

## ATOMIC STRUCTURE

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

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

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

(b)  $n_X^2 + n_Y^2 + n_Z^2 = 9$ . Occurs for  $n_X = 2$ ,  $n_Y = 1$ ,  $n_Z = 1$ , for  $n_X = 1$ ,  $n_Y = 2$ ,  $n_Z = 1$  and for  $n_X = 1$ ,  $n_Y = 1$ ,  $n_Z = 2$ . 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,

$E = -\frac{13.6 \text{ eV}}{n^2}$ . 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  $\left(\frac{L}{4}, \frac{L}{4}, \frac{L}{2}\right)$ ,  $\left(\frac{L}{4}, \frac{3L}{4}, \frac{L}{2}\right)$ ,  $\left(\frac{3L}{4}, \frac{L}{4}, \frac{L}{2}\right)$  and  $\left(\frac{3L}{4}, \frac{3L}{4}, \frac{L}{2}\right)$ .

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

**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.

**41.8. 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)**  $l=0$ :  $L=0$ ,  $L_z=0$ .  $l=1$ :  $L=\sqrt{2}\hbar$ ,  $L_z=\hbar, 0, -\hbar$ .  $l=2$ :  $L=\sqrt{6}\hbar$ ,  $L_z=2\hbar, \hbar, 0, -\hbar, -2\hbar$ .

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

(b)  $L=0$ :  $\theta$  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.

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

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

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

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

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

**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  $m_l = 2$ ,  $144.7^\circ$ ,  $114.1^\circ$ ,  $90.0^\circ$ ,  $65.9^\circ$ ,  $35.3^\circ$ .

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

**41.11. IDENTIFY and SET UP:** The angular momentum  $L$  is related to the quantum number  $l$  by Eq. (41.22),  $L = \sqrt{l(l+1)}\hbar$ . The maximum  $l$ ,  $l_{\max}$ , for a given  $n$  is  $l_{\max} = n-1$ .

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

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

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

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

**41.12. 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:** The  $(l, m_l)$  combinations are  $(0, 0)$ ,  $(1, 0)$ ,  $(1, \pm 1)$ ,  $(2, 0)$ ,  $(2, \pm 1)$ ,  $(2, \pm 2)$ ,  $(3, 0)$ ,  $(3, \pm 1)$ ,  $(3, \pm 2)$ ,  $(3, \pm 3)$ ,  $(4, 0)$ ,  $(4, \pm 1)$ ,  $(4, \pm 2)$ ,  $(4, \pm 3)$  and  $(4, \pm 4)$  a total of 25.

(b) Each state has the same energy ( $n$  is the same),  $-\frac{13.60 \text{ eV}}{25} = -0.544 \text{ eV}$ .

**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  $n$ .

**41.13. 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  $m_l$ ,  $\cos\theta = \frac{l}{\sqrt{l(l+1)}}$ .

**41.14. 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.

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

(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  $r = a$ .

**41.15. IDENTIFY:**  $P(a) = \int_0^a |\psi_{1s}|^2 dV = \int_0^a \frac{1}{\pi a^3} e^{-2r/a} (4\pi r^2 dr)$ .

$$\text{SET UP: From Example 41.4, } \int r^2 e^{-2r/a} dr = \left( -\frac{ar^2}{2} - \frac{a^2r}{2} - \frac{a^3}{4} \right) e^{-2r/a}.$$

**EXECUTE:**

$$P(a) = \frac{4}{a^3} \int_0^a r^2 e^{-2r/a} dr = \frac{4}{a^3} \left[ \left( -\frac{ar^2}{2} - \frac{a^2r}{2} - \frac{a^3}{4} \right) e^{-2r/a} \right]_0^a = \frac{4}{a^3} \left[ \left( -\frac{a^3}{2} - \frac{a^3}{2} - \frac{a^3}{4} \right) e^{-2} + \frac{a^3}{4} e^0 \right] = 1 - 5e^{-2}.$$

**EVALUATE:**  $P(a) < 1$ , as it must be.

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

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

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

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

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

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

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

(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.

**41.18. IDENTIFY:** Apply Eq. (41.36).

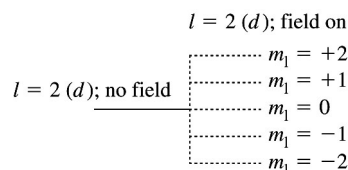
**SET UP:**  $\mu_B = 5.788 \times 10^{-5} \text{ eV/T}$

**EXECUTE: (a)**  $\Delta E = \mu_B B = (5.79 \times 10^{-5} \text{ eV/T})(0.400 \text{ T}) = 2.32 \times 10^{-5} \text{ eV}$ .

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

**(c)** The energy level diagram is sketched in Figure 41.18.

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



**Figure 41.18**

**41.19. IDENTIFY and SET UP:** The interaction energy between an external magnetic field and the orbital angular momentum of the atom is given by Eq. (41.36). 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.

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

**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.

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

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

**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.

**41.22. IDENTIFY:** Apply Eq. (41.40), with  $S_z = -\frac{\hbar}{2}$ .

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

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

$$U = -\frac{(2.00232)}{2}(5.788 \times 10^{-5} \text{ eV/T})(0.480 \text{ T}) = -2.78 \times 10^{-5} \text{ eV}.$$

(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.

