

41

ATOMIC STRUCTURE

LEARNING GOALS

By studying this chapter, you will learn:

- How to extend quantum-mechanical calculations to three-dimensional problems.
- How to solve the Schrödinger equation for a particle trapped in a cubical box.
- How to describe the states of a hydrogen atom in terms of quantum numbers.
- How magnetic fields affect the orbital motion of atomic electrons.
- How we know that electrons have their own intrinsic angular momentum.
- How to analyze the structure of many-electron atoms.
- How x rays emitted by atoms reveal their inner structure.



? Lithium (with three electrons per atom) is a metal that burns spontaneously in water, while helium (with two electrons per atom) is a gas that undergoes almost no chemical reactions. How can one extra electron make these two elements so dramatically different?

Some physicists claim that all of chemistry is contained in the Schrödinger equation. This is somewhat of an exaggeration, but this equation can teach us a great deal about the chemical behavior of elements and the nature of chemical bonds. It provides insight into the periodic table of the elements and the microscopic basis of magnetism.

In order to learn about the quantum-mechanical structure of atoms, we'll first construct a three-dimensional version of the Schrödinger equation. We'll try this equation out by looking at a three-dimensional version of a particle in a box: a particle confined to a cubical volume.

We'll then see that we can learn a great deal about the structure and properties of *all* atoms from the solutions to the Schrödinger equation for the hydrogen atom. These solutions have quantized values of angular momentum; we don't need to make a separate statement about quantization as we did with the Bohr model. We label the states with a set of quantum numbers, which we'll use later with many-electron atoms as well. We'll find that the electron also has an intrinsic *spin* angular momentum in addition to the orbital angular momentum associated with its motion.

We'll also encounter the exclusion principle, a kind of microscopic zoning ordinance that is the key to understanding many-electron atoms. This principle says that no two electrons in an atom can have the same quantum-mechanical state. Finally, we'll use the principles of this chapter to explain the characteristic x-ray spectra of atoms.

41.1 The Schrödinger Equation in Three Dimensions

We have discussed the Schrödinger equation and its applications only for *one-dimensional* problems, the analog of a Newtonian particle moving along a straight line. The straight-line model is adequate for some applications, but to understand atomic structure, we need a three-dimensional generalization.

It's not difficult to guess what the three-dimensional Schrödinger equation should look like. First, the wave function Ψ is a function of time and all three space coordinates (x, y, z) . In general, the potential-energy function also depends on all three coordinates and can be written as $U(x, y, z)$. Next, recall from Section 40.1 that the term $-(\hbar^2/2m)\partial^2\Psi/\partial x^2$ in the one-dimensional Schrödinger equation, Eq. (40.20), is related to the kinetic energy of the particle in the state described by the wave function Ψ . For example, if we insert into this term the wave function $\Psi(x, t) = Ae^{ikx}e^{-i\omega t}$ for a free particle with magnitude of momentum $p = \hbar k$ and kinetic energy $K = p^2/2m$, we obtain $-(\hbar^2/2m)(ik)^2 Ae^{ikx}e^{-i\omega t} = (\hbar^2 k^2/2m) Ae^{ikx}e^{-i\omega t} = (p^2/2m)\Psi(x, t) = K\Psi(x, t)$. If the particle can move in three dimensions, its momentum has three components (p_x, p_y, p_z) and its kinetic energy is

$$K = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \quad (41.1)$$

These observations, taken together, suggest that the correct generalization of the Schrödinger equation to three dimensions is

$$\begin{aligned} -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \Psi(x, y, z, t)}{\partial x^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial y^2} + \frac{\partial^2 \Psi(x, y, z, t)}{\partial z^2} \right) \\ + U(x, y, z) \Psi(x, y, z, t) = i\hbar \frac{\partial \Psi(x, y, z, t)}{\partial t} \end{aligned} \quad (41.2)$$

(general three-dimensional Schrödinger equation)

The three-dimensional wave function $\Psi(x, y, z, t)$ has a similar interpretation as in one dimension. The wave function itself is a complex quantity with both a real part and an imaginary part, but $|\Psi(x, y, z, t)|^2$ —the square of its absolute value, equal to the product of $\Psi(x, y, z, t)$ and its complex conjugate $\Psi^*(x, y, z, t)$ —is real and either positive or zero at every point in space. We interpret $|\Psi(x, y, z, t)|^2 dV$ as the *probability* of finding the particle within a small volume dV centered on the point (x, y, z) at time t , so $|\Psi(x, y, z, t)|^2$ is the *probability distribution function* in three dimensions. The *normalization condition* on the wave function is that the probability that the particle is *somewhere* in space is exactly 1. Hence the integral of $|\Psi(x, y, z, t)|^2$ over all space must equal 1:

$$\int |\Psi(x, y, z, t)|^2 dV = 1 \quad \begin{array}{l} \text{(normalization condition} \\ \text{in three dimensions)} \end{array} \quad (41.3)$$

If the wave function $\Psi(x, y, z, t)$ represents a state of a definite energy E —that is, a stationary state—we can write it as the product of a spatial wave function $\psi(x, y, z)$ and a function of time $e^{-iEt/\hbar}$:

$$\Psi(x, y, z, t) = \psi(x, y, z) e^{-iEt/\hbar} \quad \begin{array}{l} \text{(time-dependent wave function} \\ \text{for a state of definite energy)} \end{array} \quad (41.4)$$

(Compare this to Eq. (40.21) for a one-dimensional state of definite energy.) If we substitute Eq. (41.4) into Eq. (41.2), the right-hand side of the equation becomes $i\hbar\psi(x, y, z)(-iE/\hbar)e^{-iEt/\hbar} = E\psi(x, y, z)e^{-iEt/\hbar}$. We can then divide

both sides by the factor $e^{-iEt/\hbar}$, leaving the *time-independent* Schrödinger equation in three dimensions for a stationary state:

$$\begin{aligned}
 & -\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right) + U(x, y, z) \psi(x, y, z) \\
 & = E \psi(x, y, z) \quad \text{(three-dimensional time-independent Schrödinger equation)} \quad (41.5)
 \end{aligned}$$

The probability distribution function for a stationary state is just the square of the absolute value of the spatial wave function: $|\psi(x, y, z)e^{-iEt/\hbar}|^2 = \psi^*(x, y, z)e^{+iEt/\hbar}\psi(x, y, z)e^{-iEt/\hbar} = |\psi(x, y, z)|^2$. Note that this doesn't depend on time. (As we discussed in Section 40.1, that's why we call these states *stationary*.) Hence for a stationary state the wave function normalization condition, Eq. (41.3), becomes

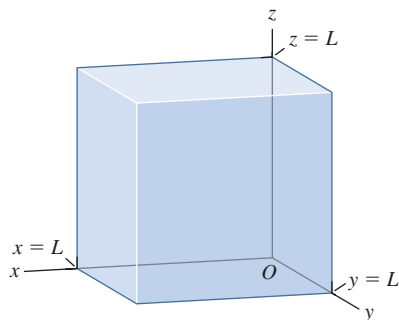
$$\int |\psi(x, y, z)|^2 dV = 1 \quad \text{(normalization condition for a stationary state in three dimensions)} \quad (41.6)$$

We won't pretend that we have *derived* Eqs. (41.2) and (41.5). Like their one-dimensional versions, these equations have to be tested by comparison of their predictions with experimental results. Happily, Eqs. (41.2) and (41.5) both pass this test with flying colors, so we are confident that they *are* the correct equations.

An important topic that we will address in this chapter is the solutions for Eq. (41.5) for the stationary states of the hydrogen atom. The potential-energy function for an electron in a hydrogen atom is *spherically symmetric*; it depends only on the distance $r = (x^2 + y^2 + z^2)^{1/2}$ from the origin of coordinates. To take advantage of this symmetry, it's best to use *spherical coordinates* rather than the Cartesian coordinates (x, y, z) to solve the Schrödinger equation for the hydrogen atom. Before introducing these new coordinates and investigating the hydrogen atom, it's useful to look at the three-dimensional version of the particle in a box that we considered in Section 40.2. Solving this simpler problem will give us insight into the more complicated stationary states found in atomic physics.

Test Your Understanding of Section 41.1 In a certain region of space the potential-energy function for a quantum-mechanical particle is zero. In this region the wave function $\psi(x, y, z)$ for a certain stationary state satisfies $\partial^2 \psi / \partial x^2 > 0$, $\partial^2 \psi / \partial y^2 > 0$, and $\partial^2 \psi / \partial z^2 > 0$. The particle has a definite energy E that is positive. What can you conclude about $\psi(x, y, z)$ in this region? (i) It must be positive; (ii) it must be negative; (iii) it must be zero; (iv) not enough information given to decide.

41.1 A particle is confined in a cubical box with walls at $x = 0$, $x = L$, $y = 0$, $y = L$, $z = 0$, and $z = L$.



41.2 Particle in a Three-Dimensional Box

Consider a particle enclosed within a cubical box of side L . This could represent an electron that's free to move anywhere within the interior of a solid metal cube but cannot escape the cube. We'll choose the origin to be at one corner of the box, with the x -, y -, and z -axes along edges of the box. Then the particle is confined to the region $0 \leq x \leq L$, $0 \leq y \leq L$, $0 \leq z \leq L$ (Fig. 41.1). What are the stationary states of this system?

As for the particle in a one-dimensional box that we considered in Section 40.2, we'll say that the potential energy is zero inside the box but infinite outside. Hence the spatial wave function $\psi(x, y, z)$ must be zero outside the box in order that the term $U(x, y, z)\psi(x, y, z)$ in the time-independent Schrödinger equation, Eq. (41.5), not be infinite. Hence the probability distribution function $|\psi(x, y, z)|^2$ is zero outside the box, and there is zero probability that the particle will be found

there. Inside the box, the spatial wave function for a stationary state obeys the time-independent Schrödinger equation, Eq. (41.5), with $U(x, y, z) = 0$:

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right) = E \psi(x, y, z)$$

(particle in a three-dimensional box) (41.7)

In order for the wave function to be continuous from the inside to the outside of the box, $\psi(x, y, z)$ must equal zero on the walls. Hence our boundary conditions are that $\psi(x, y, z) = 0$ at $x = 0$, $x = L$, $y = 0$, $y = L$, $z = 0$, and $z = L$.

Guessing a solution to a complicated partial differential equation like Eq. (41.7) seems like quite a challenge. To make progress, recall that we wrote the time-dependent wave function for a stationary state as the product of one function that depends only on the spatial coordinates x , y , and z and a second function that depends only on the time t : $\Psi(x, y, z, t) = \psi(x, y, z)e^{-iEt/\hbar}$. In the same way, let's try a technique called *separation of variables*: We'll write the spatial wave function $\psi(x, y, z)$ as a product of one function X that depends only on x , a second function Y that depends only on y , and a third function Z that depends only on z :

$$\psi(x, y, z) = X(x)Y(y)Z(z) \quad (41.8)$$

If we substitute Eq. (41.8) into Eq. (41.7), we get

$$-\frac{\hbar^2}{2m} \left(Y(y)Z(z) \frac{d^2 X(x)}{dx^2} + X(x)Z(z) \frac{d^2 Y(y)}{dy^2} + X(x)Y(y) \frac{d^2 Z(z)}{dz^2} \right) = EX(x)Y(y)Z(z) \quad (41.9)$$

The partial derivatives in Eq. (41.7) have become ordinary derivatives since they act on functions of a single variable. Now we divide both sides of Eq. (41.9) by the product $X(x)Y(y)Z(z)$:

$$\left(-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} \right) + \left(-\frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{d^2 Y(y)}{dy^2} \right) + \left(-\frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{d^2 Z(z)}{dz^2} \right) = E \quad (41.10)$$

The right-hand side of Eq. (41.10) is the energy of the stationary state, which does not and cannot depend on the values of x , y , or z . For this to be true, the left-hand side of the equation must also be independent of the values of x , y , and z . Hence the first term in parentheses on the left-hand side of Eq. (41.10) must equal a constant that doesn't depend on x , the second term in parentheses must equal another constant that doesn't depend on y , and the third term in parentheses must equal a third constant that doesn't depend on z . Let's call these constants E_X , E_Y , and E_Z , respectively. We then have a separate equation for each of the three functions $X(x)$, $Y(y)$, and $Z(z)$:

$$-\frac{\hbar^2}{2m} \frac{d^2 X(x)}{dx^2} = E_X X(x) \quad (41.11a)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 Y(y)}{dy^2} = E_Y Y(y) \quad (41.11b)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 Z(z)}{dz^2} = E_Z Z(z) \quad (41.11c)$$

To satisfy the boundary conditions that $\psi(x, y, z) = X(x)Y(y)Z(z)$ be equal to zero on the walls of the box, we demand that $X(x) = 0$ at $x = 0$ and $x = L$, $Y(y) = 0$ at $y = 0$ and $y = L$, and $Z(z) = 0$ at $z = 0$ and $z = L$.

How can we interpret the three constants E_X , E_Y , and E_Z in Eqs. (41.11)? From Eq. (41.10), they are related to the energy E by

$$E_X + E_Y + E_Z = E \quad (41.12)$$

Equation (41.12) should remind you of Eq. (41.1) in Section 41.1, which states that the kinetic energy of a particle is the sum of contributions coming from its x -, y -, and z -components of momentum. Hence the constants E_X , E_Y , and E_Z tell us how much of the particle's energy is due to motion along each of the three coordinate axes. (Inside the box the potential energy is zero, so the particle's energy is purely kinetic.)

Equations (41.11) represent an enormous simplification; we've reduced the problem of solving a fairly complex *partial* differential equation with three independent variables to the much simpler problem of solving three separate *ordinary* differential equations with one independent variable each. What's more, each of these ordinary differential equations is just the same as the time-independent Schrödinger equation for a particle in a *one-dimensional* box, Eq. (40.25), and with exactly the same boundary conditions at 0 and L . (The only differences are that some of the quantities are labeled by different symbols.) By comparing with our work in Section 40.2, you can see that the solutions to Eqs. (41.11) are

$$X_{n_X}(x) = C_X \sin \frac{n_X \pi x}{L} \quad (n_X = 1, 2, 3, \dots) \quad (41.13a)$$

$$Y_{n_Y}(y) = C_Y \sin \frac{n_Y \pi y}{L} \quad (n_Y = 1, 2, 3, \dots) \quad (41.13b)$$

$$Z_{n_Z}(z) = C_Z \sin \frac{n_Z \pi z}{L} \quad (n_Z = 1, 2, 3, \dots) \quad (41.13c)$$

where C_X , C_Y , and C_Z are constants. The corresponding values of E_X , E_Y , and E_Z are

$$E_X = \frac{n_X^2 \pi^2 \hbar^2}{2mL^2} \quad (n_X = 1, 2, 3, \dots) \quad (41.14a)$$

$$E_Y = \frac{n_Y^2 \pi^2 \hbar^2}{2mL^2} \quad (n_Y = 1, 2, 3, \dots) \quad (41.14b)$$

$$E_Z = \frac{n_Z^2 \pi^2 \hbar^2}{2mL^2} \quad (n_Z = 1, 2, 3, \dots) \quad (41.14c)$$

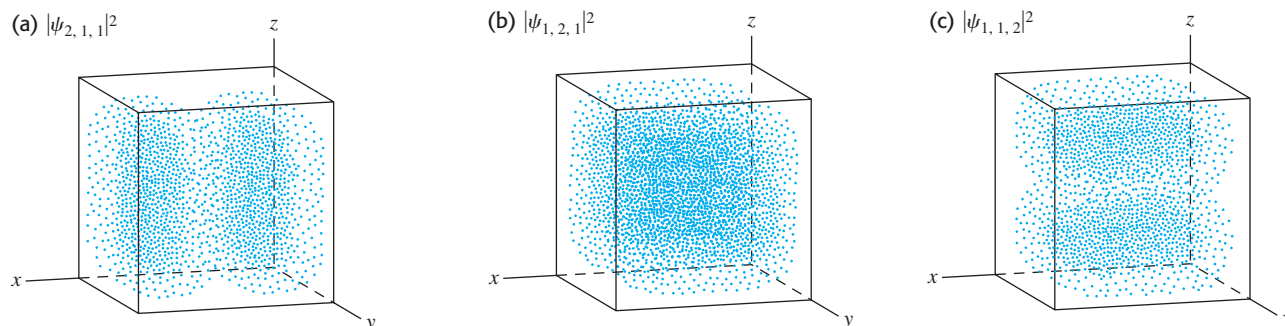
There is only one quantum number n for the one-dimensional particle in a box, but *three* quantum numbers n_X , n_Y , and n_Z for the three-dimensional box. If we substitute Eqs. (41.13) back into Eq. (41.8) for the total spatial wave function, $\psi(x, y, z) = X(x)Y(y)Z(z)$, we get the following stationary-state wave functions for a particle in a three-dimensional cubical box:

$$\begin{aligned} \psi_{n_X, n_Y, n_Z}(x, y, z) &= C \sin \frac{n_X \pi x}{L} \sin \frac{n_Y \pi y}{L} \sin \frac{n_Z \pi z}{L} \\ &\quad (n_X = 1, 2, 3, \dots; n_Y = 1, 2, 3, \dots; n_Z = 1, 2, 3, \dots) \end{aligned} \quad (41.15)$$

where $C = C_X C_Y C_Z$. The value of the constant C is determined by the normalization condition, Eq. (41.6).

In Section 40.2 we saw that the stationary-state wave functions for a particle in a one-dimensional box were analogous to standing waves on a string. In a similar way, the *three*-dimensional wave functions given by Eq. (41.15) are analogous to standing electromagnetic waves in a cubical cavity like the interior of a microwave oven (see Section 32.5). In a microwave oven there are “dead spots” where the wave intensity is zero, corresponding to the nodes of the standing wave. (The rotating platform in a microwave oven ensures even cooking by making sure that no part of the food sits at any “dead spot.”) In a similar fashion, the probability distribution function corresponding to Eq. (41.15) can have “dead

41.2 Probability distribution function $|\psi_{n_X, n_Y, n_Z}(x, y, z)|^2$ for (n_X, n_Y, n_Z) equal to (a) (2, 1, 1), (b) (1, 2, 1), and (c) (1, 1, 2). The value of $|\psi|^2$ is proportional to the density of dots. The wave function is zero on the walls of the box and on the midplane of the box, so $|\psi|^2 = 0$ at these locations.



spots” where there is zero probability of finding the particle. As an example, consider the case $(n_X, n_Y, n_Z) = (2, 1, 1)$. From Eq. (41.15), the probability distribution function for this case is

$$|\psi_{2,1,1}(x, y, z)|^2 = |C|^2 \sin^2 \frac{2\pi x}{L} \sin^2 \frac{\pi y}{L} \sin^2 \frac{\pi z}{L}$$

As Fig. 41.2a shows, the probability distribution function is zero on the plane $x = L/2$, where $\sin^2(2\pi x/L) = \sin^2 \pi = 0$. The particle is most likely to be found near where all three of the sine-squared functions are greatest, at $(x, y, z) = (L/4, L/2, L/2)$ or $(x, y, z) = (3L/4, L/2, L/2)$. Figures 41.2b and 41.2c show the similar cases $(n_X, n_Y, n_Z) = (1, 2, 1)$ and $(n_X, n_Y, n_Z) = (1, 1, 2)$. For higher values of the quantum numbers n_X , n_Y , and n_Z there are additional planes on which the probability distribution function equals zero, just as the probability distribution function $|\psi(x)|^2$ for a one-dimensional box has more zeros for higher values of n (see Fig. 40.12).

Example 41.1 Probability in a three-dimensional box

(a) Find the value of the constant C that normalizes the wave function of Eq. (41.15). (b) Find the probability that the particle will be found somewhere in the region $0 \leq x \leq L/4$ (Fig. 41.3) for the cases (i) $(n_X, n_Y, n_Z) = (1, 2, 1)$, (ii) $(n_X, n_Y, n_Z) = (2, 1, 1)$, and (iii) $(n_X, n_Y, n_Z) = (3, 1, 1)$.

SOLUTION

IDENTIFY and SET UP: Equation (41.6) tells us that to normalize the wave function, we have to choose the value of C so that the

integral of the probability distribution function $|\psi_{n_X, n_Y, n_Z}(x, y, z)|^2$ over the volume within the box equals 1. (The integral is actually over *all* space, but the particle-in-a-box wave functions are zero outside the box.)

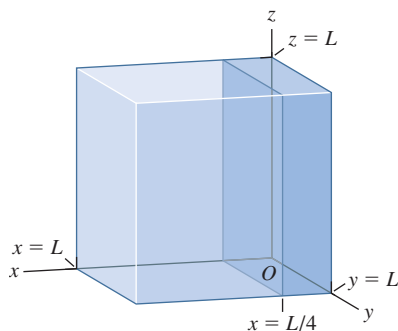
The probability of finding the particle within a certain volume within the box equals the integral of the probability distribution function over that volume. Hence in part (b) we’ll integrate $|\psi_{n_X, n_Y, n_Z}(x, y, z)|^2$ for the given values of (n_X, n_Y, n_Z) over the volume $0 \leq x \leq L/4$, $0 \leq y \leq L$, $0 \leq z \leq L$.

EXECUTE: (a) From Eq. (41.15),

$$|\psi_{n_X, n_Y, n_Z}(x, y, z)|^2 = |C|^2 \sin^2 \frac{n_X \pi x}{L} \sin^2 \frac{n_Y \pi y}{L} \sin^2 \frac{n_Z \pi z}{L}$$

Hence the normalization condition is

$$\begin{aligned} & \int |\psi_{n_X, n_Y, n_Z}(x, y, z)|^2 dV \\ &= |C|^2 \int_{x=0}^{x=L} \int_{y=0}^{y=L} \int_{z=0}^{z=L} \sin^2 \frac{n_X \pi x}{L} \sin^2 \frac{n_Y \pi y}{L} \sin^2 \frac{n_Z \pi z}{L} dx dy dz \\ &= |C|^2 \left(\int_{x=0}^{x=L} \sin^2 \frac{n_X \pi x}{L} dx \right) \left(\int_{y=0}^{y=L} \sin^2 \frac{n_Y \pi y}{L} dy \right) \\ & \quad \times \left(\int_{z=0}^{z=L} \sin^2 \frac{n_Z \pi z}{L} dz \right) = 1 \end{aligned}$$



41.3 What is the probability that the particle is in the dark-colored quarter of the box?

Continued

We can use the identity $\sin^2\theta = \frac{1}{2}(1 - \cos 2\theta)$ and the variable substitution $\theta = n_X\pi x/L$ to show that

$$\begin{aligned}\int \sin^2 \frac{n_X\pi x}{L} dx &= \frac{L}{2n_X\pi} \left[\frac{n_X\pi x}{L} - \frac{1}{2} \sin\left(\frac{2n_X\pi x}{L}\right) \right] \\ &= \frac{x}{2} - \frac{L}{4n_X\pi} \sin\left(\frac{2n_X\pi x}{L}\right)\end{aligned}$$

If we evaluate this integral between $x = 0$ and $x = L$, the result is $L/2$ (recall that $\sin 0 = 0$ and $\sin 2n_X\pi = 0$ for any integer n_X). The y - and z -integrals each yield the same result, so the normalization condition is

$$|C|^2 \left(\frac{L}{2}\right) \left(\frac{L}{2}\right) \left(\frac{L}{2}\right) = |C|^2 \left(\frac{L}{2}\right)^3 = 1$$

or $|C|^2 = (2/L)^3$. If we choose C to be real and positive, then $C = (2/L)^{3/2}$.

