

8.2 Atomic Line Spectra Are Experimental Evidence That Electrons in Atoms Have Quantized Energies • 313

Figure 8.8. Another series is in the ultraviolet region, and the rest are in the infrared. In 1885, J. J. Balmer found an equation that was able to give the wavelengths of the lines in the visible portion of the spectrum. This was soon extended to a more general equation, called the **Rydberg equation**, that could be used to calculate the wavelengths of *all* the spectral lines of hydrogen.

Rydberg equation:

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

The symbol λ stands for the wavelength, R_H is a constant ($109,678 \text{ cm}^{-1}$), and n_1 and n_2 are variables whose values are whole numbers that range from 1 to ∞ . The only restriction is that the value of n_2 must be larger than n_1 . (This assures that the calculated wavelength has a positive value.) Thus, if $n_1 = 1$, acceptable values of n_2 are 2, 3, 4, . . . , ∞ . The Rydberg constant, R_H , is an *empirical constant*, which means its value was chosen so that the equation gives values for λ that match the ones determined experimentally. The use of the Rydberg equation is straightforward, as illustrated in the following example.

The lines in the visible portion of the hydrogen spectrum are called the *Balmer series*, for which $n_1 = 2$ in the Rydberg equation. Calculate, to four significant figures, the wavelength in nanometers of the spectral line in this series for which $n_2 = 4$.

ANALYSIS and SOLUTION: To solve this problem, we substitute values into the Rydberg equation, which will give us $1/\lambda$. Taking the reciprocal will then give the wavelength. As usual, we must be careful with the units.

Substituting $n_1 = 2$ and $n_2 = 4$ into the Rydberg equation gives

$$\begin{aligned} \frac{1}{\lambda} &= 109,678 \text{ cm}^{-1} \left(\frac{1}{2^2} - \frac{1}{4^2} \right) \\ &= 109,678 \text{ cm}^{-1} \left(\frac{1}{4} - \frac{1}{16} \right) \\ &= 109,678 \text{ cm}^{-1} (0.2500 - 0.0625) \\ &= 109,678 \text{ cm}^{-1} (0.1875) \\ &= 2.056 \times 10^4 \text{ cm}^{-1} \end{aligned}$$

Taking the reciprocal gives the wavelength in centimeters.

$$\begin{aligned} \lambda &= \frac{1}{2.056 \times 10^4 \text{ cm}^{-1}} \\ &= 4.864 \times 10^{-5} \text{ cm} \end{aligned}$$

Finally, we convert to nanometers.

$$\begin{aligned} \lambda &= 4.864 \times 10^{-5} \text{ cm} \times \frac{10^{-2} \text{ m}}{1 \text{ cm}} \times \frac{1 \text{ nm}}{10^{-9} \text{ m}} \\ &= 486.4 \text{ nm} \end{aligned}$$

Is the Answer Reasonable?

Besides double-checking the arithmetic, we can check the answer against the experimental spectrum of hydrogen in Figure 8.8. This wavelength corresponds to the turquoise line in the hydrogen spectrum.

PRACTICE EXERCISE 3: Calculate the wavelength in nanometers of the spectral line in the visible spectrum of hydrogen for which $n_1 = 2$ and $n_2 = 3$. What color is this line?

EXAMPLE 8.3 **Calculating the Wavelength of a Line in the Hydrogen Spectrum**

The discovery of the Rydberg equation was both exciting and perplexing. The fact that the wavelength of any line in the hydrogen spectrum can be calculated by a simple equation involving just one constant and the reciprocals of the squares of two whole numbers is remarkable. What is there about the behavior of the electron in the atom that could account for such simplicity?

The energy of electrons in atoms is quantized

Earlier you saw that there is a simple relationship between the frequency of light and its energy, $E = h\nu$. Because excited atoms emit light of only certain specific frequencies, it must be true that only certain characteristic energy changes are able to take place within the atoms. For instance, in the spectrum of hydrogen there is a red line (see Figure 8.8) that has a wavelength of 656.4 nm and a frequency of 4.567×10^{14} Hz. As shown in the margin, the energy of a photon of this light is 3.026×10^{-19} J. Whenever a hydrogen atom emits red light, the frequency of the light is always precisely 4.567×10^{14} Hz and the energy of the atom decreases by *exactly* 3.026×10^{-19} J, never more and never less. Atomic spectra, then, tell us that *when an excited atom loses energy, not just any arbitrary amount can be lost*. The same is true if the atom gains energy.

$$\begin{aligned} E &= h\nu \\ h &= 6.626 \times 10^{-34} \text{ J s} \\ E &= (6.626 \times 10^{-34} \text{ J s}) \\ &\quad \times (4.567 \times 10^{14} \text{ s}^{-1}) \\ &= 3.026 \times 10^{-19} \text{ J} \end{aligned}$$

How is it that atoms of a given element always undergo exactly the same specific energy changes? The answer seems to be that in an atom an electron can have only certain definite amounts of energy and no others. We say that the electron is restricted to certain **energy levels** and that the energy of the electron is **quantized**.