**41.23. IDENTIFY and SET UP:** The interaction energy is  $U = -\vec{\mu} \cdot \vec{B}$ , with  $\mu_z$  given by Eq. (41.40).

**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.

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

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

**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.

**41.24. 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  $B \equiv \Delta E / 2\mu_B = 5.1 \times 10^{-2}$  T, far smaller than that found in Example 41.7 for spin-orbit coupling.

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

**41.25. IDENTIFY and SET UP:**  $j$  can have the values  $l + 1/2$  and  $l - 1/2$ .

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

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

**41.26. 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.

**41.27. 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.

**41.28. 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.

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

**SET UP:** Beryllium has 4 electrons.

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

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

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

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

**41.30. IDENTIFY and SET UP:** Apply Eq. (41.45). The ionization potential is  $-E_n$ , where  $E_n$  is the level energy for the least tightly bound electron.

**EXECUTE:** As electrons are removed, for the outermost electron the screening of the nucleus by the remaining electrons decreases. The ground state electron configuration of magnesium is  $1s^2 2s^2 2p^6 3s^2$ .

For a  $3s$  electron the other electrons screen the nucleus and  $Z_{\text{eff}} \approx 1$ . For  $\text{Mg}^+$  the electron configuration is  $1s^2 2s^2 2p^6 3s$  and the 10 inner electrons screen the nucleus from the  $3s$  electron.  $Z_{\text{eff}} \approx 2$ . For  $\text{Mg}^{2+}$  the electron configuration is  $1s^2 2s^2 2p^6$ . The screening for an outershell electron is further reduced and now it is a  $n = 2$  rather than an  $n = 3$  electron that will be removed in ionization.

**EVALUATE:** Both screening and the shell structure of the atom determine the successive ionization potentials.

**41.31. IDENTIFY and SET UP:** The energy of an atomic level is given in terms of  $n$  and  $Z_{\text{eff}}$  by Eq. (41.45),

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

**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  $Z_{\text{eff}}^2$ .

**41.32. IDENTIFY and SET UP:** Apply Eq. (41.45).

**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.

**41.33. IDENTIFY and SET UP:** Use the exclusion principle to determine the ground-state electron configuration, as in Table 41.3. Estimate the energy by estimating  $Z_{\text{eff}}$ , 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.

**41.34. IDENTIFY and SET UP:** Apply Eq. (41.45).

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

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

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

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

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

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

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

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

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

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

Nickel (Ni).



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

**41.37. IDENTIFY and SET UP:** Apply Eq. (41.47).  $E = hf$  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.

**41.40. 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).

**41.41. 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  $\frac{L}{8} - \frac{L}{4\pi} = \frac{1}{2} \left( \frac{L}{2} \right) \left( \frac{1}{2} - \frac{1}{\pi} \right)$ .

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

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

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

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

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

**EVALUATE:** This is about a factor of three larger than the probability when the particle is in the ground state.

**41.42. IDENTIFY:** The probability is a maximum where  $|\psi|^2$  is a maximum, and this is where  $\frac{\partial}{\partial x} |\psi|^2 = 0$ . The probability is zero where  $|\psi|^2$  is zero.

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

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

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

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

**41.43. (a) IDENTIFY and SET UP:** The probability is  $P = |\psi|^2 dV$  with  $dV = 4\pi r^2 dr$ .

**EXECUTE:**  $|\psi|^2 = A^2 e^{-2\alpha r^2}$  so  $P = 4\pi A^2 r^2 e^{-2\alpha r^2} dr$

**(b) IDENTIFY and SET UP:**  $P$  is maximum where  $\frac{dP}{dr} = 0$ .

**EXECUTE:**  $\frac{d}{dr} (r^2 e^{-2\alpha r^2}) = 0$

$$2r e^{-2\alpha r^2} - 4\alpha r^3 e^{-2\alpha r^2} = 0 \text{ and this reduces to } 2r - 4\alpha r^3 = 0$$

$r = 0$  is a solution of the equation but corresponds to a minimum not a maximum. Seek  $r$  not equal to 0 so divide by  $r$  and get  $2 - 4\alpha r^2 = 0$ .

This gives  $r = \frac{1}{\sqrt{2\alpha}}$ . (We took the positive square root since  $r$  must be positive.)

**EVALUATE:** This is different from the value of  $r$ ,  $r = 0$ , where  $|\psi|^2$  is a maximum. At  $r = 0$ ,  $|\psi|^2$  has a maximum but the volume element  $dV = 4\pi r^2 dr$  is zero here so  $P$  does not have a maximum at  $r = 0$ .

**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 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 
$$-\frac{\hbar^2}{2m}\frac{d^2\psi_{n_x}}{dx^2} + \frac{1}{2}k'x^2\psi_{n_x} = E_{n_x}\psi_{n_x}.$$

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

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

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

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

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

Therefore, we have shown that this  $\psi$  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:

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

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

$E_{n_x} = \left(n_x + \frac{1}{2}\right)\hbar\omega_1$ ,  $\psi_{n_y}(y)$  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  $E_{n_z} = \left(n_z + \frac{1}{2}\right)\hbar\omega_2$ .