(b) We have the same y - and z -integrals as in part (a), but now the limits of integration on the x -integral are $x = 0$ and $x = L/4$:

$$\begin{aligned}P &= \int_{0 \leq x \leq L/4} |\psi_{n_X n_Y n_Z}|^2 dV = |C|^2 \left(\int_{x=0}^{x=L/4} \sin^2 \frac{n_X\pi x}{L} dx \right) \\ &\quad \times \left(\int_{y=0}^{y=L} \sin^2 \frac{n_Y\pi y}{L} dy \right) \left(\int_{z=0}^{z=L} \sin^2 \frac{n_Z\pi z}{L} dz \right)\end{aligned}$$

The x -integral is

$$\begin{aligned}\int_{x=0}^{x=L/4} \sin^2 \frac{n_X\pi x}{L} dx &= \left(\frac{x}{2} - \frac{L}{4n_X\pi} \sin\left(\frac{2n_X\pi x}{L}\right) \right) \Big|_{x=0}^{x=L/4} \\ &= \frac{L}{8} - \frac{L}{4n_X\pi} \sin\left(\frac{n_X\pi}{2}\right)\end{aligned}$$

Hence the probability of finding the particle somewhere in the region $0 \leq x \leq L/4$ is

$$\begin{aligned}P &= \left(\frac{2}{L}\right)^3 \left(\frac{L}{8} - \frac{L}{4n_X\pi} \sin\left(\frac{n_X\pi}{2}\right)\right) \left(\frac{L}{2}\right) \left(\frac{L}{2}\right) \\ &= \frac{1}{4} - \frac{1}{2n_X\pi} \sin\left(\frac{n_X\pi}{2}\right)\end{aligned}$$

This depends only on the value of n_X , not on n_Y or n_Z . Hence for the three cases we have

$$\begin{aligned}\text{(i) } n_X = 1: P &= \frac{1}{4} - \frac{1}{2(1)\pi} \sin\left(\frac{\pi}{2}\right) = \frac{1}{4} - \frac{1}{2\pi} (1) \\ &= \frac{1}{4} - \frac{1}{2\pi} = 0.091\end{aligned}$$

$$\begin{aligned}\text{(ii) } n_X = 2: P &= \frac{1}{4} - \frac{1}{2(2)\pi} \sin\left(\frac{2\pi}{2}\right) = \frac{1}{4} - \frac{1}{4\pi} \sin \pi \\ &= \frac{1}{4} - 0 = 0.250\end{aligned}$$

$$\begin{aligned}\text{(iii) } n_X = 3: P &= \frac{1}{4} - \frac{1}{2(3)\pi} \sin\left(\frac{3\pi}{2}\right) = \frac{1}{4} - \frac{1}{6\pi} (-1) \\ &= \frac{1}{4} + \frac{1}{6\pi} = 0.303\end{aligned}$$

EVALUATE: You can see why the probabilities in part (b) are different by looking at part (b) of Fig. 40.12, which shows $\sin^2 n_X\pi x/L$ for $n_X = 1, 2$, and 3 . For $n_X = 2$ the area under the curve between $x = 0$ and $x = L/4$ (equal to the integral between these two points) is exactly $\frac{1}{4}$ of the total area between $x = 0$ and $x = L$. For $n_X = 1$ the area between $x = 0$ and $x = L/4$ is less than $\frac{1}{4}$ of the total area, and for $n_X = 3$ it is greater than $\frac{1}{4}$ of the total area.

Energy Levels, Degeneracy, and Symmetry

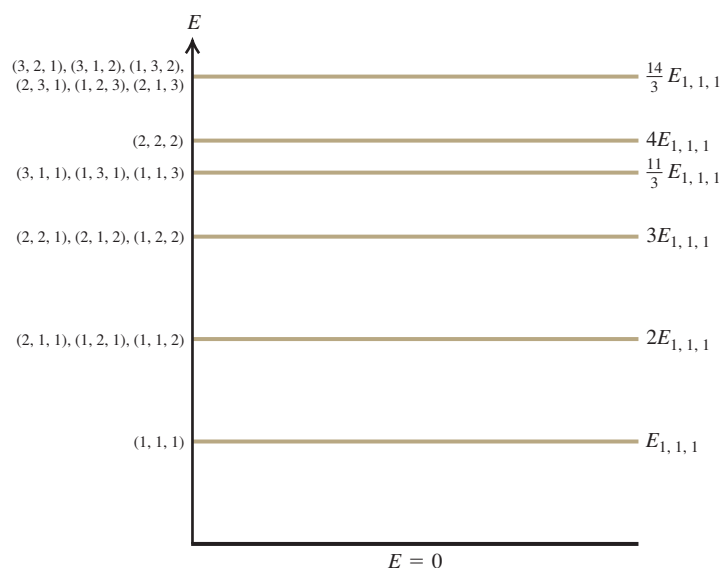
From Eqs. (41.12) and (41.14), the allowed energies for a particle of mass m in a cubical box of side L are

$$E_{n_X, n_Y, n_Z} = \frac{(n_X^2 + n_Y^2 + n_Z^2)\pi^2\hbar^2}{2mL^2} \quad (n_X = 1, 2, 3, \dots; n_Y = 1, 2, 3, \dots; n_Z = 1, 2, 3, \dots) \quad (41.16)$$

(energy levels, particle in a three-dimensional cubical box)

Figure 41.4 shows the six lowest energy levels given by Eq. (41.16). Note that most energy levels correspond to more than one set of quantum numbers (n_X, n_Y, n_Z) and hence to more than one quantum state. Having two or more distinct quantum states with the same energy is called **degeneracy**, and states with the same energy are said to be **degenerate**. For example, Fig. 41.4 shows that the states $(n_X, n_Y, n_Z) = (2, 1, 1)$, $(1, 2, 1)$, and $(1, 1, 2)$ are degenerate. By comparison, for a particle in a one-dimensional box there is just one state for each energy level (see Fig. 40.11a) and no degeneracy.

The reason the cubical box exhibits degeneracy is that it is *symmetric*: All sides of the box have the same dimensions. As an illustration, Fig. 41.2 shows the probability distribution functions for the three states $(n_X, n_Y, n_Z) = (2, 1, 1)$, $(1, 2, 1)$, and $(1, 1, 2)$. You can transform any one of these three states into a different one by simply rotating the cubical box by 90° . This rotation doesn't change the energy, so the three states are degenerate.



41.4 Energy-level diagram for a particle in a three-dimensional cubical box. We label each level with the quantum numbers of the states (n_X, n_Y, n_Z) with that energy. Several of the levels are degenerate (more than one state has the same energy). The lowest (ground) level, $(n_X, n_Y, n_Z) = (1, 1, 1)$, has energy $E_{1,1,1} = (1^2 + 1^2 + 1^2)\pi^2\hbar^2/2mL^2 = 3\pi^2\hbar^2/2mL^2$; we show the energies of the other levels as multiples of $E_{1,1,1}$.

Since degeneracy is a consequence of symmetry, we can remove the degeneracy by making the box asymmetric. We do this by giving the three sides of the box different lengths L_X , L_Y , and L_Z . If we repeat the steps that we followed to solve the time-independent Schrödinger equation, we find that the energy levels are given by

$$E_{n_X, n_Y, n_Z} = \left(\frac{n_X^2}{L_X^2} + \frac{n_Y^2}{L_Y^2} + \frac{n_Z^2}{L_Z^2} \right) \frac{\pi^2 \hbar^2}{2m} \quad (n_X = 1, 2, 3, \dots; n_Y = 1, 2, 3, \dots; n_Z = 1, 2, 3, \dots) \quad (41.17)$$

(energy levels, particle in a three-dimensional box with sides of length L_X , L_Y , and L_Z)

If L_X , L_Y , and L_Z are all different, the states $(n_X, n_Y, n_Z) = (2, 1, 1)$, $(1, 2, 1)$, and $(1, 1, 2)$ have different energies and hence are no longer degenerate. Note that Eq. (41.17) reduces to Eq. (41.16) if the lengths are all the same ($L_X = L_Y = L_Z = L$).

Let's summarize the key differences between the three-dimensional particle in a box and the one-dimensional case that we examined in Section 40.2:

- We can write the wave function for a three-dimensional stationary state as a product of three functions, one for each spatial coordinate. Only a single function of the coordinate x is needed in one dimension.
- In the three-dimensional case, three quantum numbers are needed to describe each stationary state. Only one quantum number is needed in the one-dimensional case.
- Most of the energy levels for the three-dimensional case are degenerate: More than one stationary state has this energy. There is no degeneracy in the one-dimensional case.
- For a stationary state of the three-dimensional case, there are surfaces on which the probability distribution function $|\psi|^2$ is zero. In the one-dimensional case there are positions on the x -axis where $|\psi|^2$ is zero.

We'll see these same features in the following section as we examine a three-dimensional situation that's more realistic than a particle in a box: a hydrogen atom in which a negatively charged electron orbits a positively charged nucleus.

Test Your Understanding of Section 41.2 Rank the following states of a particle in a cubical box of side L in order from highest to lowest energy: (i) $(n_X, n_Y, n_Z) = (2, 3, 2)$; (ii) $(n_X, n_Y, n_Z) = (4, 1, 1)$; (iii) $(n_X, n_Y, n_Z) = (2, 2, 3)$; (iv) $(n_X, n_Y, n_Z) = (1, 3, 3)$.

41.3 The Hydrogen Atom

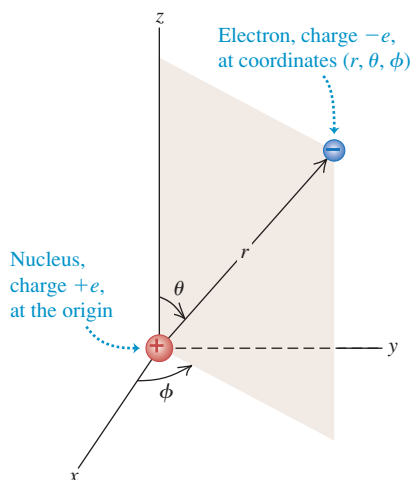
Let's continue the discussion of the hydrogen atom that we began in Chapter 39. In the Bohr model, electrons move in circular orbits like Newtonian particles, but with quantized values of angular momentum. While this model gave the correct energy levels of the hydrogen atom, as deduced from spectra, it had many conceptual difficulties. It mixed classical physics with new and seemingly contradictory concepts. It provided no insight into the process by which photons are emitted and absorbed. It could not be generalized to atoms with more than one electron. It predicted the wrong magnetic properties for the hydrogen atom. And perhaps most important, its picture of the electron as a localized point particle was inconsistent with the more general view we developed in Chapters 39 and 40. To go beyond the Bohr model, let's apply the Schrödinger equation to find the wave functions for stationary states (states of definite energy) of the hydrogen atom. As in Section 39.3, we include the motion of the nucleus by simply replacing the electron mass m with the reduced mass m_r .

The Schrödinger Equation for the Hydrogen Atom

We discussed the three-dimensional version of the Schrödinger equation in Section 41.1. The potential-energy function is *spherically symmetric*: It depends only on the distance $r = (x^2 + y^2 + z^2)^{1/2}$ from the origin of coordinates:

$$U(r) = -\frac{1}{4\pi\epsilon_0} \frac{e^2}{r} \quad (41.18)$$

41.5 The Schrödinger equation for the hydrogen atom can be solved most readily using spherical coordinates.



The hydrogen-atom problem is best formulated in spherical coordinates (r, θ, ϕ) , shown in Fig. 41.5; the spherically symmetric potential-energy function depends only on r , not on θ or ϕ . The Schrödinger equation with this potential-energy function can be solved exactly; the solutions are combinations of familiar functions. Without going into a lot of detail, we can describe the most important features of the procedure and the results.

First, we find the solutions using the same method of separation of variables that we employed for a particle in a cubical box in Section 41.2. We express the wave function $\psi(r, \theta, \phi)$ as a product of three functions, each one a function of only one of the three coordinates:

$$\psi(r, \theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \quad (41.19)$$

That is, the function $R(r)$ depends only on r , $\Theta(\theta)$ depends only on θ , and $\Phi(\phi)$ depends only on ϕ . Just as for a particle in a three-dimensional box, when we substitute Eq. (41.19) into the Schrödinger equation, we get three separate ordinary differential equations. One equation involves only r and $R(r)$, a second involves only θ and $\Theta(\theta)$, and a third involves only ϕ and $\Phi(\phi)$:

$$-\frac{\hbar^2}{2m_r r^2} \frac{d}{dr} \left(r^2 \frac{dR(r)}{dr} \right) + \left(\frac{\hbar^2 l(l+1)}{2m_r r^2} + U(r) \right) R(r) = ER(r) \quad (41.20a)$$

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta(\theta)}{d\theta} \right) + \left(l(l+1) - \frac{m_l^2}{\sin^2 \theta} \right) \Theta(\theta) = 0 \quad (41.20b)$$

$$\frac{d^2 \Phi(\phi)}{d\phi^2} + m_l^2 \Phi(\phi) = 0 \quad (41.20c)$$

In Eqs. (41.20) E is the energy of the stationary state and l and m_l are constants that we'll discuss later. (Be careful! Don't confuse the constant m_l with the reduced mass m_r .)

We won't attempt to solve this set of three equations, but we can describe how it's done. As for the particle in a cubical box, the physically acceptable solutions of these three equations are determined by boundary conditions. The radial function $R(r)$ in Eq. (41.20a) must approach zero at large r , because we are describing

bound states of the electron that are localized near the nucleus. This is analogous to the requirement that the harmonic-oscillator wave functions (see Section 40.5) must approach zero at large x . The angular functions $\Theta(\theta)$ and $\Phi(\phi)$ in Eqs. (41.20b) and (41.20c) must be *finite* for all relevant values of the angles. For example, there are solutions of the Θ equation that become infinite at $\theta = 0$ and $\theta = \pi$; these are unacceptable, since $\psi(r, \theta, \phi)$ must be normalizable. Furthermore, the angular function $\Phi(\phi)$ in Eq. (41.20c) must be *periodic*. For example, (r, θ, ϕ) and $(r, \theta, \phi + 2\pi)$ describe the same point, so $\Phi(\phi + 2\pi)$ must equal $\Phi(\phi)$.

The allowed radial functions $R(r)$ turn out to be an exponential function $e^{-\alpha r}$ (where α is positive) multiplied by a polynomial in r . The functions $\Theta(\theta)$ are polynomials containing various powers of $\sin\theta$ and $\cos\theta$, and the functions $\Phi(\phi)$ are simply proportional to $e^{im_l\phi}$, where $i = \sqrt{-1}$ and m_l is an integer that may be positive, zero, or negative.

In the process of finding solutions that satisfy the boundary conditions, we also find the corresponding energy levels. We denote the energies of these levels [E in Eq. (41.20a)] by E_n ($n = 1, 2, 3, \dots$). These turn out to be *identical* to those from the Bohr model, as given by Eq. (39.15), with the electron rest mass m replaced by the reduced mass m_r . Rewriting that equation using $\hbar = h/2\pi$, we have

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m_r e^4}{2n^2\hbar^2} = -\frac{13.60 \text{ eV}}{n^2} \quad (\text{energy levels of hydrogen}) \quad (41.21)$$

As in Section 39.3, we call n the **principal quantum number** for the level of energy E_n .

Equation (41.21) is an important validation of our Schrödinger-equation analysis of the hydrogen atom. The Schrödinger analysis is quite different from the Bohr model, both mathematically and conceptually, yet both yield the same energy-level scheme—a scheme that agrees with the energies determined from spectra. As we will see, the Schrödinger analysis can explain many more aspects of the hydrogen atom than can the Bohr model.

Quantization of Orbital Angular Momentum

The solutions to Eqs. (41.20) that satisfy the boundary conditions mentioned above also have quantized values of *orbital angular momentum*. That is, only certain discrete values of the magnitude and components of orbital angular momentum are permitted. In discussing the Bohr model in Section 39.3, we mentioned that quantization of angular momentum was a result with little fundamental justification. With the Schrödinger equation it appears automatically.

The possible values of the magnitude L of orbital angular momentum \vec{L} are determined by the requirement that the $\Theta(\theta)$ function in Eq. (41.20b) must be finite at $\theta = 0$ and $\theta = \pi$. In a level with energy E_n and principal quantum number n , the possible values of L are

$$L = \sqrt{l(l+1)}\hbar \quad (l = 0, 1, 2, \dots, n-1) \quad \begin{array}{l} \text{(magnitude of} \\ \text{orbital angular} \\ \text{momentum)} \end{array} \quad (41.22)$$

The *orbital angular-momentum quantum number* l , which is the same l that appears in Eqs. (41.20a) and (41.20b), is called the **orbital quantum number** for short. In the Bohr model, each energy level corresponded to a single value of angular momentum. Equation (41.22) shows that in fact there are n different possible values of L for the n th energy level.

An interesting feature of Eq. (41.22) is that the orbital angular momentum is *zero* for $l = 0$ states. This result disagrees with the Bohr model, in which the electron always moved in a circle of definite radius and L was never zero. The $l = 0$ wave functions ψ depend only on r ; for these states, the functions $\Theta(\theta)$ and $\Phi(\phi)$ are constants. Thus the wave functions for $l = 0$ states are spherically

symmetric. There is nothing in their probability distribution $|\psi|^2$ to favor one direction over any other, and there is no orbital angular momentum.

The permitted values of the *component* of \vec{L} in a given direction, say the z -component L_z , are determined by the requirement that the $\Phi(\phi)$ function must equal $\Phi(\phi + 2\pi)$. The possible values of L_z are

$L_z = m_l \hbar$	$(m_l = 0, \pm 1, \pm 2, \dots, \pm l)$	(components of orbital angular momentum)	(41.23)
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The quantum number m_l is the same as that in Eqs. (41.20b) and (41.20c). We see that m_l can be zero or a positive or negative integer up to, but no larger in magnitude than, l . That is, $|m_l| \leq l$. For example, if $l = 1$, m_l can equal 1, 0, or -1 . For reasons that will emerge later, we call m_l the *orbital magnetic quantum number*, or **magnetic quantum number** for short.

The component L_z can never be quite as large as L (unless both are zero). For example, when $l = 2$, the largest possible value of m_l is also 2; then Eqs. (41.22) and (41.23) give

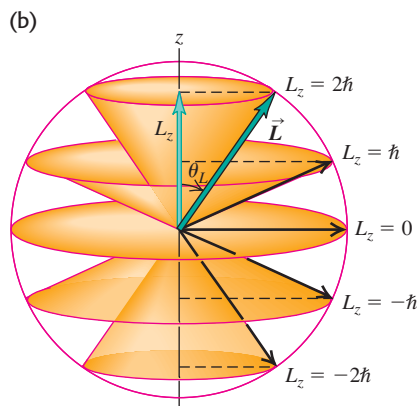
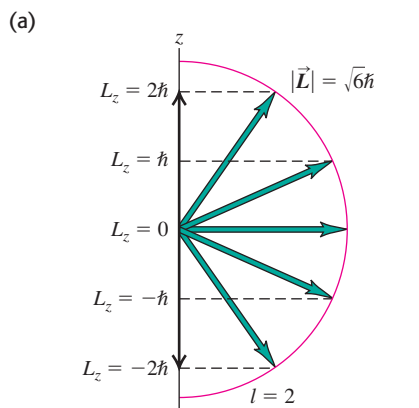
$$L = \sqrt{2(2 + 1)}\hbar = \sqrt{6}\hbar = 2.45\hbar$$

$$L_z = 2\hbar$$

Figure 41.6 shows the situation. The minimum value of the angle θ_L between the vector \vec{L} and the z -axis is given by

$$\theta_L = \arccos \frac{L_z}{L} = \arccos \frac{2}{2.45} = 35.3^\circ$$

41.6 (a) When $l = 2$, the magnitude of the angular momentum vector \vec{L} is $\sqrt{6}\hbar = 2.45\hbar$, but \vec{L} does not have a definite direction. In this semiclassical vector picture, \vec{L} makes an angle of 35.3° with the z -axis when the z -component has its maximum value of $2\hbar$. (b) These cones show the possible directions of \vec{L} for different values of L_z .



That $|L_z|$ is always less than L is also required by the uncertainty principle. Suppose we could know the precise *direction* of the orbital angular momentum vector. Then we could let that be the direction of the z -axis, and L_z would equal L . This corresponds to a particle moving in the xy -plane only, in which case the z -component of the linear momentum \vec{p} would be zero with no uncertainty Δp_z . Then the uncertainty principle $\Delta z \Delta p_z \geq \hbar$ requires infinite uncertainty Δz in the coordinate z . This is impossible for a localized state; we conclude that we can't know the direction of \vec{L} precisely. Thus, as we've already stated, the component of \vec{L} in a given direction can never be quite as large as its magnitude L . Also, if we can't know the direction of \vec{L} precisely, we can't determine the components L_x and L_y precisely. Thus we show *cones* of possible directions for \vec{L} in Fig. 41.6b.

You may wonder why we have singled out the z -axis for special attention. There's no fundamental reason for this; the atom certainly doesn't care what coordinate system we use. The point is that we can't determine all three components of orbital angular momentum with certainty, so we arbitrarily pick one as the component we want to measure. When we discuss interactions of the atom with a magnetic field, we will consistently choose the positive z -axis to be in the direction of \vec{B} .

Quantum Number Notation

The wave functions for the hydrogen atom are determined by the values of three quantum numbers n , l , and m_l . (Compare this to the particle in a three-dimensional box that we considered in Section 41.2. There, too, three quantum numbers were needed to describe each stationary state.) The energy E_n is determined by the principal quantum number n according to Eq. (41.21). The magnitude of orbital angular momentum is determined by the orbital quantum number l , as in Eq. (41.22). The component of orbital angular momentum in a specified axis direction (customarily the z -axis) is determined by the magnetic quantum number m_l , as in Eq. (41.23). The energy does not depend on the values of l or m_l (Fig. 41.7), so for each energy level E_n given by Eq. (41.21), there is more than one distinct state having the same energy but different quantum numbers. That is, these states are *degenerate*, just like most of the states of a particle in a

three-dimensional box. As for the three-dimensional box, degeneracy arises because the hydrogen atom is symmetric: If you rotate the atom through any angle, the potential-energy function at a distance r from the nucleus has the same value.

