2 \times 10^{-36} \text{ m}^3$ , so  $L = 1.9 \text{ pm}$ .

**(e)**  $n_X, n_Y, n_Z$  can be 1, 2, 3, ..., and  $m_z = \pm 1/2$ . The possible states for 6 electrons are:

Lowest state: (1, 1, 1,  $\pm 1/2$ )

Possible higher states: (1, 1, 2,  $\pm 1/2$ ), (1, 2, 1,  $\pm 1/2$ ), (2, 1, 1,  $\pm 1/2$ ).

**(f)** We want the highest energy. Use Eq. (41.16). These states are degenerate, so we only need to calculate one of them, and we use  $L = 1.9 \text{ pm}$ .

$$E_{1,1,2} = \frac{(1^2 + 1^2 + 2^2) \pi^2 \hbar^2}{2mL^2} = 1.0 \times 10^{-13} \text{ J} = 630 \text{ keV}.$$

**EVALUATE:** Modeling such as this gives only very rough approximations, but it can give reasonable order-of-magnitude estimates.

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

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

$$U(r) = \frac{1}{4\pi\epsilon_0} \frac{q_1 q_2}{r}, \text{ with } q_1 = +Ze \text{ and } q_2 = -e.$$

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

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

$$r = \frac{(4\pi\epsilon_0)2\hbar^2}{me^2} = 2a.$$

**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  $\alpha = 2/a$ .

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

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

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

**41.50. 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,  $r^2|\psi|^2 = Cr^2e^{-2r/a}$ .

**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  $r \rightarrow \infty$ .

**41.52. IDENTIFY:** This problem involves the Zeeman effect.

**SET UP and EXECUTE:** (a) We want the current.  $\mu = IA = I\pi r^2$ , so  $I = \mu/\pi r^2$ . Using  $\mu$  from the problem gives

$$I = \frac{\frac{e}{2m_p} S_z}{\pi r^2} = \frac{\left(\frac{e}{2m_p}\right) \frac{\hbar}{2}}{\pi (0.85 \text{ fm})^2} = 1100 \text{ A}.$$

(b) We want the magnetic field at  $x = 0.40a_0$  from the proton. Use Eq. (28.15) for a circular loop.

$$B_x = \frac{\mu_0 I a^2}{2(x^2 + a^2)^{3/2}}.$$

In our case,  $a$  is the radius of the “loop” (which is the proton), so  $a = R_p$ .  $x = 0.40a_0 \gg R_p$ . So

$$B_x = \frac{\mu_0 I R_p^2}{2(0.40a_0)^3}.$$

Using  $R_p = 0.85 \text{ fm}$ ,  $I = 1100 \text{ A}$ , and  $a_0 = 5.29 \times 10^{-11} \text{ m}$  gives  $B = 52 \text{ mT}$ .

(c) We want the potential energy due to the electron spin. Use Eq. (41.38) and  $U = \pm \mu_B B$ .

$$\mu_z = (2.00232)(e/2m)S_z \approx 2(e/2m)(\hbar/2) = \hbar e/2m = \mu_B.$$

$$U = \mu_B B = (5.788 \times 10^{-5} \text{ eV/T})(52 \text{ mT}) = 3.0 \text{ } \mu\text{eV}.$$

(d) We want the wavelength.  $hc/\lambda = 2U$ , so  $\lambda = hc/2U = hc/[2(3.0 \text{ } \mu\text{eV})] = 0.21 \text{ m} = 21 \text{ cm}$ .

**EVALUATE:** (e) The observed radiation has a wavelength of precisely 21 cm, so it definitely could be from electron spin flip.

**41.53. IDENTIFY:** This problem is about the broadening of spectral lines in hydrogen due to spin-orbit coupling.

**SET UP:** The blue spectral line of wavelength 434 nm is due to a transition from the  $n = 5$  to the  $n = 2$  shell. Eq. (41.41) applies, with  $l = 0, 1, 2, 3, 4$  and  $j = |l \pm 1/2|$ . In any transition  $\Delta l = \pm 1$ . Use Example 41.8 as a guide.