**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,  $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = \left(E_{n_x} - \frac{1}{2}k'_1x^2\right)\psi$  with similar relations for  $\frac{\partial^2\psi}{\partial y^2}$  and  $\frac{\partial^2\psi}{\partial z^2}$ . Adding,

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = \left(E_{n_x} + E_{n_y} + E_{n_z} - \frac{1}{2}k'_1x^2 - \frac{1}{2}k'_1y^2 - \frac{1}{2}k'_2z^2\right)\psi$$

$$= (E_{n_x} + E_{n_y} + E_{n_z} - U)\psi = (E - U)\psi$$

where the energy  $E$  is  $E = E_{n_x} + E_{n_y} + E_{n_z} = \hbar\left[(n_x + n_y + 1)\omega_1^2 + \left(n_z + \frac{1}{2}\right)\omega_2^2\right]$ , 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  $E = \hbar\left(\omega_1^2 + \frac{1}{2}\omega_2^2\right)$ . The first excited level

corresponds to  $n_x = n_y = 0$  and  $n_z = 1$ , since  $\omega_1^2 > \omega_2^2$ , and  $E = \hbar\left(\omega_1^2 + \frac{3}{2}\omega_2^2\right)$ .

**(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:** An electron is in the  $5f$  state in hydrogen. We want to find out about its angular momentum.

**SET UP:** For the  $5f$  state,  $l = 3$ .  $L_z = m_l\hbar$ .  $m_l = 0, \pm 1, \dots, \pm l$ .  $L = \sqrt{l(l+1)}\hbar$ .

**EXECUTE: (a)** The largest possible  $m_l$  is  $m_l = 3$ .  $L_z = 3\hbar$ .

**(b)**  $L_x^2 + L_y^2 + L_z^2 = L^2$ .  $L^2 = 3(4)\hbar^2 = 12\hbar^2$ .

$$\sqrt{L_x^2 + L_y^2} = \sqrt{L^2 - L_z^2} = \sqrt{12\hbar^2 - 9\hbar^2} = \sqrt{3}\hbar.$$

**EVALUATE:** The restriction on  $L_z$  also places restrictions on  $L_x$  and  $L_y$ .

**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:** The total number of states is

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

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

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

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

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

**EXECUTE:** (a)  $L = \sqrt{l(l+1)}\hbar = 12\hbar \Rightarrow l = 3$ . Therefore the smallest that  $n$  can be is 4, so

$$E_n = -(13.6\text{ eV})/n^2 = -(13.6\text{ eV})/4^2 = -0.8500\text{ eV}.$$

(b) For  $l = 3$ ,  $m_l = \pm 3, \pm 2, \pm 1, 0$ . Since  $L_z = m_l\hbar$ , the largest  $L_z$  can be is  $3\hbar$  and the smallest it can be is  $-3\hbar$ .

(c)  $S = \sqrt{3/4}\hbar$  for all electrons.

(d) In this case,  $n = 3$ , so  $l = 2, 1, 0$ . Therefore the maximum that  $L$  can be is  $L_{\max} = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ .

The minimum  $L$  can be is zero when  $l = 0$ .

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

**41.49. IDENTIFY:** The total energy determines what shell the electron is in, which limits its angular momentum.

**SET UP:** The electron's orbital angular momentum is given by  $L = \sqrt{l(l+1)}\hbar$ , and its total energy in the  $n^{\text{th}}$  shell is  $E_n = -(13.6\text{ eV})/n^2$ .

**EXECUTE:** (a) First find  $n$ :  $E_n = -(13.6\text{ eV})/n^2 = -0.5440\text{ eV}$  which gives  $n = 5$ , so  $l = 4, 3, 2, 1, 0$ .

Therefore the possible values of  $L$  are given by  $L = \sqrt{l(l+1)}\hbar$ , giving  $L = 0, \sqrt{2}\hbar, \sqrt{6}\hbar, \sqrt{12}\hbar, \sqrt{20}\hbar$ .

(b)  $E_6 = -(13.6\text{ eV})/6^2 = -0.3778\text{ eV}$ .  $\Delta E = E_6 - E_5 = -0.3778\text{ eV} - (-0.5440\text{ eV}) = +0.1662\text{ eV}$

This must be the energy of the photon, so  $\Delta E = hc/\lambda$ , which gives

$\lambda = hc/\Delta E = (4.136 \times 10^{-15}\text{ eV} \cdot \text{s})(3.00 \times 10^8\text{ m/s})/(0.1662\text{ eV}) = 7.47 \times 10^{-6}\text{ m} = 7470\text{ nm}$ , which is in the infrared and hence not visible.

**EVALUATE:** The electron can have any of the five possible values for its angular momentum, but it cannot have any others.

**41.50. IDENTIFY:** For the  $N$  shell,  $n = 4$ , which limits the values of the other quantum numbers.

**SET UP:** In the  $n^{\text{th}}$  shell,  $0 \leq l < n-1$ ,  $m_l = 0, \pm 1, \dots, \pm l$ , and  $m_s = \pm 1/2$ . The orbital angular momentum of the electron is  $L = \sqrt{l(l+1)}\hbar$  and its spin angular momentum is  $S = \sqrt{3/4}\hbar$ .