States with various values of the orbital quantum number l are often labeled with letters, according to the following scheme:

- $l = 0$: s states
- $l = 1$: p states
- $l = 2$: d states
- $l = 3$: f states
- $l = 4$: g states
- $l = 5$: h states

and so on alphabetically. This seemingly irrational choice of the letters s , p , d , and f originated in the early days of spectroscopy and has no fundamental significance. In an important form of *spectroscopic notation* that we'll use often, a state with $n = 2$ and $l = 1$ is called a $2p$ state; a state with $n = 4$ and $l = 0$ is a $4s$ state; and so on. Only s states ($l = 0$) are spherically symmetric.

Here's another bit of notation. The radial extent of the wave functions increases with the principal quantum number n , and we can speak of a region of space associated with a particular value of n as a **shell**. Especially in discussions of many-electron atoms, these shells are denoted by capital letters:

- $n = 1$: K shell
- $n = 2$: L shell
- $n = 3$: M shell
- $n = 4$: N shell

and so on alphabetically. For each n , different values of l correspond to different *subshells*. For example, the L shell ($n = 2$) contains the $2s$ and $2p$ subshells.

Table 41.1 shows some of the possible combinations of the quantum numbers n , l , and m_l for hydrogen-atom wave functions. The spectroscopic notation and the shell notation for each are also shown.

Table 41.1 Quantum States of the Hydrogen Atom

n	l	m_l	Spectroscopic Notation	Shell
1	0	0	$1s$	K
2	0	0	$2s$	L
2	1	$-1, 0, 1$	$2p$	
3	0	0	$3s$	M
3	1	$-1, 0, 1$	$3p$	
3	2	$-2, -1, 0, 1, 2$	$3d$	
4	0	0	$4s$	N
and so on				

41.7 The energy for an orbiting satellite such as the Hubble Space Telescope depends on the average distance between the satellite and the center of the earth. It does *not* depend on whether the orbit is circular (with a large orbital angular momentum L) or elliptical (in which case L is smaller). In the same way, the energy of a hydrogen atom does not depend on the orbital angular momentum.



Problem-Solving Strategy 41.1 Atomic Structure



IDENTIFY the relevant concepts: Many problems in atomic structure can be solved simply by reference to the quantum numbers n , l , and m_l that describe the total energy E , the magnitude of the orbital angular momentum \vec{L} , the z -component of \vec{L} , and other properties of an atom.

SET UP the problem: Identify the target variables and choose the appropriate equations, which may include Eqs. (41.21), (41.22), and (41.23).

EXECUTE the solution as follows:

- Be sure you understand the possible values of the quantum numbers n , l , and m_l for the hydrogen atom. They are all integers; n is always greater than zero, l can be zero or positive up

to $n - 1$, and m_l can range from $-l$ to l . You should know how to count the number of (n, l, m_l) states in each shell (K , L , M , and so on) and subshell ($3s$, $3p$, $3d$, and so on). Be able to *construct* Table 41.1, not just to write it from memory.

- Solve for the target variables.

EVALUATE your answer: It helps to be familiar with typical magnitudes in atomic physics. For example, the electric potential energy of a proton and electron 0.10 nm apart (typical of atomic dimensions) is about -15 eV. Visible light has wavelengths around 500 nm and frequencies around 5×10^{14} Hz. Problem-Solving Strategy 39.1 (Section 39.1) gives other typical magnitudes.

Example 41.2 Counting hydrogen states

How many distinct (n, l, m_l) states of the hydrogen atom with $n = 3$ are there? What are their energies?

SOLUTION

IDENTIFY and SET UP: This problem uses the relationships among the principal quantum number n , orbital quantum number l , magnetic quantum number m_l , and energy of a state for the hydrogen atom. We use the rule that l can have n integer values, from 0 to $n - 1$, and that m_l can have $2l + 1$ values, from $-l$ to l . Equation (41.21) gives the energy of any particular state.

EXECUTE: When $n = 3$, l can be 0, 1, or 2. When $l = 0$, m_l can be only 0 (1 state). When $l = 1$, m_l can be $-1, 0$, or 1 (3 states). When $l = 2$, m_l can be $-2, -1, 0, 1$, or 2 (5 states). The total number of

(n, l, m_l) states with $n = 3$ is therefore $1 + 3 + 5 = 9$. (In Section 41.5 we'll find that the total number of $n = 3$ states is in fact twice this, or 18, because of electron spin.)

The energy of a hydrogen-atom state depends only on n , so all 9 of these states have the same energy. From Eq. (41.21),

$$E_3 = \frac{-13.60 \text{ eV}}{3^2} = -1.51 \text{ eV}$$

EVALUATE: For a given value of n , the total number of (n, l, m_l) states turns out to be n^2 . In this case $n = 3$ and there are $3^2 = 9$ states. Remember that the ground level of hydrogen has $n = 1$ and $E_1 = -13.6 \text{ eV}$; the $n = 3$ excited states have a higher (less negative) energy.

Example 41.3 Angular momentum in an excited level of hydrogen

Consider the $n = 4$ states of hydrogen. (a) What is the maximum magnitude L of the orbital angular momentum? (b) What is the maximum value of L_z ? (c) What is the minimum angle between \vec{L} and the z -axis? Give your answers to parts (a) and (b) in terms of \hbar .

SOLUTION

IDENTIFY and SET UP: We again need to relate the principal quantum number n and the orbital quantum number l for a hydrogen atom. We also need to relate the value of l and the magnitude and possible directions of the orbital angular momentum vector. We'll use Eq. (41.22) in part (a) to determine the maximum value of L ; then we'll use Eq. (41.23) in part (b) to determine the maximum value of L_z . The angle between \vec{L} and the z -axis is minimum when L_z is maximum (so that \vec{L} is most nearly aligned with the positive z -axis).

EXECUTE: (a) When $n = 4$, the maximum value of the orbital angular-momentum quantum number l is $(n - 1) = (4 - 1) = 3$; from Eq. (41.22),

$$L_{\max} = \sqrt{3(3 + 1)}\hbar = \sqrt{12}\hbar = 3.464\hbar$$

(b) For $l = 3$ the maximum value of m_l is 3. From Eq. (41.23),

$$(L_z)_{\max} = 3\hbar$$

(c) The *minimum* allowed angle between \vec{L} and the z -axis corresponds to the *maximum* allowed values of L_z and m_l (Fig. 41.6b shows an $l = 2$ example). For the state with $l = 3$ and $m_l = 3$,

$$\theta_{\min} = \arccos \frac{(L_z)_{\max}}{L} = \arccos \frac{3\hbar}{3.464\hbar} = 30.0^\circ$$

EVALUATE: As a check, you can verify that θ is greater than 30.0° for all states with smaller values of l .

Electron Probability Distributions

Rather than picturing the electron as a point particle moving in a precise circle, the Schrödinger equation gives an electron *probability distribution* surrounding the nucleus. The hydrogen-atom probability distributions are three-dimensional, so they are harder to visualize than the two-dimensional circular orbits of the Bohr model. It's helpful to look at the *radial probability distribution function* $P(r)$ —that is, the probability per radial length for the electron to be found at various distances from the proton. From Section 41.1 the probability for finding the electron in a small volume element dV is $|\psi|^2 dV$. (We assume that ψ is normalized in accordance with Eq. (41.6)—that is, that the integral of $|\psi|^2 dV$ over all space equals unity so that there is 100% probability of finding the electron somewhere in the universe.) Let's take as our volume element a thin spherical shell with inner radius r and outer radius $r + dr$. The volume dV of this shell is approximately its area $4\pi r^2$ multiplied by its thickness dr :

$$dV = 4\pi r^2 dr \quad (41.24)$$

We denote by $P(r) dr$ the probability of finding the particle within the radial range dr ; then, using Eq. (41.24),

$$P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr \quad \text{(probability that the electron is between } r \text{ and } r + dr) \quad (41.25)$$

For wave functions that depend on θ and ϕ as well as r , we use the value of $|\psi|^2$ averaged over all angles in Eq. (41.25).

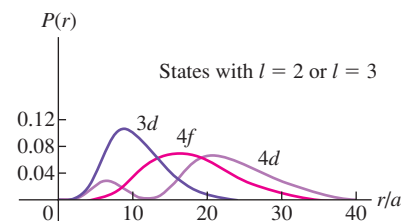
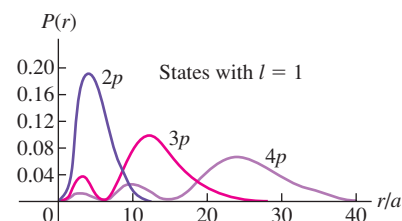
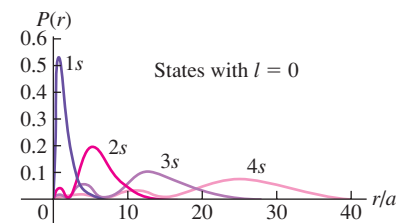
Figure 41.8 shows graphs of $P(r)$ for several hydrogen-atom wave functions. The r scales are labeled in multiples of a , the smallest distance between the electron and the nucleus in the Bohr model:

$$a = \frac{\epsilon_0 \hbar^2}{\pi m_e e^2} = \frac{4\pi\epsilon_0 \hbar^2}{m_e e^2} = 5.29 \times 10^{-11} \text{ m} \quad \text{(smallest } r, \text{ Bohr model)} \quad (41.26)$$

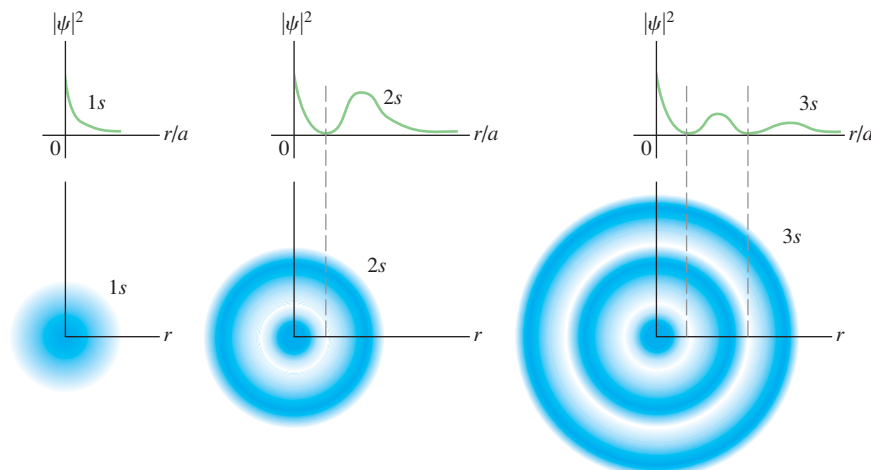
Just as for a particle in a cubical box (see Section 41.2), there are some locations where the probability is zero. These surfaces are planes for a particle in a box; for a hydrogen atom these are spherical surfaces (that is, surfaces of constant r). But again, the uncertainty principle tells us not to worry; we can't localize the electron exactly anyway. Note that for the states having the largest possible l for each n (such as $1s$, $2p$, $3d$, and $4f$ states), $P(r)$ has a single maximum at $n^2 a$. For these states, the electron is most likely to be found at the distance from the nucleus that is predicted by the Bohr model, $r = n^2 a$.

Figure 41.8 shows *radial* probability distribution functions $P(r) = 4\pi r^2 |\psi|^2$, which indicate the relative probability of finding the electron within a thin spherical shell of radius r . By contrast, Figs. 41.9 and 41.10 show the *three-dimensional* probability distribution functions $|\psi|^2$, which indicate the relative probability of finding the electron within a small box at a given position. The darker the blue “cloud,” the greater the value of $|\psi|^2$. (These are similar to the “clouds” shown in Fig. 41.2.) Figure 41.9 shows cross sections of the spherically symmetric probability clouds for the lowest three s subshells, for which $|\psi|^2$ depends only on the radial coordinate r . Figure 41.10 shows cross sections of the clouds for other electron states for which $|\psi|^2$ depends on both r and θ . For these states the probability distribution function is zero for certain values of θ as well as for certain values of r . In *any* stationary state of the hydrogen atom, $|\psi|^2$ is independent of ϕ .

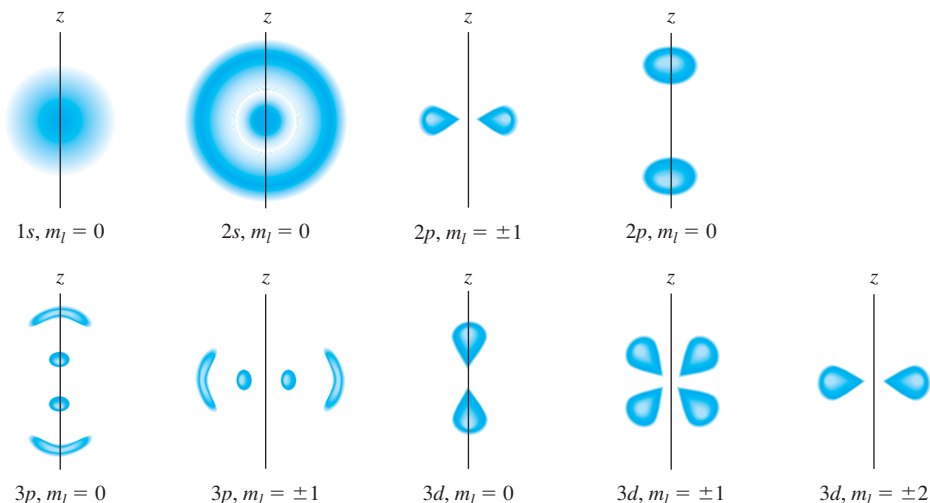
41.8 Radial probability distribution functions $P(r)$ for several hydrogen-atom wave functions, plotted as functions of the ratio r/a [see Eq. (41.26)]. For each function, the number of maxima is $(n - l)$. The curves for which $l = n - 1$ ($1s$, $2p$, $3d$, ...) have only one maximum, located at $r = n^2 a$.



41.9 Three-dimensional probability distribution functions $|\psi|^2$ for the spherically symmetric $1s$, $2s$, and $3s$ hydrogen-atom wave functions.



41.10 Cross sections of three-dimensional probability distributions for a few quantum states of the hydrogen atom. They are not to the same scale. Mentally rotate each drawing about the z -axis to obtain the three-dimensional representation of $|\psi|^2$. For example, the $2p, m_l = \pm 1$ probability distribution looks like a fuzzy donut.



Example 41.4 A hydrogen wave function

The ground-state wave function for hydrogen (a $1s$ state) is

$$\psi_{1s}(r) = \frac{1}{\sqrt{\pi a^3}} e^{-r/a}$$

(a) Verify that this function is normalized. (b) What is the probability that the electron will be found at a distance less than a from the nucleus?

SOLUTION

IDENTIFY and SET UP: This example is similar to Example 41.1 in Section 41.2. We need to show that this wave function satisfies the condition that the probability of finding the electron *somewhere* is 1. We then need to find the probability that it will be found in the region $r < a$. In part (a) we'll carry out the integral $\int |\psi|^2 dV$ over all space; if it is equal to 1, the wave function is normalized. In part (b) we'll carry out the same integral over a spherical volume that extends from the origin (the nucleus) out to a distance a from the nucleus.

EXECUTE: (a) Since the wave function depends only on the radial coordinate r , we can choose our volume elements to be spherical shells of radius r , thickness dr , and volume dV given by Eq. (41.24). We then have

$$\begin{aligned} \int_{\text{all space}} |\psi_{1s}|^2 dV &= \int_0^\infty \frac{1}{\pi a^3} e^{-2r/a} (4\pi r^2 dr) \\ &= \frac{4}{a^3} \int_0^\infty r^2 e^{-2r/a} dr \end{aligned}$$

You can find the following indefinite integral in a table of integrals or by integrating by parts:

$$\int r^2 e^{-2r/a} dr = \left(-\frac{ar^2}{2} - \frac{a^2 r}{2} - \frac{a^3}{4} \right) e^{-2r/a}$$

Evaluating this between the limits $r = 0$ and $r = \infty$ is simple; it is zero at $r = \infty$ because of the exponential factor, and at $r = 0$ only the last term in the parentheses survives. Thus the value of the definite integral is $a^3/4$. Putting it all together, we find

$$\int_0^\infty |\psi_{1s}|^2 dV = \frac{4}{a^3} \int_0^\infty r^2 e^{-2r/a} dr = \frac{4}{a^3} \frac{a^3}{4} = 1$$

The wave function *is* normalized.

(b) To find the probability P that the electron is found within $r < a$, we carry out the same integration but with the limits 0 and a . We'll leave the details to you (Exercise 41.15). From the upper limit we get $-5e^{-2}a^3/4$; the final result is

$$\begin{aligned} P &= \int_0^a |\psi_{1s}|^2 4\pi r^2 dr = \frac{4}{a^3} \left(-\frac{5a^3 e^{-2}}{4} + \frac{a^3}{4} \right) \\ &= (-5e^{-2} + 1) = 1 - 5e^{-2} = 0.323 \end{aligned}$$

EVALUATE: Our results tell us that in a ground state we expect to find the electron at a distance from the nucleus less than a about $\frac{1}{3}$ of the time and at a greater distance about $\frac{2}{3}$ of the time. It's hard to tell, but in Fig. 41.8, about $\frac{2}{3}$ of the area under the $1s$ curve is at distances greater than a (that is, $r/a > 1$).

Hydrogenlike Atoms

Two generalizations that we discussed with the Bohr model in Section 39.3 are equally valid in the Schrödinger analysis. First, if the “atom” is not composed of a single proton and a single electron, using the reduced mass m_r of the system in Eqs. (41.21) and (41.26) will lead to changes that are substantial for some exotic

systems. One example is *positronium*, in which a positron and an electron orbit each other; another is a *muonic atom*, in which the electron is replaced by an unstable particle called a muon that has the same charge as an electron but is 207 times more massive. Second, our analysis is applicable to single-electron ions, such as He^+ , Li^{2+} , and so on. For such ions we replace e^2 by Ze^2 in Eqs. (41.21) and (41.26), where Z is the number of protons (the **atomic number**).

Test Your Understanding of Section 41.3 Rank the following states of the hydrogen atom in order from highest to lowest probability of finding the electron in the vicinity of $r = 5a$: (i) $n = 1, l = 0, m_l = 0$; (ii) $n = 2, l = 1, m_l = +1$; (iii) $n = 2, l = 1, m_l = 0$.



41.4 The Zeeman Effect

The **Zeeman effect** is the splitting of atomic energy levels and the associated spectral lines when the atoms are placed in a magnetic field (Fig. 41.11). This effect confirms experimentally the quantization of angular momentum. The discussion in this section, which assumes that the only angular momentum is the *orbital* angular momentum of a single electron, also shows why we call m_l the magnetic quantum number.

Atoms contain charges in motion, so it should not be surprising that magnetic forces cause changes in that motion and in the energy levels. As early as the middle of the 19th century, physicists speculated that the sources of visible light might be vibrating electric charge on an atomic scale. In 1896 the Dutch physicist Pieter Zeeman was the first to show that in the presence of a magnetic field, some spectral lines were split into groups of closely spaced lines (Fig. 41.12). This effect now bears his name.

Magnetic Moment of an Orbiting Electron

Let's begin our analysis of the Zeeman effect by reviewing the concept of *magnetic dipole moment* or *magnetic moment*, introduced in Section 27.7. A plane current loop with vector area \vec{A} carrying current I has a magnetic moment $\vec{\mu}$ given by

$$\vec{\mu} = I\vec{A} \quad (41.27)$$

When a magnetic dipole of moment $\vec{\mu}$ is placed in a magnetic field \vec{B} , the field exerts a torque $\vec{\tau} = \vec{\mu} \times \vec{B}$ on the dipole. The potential energy U associated with this interaction is given by Eq. (27.27):

$$U = -\vec{\mu} \cdot \vec{B} \quad (41.28)$$

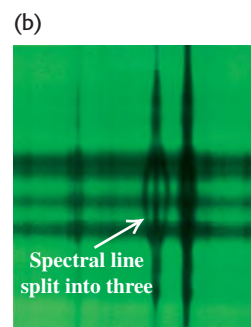
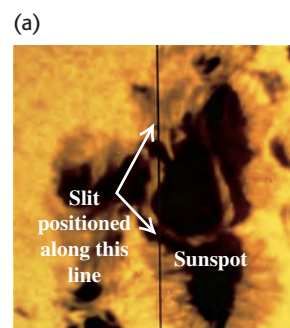
Now let's use Eqs. (41.27) and (41.28) and the Bohr model to look at the interaction of a hydrogen atom with a magnetic field. The orbiting electron with speed v is equivalent to a current loop with radius r and area πr^2 . The average current I is the average charge per unit time that passes a given point of the orbit. This is equal to the charge magnitude e divided by the time T for one revolution, given by $T = 2\pi r/v$. Thus $I = ev/2\pi r$, and from Eq. (41.27) the magnitude μ of the magnetic moment is

$$\mu = IA = \frac{ev}{2\pi r} \pi r^2 = \frac{evr}{2} \quad (41.29)$$

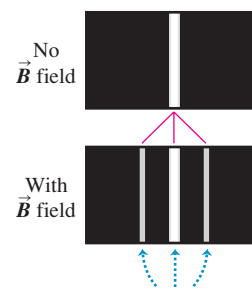
We can also express this in terms of the magnitude L of the orbital angular momentum. From Eq. (10.28) the angular momentum of a particle in a circular orbit is $L = mvr$, so Eq. (41.29) becomes

$$\mu = \frac{e}{2m} L \quad (41.30)$$

41.11 Magnetic effects on the spectrum of sunlight. (a) The slit of a spectrograph is positioned along the black line crossing a portion of a sunspot. (b) The 0.4-T magnetic field in the sunspot (a thousand times greater than the earth's field) splits the middle spectral line into three lines.



41.12 The normal Zeeman effect. Compare this to the magnetic splitting in the solar spectrum shown in Fig. 41.11b.



When an excited gas is placed in a magnetic field, the interaction of orbital magnetic moments with the field splits individual spectral lines of the gas into sets of three lines.

The ratio of the magnitude of $\vec{\mu}$ to the magnitude of \vec{L} is $\mu/L = e/2m$ and is called the *gyromagnetic ratio*.

In the Bohr model, $L = nh/2\pi = n\hbar$, where $n = 1, 2, \dots$. For an $n = 1$ state (a ground state), Eq. (41.30) becomes $\mu = (e/2m)\hbar$. This quantity is a natural unit for magnetic moment; it is called one **Bohr magneton**, denoted by μ_B :

$$\mu_B = \frac{e\hbar}{2m} \quad (\text{definition of the Bohr magneton}) \quad (41.31)$$

Evaluating Eq. (41.31) gives

$$\mu_B = 5.788 \times 10^{-5} \text{ eV/T} = 9.274 \times 10^{-24} \text{ J/T or A} \cdot \text{m}^2$$

Note that the units J/T and $\text{A} \cdot \text{m}^2$ are equivalent. We defined this quantity previously in Section 28.8.

While the Bohr model suggests that the orbital motion of an atomic electron gives rise to a magnetic moment, this model does *not* give correct predictions about magnetic interactions. As an example, the Bohr model predicts that an electron in a hydrogen-atom ground state has an orbital magnetic moment of magnitude μ_B . But the Schrödinger picture tells us that such a ground-state electron is in an s state with zero angular momentum, so the orbital magnetic moment must be *zero*! To get the correct results, we must describe the states by using Schrödinger wave functions.