**EXECUTE:** (a) We want the number of states.

For the  $n = 2$  level:  $l = 0$  and  $1$ . For  $l = 0$ ,  $j = |0 \pm 1/2| = 1/2$ . For  $l = 1$ ,  $j = 1 \pm 1/2 = 1/2$  and  $3/2$ . The possible states are  $(0, 1/2)$ ,  $(1, 1/2)$ , and  $(1, 3/2)$ , so there are 3 states.

For the  $n = 5$  level:  $l = 0, 1, 2, 3$ , or  $4$ . The possible values of  $j$  are

$$l = 0: j = 1/2$$

$$l = 1: j = 1/2, 3/2$$

$$l = 2: j = 3/2, 5/2$$

$$l = 3: j = 5/2, 7/2$$

$$l = 4: j = 7/2, 9/2$$

The possible states are  $(0, 1/2)$ ,  $(1, 1/2)$ ,  $(1, 3/2)$ ,  $(2, 3/2)$ ,  $(2, 5/2)$ ,  $(3, 5/2)$ ,  $(3, 7/2)$ ,  $(4, 7/2)$ ,  $(4, 9/2)$ .

There are a total of 9 states.

(b) We want the number of different energy levels for each value of  $n$ . From Eq. (41.41) we see that for a given  $n$ , the energy  $E_{n,j}$  depends only on  $j$ . Therefore all states having the same  $n$  and  $j$  have the same energy.

$n = 2$  level: Since  $j$  has only 2 different possible values ( $1/2$  and  $3/2$ ), there are only 2 different energy levels.

$n = 5$  level: Since  $j$  has 5 different values ( $1/2, 3/2, 5/2, 7/2, 9/2$ ) there are 5 different energy levels.

For each energy level, we want its difference from  $-(13.6 \text{ eV})/n^2$ . Call  $E_n = -(13.6 \text{ eV})/n^2$  and call the energy difference we want  $\Delta E_{n,j} = E_{n,j} - E_n$ , where  $E_{n,j}$  is the energy of the  $(n, j)$  level as given in Eq. (41.41). For calculations use  $\alpha^2 = 5.32514 \times 10^{-5}$ . Using Eq. (41.41), we get

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

Simplifying to a working equation gives

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

We now use this equation to calculate the energy *differences*. If  $\Delta E_{nj}$  is negative, the energy of the level is *less than*  $E_n$ .

$n = 2$  level: For  $n = 2$  and  $j = 1/2$ , we have

$$\Delta E_{2,1/2} = -\frac{13.60 \text{ eV} \alpha^2}{2^4} \left( \frac{2}{1/2+1/2} - \frac{3}{4} \right) = -5.658 \times 10^{-5} \text{ eV}.$$

For  $n = 2$  and  $j = 3/2$ , we have

$$\Delta E_{2,3/2} = -\frac{13.60 \text{ eV} \alpha^2}{2^4} \left( \frac{2}{3/2+1/2} - \frac{3}{4} \right) = -1.1316 \times 10^{-5} \text{ eV}.$$

$n = 5$  level: For  $n = 5$  and  $j = 1/2$ , we have

$$\Delta E_{5,1/2} = -\frac{13.60 \text{ eV} \alpha^2}{5^4} \left( \frac{5}{1/2+1/2} - \frac{3}{4} \right) = -4.11356 \times 10^{-5} \text{ eV}.$$

For  $n = 5$  and  $j = 3/2$ , we have

$$\Delta E_{5,3/2} = -\frac{13.60 \text{ eV} \alpha^2}{5^4} \left( \frac{5}{3/2+1/2} - \frac{3}{4} \right) = -1.69382 \times 10^{-5} \text{ eV}.$$

For  $n = 5$  and  $j = 5/2$ , we have

$$\Delta E_{5,5/2} = -\frac{13.60 \text{ eV} \alpha^2}{5^4} \left( \frac{5}{5/2+1/2} - \frac{3}{4} \right) = -8.87239 \times 10^{-6} \text{ eV}.$$

For  $n = 5$ ,  $j = 7/2$ , we have

$$\Delta E_{5,7/2} = -\frac{13.60 \text{ eV} \alpha^2}{5^4} \left( \frac{5}{7/2+1/2} - \frac{3}{4} \right) = -4.83949 \times 10^{-6} \text{ eV}.$$

For  $n = 5$ ,  $j = 9/2$ , we have

$$\Delta E_{5,9/2} = -\frac{13.60 \text{ eV} \alpha^2}{5^4} \left( \frac{5}{9/2+1/2} - \frac{3}{4} \right) = -2.41974 \times 10^{-6} \text{ eV}.$$

Notice that in every case, fine structure due to spin-orbit coupling makes the energy levels *more negative*, i.e. *lower*.