**EXECUTE:** (a) For  $l = 3$  we can have  $m_l = \pm 3, \pm 2, \pm 1, 0$  and  $m_s = \pm 1/2$ ; for  $l = 2$  we can have  $m_l = \pm 2, \pm 1, 0$  and  $m_s = \pm 1/2$ ; for  $l = 1$ , we can have  $m_l = \pm 1, 0$  and  $m_s = \pm 1/2$ ; for  $l = 0$ , we can have  $m_l = 0$  and  $m_s = \pm 1/2$ .

(b) For the  $N$  shell,  $n = 4$ , and for an  $f$ -electron,  $l = 3$ , giving  $L = \sqrt{l(l+1)}\hbar = \sqrt{3(3+1)}\hbar = \sqrt{12}\hbar$ .

$L_z = m_l\hbar = \pm 3\hbar, \pm 2\hbar, \pm \hbar, 0$ , so the maximum value is  $3\hbar$ .  $S = \sqrt{3/4}\hbar$  for all electrons.

(c) For a  $d$ -state electron,  $l = 2$ , giving  $L = \sqrt{2(2+1)}\hbar = \sqrt{6}\hbar$ .  $L_z = m_l\hbar$ , and the maximum value of  $m_l$  is 2, so the maximum value of  $L_z$  is  $2\hbar$ . The smallest angle occurs when  $L_z$  is most closely aligned along the

angular momentum vector, which is when  $L_z$  is greatest. Therefore  $\cos\theta_{\min} = \frac{L_z}{L} = \frac{2\hbar}{\sqrt{6}\hbar} = \frac{2}{\sqrt{6}}$  and

$\theta_{\min} = 35.3^\circ$ . The largest angle occurs when  $L_z$  is as far as possible from the  $L$ -vector, which is when  $L_z$  is most negative. Therefore  $\cos\theta_{\max} = \frac{-2\hbar}{\sqrt{6}\hbar} = -\frac{2}{\sqrt{6}}$  and  $\theta_{\max} = 144.7^\circ$ .

(d) This is not possible since  $l = 3$  for an  $f$ -electron, but in the  $M$  shell the maximum value of  $l$  is 2.

**EVALUATE:** The fact that the angle in part (c) cannot be zero tells us that the orbital angular momentum of the electron cannot be totally aligned along any specified direction.

**41.51. IDENTIFY:** The inner electrons shield part of the nuclear charge from the outer electron.

**SET UP:** The electron's energy in the  $n^{\text{th}}$  shell, due to shielding, is  $E_n = -\frac{Z_{\text{eff}}^2}{n^2}(13.6\text{ eV})$ , where  $Z_{\text{eff}}e$  is the effective charge that the electron "sees" for the nucleus.

**EXECUTE:** (a)  $E_n = -\frac{Z_{\text{eff}}^2}{n^2}(13.6 \text{ eV})$  and  $n = 4$  for the  $4s$  state. Solving for  $Z_{\text{eff}}$  gives

$Z_{\text{eff}} = \sqrt{-\frac{(4^2)(-1.947 \text{ eV})}{13.6 \text{ eV}}} = 1.51$ . The nucleus contains a charge of  $+11e$ , so the average number of electrons that screen this nucleus must be  $11 - 1.51 = 9.49$  electrons.

(b) (i) The charge of the nucleus is  $+19e$ , but  $17.2e$  is screened by the electrons, so the outer electron “sees”  $19e - 17.2e = 1.8e$  and  $Z_{\text{eff}} = 1.8$ .

(ii)  $E_n = -\frac{Z_{\text{eff}}^2}{n^2}(13.6 \text{ eV}) = -\frac{(1.8)^2}{4^2}(13.6 \text{ eV}) = -2.75 \text{ eV}$

**EVALUATE:** Sodium has 11 protons, so the inner 10 electrons shield a large portion of this charge from the outer electron. But they don’t shield 10 of the protons, since the inner electrons are not totally equivalent to a uniform spherical shell. (They are lumpy.)

**41.52. 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.

**41.53. (a) IDENTIFY and SET UP:** The energy is given by Eq. (39.14), which is identical to Eq. (41.21). The potential energy is given by Eq. (23.9), with  $q = +Ze$  and  $q_0 = -e$ .

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

$E_{1s} = U(r)$  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.

**41.54. IDENTIFY and SET UP:** Apply Eq. (41.45) and the concept of screening. For a level with quantum number  $n$  the ionization energy is  $-E_n$ .

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

(b)  $\frac{13.60 \text{ eV}}{350^2} = 1.11 \times 10^{-4} \text{ eV}$ ,  $r_{350} = (350)^2 a_0 = (350)^2 (0.529 \times 10^{-10} \text{ m}) = 6.48 \times 10^{-6} \text{ m}$ .

(c) Similarly for  $n = 650$ ,  $\frac{13.60 \text{ eV}}{(650)^2} = 3.22 \times 10^{-5} \text{ eV}$ ,  $r_{650} = (650)^2 (0.529 \times 10^{-10} \text{ m}) = 2.24 \times 10^{-5} \text{ m}$ .

**EVALUATE:** For a Rydberg atom with large  $n$  the Bohr radius of the electron's orbit is very large.

**41.55.**  $\psi_{2s}(r) = \frac{1}{\sqrt{32\pi a^3}} \left( 2 - \frac{r}{a} \right) e^{-r/2a}$

(a) **IDENTIFY and SET UP:** Let  $I = \int_0^\infty |\psi_{2s}|^2 dV = 4\pi \int_0^\infty |\psi_{2s}|^2 r^2 dr$ . If  $\psi_{2s}$  is normalized then we will find that  $I = 1$ .