It turns out that in the Schrödinger formulation, electrons have the same ratio of μ to L (gyromagnetic ratio) as in the Bohr model—namely, $e/2m$. Suppose the magnetic field \vec{B} is directed along the $+z$ -axis. From Eq. (41.28) the interaction energy U of the atom's magnetic moment with the field is

$$U = -\mu_z B \quad (41.32)$$

where μ_z is the z -component of the vector $\vec{\mu}$.

Now we use Eq. (41.30) to find μ_z , recalling that e is the *magnitude* of the electron charge and that the actual charge is $-e$. Because the electron charge is negative, the orbital angular momentum and magnetic moment vectors are opposite. We find

$$\mu_z = -\frac{e}{2m} L_z \quad (41.33)$$

For the Schrödinger wave functions, $L_z = m_l \hbar$, with $m_l = 0, \pm 1, \pm 2, \dots, \pm l$, so Eq. (41.33) becomes

$$\mu_z = -\frac{e}{2m} L_z = -m_l \frac{e\hbar}{2m} \quad (41.34)$$

CAUTION Two uses of the symbol m Be careful not to confuse the electron mass m with the magnetic quantum number m_l .

Finally, we can express the interaction energy, Eq. (41.32), as

$$U = -\mu_z B = m_l \frac{e\hbar}{2m} B \quad (m_l = 0, \pm 1, \pm 2, \dots, \pm l)$$

(orbital magnetic interaction energy) (41.35)

In terms of the Bohr magneton $\mu_B = e\hbar/2m$, we can write Eq. (41.35) as

$$U = m_l \mu_B B \quad (\text{orbital magnetic interaction energy}) \quad (41.36)$$

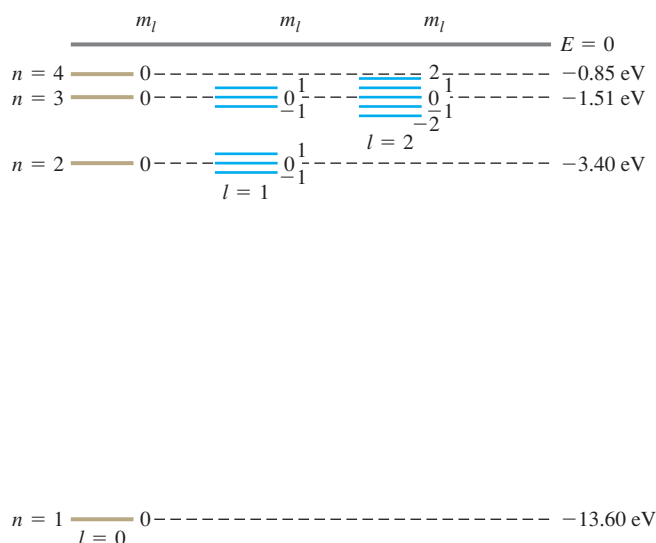
The magnetic field shifts the energy of each orbital state by an amount U . The interaction energy U depends on the value of m_l because m_l determines the

orientation of the orbital magnetic moment relative to the magnetic field. This dependence is the reason m_l is called the magnetic quantum number.

The values of m_l range from $-l$ to $+l$ in steps of one, so an energy level with a particular value of the orbital quantum number l contains $(2l + 1)$ different orbital states. Without a magnetic field these states all have the same energy; that is, they are degenerate. The magnetic field removes this degeneracy. In the presence of a magnetic field they are split into $2l + 1$ distinct energy levels; adjacent levels differ in energy by $(e\hbar/2m)B = \mu_B B$. We can understand this in terms of the connection between degeneracy and symmetry. With a magnetic field applied along the z -axis, the atom is no longer completely symmetric under rotation: There is a preferred direction in space. By removing the symmetry, we remove the degeneracy of states.

Figure 41.13 shows the effect on the energy levels of hydrogen. Spectral lines corresponding to transitions from one set of levels to another set are correspondingly split and appear as a series of three closely spaced spectral lines replacing a single line. As the following example shows, the splitting of spectral lines is quite small because the value of $\mu_B B$ is small even for substantial magnetic fields.

41.13 This energy-level diagram for hydrogen shows how the levels are split when the electron's orbital magnetic moment interacts with an external magnetic field. The values of m_l are shown adjacent to the various levels. The relative magnitudes of the level splittings are exaggerated for clarity. The $n = 4$ splittings are not shown; can you draw them in?



Example 41.5 An atom in a magnetic field

An atom in a state with $l = 1$ emits a photon with wavelength 600.000 nm as it decays to a state with $l = 0$. If the atom is placed in a magnetic field with magnitude $B = 2.00$ T, what are the shifts in the energy levels and in the wavelength that result from the interaction between the atom's orbital magnetic moment and the magnetic field?

SOLUTION

IDENTIFY and SET UP: This problem concerns the splitting of atomic energy levels by a magnetic field (the Zeeman effect). We use Eq. (41.35) or (41.36) to determine the energy-level shifts. The relationship $E = hc/\lambda$ between the energy and wavelength of a photon then lets us calculate the wavelengths emitted during transitions from the $l = 1$ states to the $l = 0$ state.

EXECUTE: The energy of a 600-nm photon is

$$E = \frac{hc}{\lambda} = \frac{(4.14 \times 10^{-15} \text{ eV} \cdot \text{s})(3.00 \times 10^8 \text{ m/s})}{600 \times 10^{-9} \text{ m}} = 2.07 \text{ eV}$$

If there is no external magnetic field, that is the difference in energy between the $l = 0$ and $l = 1$ levels.

With a 2.00-T field present, Eq. (41.36) shows that there is no shift of the $l = 0$ state (which has $m_l = 0$). For the $l = 1$ states, the splitting of levels is given by

$$U = m_l \mu_B B = m_l (5.788 \times 10^{-5} \text{ eV/T})(2.00 \text{ T}) \\ = m_l (1.16 \times 10^{-4} \text{ eV}) = m_l (1.85 \times 10^{-23} \text{ J})$$

The possible values of m_l for $l = 1$ are -1 , 0 , and $+1$, and the three corresponding levels are separated by equal intervals of

Continued

1.16×10^{-4} eV. This is a small fraction of the 2.07-eV photon energy:

$$\frac{\Delta E}{E} = \frac{1.16 \times 10^{-4} \text{ eV}}{2.07 \text{ eV}} = 5.60 \times 10^{-5}$$

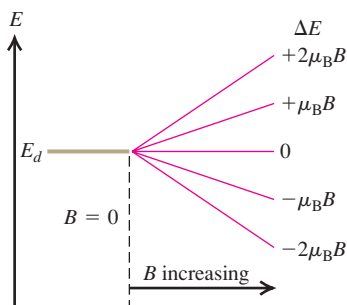
The possible values of m_l for $l = 1$ are $-1, 0$, and $+1$, and the three corresponding levels are separated by equal intervals of 1.16×10^{-4} eV. This is a small fraction of the 2.07-eV photon energy:

$$\frac{1.16 \times 10^{-4} \text{ eV}}{2.07 \text{ eV}} = 5.60 \times 10^{-5}$$

The corresponding wavelength shifts are approximately $(5.60 \times 10^{-5})(600 \text{ nm}) = 0.034 \text{ nm}$. The original 600.000-nm line is split into a triplet with wavelengths 599.966, 600.000, and 600.034 nm.

EVALUATE: Even though 2.00 T would be a strong field in most laboratories, the wavelength splittings are extremely small. Nonetheless, modern spectrographs have more than enough chromatic resolving power to measure these splittings (see Section 36.5).

41.14 This figure shows how the splitting of the energy levels of a d state ($l = 2$) depends on the magnitude B of an external magnetic field, assuming only an orbital magnetic moment.



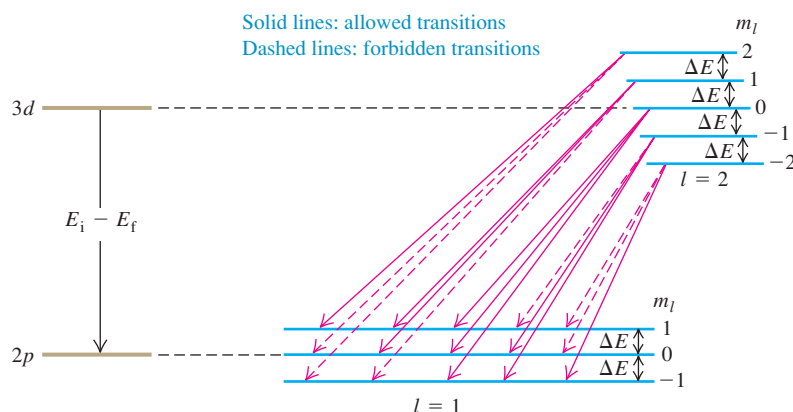
Selection Rules

Figure 41.14 shows what happens to a set of d states ($l = 2$) as the magnetic field increases. With zero field the five states $m_l = -2, -1, 0, 1$, and 2 are degenerate (have the same energy), but the applied field spreads the states out. Figure 41.15 shows the splittings of both the $3d$ and $2p$ states. Equal energy differences $(e\hbar/2m)B = \mu_B B$ separate adjacent levels. In the absence of a magnetic field, a transition from a $3d$ to a $2p$ state would yield a single spectral line with photon energy $E_i - E_f$. With the levels split as shown, it might seem that there are five possible photon energies.

In fact, there are only three possibilities. Not all combinations of initial and final levels are possible because of a restriction associated with conservation of angular momentum. The photon ordinarily carries off one unit (\hbar) of angular momentum, which leads to the requirements that in a transition l must change by 1 and m_l must change by 0 or ± 1 . These requirements are called **selection rules**. Transitions that obey these rules are called *allowed transitions*; those that don't are *forbidden transitions*. In Fig. 41.15 we show the allowed transitions by solid arrows. You should count the possible transition energies to convince yourself that the nine solid arrows give only three possible energies; the zero-field value $E_i - E_f$, and that value plus or minus $\Delta E = (e\hbar/2m)B = \mu_B B$. Figure 41.12 shows the corresponding spectral lines.

What we have described is called the *normal Zeeman effect*. It is based entirely on the orbital angular momentum of the electron. However, it leaves out a very important consideration: the electron *spin* angular momentum, the subject of the next section.

41.15 The cause of the normal Zeeman effect. The magnetic field splits the levels, but selection rules allow transitions with only three different photon energy changes, giving three different photon frequencies and wavelengths.



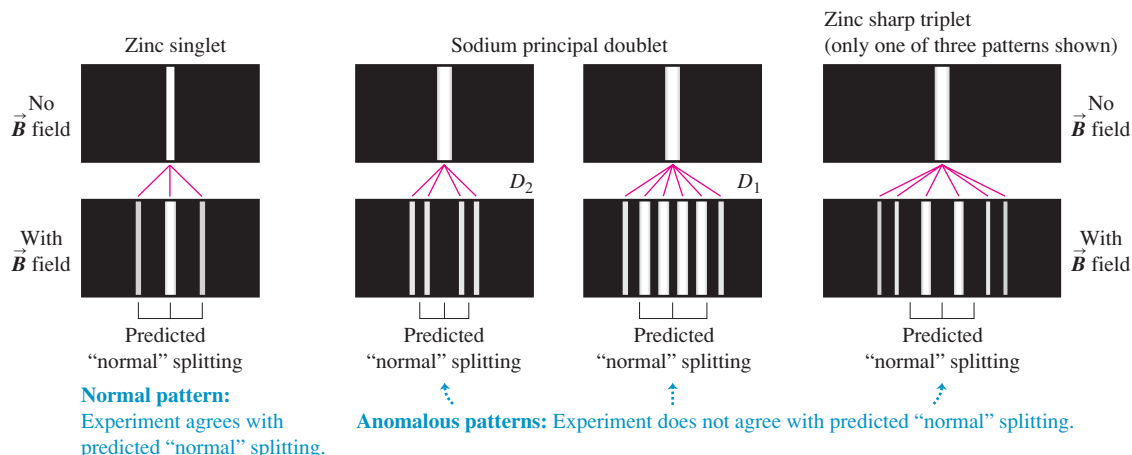
Test Your Understanding of Section 41.4 In this section we assumed that the magnetic field points in the positive z -direction. Would the results be different if the magnetic field pointed in the positive x -direction?

41.5 Electron Spin

Despite the success of the Schrödinger equation in predicting the energy levels of the hydrogen atom, experimental observations indicate that it doesn't tell the whole story of the behavior of electrons in atoms. First, spectroscopists have found magnetic-field splitting into other than the three lines we've explained, sometimes unequally spaced. Before this effect was understood, it was called the *anomalous* Zeeman effect to distinguish it from the “normal” effect discussed in the preceding section. Figure 41.16 shows both kinds of splittings.

Second, some energy levels show splittings that resemble the Zeeman effect even when there is *no* external magnetic field. For example, when the lines in the hydrogen spectrum are examined with a high-resolution spectrograph, some lines are found to consist of sets of closely spaced lines called *multiplets*. Similarly, the orange-yellow line of sodium, corresponding to the transition $4p \rightarrow 3s$ of the outer electron, is found to be a doublet ($\lambda = 589.0, 589.6 \text{ nm}$), suggesting that the $4p$ level might in fact be two closely spaced levels. The Schrödinger equation in its original form didn't predict any of this.

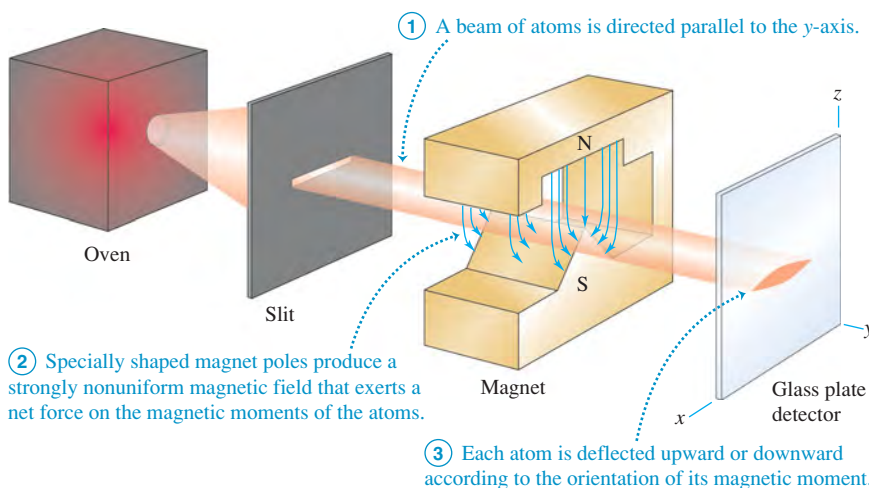
41.16 Illustrations of the normal and anomalous Zeeman effects for two elements, zinc and sodium. The brackets under each illustration show the “normal” splitting predicted by neglecting the effect of electron spin.



The Stern–Gerlach Experiment

Similar anomalies appeared in 1922 in atomic-beam experiments performed in Germany by Otto Stern and Walter Gerlach. When they passed a beam of neutral atoms through a nonuniform magnetic field (Fig. 41.17), atoms were deflected

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41.17 The Stern–Gerlach experiment.

according to the orientation of their magnetic moments with respect to the field. These experiments demonstrated the quantization of angular momentum in a very direct way. If there were only orbital angular momentum, the deflections would split the beam into an odd number $(2l + 1)$ of different components. However, some atomic beams were split into an *even* number of components. If we use a different symbol j for an angular momentum quantum number, setting $2j + 1$ equal to an even number gives $j = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$, suggesting a half-integer angular momentum. This can't be understood on the basis of the Bohr model and similar pictures of atomic structure.

In 1925 two graduate students in the Netherlands, Samuel Goudsmidt and George Uhlenbeck, proposed that the electron might have some additional motion. Using a semiclassical model, they suggested that the electron might behave like a spinning sphere of charge instead of a particle. If so, it would have an additional *spin* angular momentum and magnetic moment. If these were quantized in much the same way as *orbital* angular momentum and magnetic moment, they might help to explain the observed energy-level anomalies.

An Analogy for Electron Spin

To introduce the concept of **electron spin**, let's start with an analogy. The earth travels in a nearly circular orbit around the sun, and at the same time it *rotates* on its axis. Each motion has its associated angular momentum, which we call the *orbital* and *spin* angular momentum, respectively. The total angular momentum of the earth is the vector sum of the two. If we were to model the earth as a single point, it would have no moment of inertia about its spin axis and thus no spin angular momentum. But when our model includes the finite size of the earth, spin angular momentum becomes possible.

In the Bohr model, suppose the electron is not just a point charge but a small spinning sphere moving in orbit. Then the electron has not only orbital angular momentum but also spin angular momentum associated with the rotation of its mass about its axis. The sphere carries an electric charge, so the spinning motion leads to current loops and to a magnetic moment, as we discussed in Section 27.7. In a magnetic field, the *spin* magnetic moment has an interaction energy in addition to that of the *orbital* magnetic moment (the normal Zeeman-effect interaction that we discussed in Section 41.4). We should see additional Zeeman shifts due to the spin magnetic moment.

As we mentioned, such shifts *are* indeed observed in precise spectroscopic analysis. This and a variety of other experimental evidence have shown conclusively that the electron *does* have a spin angular momentum and a spin magnetic moment that do not depend on its orbital motion but are intrinsic to the electron itself. The origin of this spin angular momentum is fundamentally quantum-mechanical, so it's not correct to model the electron as a spinning charged sphere. But just as the Bohr model can be a useful conceptual picture for the motion of an electron in an atom, the spinning-sphere analogy can help you visualize the intrinsic spin angular momentum of an electron.

Spin Quantum Numbers

Like orbital angular momentum, the spin angular momentum of an electron (denoted by \vec{S}) is found to be quantized. Suppose we have an apparatus that measures a particular component of \vec{S} , say the z -component S_z . We find that the only possible values are

$$S_z = \pm \frac{1}{2} \hbar \text{ (components of spin angular momentum)} \quad (41.37)$$

This relationship is reminiscent of the expression $L_z = m_l \hbar$ for the z -component of orbital angular momentum, except that $|S_z|$ is *one-half* of \hbar instead of an

integer multiple. Equation (41.37) also suggests that the magnitude S of the spin angular momentum is given by an expression analogous to Eq. (41.22) with the orbital quantum number l replaced by the **spin quantum number** $s = \frac{1}{2}$:

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)}\hbar = \sqrt{\frac{3}{4}}\hbar \quad \text{(magnitude of spin angular momentum)} \quad (41.38)$$

The electron is often called a “spin $-\frac{1}{2}$ particle.”

To visualize the quantized spin of an electron in a hydrogen atom, think of the electron probability distribution function $|\psi|^2$ as a cloud surrounding the nucleus like those shown in Figs. 41.9 and 41.10. Then imagine many tiny spin arrows distributed throughout the cloud, either all with components in the $+z$ -direction or all with components in the $-z$ -direction. But don’t take this picture too seriously.

To label completely the state of the electron in a hydrogen atom, we now need a fourth quantum number m_s to specify the electron spin orientation. In analogy to the orbital magnetic quantum number m_l , we call m_s the **spin magnetic quantum number**. For an electron we give m_s the value $+\frac{1}{2}$ or $-\frac{1}{2}$ to agree with Eq. (41.37):

$$S_z = m_s \hbar \quad \left(m_s = \pm \frac{1}{2}\right) \quad \text{(allowed values of } m_s \text{ and } S_z \text{ for an electron)} \quad (41.39)$$

The spin angular momentum vector \vec{S} can have only two orientations in space relative to the z -axis: “*spin up*” with a z -component of $+\frac{1}{2}\hbar$ and “*spin down*” with a z -component of $-\frac{1}{2}\hbar$.

The z -component of the associated spin magnetic moment (μ_z) turns out to be related to S_z by

$$\mu_z = -(2.00232)\frac{e}{2m}S_z \quad (41.40)$$

where $-e$ and m are (as usual) the charge and mass of the electron. When the atom is placed in a magnetic field, the interaction energy $-\vec{\mu} \cdot \vec{B}$ of the spin magnetic dipole moment with the field causes further splittings in energy levels and in the corresponding spectral lines.

Equation (41.40) shows that the gyromagnetic ratio for electron spin is approximately *twice* as great as the value $e/2m$ for *orbital* angular momentum and magnetic dipole moment. This result has no classical analog. But in 1928 Paul Dirac developed a relativistic generalization of the Schrödinger equation for electrons. His equation gave a spin gyromagnetic ratio of exactly $2(e/2m)$. It took another two decades to develop the area of physics called *quantum electrodynamics*, abbreviated QED, which predicts the value we’ve given to “only” six significant figures as 2.00232. QED now predicts a value that agrees with a recent (2006) measurement of 2.00231930436170(152), making QED the most precise theory in all science.

Example 41.6 Energy of electron spin in a magnetic field

Calculate the interaction energy for an electron in an $l = 0$ state in a magnetic field with magnitude 2.00 T.

EXECUTE: Combining Eqs. (41.37) and (41.40), we have

$$\begin{aligned} \mu_z &= -(2.00232)\left(\frac{e}{2m}\right)\left(\pm \frac{1}{2}\hbar\right) \\ &= \mp \frac{1}{2}(2.00232)\left(\frac{e\hbar}{2m}\right) = \mp (1.00116)\mu_B \\ &= \mp (1.00116)(9.274 \times 10^{-24} \text{ J/T}) \\ &= \mp 9.285 \times 10^{-24} \text{ J/T} \\ &= \mp 5.795 \times 10^{-5} \text{ eV/T} \end{aligned}$$

SOLUTION

IDENTIFY and SET UP: For $l = 0$ the electron has zero orbital angular momentum and zero orbital magnetic moment. Hence the only magnetic interaction is that between the \vec{B} field and the spin magnetic moment $\vec{\mu}$. From Eq. (41.28), the interaction energy is $U = -\vec{\mu} \cdot \vec{B}$. As in Section 41.4, we take \vec{B} to be in the positive z -direction so that $U = -\mu_z B$ [Eq. (41.32)]. Equation (41.40) gives μ_z in terms of S_z , and Eq. (41.37) gives S_z .

Continued

Then from Eq. (41.32),

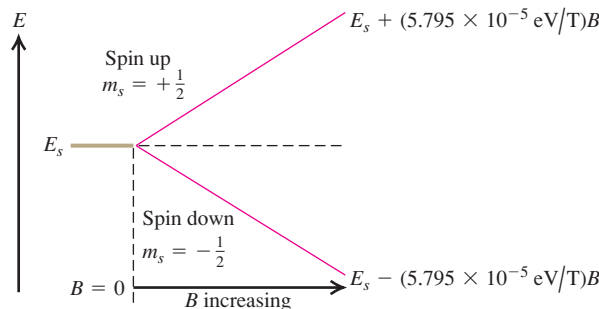
$$U = -\mu_z B = \pm (9.285 \times 10^{-24} \text{ J/T})(2.00 \text{ T}) \\ = \pm 1.86 \times 10^{-23} \text{ J} = \pm 1.16 \times 10^{-4} \text{ eV}$$

The positive value of U and the negative value of μ_z correspond to $S_z = +\frac{1}{2}\hbar$ (spin up); the negative value of U and the positive value of μ_z correspond to $S_z = -\frac{1}{2}\hbar$ (spin down).