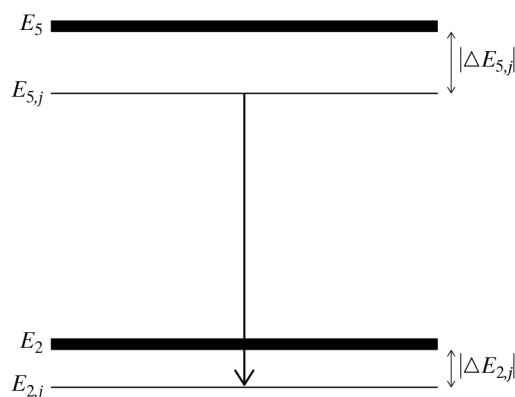


Figure 41.53

(c) We want the transition that emits the *shortest* wavelength of light. The shortest wavelength photon will have the highest energy, so it is between energy levels that have the *greatest* energy difference between them. Figure 41.53 illustrates a transition from a  $(5, j)$  level to a  $(2, j)$  level, where the two values of  $j$  are *not* the same. For the energy difference between these two levels to be as large as possible,  $|\Delta E_{5,j}|$  should be the *smallest* it can be, and  $|\Delta E_{2,j}|$  should be the *largest* it can be. But the transition must also obey  $\Delta l = \pm 1$ . For the  $n = 2$  level,  $l = 0$  or  $1$ , which means that in the  $n = 5$  level,  $l = 0, 1$ , or  $2$ . The energy levels, for a given  $n$ , depend only on  $j$ , so the  $j$  values for possible transitions that result in an energy difference and obey  $\Delta l = \pm 1$  are

$$j = 1/2 \rightarrow j = 3/2 \quad (l = 0 \rightarrow l = 1)$$

$$j = 3/2 \rightarrow j = 1/2 \quad (l = 1 \rightarrow l = 0)$$

$$j = 5/2 \rightarrow j = 1/2 \quad (l = 2 \rightarrow l = 1)$$

$$j = 5/2 \rightarrow j = 3/2 \quad (l = 2 \rightarrow l = 1)$$

Using our results from part (b), we see that  $|\Delta E_{2,j}|$  is greatest when  $j = 1/2$  ( $l = 1$ ), and  $|\Delta E_{5,j}|$  is smallest when  $j = 5/2$  ( $l = 2$ ). Therefore the transition from the  $(5, 2, 5/2)$  level to the  $(2, 1, 1/2)$  level emits a photon of the greatest energy and therefore the shortest wavelength. The energy of this photon is  $E_{\text{photon}} = E_5 + \Delta E_{5,5/2} - (E_2 + \Delta E_{2,1/2})$ . Using this condition with  $E_n = -(13.60 \text{ eV})/n^2$  and our results from part (b), we have

$$\begin{aligned} E_{\text{photon}} &= E_5 - E_2 + \Delta E_{5,5/2} - \Delta E_{2,1/2} \\ E_{\text{photon}} &= -\frac{13.60 \text{ eV}}{5^2} - \left( -\frac{13.60 \text{ eV}}{2^2} \right) + (-8.87239 \times 10^{-5} \text{ eV}) - (-5.658 \times 10^{-5} \text{ eV}). \\ E_{\text{photon}} &= \underbrace{2.856 \text{ eV}}_{E_5 \rightarrow E_2} + \underbrace{4.7708 \times 10^{-5} \text{ eV}}_{\Delta E_{5/2 \rightarrow 1/2}}. \end{aligned}$$