**EXECUTE:**  $I = 4\pi \left( \frac{1}{32\pi a^3} \right) \int_0^\infty \left( 2 - \frac{r}{a} \right)^2 e^{-r/a} r^2 dr = \frac{1}{8a^3} \int_0^\infty \left( 4r^2 - \frac{4r^3}{a} + \frac{r^4}{a^2} \right) e^{-r/a} dr$

Use the integral formula  $\int_0^\infty x^n e^{-\alpha x} dx = \frac{n!}{\alpha^{n+1}}$ , with  $\alpha = 1/a$ .

$I = \frac{1}{8a^3} \left( 4(2!)(a^3) - \frac{4}{a}(3!)(a^4) + \frac{1}{a^2}(4!)(a^5) \right) = \frac{1}{8}(8 - 24 + 24) = 1$ ; this  $\psi_{2s}$  is normalized.

(b) **SET UP:** For a spherically symmetric state such as the  $2s$ , the probability that the electron will be found at  $r < 4a$  is  $P(r < 4a) = \int_0^{4a} |\psi_{2s}|^2 dV = 4\pi \int_0^{4a} |\psi_{2s}|^2 r^2 dr$ .

**EXECUTE:**  $P(r < 4a) = \frac{1}{8a^3} \int_0^{4a} \left( 4r^2 - \frac{4r^3}{a} + \frac{r^4}{a^2} \right) e^{-r/a} dr$

Let  $P(r < 4a) = \frac{1}{8a^3} (I_1 + I_2 + I_3)$ .

$I_1 = 4 \int_0^{4a} r^2 e^{-r/a} dr$

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  $\alpha = 1/a$ .

$I_1 = -4 \left[ e^{-r/a} (r^2 a + 2ra^2 + 2a^3) \right]_0^{4a} = (-104e^{-4} + 8)a^3$ .

$I_2 = -\frac{4}{a} \int_0^{4a} r^3 e^{-r/a} dr$

Use the integral formula  $\int r^3 e^{-\alpha r} dr = -e^{-\alpha r} \left( \frac{r^3}{\alpha} + \frac{3r^2}{\alpha^2} + \frac{6r}{\alpha^3} + \frac{6}{\alpha^4} \right)$  with  $\alpha = 1/a$ .

$I_2 = \frac{4}{a} \left[ e^{-r/a} (r^3 a + 3r^2 a^2 + 6ra^3 + 6a^4) \right]_0^{4a} = (568e^{-4} - 24)a^3$ .

$I_3 = \frac{1}{a^2} \int_0^{4a} r^4 e^{-r/a} dr$

Use the integral formula  $\int r^4 e^{-\alpha r} dr = -e^{-\alpha r} \left( \frac{r^4}{\alpha} + \frac{4r^3}{\alpha^2} + \frac{12r^2}{\alpha^3} + \frac{24r}{\alpha^4} + \frac{24}{\alpha^5} \right)$  with  $\alpha = 1/a$ .

$$I_3 = -\frac{1}{a^2} \left[ e^{-r/a} (r^4 a + 4r^3 a^2 + 12r^2 a^3 + 24ra^4 + 24a^5) \right]_0^{4a} = (-824e^{-4} + 24)a^3.$$

$$\text{Thus } P(r < 4a) = \frac{1}{8a^3} (I_1 + I_2 + I_3) = \frac{1}{8a^3} a^3 ([8 - 24 + 24] + e^{-4} [-104 + 568 - 824])$$

$$P(r < 4a) = \frac{1}{8} (8 - 360e^{-4}) = 1 - 45e^{-4} = 0.176.$$

**EVALUATE:** There is an 82.4% probability that the electron will be found at  $r > 4a$ . In the Bohr model the electron is for certain at  $r = 4a$ ; this is a poor description of the radial probability distribution for this state.

**41.56. IDENTIFY:**  $P(r)$  is a maximum or minimum when  $\frac{d(r^2|\psi|^2)}{dr} = 0$ .

$$\text{SET UP: From Problem 41.55, } \psi_{2s}(r) = \frac{1}{\sqrt{32\pi a^3}} \left( 2 - \frac{r}{a} \right) e^{-r/2a}.$$

**EXECUTE: (a)** Since the given  $\psi(r)$  is real,  $r^2|\psi|^2 = r^2\psi^2$ . The probability density will be an extreme when  $\frac{d}{dr}(r^2\psi^2) = 2 \left( r\psi^2 + r^2\psi \frac{d\psi}{dr} \right) = 2r\psi \left( \psi + r \frac{d\psi}{dr} \right) = 0$ . This occurs at  $r = 0$ , a minimum, and when

$\psi = 0$ , also a minimum. A maximum must correspond to  $\psi + r \frac{d\psi}{dr} = 0$ . Within a multiplicative constant,

$$\psi(r) = (2 - r/a)e^{-r/2a}, \quad \frac{d\psi}{dr} = -\frac{1}{a}(2 - r/2a)e^{-r/2a}, \quad \text{and the condition for a maximum is}$$

$(2 - r/a) = (r/a)(2 - r/2a)$ , or  $r^2 - 6ra + 4a^2 = 0$ . The solutions to the quadratic are  $r = a(3 \pm \sqrt{5})$ . The ratio of the probability densities at these radii is 3.68, with the larger density at  $r = a(3 + \sqrt{5}) = 5.24a$  and the smaller density at  $r = a(3 - \sqrt{5}) = 0.76a$ . The maximum of  $P(r)$  occurs at a value of  $r$  somewhat larger than the Bohr radius of  $4a$ .