EVALUATE: Let's check the *signs* of our results. If the electron is spin down, \vec{S} points generally opposite to \vec{B} . Then the magnetic moment $\vec{\mu}$ (which is opposite to \vec{S} because the electron charge is negative) points generally parallel to \vec{B} , and μ_z is positive. From Eq. (41.28), $U = -\vec{\mu} \cdot \vec{B}$, the interaction energy is negative if $\vec{\mu}$ and \vec{B} are parallel. Our results show that U is indeed negative in this case. We can similarly confirm that U must be positive and μ_z negative for a spin-up electron.

The red lines in Fig. 41.18 show how the interaction energies for the two spin states vary with the magnetic field magnitude B . The graphs are straight lines because, from Eq. (41.32), U is proportional to B .

41.18 An $l = 0$ level of a single electron is split by interaction of the spin magnetic moment with an external magnetic field. The greater the magnitude B of the magnetic field, the greater the splitting. The quantity $5.795 \times 10^{-5} \text{ eV/T}$ is just $(1.00116)\mu_B$.



Spin-Orbit Coupling

We mentioned earlier that the spin magnetic dipole moment also gives splitting of energy levels even when there is *no* external field. One cause involves the orbital motion of the electron. In the Bohr model, observers moving with the electron would see the positively charged nucleus revolving around them (just as to earthbound observers the sun seems to be orbiting the earth). This apparent motion of charge causes a magnetic field at the location of the electron, as measured in the electron's moving frame of reference. The resulting interaction with the spin magnetic moment causes a twofold splitting of this level, corresponding to the two possible orientations of electron spin.

Discussions based on the Bohr model can't be taken too seriously, but a similar result can be derived from the Schrödinger equation. The interaction energy U can be expressed in terms of the scalar product of the angular momentum vectors \vec{L} and \vec{S} . This effect is called **spin-orbit coupling**; it is responsible for the small energy difference between the two closely spaced, lowest excited levels of sodium shown in Fig. 39.19a and for the corresponding doublet (589.0, 589.6 nm) in the spectrum of sodium.

Example 41.7 An effective magnetic field

To six significant figures, the wavelengths of the two spectral lines that make up the sodium doublet are $\lambda_1 = 588.995 \text{ nm}$ and $\lambda_2 = 589.592 \text{ nm}$. Calculate the effective magnetic field experienced by the electron in the $3p$ levels of the sodium atom.

SOLUTION

IDENTIFY and SET UP: The two lines in the sodium doublet result from transitions from the two $3p$ levels, which are split by spin-orbit coupling, to the $3s$ level, which is *not* split because it has $L = 0$. We picture the spin-orbit coupling as an interaction between the electron spin magnetic moment and an effective magnetic field due to the nucleus. This example is like Example 41.6 in reverse: There we were given B and found the difference between the energies of the two spin states, while here we use the energy difference to find the target variable B . The difference in energy between the two $3p$ levels is equal to the difference in energy

between the two photons of the sodium doublet. We use this relationship and the results of Example 41.6 to determine B .

EXECUTE: The energies of the two photons are $E_1 = hc/\lambda_1$ and $E_2 = hc/\lambda_2$. Here $E_1 > E_2$ because $\lambda_1 < \lambda_2$, so the difference in their energies is

$$\Delta E = \frac{hc}{\lambda_1} - \frac{hc}{\lambda_2} = hc \left(\frac{\lambda_2 - \lambda_1}{\lambda_2 \lambda_1} \right) \\ = (4.136 \times 10^{-15} \text{ eV} \cdot \text{s})(2.998 \times 10^8 \text{ m/s}) \\ \times \frac{(589.592 \times 10^{-9} \text{ m}) - (588.995 \times 10^{-9} \text{ m})}{(589.592 \times 10^{-9} \text{ m})(588.995 \times 10^{-9} \text{ m})} \\ = 0.00213 \text{ eV} = 3.41 \times 10^{-22} \text{ J}$$

This equals the energy difference between the two $3p$ levels. The spin-orbit interaction raises one level by $1.70 \times 10^{-22} \text{ J}$ (one-half

of 3.41×10^{-22} J) and lowers the other by 1.70×10^{-22} J. From Example 41.6, the amount each state is raised or lowered is $|U| = (1.00116)\mu_B B$, so

$$B = \left| \frac{U}{(1.00116)\mu_B} \right| = \frac{1.70 \times 10^{-22} \text{ J}}{9.28 \times 10^{-24} \text{ J/T}} = 18.0 \text{ T}$$

EVALUATE: The electron experiences a *very* strong effective magnetic field. To produce a steady, macroscopic field of this magnitude in the laboratory requires state-of-the-art electromagnets.

Combining Orbital and Spin Angular Momenta

The orbital and spin angular momenta (\vec{L} and \vec{S} , respectively) can combine in various ways. The vector sum of \vec{L} and \vec{S} is the *total* angular momentum \vec{J} :

$$\vec{J} = \vec{L} + \vec{S} \quad (41.41)$$

The possible values of the magnitude J are given in terms of a quantum number j by

$$J = \sqrt{j(j+1)}\hbar \quad (41.42)$$

We can then have states in which $j = |l \pm \frac{1}{2}|$. The $l + \frac{1}{2}$ states correspond to the case in which the vectors \vec{L} and \vec{S} have parallel z -components; for the $l - \frac{1}{2}$ states, \vec{L} and \vec{S} have antiparallel z -components. For example, when $l = 1$, j can be $\frac{1}{2}$ or $\frac{3}{2}$. In another spectroscopic notation these p states are labeled $^2P_{1/2}$ and $^2P_{3/2}$, respectively. The superscript is the number of possible spin orientations, the letter P (now capitalized) indicates states with $l = 1$, and the subscript is the value of j . We used this scheme to label the energy levels of the sodium atom in Fig. 39.19a.

The various line splittings resulting from magnetic interactions are collectively called *fine structure*. There are also additional, much smaller splittings associated with the fact that the *nucleus* of the atom has a magnetic dipole moment that interacts with the orbital and/or spin magnetic dipole moments of the electrons. These effects are called *hyperfine structure*. For example, the ground level of hydrogen is split into two states, separated by only 5.9×10^{-6} eV. The photon that is emitted in the transitions between these states has a wavelength of 21 cm. Radio astronomers use this wavelength to map clouds of interstellar hydrogen gas that are too cold to emit visible light (Fig. 41.19).

Test Your Understanding of Section 41.5 In which of the following situations is the magnetic moment of an electron perfectly aligned with a magnetic field that points in the positive z -direction? (i) $m_s = +\frac{1}{2}$; (ii) $m_s = -\frac{1}{2}$; (iii) both (i) and (ii); (iv) neither (i) nor (ii).



41.6 Many-Electron Atoms and the Exclusion Principle

So far our analysis of atomic structure has concentrated on the hydrogen atom. That's natural; neutral hydrogen, with only one electron, is the simplest atom. If we can't understand hydrogen, we certainly can't understand anything more complex. But now let's move on to many-electron atoms.

In general, an atom in its normal (electrically neutral) state has Z electrons and Z protons. Recall from Section 41.3 that we call Z the *atomic number*. The total electric charge of such an atom is exactly zero because the neutron has no charge while the proton and electron charges have the same magnitude but opposite sign.

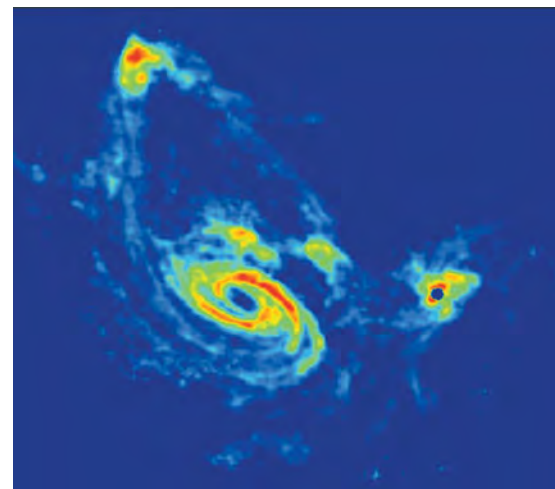
We can apply the Schrödinger equation to this general atom. However, the complexity of the analysis increases very rapidly with increasing Z . Each of the Z electrons interacts not only with the nucleus but also with every other electron.

41.19 In a visible-light image (top), these three distant galaxies appear to be unrelated. But in fact these galaxies are connected by immense streamers of hydrogen gas. This is revealed by the false-color image (bottom) made with a radio telescope tuned to the 21-cm wavelength emitted by hydrogen atoms.

Galaxies in visible light (negative image; galaxies appear dark)



Radio image at wavelength 21 cm



The wave functions and the potential energy are functions of $3Z$ coordinates, and the equation contains second derivatives with respect to all of them. The mathematical problem of finding solutions of such equations is so complex that it has not been solved exactly even for the neutral helium atom, which has only two electrons.

Fortunately, various approximation schemes are available. The simplest approximation is to ignore all interactions between electrons and consider each electron as moving under the action only of the nucleus (considered to be a point charge). In this approximation the wave function for each individual electron is a function like that for the hydrogen atom, specified by four quantum numbers (n, l, m_l, m_s) . The nuclear charge is Ze instead of e , so we replace every factor of e^2 in the wave functions and the energy levels by Ze^2 . In particular, the energy levels are given by Eq. (41.21) with e^4 replaced by Z^2e^4 :

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m_r Z^2 e^4}{2n^2 \hbar^2} = -\frac{Z^2}{n^2} (13.6 \text{ eV}) \quad (41.43)$$

This approximation is fairly drastic; when there are many electrons, their interactions with each other are as important as the interaction of each with the nucleus. So this model isn't very useful for quantitative predictions.

The Central-Field Approximation

A less drastic and more useful approximation is to think of all the electrons together as making up a charge cloud that is, on average, *spherically symmetric*. We can then think of each individual electron as moving in the total electric field due to the nucleus and this averaged-out cloud of all the other electrons. There is a corresponding spherically symmetric potential-energy function $U(r)$. This picture is called the **central-field approximation**; it provides a useful starting point for understanding atomic structure.

In the central-field approximation we can again deal with one-electron wave functions. The Schrödinger equation differs from the equation for hydrogen only in that the $1/r$ potential-energy function is replaced by a different function $U(r)$. But it turns out that $U(r)$ does not enter the differential equations for $\Theta(\theta)$ and $\Phi(\phi)$, so those angular functions are exactly the same as for hydrogen, and the orbital angular-momentum *states* are also the same as before. The quantum numbers l , m_l , and m_s have the same meanings as before, and Eqs. (41.22) and (41.23) again give the magnitude and z -component of the orbital angular momentum.

The radial wave functions and probabilities are different than for hydrogen because of the change in $U(r)$, so the energy levels are no longer given by Eq. (41.21). We can still label a state using the four quantum numbers (n, l, m_l, m_s) . In general, the energy of a state now depends on both n and l , rather than just on n as with hydrogen. The restrictions on values of the quantum numbers are the same as before:

$$n \geq 1 \quad 0 \leq l \leq n - 1 \quad |m_l| \leq l \quad m_s = \pm \frac{1}{2} \quad \begin{array}{l} \text{(allowed values of} \\ \text{quantum numbers)} \end{array} \quad (41.44)$$

The Exclusion Principle

To understand the structure of many-electron atoms, we need an additional principle, the *exclusion principle*. To see why this principle is needed, let's consider the lowest-energy state, or *ground state*, of a many-electron atom. In the one-electron states of the central-field model, there is a lowest-energy state (corresponding to an $n = 1$ state of hydrogen). We might expect that in the ground state of a complex atom, *all* the electrons should be in this lowest state. If so, then we should see only gradual changes in physical and chemical properties when we look at the behavior of atoms with increasing numbers of electrons (Z).

Such gradual changes are *not* what is observed. Instead, properties of elements vary widely from one to the next, with each element having its own distinct personality. For example, the elements fluorine, neon, and sodium have 9, 10, and 11 electrons, respectively, per atom. Fluorine ($Z = 9$) is a *halogen*; it tends strongly to form compounds in which each fluorine atom acquires an extra electron. Sodium ($Z = 11$) is an *alkali metal*; it forms compounds in which each sodium atom *loses* an electron. Neon ($Z = 10$) is a *noble gas*, forming no compounds at all. Such observations show that in the ground state of a complex atom the electrons *cannot* all be in the lowest-energy states. But why not?

The key to this puzzle, discovered by the Austrian physicist Wolfgang Pauli (Fig. 41.20) in 1925, is called the **exclusion principle**. This principle states that **no two electrons can occupy the same quantum-mechanical state** in a given system. That is, **no two electrons in an atom can have the same values of all four quantum numbers (n, l, m_l, m_s)**. Each quantum state corresponds to a certain distribution of the electron “cloud” in space. Therefore the principle also says, in effect, that no more than two electrons with opposite values of the quantum number m_s can occupy the same region of space. We shouldn’t take this last statement too seriously because the electron probability functions don’t have sharp, definite boundaries. But the exclusion principle limits the amount by which electron wave functions can overlap. Think of it as the quantum-mechanical analog of a university rule that allows only one student per desk.

CAUTION **The meaning of the exclusion principle** Don’t confuse the exclusion principle with the electric repulsion between electrons. While both effects tend to keep electrons within an atom separated from each other, they are very different in character. Two electrons can always be pushed closer together by adding energy to combat electric repulsion; in contrast, *nothing* can overcome the exclusion principle and force two electrons into the same quantum-mechanical state. ■

Table 41.2 lists some of the sets of quantum numbers for electron states in an atom. It’s similar to Table 41.1 (Section 41.3), but we’ve added the number of states in each subshell and shell. Because of the exclusion principle, the “number of states” is the same as the *maximum* number of electrons that can be found in those states. For each state, m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$.

As with the hydrogen wave functions, different states correspond to different spatial distributions; electrons with larger values of n are concentrated at larger distances from the nucleus. Figure 41.8 (Section 41.3) shows this effect. When an atom has more than two electrons, they can’t all huddle down in the low-energy $n = 1$ states nearest to the nucleus because there are only two of these states; the exclusion principle forbids multiple occupancy of a state. Some electrons are forced into states farther away, with higher energies. Each value of n corresponds roughly to a region of space around the nucleus in the form of a spherical *shell*. Hence we speak of the *K* shell as the region that is occupied by the electrons in the $n = 1$ states, the *L* shell as the region of the $n = 2$ states, and so on. States with the same n but different l form *subshells*, such as the $3p$ subshell.

Table 41.2 Quantum States of Electrons in the First Four Shells

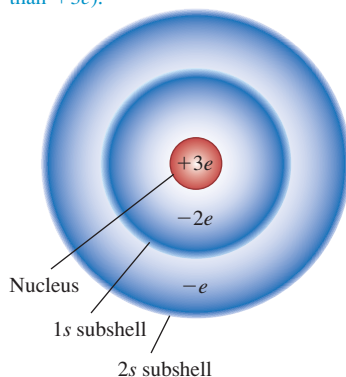
n	l	m_l	Spectroscopic Notation	Number of States	Shell
1	0	0	1s	2	K
2	0	0	2s	2	
2	1	-1, 0, 1	2p	6	L
3	0	0	3s	2	
3	1	-1, 0, 1	3p	6	M
3	2	-2, -1, 0, 1, 2	3d	10	
4	0	0	4s	2	N
4	1	-1, 0, 1	4p	6	
4	2	-2, -1, 0, 1, 2	4d	10	
4	3	-3, -2, -1, 0, 1, 2, 3	4f	14	

41.20 The key to understanding the periodic table of the elements was the discovery by Wolfgang Pauli (1900–1958) of the exclusion principle. Pauli received the 1945 Nobel Prize in physics for his accomplishment. This photo shows Pauli (on the left) and Niels Bohr watching the physics of a toy top spinning on the floor—a macroscopic analog of a microscopic electron with spin.



41.21 Schematic representation of the charge distribution in a lithium atom. The nucleus has a charge of $+3e$.

On average, the $2s$ electron is considerably farther from the nucleus than the $1s$ electrons. Therefore, it experiences a net nuclear charge of approximately $+3e - 2e = +e$ (rather than $+3e$).



41.22 Salt (sodium chloride, NaCl) dissolves readily in water, making seawater salty. This is due to the electron configurations of sodium and chlorine: Sodium can easily lose an electron to form an Na^+ ion, and chlorine can easily gain an electron to form a Cl^- ion. These ions are held in solution because they are attracted to the polar ends of water molecules (see Fig. 21.30a).



The Periodic Table

We can use the exclusion principle to derive the most important features of the structure and chemical behavior of multielectron atoms, including the periodic table of the elements. Let's imagine constructing a neutral atom by starting with a bare nucleus with Z protons and then adding Z electrons, one by one. To obtain the ground state of the atom as a whole, we fill the lowest-energy electron states (those closest to the nucleus, with the smallest values of n and l) first, and we use successively higher states until all the electrons are in place. The chemical properties of an atom are determined principally by interactions involving the outermost, or *valence*, electrons, so we particularly want to learn how these electrons are arranged.

Let's look at the ground-state electron configurations for the first few atoms (in order of increasing Z). For hydrogen the ground state is $1s$; the single electron is in a state $n = 1$, $l = 0$, $m_l = 0$, and $m_s = \pm \frac{1}{2}$. In the helium atom ($Z = 2$), both electrons are in $1s$ states, with opposite spins; one has $m_s = -\frac{1}{2}$ and the other has $m_s = +\frac{1}{2}$. We denote the helium ground state as $1s^2$. (The superscript 2 is not an exponent; the notation $1s^2$ tells us that there are two electrons in the $1s$ subshell. Also, the superscript 1 is understood, as in $2s$.) For helium the K shell is completely filled, and all others are empty. Helium is a noble gas; it has no tendency to gain or lose an electron, and it forms no compounds.

Lithium ($Z = 3$) has three electrons. In its ground state, two are in $1s$ states and one is in a $2s$ state, so we denote the lithium ground state as $1s^2 2s$. On average, the $2s$ electron is considerably farther from the nucleus than are the $1s$ electrons (Fig. 41.21). According to Gauss's law, the *net* charge Q_{encl} attracting the $2s$ electron is nearer to $+e$ than to the value $+3e$ it would have without the two $1s$ electrons present. As a result, the $2s$ electron is loosely bound; only 5.4 eV is required to remove it, compared with the 30.6 eV given by Eq. (41.43) with $Z = 3$ and $n = 2$. In chemical behavior, lithium is an *alkali metal*. It forms ionic compounds in which each lithium atom loses an electron and has a valence of $+1$.

Next is beryllium ($Z = 4$); its ground-state configuration is $1s^2 2s^2$, with its two valence electrons filling the s subshell of the L shell. Beryllium is the first of the *alkaline earth* elements, forming ionic compounds in which the valence of the atoms is $+2$.

Table 41.3 shows the ground-state electron configurations of the first 30 elements. The L shell can hold eight electrons. At $Z = 10$, both the K and L shells are filled, and there are no electrons in the M shell. We expect this to be a particularly stable configuration, with little tendency to gain or lose electrons. This element is neon, a noble gas with no known compounds. The next element after neon is sodium ($Z = 11$), with filled K and L shells and one electron in the M shell. Its "noble-gas-plus-one-electron" structure resembles that of lithium; both are alkali metals. The element *before* neon is fluorine, with $Z = 9$. It has a vacancy in the L shell and has an affinity for an extra electron to fill the shell. Fluorine forms ionic compounds in which it has a valence of -1 . This behavior is characteristic of the *halogens* (fluorine, chlorine, bromine, iodine, and astatine), all of which have "noble-gas-minus-one" configurations (Fig. 41.22).

Proceeding down the list, we can understand the regularities in chemical behavior displayed by the **periodic table of the elements** (Appendix D) on the basis of electron configurations. The similarity of elements in each *group* (vertical column) of the periodic table is the result of similarity in outer-electron configuration. All the noble gases (helium, neon, argon, krypton, xenon, and radon) have filled-shell or filled-shell plus filled p subshell configurations. All the alkali metals (lithium, sodium, potassium, rubidium, cesium, and francium) have "noble-gas-plus-one" configurations. All the alkaline earth metals (beryllium, magnesium, calcium, strontium, barium, and radium) have "noble-gas-plus-two" configurations, and, as we just mentioned, all the halogens (fluorine, chlorine, bromine, iodine, and astatine) have "noble-gas-minus-one" structures.

Table 41.3 Ground-State Electron Configurations

Element	Symbol	Atomic Number (Z)	Electron Configuration
Hydrogen	H	1	$1s$
Helium	He	2	$1s^2$
Lithium	Li	3	$1s^2 2s$
Beryllium	Be	4	$1s^2 2s^2$
Boron	B	5	$1s^2 2s^2 2p$
Carbon	C	6	$1s^2 2s^2 2p^2$
Nitrogen	N	7	$1s^2 2s^2 2p^3$
Oxygen	O	8	$1s^2 2s^2 2p^4$
Fluorine	F	9	$1s^2 2s^2 2p^5$
Neon	Ne	10	$1s^2 2s^2 2p^6$
Sodium	Na	11	$1s^2 2s^2 2p^6 3s$
Magnesium	Mg	12	$1s^2 2s^2 2p^6 3s^2$
Aluminum	Al	13	$1s^2 2s^2 2p^6 3s^2 3p$
Silicon	Si	14	$1s^2 2s^2 2p^6 3s^2 3p^2$
Phosphorus	P	15	$1s^2 2s^2 2p^6 3s^2 3p^3$
Sulfur	S	16	$1s^2 2s^2 2p^6 3s^2 3p^4$
Chlorine	Cl	17	$1s^2 2s^2 2p^6 3s^2 3p^5$
Argon	Ar	18	$1s^2 2s^2 2p^6 3s^2 3p^6$
Potassium	K	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s$
Calcium	Ca	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$
Scandium	Sc	21	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d$
Titanium	Ti	22	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$
Vanadium	V	23	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
Chromium	Cr	24	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Manganese	Mn	25	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$
Iron	Fe	26	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
Cobalt	Co	27	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
Nickel	Ni	28	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$
Copper	Cu	29	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$
Zinc	Zn	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

A slight complication occurs with the M and N shells because the $3d$ and $4s$ subshell levels ($n = 3, l = 2$, and $n = 4, l = 0$, respectively) have similar energies. (We'll discuss in the next subsection why this happens.) Argon ($Z = 18$) has all the $1s, 2s, 2p, 3s$, and $3p$ subshells filled, but in potassium ($Z = 19$) the additional electron goes into a $4s$ energy state rather than a $3d$ state (because the $4s$ state has slightly lower energy).