If there were no spin-orbit coupling, the wavelength of the photon would be 434 nm, as given in the problem. But, due to spin-orbit coupling, what appears as a single spectral line is made up of a number of lines, each of slightly different wavelength. To find the difference of the shortest-wavelength line from 434 nm, we use the approach in Example 41.8. The energy of the photon is  $E = hc/\lambda$ . As in the example, we can express this as

$$\Delta E = -\frac{hc}{\lambda^2} \Delta \lambda$$

$$\Delta \lambda = \frac{\lambda^2 \Delta E}{hc} = -\frac{(434 \text{ nm})^2 (4.7708 \times 10^{-5} \text{ eV})}{(4.13567 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})} = -7.26 \times 10^{-12} \text{ m} = -7.26 \times 10^{-3} \text{ nm}.$$

(d) We want the longest wavelength photon. Refer to Figure 41.53. The longest wavelength is due to a transition between levels having the smallest energy difference between them. Using the allowed transitions from part (c), we see that the energy difference is *smallest* when  $|\Delta E_{5,j}|$  is a *maximum* and  $|E_{2,j}|$  is a *minimum*. For the allowed transitions, we see that  $|E_{2,j}|$  is smallest when  $j = 3/2$  ( $l = 1$ ), and  $|\Delta E_{5,j}|$  is largest when  $j = 1/2$  ( $l = 0$ ). So this transition is from the  $(5, 0, 1/2)$  level to the  $(2, 1, 3/2)$  level. Follow the same approach as for part (c), which gives

$$\begin{aligned} E_{\text{photon}} &= E_5 - E_2 + \Delta E_{5,1/2} - \Delta E_{2,3/2} \\ E_{\text{photon}} &= -\frac{13.60 \text{ eV}}{5^2} - \left( -\frac{13.60 \text{ eV}}{2^2} \right) + (-4.11356 \times 10^{-5} \text{ eV}) - (-1.1316 \times 10^{-5} \text{ eV}). \\ E_{\text{photon}} &= \underbrace{2.856 \text{ eV}}_{E_5 \rightarrow E_2} - \underbrace{2.98196 \times 10^{-5} \text{ eV}}_{\Delta E_{1/2 \rightarrow 3/2}}. \end{aligned}$$

As before, we have

$$\Delta \lambda = -\frac{\lambda^2 \Delta E}{hc} = -\frac{(434 \text{ nm})^2 (-2.98196 \times 10^{-5} \text{ eV})}{(4.13567 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})} = +4.535 \times 10^{-12} \text{ m} = +4.54 \times 10^{-3} \text{ nm}.$$

(e) We want the total broadening of the spectral line. The width is the sum of the quantities we calculated in parts (c) and (d). The width is  $7.26 \times 10^{-3} \text{ nm} + 4.54 \times 10^{-3} \text{ nm} = 1.18 \times 10^{-2} \text{ nm}$ .

**EVALUATE:** Notice that fine structure effects make very small changes in the wavelength. That is why they are called *fine* structure.

**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  $\pm 1$ .

**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  $\pm 1$ . 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:

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

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

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

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

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

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

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

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

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

(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  $-8.50000 \text{ eV} + 0$  and  $-8.50000 \text{ eV} \pm 0.000203 \text{ eV}$ , giving energies of:  $-8.50020 \text{ eV}$ ,  $-8.50000 \text{ eV}$ , and  $-8.49980 \text{ eV}$ .

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

Therefore we get the following:

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

For  $E = 2.61176 \text{ eV} + 0.000203 \text{ eV} = 2.611963 \text{ eV}$ :

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

For  $E = 2.61176 \text{ eV} - 0.000203 \text{ eV} = 2.61156 \text{ eV}$ :

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

**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  $\pm 1$ , and for the  $s$  state  $m_l = 0$ . Between any two adjacent lines,  $\Delta E = \mu_B B$ . Since the change in the wavelength ( $\Delta \lambda$ ) is very small, the energy change ( $\Delta E$ ) 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