**(b)**  $\psi = 0$  at  $r = 2a$

**EVALUATE:** Parts (a) and (b) are consistent with Figure 41.8 in the textbook; note the two relative maxima, one on each side of the minimum of zero at  $r = 2a$ .

**41.57. IDENTIFY:** Use Figure 41.6 in the textbook to relate  $\theta_L$  to  $L_z$  and  $L$ :  $\cos\theta_L = \frac{L_z}{L}$  so  $\theta_L = \arccos\left(\frac{L_z}{L}\right)$ .

**(a) SET UP:** The smallest angle  $(\theta_L)_{\min}$  is for the state with the largest  $L$  and the largest  $L_z$ . This is the state with  $l = n - 1$  and  $m_l = l = n - 1$ .

$$\text{EXECUTE: } L_z = m_l \hbar = (n - 1)\hbar$$

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

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

**EVALUATE:** Note that  $(\theta_L)_{\min}$  approaches  $0^\circ$  as  $n \rightarrow \infty$ .

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

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

**EVALUATE:** Note that  $(\theta_L)_{\max}$  approaches  $180^\circ$  as  $n \rightarrow \infty$ .

**41.58. IDENTIFY and SET UP:**  $L_x^2 + L_y^2 + L_z^2 = L^2$ .  $L^2 = l(l + 1)\hbar^2$ .  $L_z = m_l \hbar$ .

$$\text{EXECUTE: (a) } L_x^2 + L_y^2 = L^2 - L_z^2 = l(l + 1)\hbar^2 - m_l^2 \hbar^2 \text{ so } \sqrt{L_x^2 + L_y^2} = \sqrt{l(l + 1) - m_l^2} \hbar.$$

**(b)** This is the magnitude of the component of angular momentum perpendicular to the  $z$ -axis.



(c) The maximum value is  $\sqrt{l(l+1)}\hbar = L$ , when  $m_l = 0$ . That is, if the electron is known to have no  $z$ -component of angular momentum, the angular momentum must be perpendicular to the  $z$ -axis. The minimum is  $\sqrt{l}\hbar$  when  $m_l = \pm l$ .

**EVALUATE:** For  $l \neq 0$  the minimum value of  $L_x^2 + L_y^2$  is not zero. The angular momentum vector cannot be totally aligned along the  $z$ -axis. For  $l \neq 0$ ,  $\vec{L}$  must always have a component perpendicular to the  $z$ -axis.

**41.59. 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  $r \rightarrow \infty$ .

**41.60. IDENTIFY:** Apply constant acceleration equations to relate  $F_z$  to the motion of an atom.

**SET UP:** According to Eq. (41.40), the magnitude of  $\mu_z$  is  $|\mu_z| = 9.28 \times 10^{-24} \text{ A} \cdot \text{m}^2$ . The atomic mass of silver is  $0.1079 \text{ kg/mol}$ .

**EXECUTE:** The time required to transit the horizontal  $50 \text{ cm}$  region is  $t = \frac{\Delta x}{v_x} = \frac{0.500 \text{ m}}{525 \text{ m/s}} = 0.952 \text{ ms}$ . The force required to deflect each spin component by  $0.50 \text{ mm}$  is

$$F_z = ma_z = \pm m \frac{2\Delta z}{t^2} = \pm \left( \frac{0.1079 \text{ kg/mol}}{6.022 \times 10^{23} \text{ atoms/mol}} \right) \frac{2(0.50 \times 10^{-3} \text{ m})}{(0.952 \times 10^{-3} \text{ s})^2} = \pm 1.98 \times 10^{-22} \text{ N. Thus, the required}$$

magnetic-field gradient is  $\left| \frac{dB_z}{dz} \right| = \left| \frac{F_z}{\mu_z} \right| = \frac{1.98 \times 10^{-22} \text{ N}}{9.28 \times 10^{-24} \text{ J/T}} = 21.3 \text{ T/m}.$

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

**41.61. IDENTIFY:** Apply Eq. (41.36).

**SET UP:** Decay from a  $3d$  to  $2p$  state in hydrogen means that  $n = 3 \rightarrow n = 2$  and

$m_l = \pm 2, \pm 1, 0 \rightarrow m_l = \pm 1, 0$ . However, selection rules limit the possibilities for decay. The emitted photon carries off one unit of angular momentum so  $l$  must change by 1 and hence  $m_l$  must change by 0 or  $\pm 1$ .