The next several elements have one or two electrons in the $4s$ subshell and increasing numbers in the $3d$ subshell. These elements are all metals with rather similar chemical and physical properties; they form the first *transition series*, starting with scandium ($Z = 21$) and ending with zinc ($Z = 30$), for which all the $3d$ and $4s$ subshells are filled.

Something similar happens with $Z = 57$ through $Z = 71$, which have one or two electrons in the $6s$ subshell but only partially filled $4f$ and $5d$ subshells. These are the *rare earth* elements; they all have very similar physical and chemical properties. Yet another such series, called the *actinide* series, starts with $Z = 91$.

Screening

We have mentioned that in the central-field picture, the energy levels depend on l as well as n . Let's take sodium ($Z = 11$) as an example. If 10 of its electrons fill its K and L shells, the energies of some of the states for the remaining electron are found experimentally to be

- $3s$ states: -5.138 eV
- $3p$ states: -3.035 eV
- $3d$ states: -1.521 eV
- $4s$ states: -1.947 eV

Application Electron Configurations and Bone Cancer Radiotherapy

The orange spots in this colored x-ray image are bone cancer tumors. One method of treating bone cancer is to inject a radioactive isotope of strontium (^{89}Sr) into a patient's vein. Strontium is chemically similar to calcium because in both atoms the two outer electrons are in an s state (the structures are $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$ for strontium and $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$ for calcium). Hence the strontium is readily taken up by the tumors, where calcium turnover is more rapid than in healthy bone. Radiation from the strontium helps to destroy the tumors.



The $3s$ states are the lowest (most negative); one is the ground state for the 11th electron in sodium. The energy of the $3d$ states is quite close to the energy of the $n = 3$ state in hydrogen. The surprise is that the $4s$ state energy is 0.426 eV *below* the $3d$ state, even though the $4s$ state has larger n .

We can understand these results using Gauss's law and the radial probability distribution. For any spherically symmetric charge distribution, the electric-field magnitude at a distance r from the center is $Q_{\text{encl}}/4\pi\epsilon_0 r^2$, where Q_{encl} is the total charge enclosed within a sphere with radius r . Mentally remove the outer (valence) electron atom from a sodium atom. What you have left is a spherically symmetric collection of 10 electrons (filling the K and L shells) and 11 protons, so $Q_{\text{encl}} = -10e + 11e = +e$. If the 11th electron is completely outside this collection of charges, it is attracted by an effective charge of $+e$, not $+11e$. This is a more extreme example of the effect depicted in Fig. 41.21.

This effect is called **screening**; the 10 electrons *screen* 10 of the 11 protons, leaving an effective net charge of $+e$. In general, an electron that spends all its time completely outside a positive charge $Z_{\text{eff}}e$ has energy levels given by the hydrogen expression with e^2 replaced by $Z_{\text{eff}}e^2$. From Eq. (41.43) this is

$$E_n = -\frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV}) \quad (\text{energy levels with screening}) \quad (41.45)$$

If the 11th electron in the sodium atom is completely outside the remaining charge distribution, then $Z_{\text{eff}} = 1$.

CAUTION Different equations for different atoms Equations (41.21), (41.43), and (41.45) all give values of E_n in terms of $(13.6 \text{ eV})/n^2$, but they don't apply in general to the same atoms. Equation (41.21) is *only* for hydrogen. Equation (41.43) is only for the case in which there is no interaction with any other electron (and is thus accurate only when the atom has just one electron). Equation (41.45) is useful when one electron is screened from the nucleus by other electrons. ■

Now let's use the radial probability functions shown in Fig. 41.8 to explain why the energy of a sodium $3d$ state is approximately the same as the $n = 3$ value of hydrogen, -1.51 eV . The distribution for the $3d$ state (for which l has the maximum value $n - 1$) has one peak, and its most probable radius is *outside* the positions of the electrons with $n = 1$ or 2 . (Those electrons also are pulled closer to the nucleus than in hydrogen because they are less effectively screened from the positive charge $11e$ of the nucleus.) Thus in sodium a $3d$ electron spends most of its time well outside the $n = 1$ and $n = 2$ states (the K and L shells). The 10 electrons in these shells screen about ten-elevenths of the charge of the 11 protons, leaving a net charge of about $Z_{\text{eff}}e = (1)e$. Then, from Eq. (41.45), the corresponding energy is approximately $-(1)^2(13.6 \text{ eV})/3^2 = -1.51 \text{ eV}$. This approximation is very close to the experimental value of -1.521 eV .

Looking again at Fig. 41.8, we see that the radial probability density for the $3p$ state (for which $l = n - 2$) has two peaks and that for the $3s$ state ($l = n - 3$) has three peaks. For sodium the first small peak in the $3p$ distribution gives a $3p$ electron a higher probability (compared to the $3d$ state) of being *inside* the charge distributions for the electrons in the $n = 2$ states. That is, a $3p$ electron is less completely screened from the nucleus than is a $3d$ electron because it spends some of its time within the filled K and L shells. Thus for the $3p$ electrons, Z_{eff} is greater than unity. From Eq. (41.45) the $3p$ energy is lower (more negative) than the $3d$ energy of -1.521 eV . The actual value is -3.035 eV . A $3s$ electron spends even more time within the inner electron shells than a $3p$ electron does, giving an even larger Z_{eff} and an even more negative energy.

Example 41.8 Determining Z_{eff} experimentally

The measured energy of a $3s$ state of sodium is -5.138 eV. Calculate the value of Z_{eff} .

SOLUTION

IDENTIFY and SET UP: Sodium has a single electron in the M shell outside filled K and L shells. The ten K and L electrons partially screen the single M electron from the $+11e$ charge of the nucleus; our goal is to determine the extent of this screening. We are given $n = 3$ and $E_n = -5.138$ eV, so we can use Eq. (41.45) to determine Z_{eff} .

EXECUTE: Solving Eq. (41.45) for Z_{eff} , we have

$$Z_{\text{eff}}^2 = -\frac{n^2 E_n}{13.6 \text{ eV}} = -\frac{3^2(-5.138 \text{ eV})}{13.6 \text{ eV}} = 3.40$$

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

EVALUATE: The effective charge attracting a $3s$ electron is $1.84e$. Sodium's 11 protons are screened by an average of $11 - 1.84 = 9.16$ electrons instead of 10 electrons because the $3s$ electron spends some time within the inner (K and L) shells.

Each alkali metal (lithium, sodium, potassium, rubidium, and cesium) has one more electron than the corresponding noble gas (helium, neon, argon, krypton, and xenon). This extra electron is mostly outside the other electrons in the filled shells and subshells. Therefore all the alkali metals behave similarly to sodium.

Example 41.9 Energies for a valence electron

The valence electron in potassium has a $4s$ ground state. Calculate the approximate energy of the $n = 4$ state having the smallest Z_{eff} , and discuss the relative energies of the $4s$, $4p$, $4d$, and $4f$ states.

SOLUTION

IDENTIFY and SET UP: The state with the smallest Z_{eff} is the one in which the valence electron spends the most time outside the inner filled shells and subshells, so that it is most effectively screened from the charge of the nucleus. Once we have determined which state has the smallest Z_{eff} , we can use Eq. (41.45) to determine the energy of this state.

EXECUTE: A $4f$ state has $n = 4$ and $l = 3 = 4 - 1$. Thus it is the state of greatest orbital angular momentum for $n = 4$, and thus the state in which the electron spends the most time outside the electron charge clouds of the inner filled shells and subshells. This makes Z_{eff} for a $4f$ state close to unity. Equation (41.45) then gives

$$E_4 = -\frac{Z_{\text{eff}}^2}{n^2}(13.6 \text{ eV}) = -\frac{1}{4^2}(13.6 \text{ eV}) = -0.85 \text{ eV}$$

This approximation agrees with the measured energy of the sodium $4f$ state to the precision given.

An electron in a $4d$ state spends a bit more time within the inner shells, and its energy is therefore a bit more negative (measured to be -0.94 eV). For the same reason, a $4p$ state has an even lower energy (measured to be -2.73 eV) and a $4s$ state has the lowest energy (measured to be -4.339 eV).

EVALUATE: We can extend this analysis to the *singly ionized alkali line earth elements*: Be^+ , Mg^+ , Ca^+ , Sr^+ , and Ba^+ . For any allowed value of n , the highest- l state ($l = n - 1$) of the one remaining outer electron sees an effective charge of almost $+2e$, so for these states, $Z_{\text{eff}} = 2$. A $3d$ state for Mg^+ , for example, has an energy of about $-2^2(13.6 \text{ eV})/3^2 = -6.0$ eV.

Test Your Understanding of Section 41.6 If electrons did *not* obey the exclusion principle, would it be easier or more difficult to remove the first electron from sodium?

41.7 X-Ray Spectra

X-ray spectra provide yet another example of the richness and power of the Schrödinger equation and of the model of atomic structure that we derived from it in the preceding section. In Section 38.2 we discussed x-ray production on the basis of the photon concept. With the development of x-ray diffraction techniques (see Section 36.6) by von Laue, Bragg, and others, beginning in 1912, it became possible to measure x-ray wavelengths quite precisely (to within 0.1% or less).

Detailed studies of x-ray spectra showed a continuous spectrum of wavelengths (see Fig. 38.8 in Section 38.2), with minimum wavelength (corresponding to maximum frequency and photon energy) determined by the accelerating

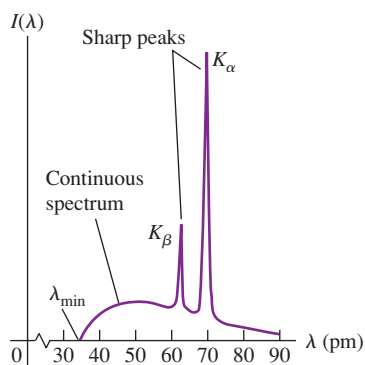
voltage V_{AC} in the x-ray tube, according to the relationship derived in Section 38.2 for *bremsstrahlung* processes:

$$\lambda_{\min} = \frac{hc}{eV_{AC}} \quad (41.46)$$

This continuous-spectrum radiation is nearly independent of the target material in the x-ray tube.

Moseley's Law and Atomic Energy Levels

41.23 Graph of intensity per unit wavelength as a function of wavelength for x rays produced with an accelerating voltage of 35 kV and a molybdenum target. The curve is a smooth function similar to the bremsstrahlung spectra in Fig. 38.8 (Section 38.2), but with two sharp spikes corresponding to part of the characteristic x-ray spectrum for molybdenum.



Depending on the accelerating voltage and the target element, we may find sharp peaks superimposed on this continuous spectrum, as in Fig. 41.23. These peaks are at different wavelengths for different elements; they form what is called a *characteristic x-ray spectrum* for each target element. In 1913 the British scientist Henry G. J. Moseley studied these spectra in detail using x-ray diffraction techniques. He found that the most intense short-wavelength line in the characteristic x-ray spectrum from a particular target element, called the K_α line, varied smoothly with that element's atomic number Z (Fig. 41.24). This is in sharp contrast to optical spectra, in which elements with adjacent Z -values have spectra that often bear no resemblance to each other.

Moseley found that the relationship could be expressed in terms of x-ray frequencies f by a simple formula called *Moseley's law*:

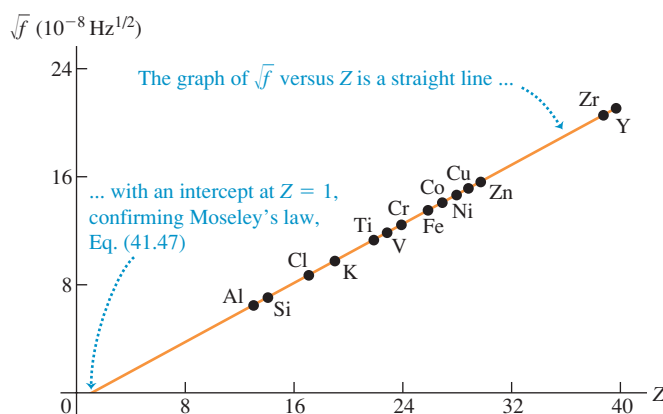
$$f = (2.48 \times 10^{15} \text{ Hz})(Z - 1)^2 \quad (\text{Moseley's law}) \quad (41.47)$$

Moseley went far beyond this empirical relationship; he showed how characteristic x-ray spectra could be understood on the basis of energy levels of atoms in the target. His analysis was based on the Bohr model, published in the same year. We will recast it somewhat, using the ideas of atomic structure that we discussed in Section 41.6. First recall that the *outer* electrons of an atom are responsible for optical spectra. Their excited states are usually only a few electron volts above their ground state. In transitions from excited states to the ground state, they usually emit photons in or near the visible region.

Characteristic x rays, by contrast, are emitted in transitions involving the *inner* shells of a complex atom. In an x-ray tube the electrons may strike the target with enough energy to knock electrons out of the inner shells of the target atoms. These inner electrons are much closer to the nucleus than are the electrons in the outer shells; they are much more tightly bound, and hundreds or thousands of electron volts may be required to remove them.

Suppose one electron is knocked out of the K shell. This process leaves a vacancy, which we'll call a *hole*. (One electron remains in the K shell.) The hole can then be filled by an electron falling in from one of the outer shells, such as the L , M , N , ... shell. This transition is accompanied by a decrease in the energy of the

41.24 The square root of Moseley's measured frequencies of the K_α line for 14 elements.



atom (because *less* energy would be needed to remove an electron from an L , M , N , ... shell), and an x-ray photon is emitted with energy equal to this decrease. Each state has definite energy, so the emitted x rays have definite wavelengths; the emitted spectrum is a *line* spectrum.

We can estimate the energy and frequency of K_α x-ray photons using the concept of screening from Section 41.6. A K_α x-ray photon is emitted when an electron in the L shell ($n = 2$) drops down to fill a hole in the K shell ($n = 1$). As the electron drops down, it is attracted by the Z protons in the nucleus screened by the one remaining electron in the K shell. We therefore approximate the energy by Eq. (41.45), with $Z_{\text{eff}} = Z - 1$, $n_i = 2$, and n_f . The energy before the transition is

$$E_i \approx -\frac{(Z-1)^2}{2^2}(13.6 \text{ eV}) = -(Z-1)^2(3.4 \text{ eV})$$

and the energy after the transition is

$$E_f \approx -\frac{(Z-1)^2}{1^2}(13.6 \text{ eV}) = -(Z-1)^2(13.6 \text{ eV})$$

The energy of the K_α x-ray photon is $E_{K\alpha} = E_i - E_f \approx (Z-1)^2(-3.4 \text{ eV} + 13.6 \text{ eV})$. That is,

$$E_{K\alpha} \approx (Z-1)^2(10.2 \text{ eV}) \quad (41.48)$$

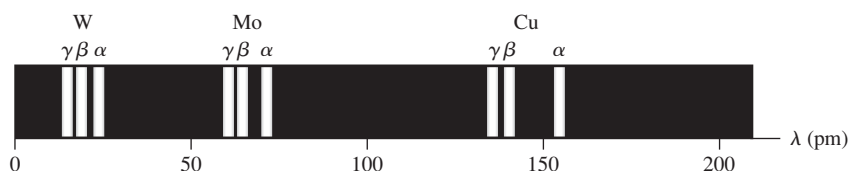
The frequency of the photon is its energy divided by Planck's constant:

$$f = \frac{E}{h} \approx \frac{(Z-1)^2(10.2 \text{ eV})}{4.136 \times 10^{-15} \text{ eV} \cdot \text{s}} = (2.47 \times 10^{15} \text{ Hz})(Z-1)^2$$

This relationship agrees almost exactly with Moseley's experimental law, Eq. (41.47). Indeed, considering the approximations we have made, the agreement is better than we have a right to expect. But our calculation does show how Moseley's law can be understood on the bases of screening and transitions between energy levels.

The hole in the K shell may also be filled by an electron falling from the M or N shell, assuming that these are occupied. If so, the x-ray spectrum of a large group of atoms of a single element shows a series, named the K series, of three lines, called the K_α , K_β , and K_γ lines. These three lines result from transitions in which the K -shell hole is filled by an L , M , or N electron, respectively. Figure 41.25 shows the K series for tungsten ($Z = 74$), molybdenum ($Z = 42$), and copper ($Z = 29$).

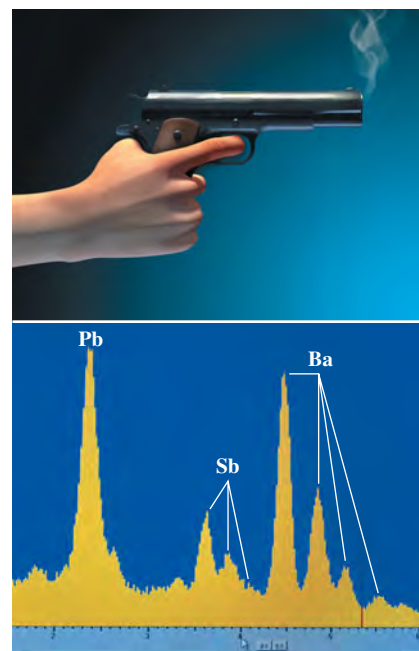
There are other series of x-ray lines, called the L , M , and N series, that are produced after the ejection of electrons from the L , M , and N shells rather than the K shell. Electrons in these outer shells are farther away from the nucleus and are not held as tightly as are those in the K shell, so removing these outer electrons requires less energy. Hence the x-ray photons that are emitted when these vacancies are filled have lower energy than those in the K series.



The three lines in each series are called the K_α , K_β , and K_γ lines. The K_α line is produced by the transition of an L electron to the vacancy in the K shell, the K_β line by an M electron, and the K_γ line by an N electron.

Application X Rays in Forensic Science

When a handgun is fired, a cloud of gunshot residue (GSR) is ejected from the barrel. The x-ray emission spectrum of GSR includes characteristic peaks from lead (Pb), antimony (Sb), and barium (Ba). If a sample taken from a suspect's skin or clothing has an x-ray emission spectrum with these characteristics, it indicates that the suspect recently fired a gun.



41.25 Wavelengths of the K_α , K_β , and K_γ lines of tungsten (W), molybdenum (Mo), and copper (Cu).

Example 41.10 Chemical analysis by x-ray emission

You measure the K_α wavelength for an unknown element, obtaining the value 0.0709 nm. What is the element?

SOLUTION

IDENTIFY and SET UP: To determine which element this is, we need to know its atomic number Z . We can find this using Moseley's law, which relates the frequency of an element's K_α x-ray emission line to that element's atomic number Z . We'll use the relationship $f = c/\lambda$ to calculate the frequency for the K_α line, and then use Eq. (41.47) to find the corresponding value of the atomic number Z . We'll then consult the periodic table (Appendix D) to determine which element has this atomic number.

EXECUTE: The frequency is

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^8 \text{ m/s}}{0.0709 \times 10^{-9} \text{ m}} = 4.23 \times 10^{18} \text{ Hz}$$

Solving Moseley's law for Z , we get

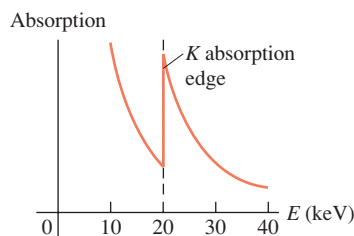
$$Z = 1 + \sqrt{\frac{f}{2.48 \times 10^{15} \text{ Hz}}} = 1 + \sqrt{\frac{4.23 \times 10^{18} \text{ Hz}}{2.48 \times 10^{15} \text{ Hz}}} = 42.3$$

We know that Z has to be an integer; we conclude that $Z = 42$, corresponding to the element molybdenum.

EVALUATE: If you're worried that our calculation did not give an integer for Z , remember that Moseley's law is an empirical relationship. There are slight variations from one atom to another due to differences in the structure of the electron shells. Nonetheless, this example suggests the power of Moseley's law.

Niels Bohr commented that it was Moseley's observations, not the alpha-particle scattering experiments of Rutherford, Geiger, and Marsden (see Section 39.2), that truly convinced physicists that the atom consists of a positive nucleus surrounded by electrons in motion. Unlike Bohr or Rutherford, Moseley did not receive a Nobel Prize for his important work; these awards are given only to living scientists, and Moseley was killed in combat during the First World War.

41.26 When a beam of x rays is passed through a slab of molybdenum, the extent to which the beam is absorbed depends on the energy E of the x-ray photons. A sharp increase in absorption occurs at the K absorption edge at 20 keV. The increase occurs because photons with energies above this value can excite an electron from the K shell of a molybdenum atom into an empty state.

**X-Ray Absorption Spectra**

We can also observe x-ray *absorption* spectra. Unlike optical spectra, the absorption wavelengths are usually not the same as those for emission, especially in many-electron atoms, and do not give simple line spectra. For example, the K_α emission line results from a transition from the L shell to a hole in the K shell. The reverse transition doesn't occur in atoms with $Z \geq 10$ because in the atom's ground state, there is no vacancy in the L shell. To be absorbed, a photon must have enough energy to move an electron to an empty state. Since empty states are only a few electron volts in energy below the free-electron continuum, the minimum absorption energies in many-electron atoms are about the same as the minimum energies that are needed to remove an electron from its shell. Experimentally, if we gradually increase the accelerating voltage and hence the maximum photon energy, we observe sudden increases in absorption when we reach these minimum energies. These sudden jumps of absorption are called *absorption edges* (Fig. 41.26).

Characteristic x-ray spectra provide a very useful analytical tool. Satellite-borne x-ray spectrometers are used to study x-ray emission lines from highly excited atoms in distant astronomical sources. X-ray spectra are also used in air-pollution monitoring and in studies of the abundance of various elements in rocks.

Test Your Understanding of Section 41.7 A beam of photons is passed through a sample of high-temperature atomic hydrogen. At what photon energy would you expect there to be an absorption edge like that shown in Fig. 41.26? (i) 13.60 eV; (ii) 3.40 eV; (iii) 1.51 eV; (iv) all of these; (v) none of these.



Three-dimensional problems: The time-independent Schrödinger equation for three-dimensional problems is given by Eq. (41.5).

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi(x, y, z)}{\partial x^2} + \frac{\partial^2 \psi(x, y, z)}{\partial y^2} + \frac{\partial^2 \psi(x, y, z)}{\partial z^2} \right) + U(x, y, z) \psi(x, y, z) = E \psi(x, y, z)$$

(three-dimensional time-independent Schrödinger equation) (41.5)

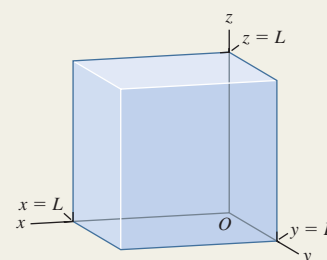
Particle in a three-dimensional box: The wave function for a particle in a cubical box is the product of a function of x only, a function of y only, and a function of z only. Each stationary state is described by three quantum numbers (n_X, n_Y, n_Z). Most of the energy levels given by Eq. (41.16) exhibit degeneracy: More than one quantum state has the same energy. (See Example 41.1.)