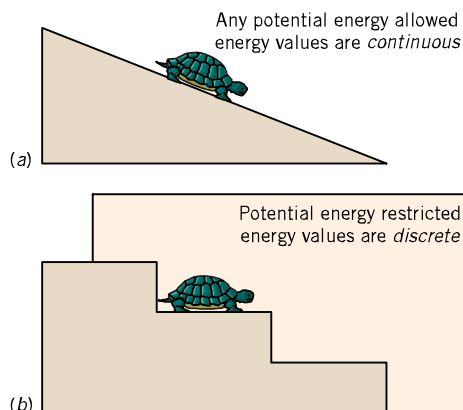
The energy of an electron in an atom might be compared to the energy of the tortoise in the zoo exhibit shown in Figure 8.9*b*. The tortoise trapped inside the zoo exhibit can only be “stable” on one of the ledges, so it has certain specific amounts of potential energy as determined by the “energy levels” of the various ledges. If the tortoise is raised to a higher ledge, its potential energy is increased. When it drops to a lower ledge, its potential energy decreases. If the tortoise tries to occupy heights between the ledges, it immediately falls to the lower ledge. Therefore, the energy changes for the tortoise are restricted to the differences in potential energy between the ledges.

The potential energy of the tortoise at rest is quantized.

So it is with an electron in an atom. The electron can only have energies corresponding to the set of electron energy levels in the atom. When the atom is supplied with energy (by an electric discharge, for example), an electron is raised from a low-energy level to a higher one. When the electron drops back, energy equal to the difference between the two levels is released and emitted as a photon. Because only certain energy jumps can occur, only certain frequencies of light can appear in the spectrum.

The existence of specific energy levels in atoms, as implied by atomic spectra, forms the foundation of all theories about electronic structure. Any model of the atom that attempts to describe the positions or motions of electrons must also account for atomic spectra.

FIGURE 8.9 *Continuous and discrete energies.* (a) The tortoise is free to move to any height less than the height of the hill. Its potential energy can take on any value between the maximum (at the hill top) and the minimum (at the bottom). Similarly, the energy of a free electron can take on any value. (b) The tortoise trapped inside a zoo exhibit is found only at three heights: at the bottom (the lowest, or *ground state*), middle, or top ledges. A fourth height, the walkway outside the exhibit, is possible but inaccessible to the tortoise. Similarly, the energy of the electron trapped inside an atom is restricted to certain values, which correspond to the various energy levels in an atom.



The Bohr model explains the simple pattern of lines seen in the spectrum of hydrogen

The first theoretical model of the hydrogen atom that successfully accounted for the Rydberg equation was proposed in 1913 by Niels Bohr (1885–1962), a Danish physicist. In his model, Bohr likened the electron moving around the nucleus to a planet circling the sun. He suggested that the electron moves around the nucleus along fixed paths, or orbits. His model broke with the classical laws of physics by placing restrictions on the sizes of the orbits and the energy that the electron could have in a given orbit. This ultimately led Bohr to an equation that described the energy of the electron in the atom. The equation includes a number of physical constants such as the mass of the electron, its charge, and Planck's constant. It also contains an integer, n , that Bohr called a **quantum number**. Each of the orbits is identified by its value of n . When all the constants are combined, Bohr's equation becomes

$$E = \frac{-b}{n^2} \quad (8.3)$$

where E is the energy of the electron and b is the combined constant (its value is 2.18×10^{-18} J). The allowed values of n are whole numbers that range from 1 to ∞ (i.e., n could equal 1, 2, 3, 4, . . . , ∞). From this equation the energy of the electron in any particular orbit could be calculated.

Because of the negative sign in Equation 8.3, the lowest (most negative) energy value occurs when $n = 1$, which corresponds to the *first Bohr orbit*. The lowest energy state of an atom is the most stable one and is called the **ground state**. For hydrogen, the ground state occurs when its electron has $n = 1$. According to Bohr's theory, this orbit brings the electron closest to the nucleus. Conversely, an atom with $n = \infty$ would correspond to an "unbound" electron that had escaped from the nucleus. Such an electron has an energy of zero in Bohr's theory. The negative sign in Equation 8.3 ensures that any electron with a finite value of n has a lower energy than an unbound electron. Thus, energy is released when a free electron is bound to a proton to form a hydrogen atom.