**EXECUTE:** The shift in the transition energy from the zero field value is

$$U = (m_{l_3} - m_{l_2})\mu_B B = \frac{e\hbar B}{2m}(m_{l_3} - m_{l_2}), \text{ where } m_{l_3} \text{ is the } 3d \text{ } m_l \text{ value and } m_{l_2} \text{ is the } 2p \text{ } m_l \text{ value. Thus}$$

there are only three different energy shifts. The shifts and the transitions that have them, labeled by the  $m_l$  values, are:

$$\frac{e\hbar B}{2m}: 2 \rightarrow 1, 1 \rightarrow 0, 0 \rightarrow -1. 0: 1 \rightarrow 1, 0 \rightarrow 0, -1 \rightarrow -1. -\frac{e\hbar B}{2m}: 0 \rightarrow 1, -1 \rightarrow 0, -2 \rightarrow -1.$$

**EVALUATE:** Our results are consistent with Figure 41.15 in the textbook.

**41.62. 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.

**41.63. 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 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.

**41.64. IDENTIFY:** Apply Eq. (41.36). Problem 39.86c says  $|\Delta\lambda/\lambda| = |\Delta E/E|$ , when these quantities are small.

**SET UP:**  $\mu_B = 5.79 \times 10^{-5} \text{ eV/T}$

**EXECUTE:** (a) The energy shift from zero field is  $\Delta U_0 = m_l \mu_B B$ .

$$\text{For } m_l = 2, \Delta U_0 = (2)(5.79 \times 10^{-5} \text{ eV/T})(1.40 \text{ T}) = 1.62 \times 10^{-4} \text{ eV}.$$

$$\text{For } m_l = 1, \Delta U_0 = (1)(5.79 \times 10^{-5} \text{ eV/T})(1.40 \text{ T}) = 8.11 \times 10^{-5} \text{ eV}.$$

(b)  $|\Delta\lambda| = \lambda_0 \frac{|\Delta E|}{E_0}$ , where  $E_0 = (13.6 \text{ eV})((1/4) - (1/9))$ ,  $\lambda_0 = \left(\frac{36}{5}\right) \frac{1}{R} = 6.563 \times 10^{-7} \text{ m}$

and  $\Delta E = 1.62 \times 10^{-4} \text{ eV} - 8.11 \times 10^{-5} \text{ eV} = 8.09 \times 10^{-5} \text{ eV}$  from part (a). Then,

$|\Delta\lambda| = 2.81 \times 10^{-11} \text{ m} = 0.0281 \text{ nm}$ . The wavelength corresponds to a larger energy change, and so the wavelength is smaller.

**EVALUATE:**  $|\Delta\lambda/\lambda| = (0.0281 \text{ nm})/(656 \text{ nm}) = 4.3 \times 10^{-5}$ .  $|\Delta\lambda/\lambda|$  is very small and the approximate expression from Problem 39.86c is very accurate.

**41.65. IDENTIFY:** The ratio according to the Boltzmann distribution is given by Eq. (39.18):  $\frac{n_1}{n_0} = e^{-(E_1 - E_0)/kT}$ ,

where 1 is the higher energy state and 0 is the lower energy state.

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

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

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

**EXECUTE:**  $U_{1/2} - U_{-1/2} = 2.00232 \left( \frac{e\hbar}{2m} \right) B \left( \frac{1}{2} - \left( -\frac{1}{2} \right) \right) = 2.00232 \left( \frac{e\hbar}{2m} \right) B = 2.00232 \mu_B B$

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

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

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

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

(b)  $B = 5.00 \times 10^{-5} \text{ T}$ ,  $\frac{n_{1/2}}{n_{-1/2}} = e^{-2.24 \times 10^{-3}} = 0.9978$

(c)  $B = 5.00 \times 10^{-5} \text{ T}$ ,  $\frac{n_{1/2}}{n_{-1/2}} = e^{-2.24 \times 10^{-2}} = 0.978$

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

**41.66. IDENTIFY:** The magnetic field at the center of a current loop of radius  $r$  is  $B = \frac{\mu_0 I}{2r}$  (Eq. 28.17).

$$I = e \left( \frac{v}{2\pi r} \right).$$

**SET UP:** Using Eq. (41.22),  $L = mvr = \sqrt{l(l+1)}\hbar$ . The Bohr radius from Eq. (39.11) 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.

**41.67. IDENTIFY and SET UP:**  $m_s$  can take on 4 different values:  $m_s = -\frac{3}{2}, -\frac{1}{2}, +\frac{1}{2}, +\frac{3}{2}$ . Each  $nlm_l$  state can have 4 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  $Z = 11$ ; 11 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.

**41.68. IDENTIFY:** Apply Eq. (41.43) and Eq. (41.26), with  $e^2$  replaced by  $Ze^2$ . The photon wavelength  $\lambda$  is related to the transition energy  $\Delta E$  for the atom by  $\Delta E = \frac{hc}{\lambda}$ .

**SET UP:** For  $N^{6+}$ ,  $Z = 7$ .

**EXECUTE:** (a)  $Z^2 (-13.6 \text{ eV}) = (7)^2 (-13.6 \text{ eV}) = -666 \text{ eV}$ .

(b) The negative of the result of part (a), 666 eV.

(c) The radius of the ground state orbit is inversely proportional to the nuclear charge, and

$$\frac{a}{Z} = (0.529 \times 10^{-10} \text{ m})/7 = 7.56 \times 10^{-12} \text{ m}.$$

(d)  $\lambda = \frac{hc}{\Delta E} = \frac{hc}{E_0 \left( \frac{1}{1^2} - \frac{1}{2^2} \right)}$ , where  $E_0$  is the energy found in part (b), and  $\lambda = 2.49 \text{ nm}$ .