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

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

**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  $\mu_z$  is

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

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

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

**41.57. IDENTIFY:** We want to calculate the magnetic moment of a spinning sphere of charge.

**SET UP:**  $\mu = g(Q/2M)L$ . Follow the directions in each step of the problem.

**EXECUTE:** (a)  $da = (Rd\theta)2\pi R \sin \theta d\theta = 2\pi R^2 \sin \theta d\theta$ .

(b)  $dI = (\sigma dA)/T$  and  $T = 2\pi/\omega$ . Combining these relations with the result from part (a) gives

$$dI = \frac{\sigma 2\pi R^2 \sin \theta d\theta}{2\pi/\omega} = \sigma \omega R^2 \sin \theta d\theta.$$

(c) Using the results from parts (a) and (b) gives

$$d\mu = AdI = \pi(R \sin \theta)^2 \sigma \omega R^2 \sin \theta d\theta = \pi \sigma \omega R^4 \sin^3 \theta d\theta.$$

(d) Integrate to find the magnetic moment.

$$\mu = \int_0^\pi \pi \sigma \omega R^4 \sin^3 \theta d\theta = \pi \sigma \omega R^4 \int_0^\pi \sin \theta (1 - \cos^2 \theta) d\theta = \frac{4\pi \sigma \omega R^4}{3}.$$

$$\sigma = Q/4\pi R^2 \text{ gives } \mu = \left( \frac{4\pi \omega R^4}{3} \right) \left( \frac{Q}{4\pi R^2} \right) = \frac{\omega R^2 Q}{3}.$$

(e) We now have a solid sphere. Consider the sphere to be a series of thin concentric shells each of thickness  $dr$ . Use the results of part (d) with  $R \rightarrow r$  and  $Q \rightarrow dq$  (the charge within the shell).

$$dq = \rho(r)dr = \rho(r)4\pi r^2 dr, \quad d\mu = \frac{\omega R^2 dq}{3} = \frac{\omega r^2}{3} \rho(r)4\pi r^2 dr, \quad \mu = \frac{4\pi \omega}{3} \int_0^R \rho(r)r^4 dr.$$

(f) We want the  $g$ -factor. Use  $L = I\omega$ ,  $I = cMR^2$ , and the results of part (e).

$$\mu = \frac{4\pi \omega}{3} \int_0^R \rho(r)r^4 dr = g \frac{Q}{2M} L = g \frac{Q}{2M} I \omega = \frac{gQ}{2M} (cMR^2 \omega).$$

$$g = \frac{8\pi}{3QcR^2} \int_0^R \rho(r)r^4 dr.$$

(g) We want  $g$  if the solid sphere has uniform density. In this case the integral is

$$\int_0^R \rho(r)r^4 dr = \frac{Q}{\frac{4}{3}\pi R^3} \frac{R^5}{5}.$$

Using  $c = 2/5$  and solving the result in (f) for  $g$  gives  $g = 1$ .

**EVALUATE:** The result shows that for any spinning uniform solid sphere the  $g$ -factor is one.



**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  $n^2 a_0$ .

**EXECUTE:**  $v = \frac{\sqrt{l(l+1)}\hbar}{m(n^2 a_0)} = \frac{\sqrt{2}(6.63 \times 10^{-34} \text{ J} \cdot \text{s})}{2\pi(9.11 \times 10^{-31} \text{ kg})(4)(5.29 \times 10^{-11} \text{ m})} = 7.74 \times 10^5 \text{ m/s}$ . 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  $3p$  electrons in sodium is much larger than the value we calculated for  $2p$  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  $1s^4 2s^4 2p^{12}$ ; 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:**  $\mu_B = \frac{e\hbar}{2m} = \frac{eh}{4\pi m}$ .

**EXECUTE:** The effective field is that which gives rise to the observed difference in the energy level

transition,  $B = \frac{\Delta E}{\mu_B} = \frac{hc}{\mu_B} \left( \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \right) = \frac{4\pi mc}{e} \left( \frac{\lambda_1 - \lambda_2}{\lambda_1 \lambda_2} \right)$ . 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:

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

**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

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

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

**(b) IDENTIFY and SET UP:** Calculate the change in  $\Delta E$  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 39.74c 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  $\Delta E$  means a larger  $\lambda$ ; the magnetic field increases the wavelength. The fractional shift in wavelength,  $\Delta\lambda/\lambda$  is small, only  $1.2 \times 10^{-5}$ .