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

$$(n_X = 1, 2, 3, \dots;$$

$$n_Y = 1, 2, 3, \dots; n_Z = 1, 2, 3, \dots)$$

(energy levels, particle in a three-dimensional cubical box) (41.16)



The hydrogen atom: The Schrödinger equation for the hydrogen atom gives the same energy levels as the Bohr model. If the nucleus has charge Ze , there is an additional factor of Z^2 in the numerator of Eq. (41.21). The possible magnitudes L of orbital angular momentum are given by Eq. (41.22), and the possible values of the z -component of orbital angular momentum are given by Eq. (41.23). (See Examples 41.2 and 41.3.)

The probability that an atomic electron is between r and $r + dr$ from the nucleus is $P(r) dr$, given by Eq. (41.25). Atomic distances are often measured in units of a , the smallest distance between the electron and the nucleus in the Bohr model. (See Example 41.4.)

$$E_n = -\frac{1}{(4\pi\epsilon_0)^2} \frac{m_r e^4}{2n^2 \hbar^2} = -\frac{13.60 \text{ eV}}{n^2}$$

(energy levels of hydrogen) (41.21)

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

($l = 0, 1, 2, \dots, n-1$) (41.22)

$$L_z = m_l \hbar$$

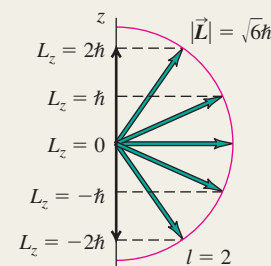
($m_l = 0, \pm 1, \pm 2, \dots, \pm l$) (41.23)

$$P(r) dr = |\psi|^2 dV = |\psi|^2 4\pi r^2 dr$$

(41.25)

$$a = \frac{\epsilon_0 \hbar^2}{\pi m_r e^2} = \frac{4\pi\epsilon_0 \hbar^2}{m_r e^2}$$

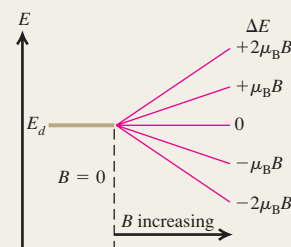
$$= 5.29 \times 10^{-11} \text{ m} \quad (41.26)$$



The Zeeman effect: The interaction energy of an electron (mass m) with magnetic quantum number m_l in a magnetic field \vec{B} along the $+z$ -direction is given by Eq. (41.35) or (41.36), where $\mu_B = e\hbar/2m$ is called the Bohr magneton. (See Example 41.5.)

$$U = -\mu_z B = m_l \frac{e\hbar}{2m} B = m_l \mu_B B$$

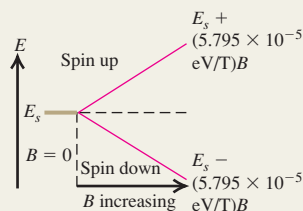
($m_l = 0, \pm 1, \pm 2, \dots, \pm l$) (41.35), (41.36)



Electron spin: An electron has an intrinsic spin angular momentum of magnitude S , given by Eq. (41.38). The possible values of the z -component of the spin angular momentum are $S_z = m_s \hbar$, where $m_s = \pm \frac{1}{2}$. (See Examples 41.6 and 41.7.)

$$S = \sqrt{\frac{1}{2}\left(\frac{1}{2} + 1\right)}\hbar = \sqrt{\frac{3}{4}}\hbar \quad (41.38)$$

$$S_z = \pm \frac{1}{2}\hbar \quad (41.37)$$

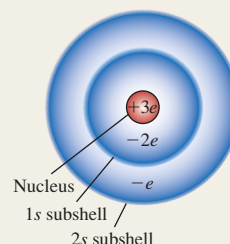


Many-electron atoms: In a hydrogen atom, the quantum numbers n , l , m_l , and m_s of the electron have certain allowed values given by Eq. (41.44). In a many-electron atom, the allowed quantum numbers for each electron are the same as in hydrogen, but the energy levels depend on both n and l because of screening, the partial cancellation of the field of the nucleus by the inner electrons. If the effective (screened) charge attracting an electron is $Z_{\text{eff}}e$, the energies of the levels are given approximately by Eq. (41.45). (See Examples 41.8 and 41.9.)

$$n \geq 1 \quad 0 \leq l \leq n - 1 \quad (41.44)$$

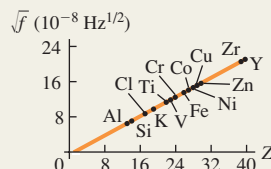
$$|m_l| \leq l \quad m_s = \pm \frac{1}{2}$$

$$E_n = -\frac{Z_{\text{eff}}^2}{n^2} (13.6 \text{ eV}) \quad (41.45)$$



X-ray spectra: Moseley's law states that the frequency of a K_α x ray from a target with atomic number Z is given by Eq. (41.47). Characteristic x-ray spectra result from transitions to a hole in an inner energy level of an atom. (See Example 41.10.)

$$f = (2.48 \times 10^{15} \text{ Hz})(Z - 1)^2 \quad (41.47)$$



BRIDGING PROBLEM

A Many-Electron Atom in a Box

An atom of titanium (Ti) has 22 electrons and has a radius of $1.47 \times 10^{-10} \text{ m}$. As a simple model of this atom, imagine putting 22 electrons into a cubical box that has the same volume as a titanium atom. (a) What is the length of each side of the box? (b) What will be the configuration of the 22 electrons? (c) Find the energies of each of the levels occupied by the electrons. (Ignore the electric forces that the electrons exert on each other.) (d) You remove one of the electrons from the lowest level. As a result, one of the electrons from the highest occupied level drops into the lowest level to fill the hole, emitting a photon in the process. What is the energy of this photon? How does this compare to the energy of the K_α photon for titanium as predicted by Moseley's law?

SOLUTION GUIDE

See MasteringPhysics® study area for a Video Tutor solution.



IDENTIFY and SET UP

- In this problem you'll use ideas from Section 41.2 about a particle in a cubical box. You'll also apply the exclusion principle from Section 41.6 to find the electron configuration of this cubical "atom." The ideas about x-ray spectra from Section 41.7 are also important.
- The target variables are (a) the dimensions of the box, (b) the electron configurations (like those given in Table 41.3 for real atoms), (c) the occupied energy levels of the cubical box, and (d) the energy of the emitted photon.

EXECUTE

- Use your knowledge of geometry to find the length of each side of the box.
- Each electron state is described by four quantum numbers: n_x , n_y , and n_z as described in Section 41.2 and the spin magnetic quantum number m_s described in Section 41.5. Use the exclusion principle to determine the quantum numbers of each of the 22 electrons in the "atom." (Hint: Figure 41.4 in Section 41.2 shows the first several energy levels of a cubical box relative to the ground level $E_{1,1,1}$.)
- Use your results from steps 3 and 4 to find the energies of each of the occupied levels.
- Use your result from step 5 to find the energy of the photon emitted when an electron makes a transition from the highest occupied level to the ground level. Compare this to the energy calculated for titanium using Moseley's law.

EVALUATE

- Is this cubical "atom" a useful model for titanium? Why or why not?
- In this problem you ignored the electric interactions between electrons. To estimate how large these are, find the electrostatic potential energy of two electrons separated by half the length of the box. How does this compare to the energy levels you calculated in step 5? Is it a good approximation to ignore these interactions?

Problems

For instructor-assigned homework, go to www.masteringphysics.com

•, ••, •••: Problems of increasing difficulty. **CP**: Cumulative problems incorporating material from earlier chapters. **CALC**: Problems requiring calculus. **BIO**: Biosciences problems.

DISCUSSION QUESTIONS

Q41.1 Particle *A* is described by the wave function $\psi(x, y, z)$. Particle *B* is described by the wave function $\psi(x, y, z)e^{i\phi}$, where ϕ is a real constant. How does the probability of finding particle *A* within a volume dV around a certain point in space compare with the probability of finding particle *B* within this same volume?

Q41.2 What are the most significant differences between the Bohr model of the hydrogen atom and the Schrödinger analysis? What are the similarities?

Q41.3 For a body orbiting the sun, such as a planet, comet, or asteroid, is there any restriction on the *z*-component of its orbital angular momentum such as there is with the *z*-component of the electron's orbital angular momentum in hydrogen? Explain.

Q41.4 Why is the analysis of the helium atom much more complex than that of the hydrogen atom, either in a Bohr type of model or using the Schrödinger equation?

Q41.5 The Stern–Gerlach experiment is always performed with beams of *neutral* atoms. Wouldn't it be easier to form beams using *ionized* atoms? Why won't this work?

Q41.6 (a) If two electrons in hydrogen atoms have the same principal quantum number, can they have different orbital angular momentum? How? (b) If two electrons in hydrogen atoms have the same orbital angular-momentum quantum number, can they have different principal quantum numbers? How?

Q41.7 In the Stern–Gerlach experiment, why is it essential for the magnetic field to be *inhomogeneous* (that is, nonuniform)?

Q41.8 In the ground state of the helium atom one electron must have “spin down” and the other “spin up.” Why?

Q41.9 An electron in a hydrogen atom is in an *s* level, and the atom is in a magnetic field $\vec{B} = B\hat{k}$. Explain why the “spin up” state ($m_s = +\frac{1}{2}$) has a higher energy than the “spin down” state ($m_s = -\frac{1}{2}$).

Q41.10 The central-field approximation is more accurate for alkali metals than for transition metals such as iron, nickel, or copper. Why?

Q41.11 Table 41.3 shows that for the ground state of the potassium atom, the outermost electron is in a *4s* state. What does this tell you about the relative energies of the *3d* and *4s* levels for this atom? Explain.

Q41.12 Do gravitational forces play a significant role in atomic structure? Explain.

Q41.13 Why do the transition elements ($Z = 21$ to 30) all have similar chemical properties?

Q41.14 Use Table 41.3 to help determine the ground-state electron configuration of the neutral gallium atom (Ga) as well as the ions Ga^+ and Ga^- . Gallium has an atomic number of 31.

Q41.15 On the basis of the Pauli exclusion principle, the structure of the periodic table of the elements shows that there must be a fourth quantum number in addition to *n*, *l*, and *m_l*. Explain.

Q41.16 A small amount of magnetic-field splitting of spectral lines occurs even when the atoms are not in a magnetic field. What causes this?

Q41.17 The ionization energies of the alkali metals (that is, the lowest energy required to remove one outer electron when the

atom is in its ground state) are about 4 or 5 eV, while those of the noble gases are in the range from 11 to 25 eV. Why is there a difference?

Q41.18 The energy required to remove the *3s* electron from a sodium atom in its ground state is about 5 eV. Would you expect the energy required to remove an additional electron to be about the same, or more, or less? Why?

Q41.19 What is the “central-field approximation” and why is it only an approximation?

Q41.20 The nucleus of a gold atom contains 79 protons. How does the energy required to remove a *1s* electron completely from a gold atom compare with the energy required to remove the electron from the ground level in a hydrogen atom? In what region of the electromagnetic spectrum would a photon with this energy for each of these two atoms lie?

Q41.21 (a) Can you show that the orbital angular momentum of an electron in any given direction (e.g., along the *z*-axis) is *always* less than or equal to its total orbital angular momentum? In which cases would the two be equal to each other? (b) Is the result in part (a) true for a classical object, such as a spinning top or planet?

Q41.22 An atom in its ground level absorbs a photon with energy equal to the *K* absorption edge. Does absorbing this photon ionize this atom? Explain.

Q41.23 Can a hydrogen atom emit x rays? If so, how? If not, why not?

EXERCISES

Section 41.2 Particle in a Three-Dimensional Box

41.1 • For a particle in a three-dimensional box, what is the degeneracy (number of different quantum states with the same energy) of the following energy levels: (a) $3\pi^2\hbar^2/2mL^2$ and (b) $9\pi^2\hbar^2/2mL^2$?

41.2 • CP Model a hydrogen atom as an electron in a cubical box with side length *L*. Set the value of *L* so that the volume of the box equals the volume of a sphere of radius $a = 5.29 \times 10^{-11}$ m, the Bohr radius. Calculate the energy separation between the ground and first excited levels, and compare the result to this energy separation calculated from the Bohr model.

41.3 • CP A photon is emitted when an electron in a three-dimensional box of side length 8.00×10^{-11} m makes a transition from the $n_X = 2, n_Y = 2, n_Z = 1$ state to the $n_X = 1, n_Y = 1, n_Z = 1$ state. What is the wavelength of this photon?

41.4 • For each of the following states of a particle in a three-dimensional box, at what points is the probability distribution function a maximum: (a) $n_X = 1, n_Y = 1, n_Z = 1$ and (b) $n_X = 2, n_Y = 2, n_Z = 1$?

41.5 •• A particle is in the three-dimensional box of Section 41.1. For the state $n_X = 2, n_Y = 2, n_Z = 1$, for what planes (in addition to the walls of the box) is the probability distribution function zero? Compare this number of planes to the corresponding number of planes where $|\psi|^2$ is zero for the lower-energy state $n_X = 2, n_Y = 1, n_Z = 1$ and for the ground state $n_X = 1, n_Y = 1, n_Z = 1$.

41.6 • What is the energy difference between the two lowest energy levels for a proton in a cubical box with side length 1.00×10^{-14} m, the approximate diameter of a nucleus?

Section 41.3 The Hydrogen Atom

41.7 •• Consider an electron in the N shell. (a) What is the smallest orbital angular momentum it could have? (b) What is the largest orbital angular momentum it could have? Express your answers in terms of \hbar and in SI units. (c) What is the largest orbital angular momentum this electron could have in any chosen direction? Express your answers in terms of \hbar and in SI units. (d) What is the largest spin angular momentum this electron could have in any chosen direction? Express your answers in terms of \hbar and in SI units. (e) For the electron in part (c), what is the ratio of its spin angular momentum in the z -direction to its orbital angular momentum in the z -direction?

41.8 • An electron is in the hydrogen atom with $n = 5$. (a) Find the possible values of L and L_z for this electron, in units of \hbar . (b) For each value of L , find all the possible angles between \vec{L} and the z -axis. (c) What are the maximum and minimum values of the magnitude of the angle between \vec{L} and the z -axis?

41.9 • The orbital angular momentum of an electron has a magnitude of 4.716×10^{-34} kg \cdot m²/s. What is the angular-momentum quantum number l for this electron?

41.10 • Consider states with angular-momentum quantum number $l = 2$. (a) In units of \hbar , what is the largest possible value of L_z ? (b) In units of \hbar , what is the value of L ? Which is larger: L or the maximum possible L_z ? (c) For each allowed value of L_z , what angle does the vector \vec{L} make with the $+z$ -axis? How does the minimum angle for $l = 2$ compare to the minimum angle for $l = 3$ calculated in Example 41.3?

41.11 • Calculate, in units of \hbar , the magnitude of the maximum orbital angular momentum for an electron in a hydrogen atom for states with a principal quantum number of 2, 20, and 200. Compare each with the value of $n\hbar$ postulated in the Bohr model. What trend do you see?

41.12 • (a) Make a chart showing all the possible sets of quantum numbers l and m_l for the states of the electron in the hydrogen atom when $n = 5$. How many combinations are there? (b) What are the energies of these states?

41.13 •• (a) How many different $5g$ states does hydrogen have? (b) Which of the states in part (a) has the largest angle between \vec{L} and the z -axis, and what is that angle? (c) Which of the states in part (a) has the smallest angle between \vec{L} and the z -axis, and what is that angle?

41.14 •• CALC (a) What is the probability that an electron in the $1s$ state of a hydrogen atom will be found at a distance less than $a/2$ from the nucleus? (b) Use the results of part (a) and of Example 41.4 to calculate the probability that the electron will be found at distances between $a/2$ and a from the nucleus.

41.15 • CALC In Example 41.4 fill in the missing details that show that $P = 1 - 5e^{-2}$.

41.16 • Show that $\Phi(\phi) = e^{im_l\phi} = \Phi(\phi + 2\pi)$ (that is, show that $\Phi(\phi)$ is periodic with period 2π) if and only if m_l is restricted to the values $0, \pm 1, \pm 2, \dots$ (Hint: Euler's formula states that $e^{i\phi} = \cos\phi + i\sin\phi$.)

Section 41.4 The Zeeman Effect

41.17 • A hydrogen atom in a $3p$ state is placed in a uniform external magnetic field \vec{B} . Consider the interaction of the magnetic field with the atom's orbital magnetic dipole moment. (a) What field magnitude B is required to split the $3p$ state into multiple lev-

els with an energy difference of 2.71×10^{-5} eV between adjacent levels? (b) How many levels will there be?

41.18 • A hydrogen atom is in a d state. In the absence of an external magnetic field the states with different m_l values have (approximately) the same energy. Consider the interaction of the magnetic field with the atom's orbital magnetic dipole moment. (a) Calculate the splitting (in electron volts) of the m_l levels when the atom is put in a 0.400-T magnetic field that is in the $+z$ -direction. (b) Which m_l level will have the lowest energy? (c) Draw an energy-level diagram that shows the d levels with and without the external magnetic field.

41.19 • A hydrogen atom in the $5g$ state is placed in a magnetic field of 0.600 T that is in the z -direction. (a) Into how many levels is this state split by the interaction of the atom's orbital magnetic dipole moment with the magnetic field? (b) What is the energy separation between adjacent levels? (c) What is the energy separation between the level of lowest energy and the level of highest energy?

41.20 •• CP A hydrogen atom undergoes a transition from a $2p$ state to the $1s$ ground state. In the absence of a magnetic field, the energy of the photon emitted is 122 nm. The atom is then placed in a strong magnetic field in the z -direction. Ignore spin effects; consider only the interaction of the magnetic field with the atom's orbital magnetic moment. (a) How many different photon wavelengths are observed for the $2p \rightarrow 1s$ transition? What are the m_l values for the initial and final states for the transition that leads to each photon wavelength? (b) One observed wavelength is exactly the same with the magnetic field as without. What are the initial and final m_l values for the transition that produces a photon of this wavelength? (c) One observed wavelength with the field is longer than the wavelength without the field. What are the initial and final m_l values for the transition that produces a photon of this wavelength? (d) Repeat part (c) for the wavelength that is shorter than the wavelength in the absence of the field.

Section 41.5 Electron Spin

41.21 •• CP Classical Electron Spin. (a) If you treat an electron as a classical spherical object with a radius of 1.0×10^{-17} m, what angular speed is necessary to produce a spin angular momentum of magnitude $\sqrt{3/4}\hbar$? (b) Use $v = r\omega$ and the result of part (a) to calculate the speed v of a point at the electron's equator. What does your result suggest about the validity of this model?

41.22 •• A hydrogen atom in the $n = 1$, $m_s = -\frac{1}{2}$ state is placed in a magnetic field with a magnitude of 0.480 T in the $+z$ -direction. (a) Find the magnetic interaction energy (in electron volts) of the electron with the field. (b) Is there any orbital magnetic dipole moment interaction for this state? Explain. Can there be an orbital magnetic dipole moment interaction for $n \neq 1$?

41.23 • Calculate the energy difference between the $m_s = \frac{1}{2}$ ("spin up") and $m_s = -\frac{1}{2}$ ("spin down") levels of a hydrogen atom in the $1s$ state when it is placed in a 1.45-T magnetic field in the negative z -direction. Which level, $m_s = \frac{1}{2}$ or $m_s = -\frac{1}{2}$, has the lower energy?

41.24 • CP The hyperfine interaction in a hydrogen atom between the magnetic dipole moment of the proton and the spin magnetic dipole moment of the electron splits the ground level into two levels separated by 5.9×10^{-6} eV. (a) Calculate the wavelength and frequency of the photon emitted when the atom makes a transition between these states, and compare your answer to the value given at the end of Section 41.5. In what part of the electromagnetic spectrum does this lie? Such photons are emitted by cold hydrogen clouds in interstellar space; by detecting these photons,

astronomers can learn about the number and density of such clouds. (b) Calculate the effective magnetic field experienced by the electron in these states (see Fig. 41.18). Compare your result to the effective magnetic field due to the spin-orbit coupling calculated in Example 41.7.

41.25 • A hydrogen atom in a particular orbital angular momentum state is found to have j quantum numbers $\frac{7}{2}$ and $\frac{9}{2}$. What is the letter that labels the value of l for the state?

Section 41.6 Many-Electron Atoms and the Exclusion Principle

41.26 • For germanium (Ge, $Z = 32$), make a list of the number of electrons in each subshell ($1s, 2s, 2p, \dots$). Use the allowed values of the quantum numbers along with the exclusion principle; do not refer to Table 41.3.

41.27 • Make a list of the four quantum numbers n, l, m_l , and m_s for each of the 10 electrons in the ground state of the neon atom. Do not refer to Table 41.2 or 41.3.

41.28 •• (a) Write out the ground-state electron configuration ($1s^2, 2s^2, \dots$) for the carbon atom. (b) What element of next-larger Z has chemical properties similar to those of carbon? Give the ground-state electron configuration for this element.

41.29 •• (a) Write out the ground-state electron configuration ($1s^2, 2s^2, \dots$) for the beryllium atom. (b) What element of next-larger Z has chemical properties similar to those of beryllium? Give the ground-state electron configuration of this element. (c) Use the procedure of part (b) to predict what element of next-larger Z than in (b) will have chemical properties similar to those of the element you found in part (b), and give its ground-state electron configuration.

41.30 • For magnesium, the first ionization potential is 7.6 eV. The second ionization potential (additional energy required to remove a second electron) is almost twice this, 15 eV, and the third ionization potential is much larger, about 80 eV. How can these numbers be understood?

41.31 • The $5s$ electron in rubidium (Rb) sees an effective charge of $2.771e$. Calculate the ionization energy of this electron.

41.32 • The energies of the $4s, 4p$, and $4d$ states of potassium are given in Example 41.9. Calculate Z_{eff} for each state. What trend do your results show? How can you explain this trend?

41.33 • (a) The doubly charged ion N^{2+} is formed by removing two electrons from a nitrogen atom. What is the ground-state electron configuration for the N^{2+} ion? (b) Estimate the energy of the least strongly bound level in the L shell of N^{2+} . (c) The doubly charged ion P^{2+} is formed by removing two electrons from a phosphorus atom. What is the ground-state electron configuration for the P^{2+} ion? (d) Estimate the energy of the least strongly bound level in the M shell of P^{2+} .

41.34 • (a) The energy of the $2s$ state of lithium is -5.391 eV. Calculate the value of Z_{eff} for this state. (b) The energy of the $4s$ state of potassium is -4.339 eV. Calculate the value of Z_{eff} for this state. (c) Compare Z_{eff} for the $2s$ state of lithium, the $3s$ state of sodium (see Example 41.8), and the $4s$ state of potassium. What trend do you see? How can you explain this trend?

41.35 • Estimate the energy of the highest- l state for (a) the L shell of Be^+ and (b) the N shell of Ca^+ .

Section 41.7 X-Ray Spectra

41.36 • A K_α x ray emitted from a sample has an energy of 7.46 keV. Of which element is the sample made?