**EVALUATE:** For hydrogen, the wavelength of the photon emitted in this transition is 122 nm (Section 39.3). The wavelength for  $N^{6+}$  is smaller by a factor of  $7^2$ .

**41.69. (a) IDENTIFY and SET UP:** The energy of the photon equals the transition energy of the atom:  $\Delta E = hc/\lambda$ . The energies of the states are given by Eq. (41.21).

**EXECUTE:**  $E_n = -\frac{13.60 \text{ eV}}{n^2}$  so  $E_2 = -\frac{13.60 \text{ eV}}{4}$  and  $E_1 = -\frac{13.60 \text{ eV}}{1}$

$$\Delta E = E_2 - E_1 = 13.60 \text{ eV} \left( -\frac{1}{4} + 1 \right) = \frac{3}{4} (13.60 \text{ eV}) = 10.20 \text{ eV} = (10.20 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV}) = 1.634 \times 10^{-18} \text{ J}$$

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

(b) **IDENTIFY and SET UP:** Calculate the change in  $\Delta E$  due to the orbital magnetic interaction energy, Eq. (41.36), 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  $U = m_l \mu_B B = (-1)(9.274 \times 10^{-24} \text{ A} \cdot \text{m}^2)(2.20 \text{ T}) = (-2.040 \times 10^{-23} \text{ J})(1 \text{ eV}/1.602 \times 10^{-19} \text{ J}) = 1.273 \times 10^{-4} \text{ eV}$ .

Note that the shift in energy due to the magnetic field is a very small fraction of the 10.2 eV transition energy. Problem 39.86c 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  $1.2 \times 10^{-5}$ .

**41.70. IDENTIFY:** Apply Eq. (41.36), 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.

**41.71. IDENTIFY:** Estimate the atomic transition energy and use Eq. (39.5) to relate this to the photon wavelength.

**(a) SET UP:** vanadium,  $Z = 23$

minimum wavelength; corresponds to largest transition energy

**EXECUTE:** The highest occupied shell is the  $N$  shell ( $n = 4$ ). The highest energy transition is  $N \rightarrow K$ ,

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

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

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

**SET UP:** maximum wavelength; corresponds to smallest transition energy, so for the  $K_\alpha$  transition

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

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

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

**(b) rhenium,  $Z = 45$**

Apply the analysis of part (a), just with this different value of  $Z$ .

minimum wavelength

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

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

maximum wavelength

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

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

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

**41.72. IDENTIFY:** The interaction energy for an electron in a magnetic field is  $U = -\mu_z B$ , where  $\mu_z$  is given by Eq. (41.40).

**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)**  $B = \frac{2\pi(9.11 \times 10^{-31} \text{ kg})(3.00 \times 10^8 \text{ m/s})}{(0.0350 \text{ m})(1.60 \times 10^{-19} \text{ C})} = 0.307 \text{ T}.$

**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  $m_s = +\frac{1}{2}$ .

- 41.73. 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  $E_n = \hbar\omega\left(n + \frac{1}{2}\right)$ . 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  $(2N)\left(\frac{1}{2}\hbar\omega\right)$ , 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  $2\left(\frac{1}{2}\hbar\omega\right) + 2\left(\frac{3}{2}\hbar\omega\right) = 4\hbar\omega$ , which is in agreement with our general result.

- 41.74. 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,

$$\frac{(+2e)(-e)}{4\pi\epsilon_0 r^2} + \frac{(-e)(-e)}{4\pi\epsilon_0 (2r)^2} = \frac{-mv^2}{r}. \text{ But, from the quantization of angular momentum in the first Bohr orbit,}$$

$$L = mvr = \hbar \Rightarrow v = \frac{\hbar}{mr}. \text{ So } \frac{-2e^2}{4\pi\epsilon_0 r^2} + \frac{e^2}{4\pi\epsilon_0 (2r)^2} = \frac{-mv^2}{r} = \frac{-m\left(\frac{\hbar}{mr}\right)^2}{r} = -\frac{\hbar^2}{mr^3} \Rightarrow \frac{-7}{4} \frac{e^2}{r^2} = -\frac{4\pi\epsilon_0 \hbar^2}{mr^3}.$$

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

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

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

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

(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.

**41.75. IDENTIFY and SET UP:** In the expression for the turning points and in the wave function replace  $a$  by  $a/Z$   
**EXECUTE:** (a) The radius is inversely proportional to  $Z$ , so the classical turning radius is  $2a/Z$ .

(b) The normalized wave function is  $\psi_{1s}(r) = \frac{1}{\sqrt{\pi a^3/Z^3}} e^{-Zr/a}$  and the probability of the electron being

found outside the classical turning point is  $P = \int_{2a/Z}^{\infty} |\psi_{1s}|^2 4\pi r^2 dr = \frac{4}{a^3/Z^3} \int_{2a/Z}^{\infty} e^{-2Zr/a} r^2 dr$ . Making the

change of variable  $u = Zr/a$ ,  $dr = (a/Z)du$  changes the integral to  $P = 4 \int_2^{\infty} e^{-2u} u^2 du$ , which is independent of  $Z$ . The probability is that found in Problem 41.53, 0.238, independent of  $Z$ .

**EVALUATE:** The probability of the electron being in the classically forbidden region is independent of  $Z$ .