- 41.62. IDENTIFY:** The interaction energy for an electron in a magnetic field is  $U = -\mu_z B$ , where  $\mu_z$  is given by  $\mu_z = -(2.00232) \left( \frac{e}{2m} \right) S_z$ .

**SET UP:**  $\Delta S_z = \hbar$ .

**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 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 41.63 shows the graph of  $f$  versus  $B$  for this data. The slope of the best-fit straight line is  $2.84 \times 10^{10} \text{ Hz/T}$ .

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

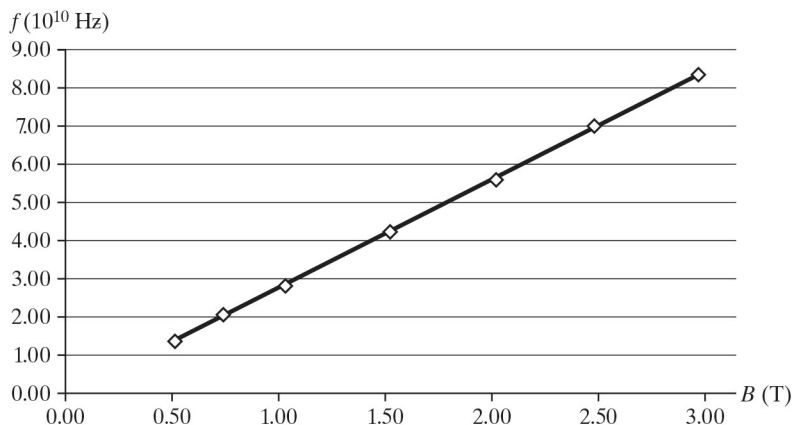


Figure 41.63

(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

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

**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.

**41.64. IDENTIFY:** The photons have different energy due to spin-orbit coupling, which shifts 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  $\Delta E$  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

$E_n = -\frac{13.60 \text{ eV}}{n^2}$  to find the energy difference  $\Delta E$ , which 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

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

$\Delta E_{\text{photon}}$  is the energy difference between the  $E_{3,3/2}$  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 is smaller.

**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  $E_n = \frac{Z_{\text{eff}}^2}{n^2}(13.6 \text{ eV})$ .

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

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

$$\text{Li: } E = (0.010364)(520.2 \text{ kJ/mol}) = 5.391 \text{ eV}$$

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

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

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

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

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

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

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

$$\text{Na: } Z = 11, n = 3$$

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

$$\text{Rb: } Z = 37, n = 5$$

$$\text{Cs: } Z = 55, n = 6$$

$$\text{Fr: } Z = 87, n = 7.$$

(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  $Z_{\text{eff}}$ . For example, for Li we have

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

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

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

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

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

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

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

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

**EVALUATE:** (d) We can see that  $Z_{\text{eff}}$  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

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

which is between the ground state (1, 1, 1) and the next higher state (2, 1, 1). The energy absorbed by

$$\text{the photon is } \Delta E = \frac{hc}{\lambda}.$$

**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)  $\lambda_1$  and the one in part (b)  $\lambda_2$ . From part (a)

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

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

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:** This problem deals with the entanglement of three spin-3/2 particles.

**SET UP:**  $s_z = m_z \hbar$ ,  $m_z = \pm 1/2, \pm 3/2$ .

**EXECUTE:** (a) These particles have spin 3/2, so their spin magnitude  $S$  is

$$S = \sqrt{\frac{3}{2} \left( \frac{3}{2} + 1 \right)} \hbar = \sqrt{15/4} \hbar.$$

(b) No particles can have identical states. We follow the reasoning of Section 41.8 in the textbook. For simplicity call the states  $A = 1/2$ ,  $B = -1/2$ ,  $C = -3/2$ . The possible combinations of  $ABC$  are  $ABC$ ,  $ACB$ ,  $BAC$ ,  $BCA$ ,  $CAB$ , and  $CBA$ . In terms of the wave functions, the normalized wave functions are

$$\psi = \frac{1}{\sqrt{6}} (\psi_{+1/2} \psi_{-1/2} \psi_{-3/2} - \psi_{+1/2} \psi_{-3/2} \psi_{-1/2} + \psi_{-1/2} \psi_{+1/2} \psi_{-3/2} - \psi_{+1/2} \psi_{-3/2} \psi_{+1/2} + \psi_{-3/2} \psi_{+1/2} \psi_{-1/2} - \psi_{-3/2} \psi_{-1/2} \psi_{+1/2}).$$

The factor of  $1/\sqrt{6}$  is present for normalization because the probability is proportional to the square of the wave function.