41.37 • Calculate the frequency, energy (in keV), and wavelength of the K_α x ray for the elements (a) calcium (Ca, $Z = 20$); (b) cobalt (Co, $Z = 27$); (c) cadmium (Cd, $Z = 48$).

41.38 •• The energies for an electron in the K, L , and M shells of the tungsten atom are $-69,500$ eV, $-12,000$ eV, and -2200 eV, respectively. Calculate the wavelengths of the K_α and K_β x rays of tungsten.

PROBLEMS

41.39 • In terms of the ground-state energy $E_{1,1,1}$, what is the energy of the highest level occupied by an electron when 10 electrons are placed into a cubical box?

41.40 •• CALC A particle in the three-dimensional box of Section 41.2 is in the ground state, where $n_x = n_y = n_z = 1$. (a) Calculate the probability that the particle will be found somewhere between $x = 0$ and $x = L/2$. (b) Calculate the probability that the particle will be found somewhere between $x = L/4$ and $x = L/2$. Compare your results to the result of Example 41.1 for the probability of finding the particle in the region $x = 0$ to $x = L/4$.

41.41 •• CALC A particle is in the three-dimensional box of Section 41.2. (a) Consider the cubical volume defined by $0 \leq x \leq L/4$, $0 \leq y \leq L/4$, and $0 \leq z \leq L/4$. What fraction of the total volume of the box is this cubical volume? (b) If the particle is in the ground state ($n_x = 1, n_y = 1, n_z = 1$) calculate the probability that the particle will be found in the cubical volume defined in part (a). (c) Repeat the calculation of part (b) when the particle is in the state $n_x = 2, n_y = 1, n_z = 1$.

41.42 •• CALC A particle is described by the normalized wave function $\psi(x, y, z) = A x e^{-\alpha x^2} e^{-\beta y^2} e^{-\gamma z^2}$, where A, α, β , and γ are all real, positive constants. The probability that the particle will be found in the infinitesimal volume $dx dy dz$ centered at the point (x_0, y_0, z_0) is $|\psi(x_0, y_0, z_0)|^2 dx dy dz$. (a) At what value of x_0 is the particle most likely to be found? (b) Are there values of x_0 for which the probability of the particle being found is zero? If so, at what x_0 ?

41.43 •• CALC A particle is described by the normalized wave function $\psi(x, y, z) = A e^{-\alpha(x^2+y^2+z^2)}$, where A and α are real, positive constants. (a) Determine the probability of finding the particle at a distance between r and $r + dr$ from the origin. (Hint: See Problem 41.42. Consider a spherical shell centered on the origin with inner radius r and thickness dr .) (b) For what value of r does the probability in part (a) have its maximum value? Is this the same value of r for which $|\psi(x, y, z)|^2$ is a maximum? Explain any differences.

41.44 •• CP CALC A Three-Dimensional Isotropic Harmonic Oscillator. An isotropic harmonic oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k'(x^2 + y^2 + z^2)$. (Isotropic means that the force constant k' is the same in all three coordinate directions.) (a) Show that for this potential, a solution to Eq. (41.5) is given by $\psi = \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z)$. In this expression, $\psi_{n_x}(x)$ is a solution to the one-dimensional harmonic oscillator Schrödinger equation, Eq. (40.44), with energy $E_{n_x} = (n_x + \frac{1}{2})\hbar\omega$. The functions $\psi_{n_y}(y)$ and $\psi_{n_z}(z)$ are analogous one-dimensional wave functions for oscillations in the y - and z -directions. Find the energy associated with this ψ . (b) From your results in part (a) what are the ground-level and first-excited-level energies of the three-dimensional isotropic oscillator? (c) Show that there is only one state (one set of quantum numbers n_x, n_y , and n_z) for the ground level but three states for the first excited level.

41.45 •• CP CALC Three-Dimensional Anisotropic Harmonic Oscillator. An oscillator has the potential-energy function $U(x, y, z) = \frac{1}{2}k'_1(x^2 + y^2) + \frac{1}{2}k'_2z^2$, where $k'_1 > k'_2$. This oscillator is called *anisotropic* because the force constant is not the same in all three coordinate directions. (a) Find a general expression

for the energy levels of the oscillator (see Problem 41.44). (b) From your results in part (a), what are the ground-level and first-excited-level energies of this oscillator? (c) How many states (different sets of quantum numbers n_x , n_y , and n_z) are there for the ground level and for the first excited level? Compare to part (c) of Problem 41.44.

41.46 •• An electron in hydrogen is in the $5f$ state. (a) Find the largest possible value of the z -component of its angular momentum. (b) Show that for the electron in part (a), the corresponding x - and y -components of its angular momentum satisfy the equation $\sqrt{L_x^2 + L_y^2} = \hbar\sqrt{3}$.

41.47 •• (a) Show that the total number of atomic states (including different spin states) in a shell of principal quantum number n is $2n^2$. [Hint: The sum of the first N integers $1 + 2 + 3 + \cdots + N$ is equal to $N(N + 1)/2$.] (b) Which shell has 50 states?

41.48 •• (a) What is the lowest possible energy (in electron volts) of an electron in hydrogen if its orbital angular momentum is $\sqrt{12}\hbar$? (b) What are the largest and smallest values of the z -component of the orbital angular momentum (in terms of \hbar) for the electron in part (a)? (c) What are the largest and smallest values of the spin angular momentum (in terms of \hbar) for the electron in part (a)? (d) What are the largest and smallest values of the orbital angular momentum (in terms of \hbar) for an electron in the M shell of hydrogen?

41.49 • Consider an electron in hydrogen having total energy -0.5440 eV. (a) What are the possible values of its orbital angular momentum (in terms of \hbar)? (b) What wavelength of light would it take to excite this electron to the next higher shell? Is this photon visible to humans?

41.50 • (a) Show all the distinct states for an electron in the N shell of hydrogen. Include all four quantum numbers. (b) For an f electron in the N shell, what is the largest possible orbital angular momentum and the greatest positive value for the component of this angular momentum along any chosen direction (the z -axis)? What is the magnitude of its spin angular momentum? Express these quantities in units of \hbar . (c) For an electron in the d state of the N shell, what are the maximum and minimum angles between its angular momentum vector and any chosen direction (the z -axis)? (d) What is the largest value of the orbital angular momentum for an f electron in the M shell?

41.51 • (a) The energy of an electron in the $4s$ state of sodium is -1.947 eV. What is the effective net charge of the nucleus “seen” by this electron? On the average, how many electrons screen the nucleus? (b) For an outer electron in the $4p$ state of potassium, on the average 17.2 inner electrons screen the nucleus. (i) What is the effective net charge of the nucleus “seen” by this outer electron? (ii) What is the energy of this outer electron?

41.52 • CALC For a hydrogen atom, the probability $P(r)$ of finding the electron within a spherical shell with inner radius r and outer radius $r + dr$ is given by Eq. (41.25). For a hydrogen atom in the $1s$ ground state, at what value of r does $P(r)$ have its maximum value? How does your result compare to the distance between the electron and the nucleus for the $n = 1$ state in the Bohr model, Eq. (41.26)?

41.53 •• CALC Consider a hydrogen atom in the $1s$ state. (a) For what value of r is the potential energy $U(r)$ equal to the total energy E ? Express your answer in terms of a . This value of r is called the *classical turning point*, since this is where a Newtonian particle would stop its motion and reverse direction. (b) For r greater than the classical turning point, $U(r) > E$. Classically, the particle cannot be in this region, since the kinetic energy cannot be negative. Calculate the probability of the electron being found in this classically forbidden region.

41.54 • CP Rydberg Atoms. *Rydberg atoms* are atoms whose outermost electron is in an excited state with a very large principal quantum number. Rydberg atoms have been produced in the laboratory and detected in interstellar space. (a) Why do all neutral Rydberg atoms with the same n value have essentially the same ionization energy, independent of the total number of electrons in the atom? (b) What is the ionization energy for a Rydberg atom with a principal quantum number of 350? What is the radius in the Bohr model of the Rydberg electron’s orbit? (c) Repeat part (b) for $n = 650$.

41.55 •• CALC The wave function for a hydrogen atom in the $2s$ state is

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

(a) Verify that this function is normalized. (b) In the Bohr model, the distance between the electron and the nucleus in the $n = 2$ state is exactly $4a$. Calculate the probability that an electron in the $2s$ state will be found at a distance less than $4a$ from the nucleus.

41.56 •• CALC The normalized wave function for a hydrogen atom in the $2s$ state is given in Problem 41.55. (a) For a hydrogen atom in the $2s$ state, at what value of r is $P(r)$ maximum? How does your result compare to $4a$, the distance between the electron and the nucleus in the $n = 2$ state of the Bohr model? (b) At what value of r (other than $r = 0$ or $r = \infty$) is $P(r)$ equal to zero, so that the probability of finding the electron at that separation from the nucleus is zero? Compare your result to Fig. 41.9.

41.57 •• (a) For an excited state of hydrogen, show that the smallest angle that the orbital angular momentum vector \vec{L} can have with the z -axis is

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

(b) What is the corresponding expression for $(\theta_L)_{\max}$, the largest possible angle between \vec{L} and the z -axis?

41.58 •• (a) If the value of L_z is known, we cannot know either L_x or L_y precisely. But we can know the value of the quantity $\sqrt{L_x^2 + L_y^2}$. Write an expression for this quantity in terms of l , m_l , and \hbar . (b) What is the meaning of $\sqrt{L_x^2 + L_y^2}$? (c) For a state of nonzero orbital angular momentum, find the maximum and minimum values of $\sqrt{L_x^2 + L_y^2}$. Explain your results.

41.59 •• CALC The normalized radial wave function for the $2p$ state of the hydrogen atom is $R_{2p} = (1/\sqrt{24a^5})re^{-r/2a}$. After we average over the angular variables, the radial probability function becomes $P(r) dr = (R_{2p})^2 r^2 dr$. At what value of r is $P(r)$ for the $2p$ state a maximum? Compare your results to the radius of the $n = 2$ state in the Bohr model.

41.60 •• CP Stern–Gerlach Experiment. In a Stern–Gerlach experiment, the deflecting force on the atom is $F_z = -\mu_z(dB_z/dz)$, where μ_z is given by Eq. (41.40) and dB_z/dz is the magnetic-field gradient. In a particular experiment the magnetic-field region is 50.0 cm long; assume the magnetic-field gradient is constant in this region. A beam of silver atoms enters the magnetic field with a speed of 525 m/s. What value of dB_z/dz is required to give a separation of 1.0 mm between the two spin components as they exit the field? (Note: The magnetic dipole moment of silver is the same as that for hydrogen, since its valence electron is in an $l = 0$ state.)

41.61 • Consider the transition from a $3d$ to a $2p$ state of hydrogen in an external magnetic field. Assume that the effects of electron

spin can be ignored (which is not actually the case) so that the magnetic field interacts only with the orbital angular momentum. Identify each allowed transition by the m_l values of the initial and final states. For each of these allowed transitions, determine the shift of the transition energy from the zero-field value and show that there are three different transition energies.

41.62 •• An atom in a $3d$ state emits a photon of wavelength 475.082 nm when it decays to a $2p$ state. (a) What is the energy (in electron volts) of the photon emitted in this transition? (b) Use the selection rules described in Section 41.4 to find the allowed transitions if the atom is now in an external magnetic field of 3.500 T. Ignore the effects of the electron's spin. (c) For the case in part (b), if the energy of the $3d$ state was originally -8.50000 eV with no magnetic field present, what will be the energies of the states into which it splits in the magnetic field? (d) What are the allowed wavelengths of the light emitted during transition in part (b)?

41.63 •• CALC Spectral Analysis. While studying the spectrum of a gas cloud in space, an astronomer magnifies a spectral line that results from a transition from a p state to an s state. She finds that the line at 575.050 nm has actually split into three lines, with adjacent lines 0.0462 nm apart, indicating that the gas is in an external magnetic field. (Ignore effects due to electron spin.) What is the strength of the external magnetic field?

41.64 •• A hydrogen atom makes a transition from an $n = 3$ state to an $n = 2$ state (the Balmer H_α line) while in a magnetic field in the $+z$ -direction and with magnitude 1.40 T. (a) If the magnetic quantum number is $m_l = 2$ in the initial ($n = 3$) state and $m_l = 1$ in the final ($n = 2$) state, by how much is each energy level shifted from the zero-field value? (b) By how much is the wavelength of the H_α line shifted from the zero-field value? Is the wavelength increased or decreased? Disregard the effect of electron spin. [Hint: Use the result of Problem 39.86(c).]

41.65 • CP A large number of hydrogen atoms in $1s$ states are placed in an external magnetic field that is in the $+z$ -direction. Assume that the atoms are in thermal equilibrium at room temperature, $T = 300$ K. According to the Maxwell-Boltzmann distribution (see Section 39.4), what is the ratio of the number of atoms in the $m_s = \frac{1}{2}$ state to the number in the $m_s = -\frac{1}{2}$ state when the magnetic-field magnitude is (a) 5.00×10^{-5} T (approximately the earth's field); (b) 0.500 T; (c) 5.00 T?

41.66 •• Effective Magnetic Field. An electron in a hydrogen atom is in the $2p$ state. In a simple model of the atom, assume that the electron circles the proton in an orbit with radius r equal to the Bohr-model radius for $n = 2$. Assume that the speed v of the orbiting electron can be calculated by setting $L = mvr$ and taking L to have the quantum-mechanical value for a $2p$ state. In the frame of the electron, the proton orbits with radius r and speed v . Model the orbiting proton as a circular current loop, and calculate the magnetic field it produces at the location of the electron.

41.67 •• Weird Universe. In another universe, the electron is a spin- $\frac{3}{2}$ rather than a spin- $\frac{1}{2}$ particle, but all other physics are the same as in our universe. In this universe, (a) what are the atomic numbers of the lightest two inert gases? (b) What is the ground-state electron configuration of sodium?

41.68 • For an ion with nuclear charge Z and a single electron, the electric potential energy is $-Ze^2/4\pi\epsilon_0 r$ and the expression for the energies of the states and for the normalized wave functions are obtained from those for hydrogen by replacing e^2 by Ze^2 . Consider the N^{6+} ion, with seven protons and one electron. (a) What is the ground-state energy in electron volts? (b) What is the ionization energy, the energy required to remove the electron from the N^{6+}

ion if it is initially in the ground state? (c) What is the distance a [given for hydrogen by Eq. (41.26)] for this ion? (d) What is the wavelength of the photon emitted when the N^{6+} ion makes a transition from the $n = 2$ state to the $n = 1$ ground state?

41.69 •• A hydrogen atom in an $n = 2$, $l = 1$, $m_l = -1$ state emits a photon when it decays to an $n = 1$, $l = 0$, $m_l = 0$ ground state. (a) In the absence of an external magnetic field, what is the wavelength of this photon? (b) If the atom is in a magnetic field in the $+z$ -direction and with a magnitude of 2.20 T, what is the shift in the wavelength of the photon from the zero-field value? Does the magnetic field increase or decrease the wavelength? Disregard the effect of electron spin. [Hint: Use the result of Problem 39.86(c).]

41.70 •• A lithium atom has three electrons, and the $2s_{1/2}$ ground-state electron configuration is $1s^2 2s$. The $1s^2 2p$ excited state is split into two closely spaced levels, $^2P_{3/2}$ and $^2P_{1/2}$, by the spin-orbit interaction (see Example 41.7 in Section 41.5). A photon with wavelength 67.09608 μm is emitted in the $^2P_{3/2} \rightarrow ^2S_{1/2}$ transition, and a photon with wavelength 67.09761 μm is emitted in the $^2P_{1/2} \rightarrow ^2S_{1/2}$ transition. Calculate the effective magnetic field seen by the electron in the $1s^2 2p$ state of the lithium atom. How does your result compare to that for the $3p$ level of sodium found in Example 41.7?

41.71 • Estimate the minimum and maximum wavelengths of the characteristic x rays emitted by (a) vanadium ($Z = 23$) and (b) rhenium ($Z = 45$). Discuss any approximations that you make.

41.72 •• CP Electron Spin Resonance. Electrons in the lower of two spin states in a magnetic field can absorb a photon of the right frequency and move to the higher state. (a) Find the magnetic-field magnitude B required for this transition in a hydrogen atom with $n = 1$ and $l = 0$ to be induced by microwaves with wavelength λ . (b) Calculate the value of B for a wavelength of 3.50 cm.

CHALLENGE PROBLEMS

41.73 ••• Each of $2N$ electrons (mass m) is free to move along the x -axis. The potential-energy function for each electron is $U(x) = \frac{1}{2}k'x^2$, where k' is a positive constant. The electric and magnetic interactions between electrons can be ignored. Use the exclusion principle to show that the minimum energy of the system of $2N$ electrons is $\hbar N^2 \sqrt{k'/m}$. (Hint: See Section 40.5 and the hint given in Problem 41.47.)

41.74 ••• CP Consider a simple model of the helium atom in which two electrons, each with mass m , move around the nucleus (charge $+2e$) in the same circular orbit. Each electron has orbital angular momentum \hbar (that is, the orbit is the smallest-radius Bohr orbit), and the two electrons are always on opposite sides of the nucleus. Ignore the effects of spin. (a) Determine the radius of the orbit and the orbital speed of each electron. [Hint: Follow the procedure used in Section 39.3 to derive Eqs. (39.8) and (39.9). Each electron experiences an attractive force from the nucleus and a repulsive force from the other electron.] (b) What is the total kinetic energy of the electrons? (c) What is the potential energy of the system (the nucleus and the two electrons)? (d) In this model, how much energy is required to remove both electrons to infinity? How does this compare to the experimental value of 79.0 eV?

41.75 ••• CALC Repeat the calculation of Problem 41.53 for a one-electron ion with nuclear charge Z . (See Problem 41.68.) How does the probability of the electron being found in the classically forbidden region depend on Z ?

Answers

Chapter Opening Question ?

Helium is inert because it has a filled K shell, while sodium is very reactive because its third electron is loosely bound in an L shell. See Section 41.6 for more details.

Test Your Understanding Questions

41.1 Answer: (iv) If $U(x, y, z) = 0$ in a certain region of space, we can rewrite the time-independent Schrödinger equation [Eq. (41.5)] for that region as $\partial^2\psi/\partial x^2 + \partial^2\psi/\partial y^2 + \partial^2\psi/\partial z^2 = (-2mE/\hbar^2)\psi$. We are told that all of the second derivatives of $\psi(x, y, z)$ are positive in this region, so the left-hand side of this equation is positive. Hence the right-hand side $(-2mE/\hbar^2)\psi$ must also be positive. Since $E > 0$, the quantity $-2mE/\hbar^2$ is negative, and so $\psi(x, y, z)$ must be negative.

41.2 Answer: (iv), (ii), (i) and (iii) (tie) Equation (41.16) shows that the energy levels for a cubical box are proportional to the quantity $n_X^2 + n_Y^2 + n_Z^2$. Hence ranking in order of this quantity is the same as ranking in order of energy. For the four cases we are given, we have (i) $n_X^2 + n_Y^2 + n_Z^2 = 2^2 + 3^2 + 2^2 = 17$; (ii) $n_X^2 + n_Y^2 + n_Z^2 = 4^2 + 1^2 + 1^2 = 18$; (iii) $n_X^2 + n_Y^2 + n_Z^2 = 2^2 + 2^2 + 3^2 = 17$; and (iv) $n_X^2 + n_Y^2 + n_Z^2 = 1^2 + 3^2 + 3^2 = 19$. The states $(n_X, n_Y, n_Z) = (2, 3, 2)$ and $(n_X, n_Y, n_Z) = (2, 2, 3)$ have the same energy (they are degenerate).

41.3 Answer: (ii) and (iii) (tie), (i) An electron in a state with principal quantum number n is most likely to be found at $r = n^2a$. This result is independent of the values of the quantum numbers l and m_l . Hence an electron with $n = 2$ (most likely to be found at $r = 4a$) is more likely to be found near $r = 5a$ than an electron with $n = 1$ (most likely to be found at $r = a$).

41.4 Answer: no All that matters is the component of the electron's orbital magnetic moment along the direction of \vec{B} . We called this quantity μ_z in Eq. (41.32) because we *defined* the positive z -axis to be in the direction of \vec{B} . In reality, the names of the axes are entirely arbitrary.

41.5 Answer: (iv) For the magnetic moment to be perfectly aligned with the z -direction, the z -component of the spin vector \vec{S} would have to have the same absolute value as \vec{S} . However, the possible values of S_z are $\pm \frac{1}{2}\hbar$ [Eq. (41.37)], while the magnitude of the spin vector is $S = \sqrt{\frac{3}{4}}\hbar$ [Eq. (41.38)]. Hence \vec{S} can never be perfectly aligned with any one direction in space.

41.6 Answer: more difficult If there were no exclusion principle, all 11 electrons in the sodium atom would be in the level of lowest energy (the $1s$ level) and the configuration would be $1s^{11}$. Consequently, it would be more difficult to remove the first electron. (In a real sodium atom the valence electron is in a screened $3s$ state, which has a comparatively high energy.)

41.7 Answer: (iv) An absorption edge appears if the photon energy is just high enough to remove an electron in a given energy level from the atom. In a sample of high-temperature hydrogen we expect to find atoms whose electron is in the ground level ($n = 1$), the first excited level ($n = 2$), and the second excited level ($n = 3$). From Eq. (41.21) these levels have energies $E_n = (-13.60 \text{ eV})/n^2 = -13.60 \text{ eV}$, -3.40 eV , and -1.51 eV (see Fig. 38.9b).

Bridging Problem

Answers: (a) $2.37 \times 10^{-10} \text{ m}$

(b) Values of (n_X, n_Y, n_Z, m_s) for the 22 electrons: $(1, 1, 1, +\frac{1}{2})$, $(1, 1, 1, -\frac{1}{2})$, $(2, 1, 1, +\frac{1}{2})$, $(2, 1, 1, -\frac{1}{2})$, $(1, 2, 1, +\frac{1}{2})$, $(1, 2, 1, -\frac{1}{2})$, $(1, 1, 2, +\frac{1}{2})$, $(1, 1, 2, -\frac{1}{2})$, $(2, 2, 1, +\frac{1}{2})$, $(2, 2, 1, -\frac{1}{2})$, $(2, 1, 2, +\frac{1}{2})$, $(2, 1, 2, -\frac{1}{2})$, $(1, 2, 2, +\frac{1}{2})$, $(1, 2, 2, -\frac{1}{2})$, $(3, 1, 1, +\frac{1}{2})$, $(3, 1, 1, -\frac{1}{2})$, $(1, 3, 1, +\frac{1}{2})$, $(1, 3, 1, -\frac{1}{2})$, $(1, 1, 3, +\frac{1}{2})$, $(1, 1, 3, -\frac{1}{2})$, $(2, 2, 2, +\frac{1}{2})$, $(2, 2, 2, -\frac{1}{2})$

(c) 20.1 eV, 40.2 eV, 60.3 eV, 73.7 eV, and 80.4 eV

(d) 60.3 eV versus $4.52 \times 10^3 \text{ eV}$