(c) Particle  $A$  has  $m_z = +1/2$ , but the other two could have  $m_z = -3/2$  or  $-1/2$ . So the wave function is

$$\text{now } \psi = \frac{1}{\sqrt{2}} (\psi_{+1/2} \psi_{-3/2} \psi_{-1/2} - \psi_{+1/2} \psi_{+1/2} \psi_{-3/2}).$$

(d) Particle  $A$  has  $m_z = +1/2$ , so particle  $B$  cannot have  $m_z = +1/2$ . But it could have  $m_z = -1/2$  or  $-3/2$ . None of them can have  $m_z = +3/2$ . So the probabilities are 1/2, 0, 1/2, 0.

(e) Now we know that particle  $C$  has  $m_z = -3/2$ , so the wave functions are  $\psi = \psi_{+1/2} \psi_{-1/2} \psi_{-3/2}$ .

(f) We know that  $m_z = -1/2$  for particle  $B$ , so the probabilities are 0, 1, 0, 0.

**EVALUATE:** We could not draw all these conclusions if the particles were not entangled.

**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

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

$\hbar\omega[N^2 - N + N] = \hbar\omega N^2 = \hbar N^2 \sqrt{\frac{k'}{m}}$ . 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,  $\frac{(+2e)(-e)}{4\pi\epsilon_0 r^2} + \frac{(-e)(-e)}{4\pi\epsilon_0 (2r)^2} = \frac{-mv^2}{r}$ . But, from the quantization of angular momentum in the first Bohr

$$\text{orbit, } L = mvr = \hbar \Rightarrow v = \frac{\hbar}{mr}. \text{ So, } \frac{-2e^2}{4\pi\epsilon_0 r^2} + \frac{e^2}{4\pi\epsilon_0 (2r)^2} = \frac{-mv^2}{r} = \frac{-m\left(\frac{\hbar}{mr}\right)^2}{r} = -\frac{\hbar^2}{mr^3}$$

$$\Rightarrow \frac{-7e^2}{4r^2} = -\frac{4\pi\epsilon_0 \hbar^2}{mr^3}. \quad r = \frac{4\left(\frac{4\pi\epsilon_0 \hbar^2}{me^2}\right)}{7} = \frac{4}{7}a_0 = \frac{4}{7}(0.529 \times 10^{-10} \text{ m}) = 3.02 \times 10^{-11} \text{ m. And}$$

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

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

$$\text{(c) } U = 2\left(\frac{-2e^2}{4\pi\epsilon_0 r}\right) + \frac{e^2}{4\pi\epsilon_0 (2r)} = \frac{-4e^2}{4\pi\epsilon_0 r} + \frac{e^2}{4\pi\epsilon_0 (2r)} = \frac{-7}{2}\left(\frac{e^2}{4\pi\epsilon_0 r}\right) = -2.67 \times 10^{-17} \text{ J} = -166.9 \text{ eV.}$$

**(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  $K + U = -83.4 \text{ eV}$ . The ground state energy of  $\text{He}^+$  is  $4(-13.6 \text{ eV}) = -54.4 \text{ eV}$ . Therefore, the energy required to remove one electron from helium in this model is  $-(-83.4 \text{ eV} + 54.4 \text{ eV}) = 29.0 \text{ eV}$ . 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  $1 \times 10^{-6} \text{ m} = 5.29 \times 10^{-11} \text{ m}$ , 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  $20 \mu\text{m}$ .

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

**EVALUATE:** For rubidium, with 85 nucleons, the mass density  $\rho$  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  $1.53 \text{ g/cm}^3$ , 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:**  $m_l = \pm l, \pm(l-1), \dots, 0$ .  $m_s = \pm \frac{1}{2}$  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  $l$ .