When a hydrogen atom absorbs energy, as it does when an electric discharge passes through it, the electron is raised from the orbit having $n = 1$ to a higher orbit, to $n = 2$ or $n = 3$ or even higher. These higher orbits are less stable than the lower ones, so the electron quickly drops to a lower orbit. When this happens, energy is emitted in the form of light (see Figure 8.10). Since the energy of the electron in a given orbit is fixed, a drop from one particular orbit to another—say, from $n = 2$ to $n = 1$ —always releases the same amount of energy, and the frequency of the light emitted because of this change is always precisely the same.

The success of Bohr's theory was in its ability to account for the Rydberg equation. When the atom emits a photon, an electron drops from a higher initial

Niels Bohr won the 1922 Nobel Prize in physics for his work on atomic structure.

Classical physical laws, such as those discovered by Issac Newton, place no restrictions on the sizes or energies of orbits.

Bohr's equation for the energy actually is

$$E = -\frac{2\pi^2me^4}{n^2h^2}$$

where m is the mass of the electron, e is the charge on the electron, n is the quantum number, and h is Planck's constant. Therefore, in Equation 8.3,

$$b = \frac{2\pi^2me^4}{h^2} = 2.18 \times 10^{-18} \text{ J}$$

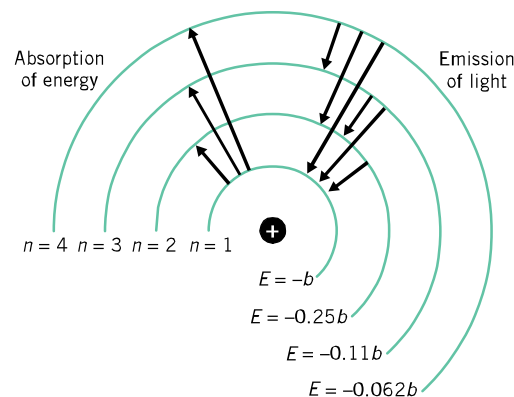


FIGURE 8.10 Absorption of energy and emission of light by the hydrogen atom. When the atom absorbs energy, the electron is raised to a higher energy level. When the electron falls to a lower energy level, light of a particular energy and frequency is emitted.

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energy E_h to a lower final energy E_l . If the initial quantum number of the electron is n_h and the final quantum number is n_l , then the energy change, calculated as a positive quantity, is

$$\begin{aligned}\Delta E &= E_h - E_l \\ &= \left(\frac{-b}{n_h^2}\right) - \left(\frac{-b}{n_l^2}\right)\end{aligned}$$

This can be rearranged to give

$$\Delta E = b \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right) \quad \text{with } n_h > n_l$$

By combining Equations 8.1 and 8.2, the relationship between the energy “ ΔE ” of a photon and its wavelength λ is

$$\Delta E = \frac{hc}{\lambda} = hc \left(\frac{1}{\lambda} \right)$$

Substituting and solving for $1/\lambda$ give

$$\frac{1}{\lambda} = \frac{b}{hc} \left(\frac{1}{n_l^2} - \frac{1}{n_h^2} \right) \quad \text{with } n_h > n_l$$

Notice how closely this equation derived from Bohr's theory matches the Rydberg equation, which was obtained solely from the experimentally measured atomic spectrum of hydrogen. Equally satisfying is that the combination of constants, b/hc , has a value of $109,730 \text{ cm}^{-1}$, which differs by only 0.05% from the experimentally derived value of R_H in the Rydberg equation.

The Bohr model fails for atoms with more than one electron

Bohr's model of the atom was both a success and a failure. By calculating the energy changes that occur between energy levels, Bohr was able to account for the Rydberg equation and, therefore, for the atomic spectrum of hydrogen. However, the theory was not able to explain quantitatively the spectra of atoms with more than one electron, and all attempts to modify the theory to make it work met with failure. Gradually, it became clear that Bohr's picture of the atom was flawed and that another theory would have to be found. Nevertheless, the concepts of quantum numbers and fixed energy levels were important steps forward.

8.3 Electron waves in atoms are called orbitals

All the objects that had been studied by scientists until the time of Bohr were large and massive in comparison with the electron, so no one had detected the limits of classical physics.

De Broglie was awarded a Nobel Prize in 1929.

Bohr's efforts to develop a theory of electronic structure were doomed from the very beginning because the classical laws of physics—those known in his day—simply do not apply to objects as small as the electron. Classical physics fails for atomic particles because matter is not really as our physical senses perceive it. When bound inside an atom, electrons behave not like solid particles, but instead like waves. This idea was proposed in 1924 by a young French graduate student, Louis de Broglie.

In Section 8.1 you learned that light waves are characterized by their wavelengths and their frequencies. The same is true of matter waves. De Broglie suggested that the wavelength of a matter wave, λ , is given by the equation

$$\lambda = \frac{h}{mv} \quad (8.4)$$

where h is Planck's constant, m is the particle's mass, and v is its velocity. Notice that this equation allows us to connect a wave property, wavelength, with particle

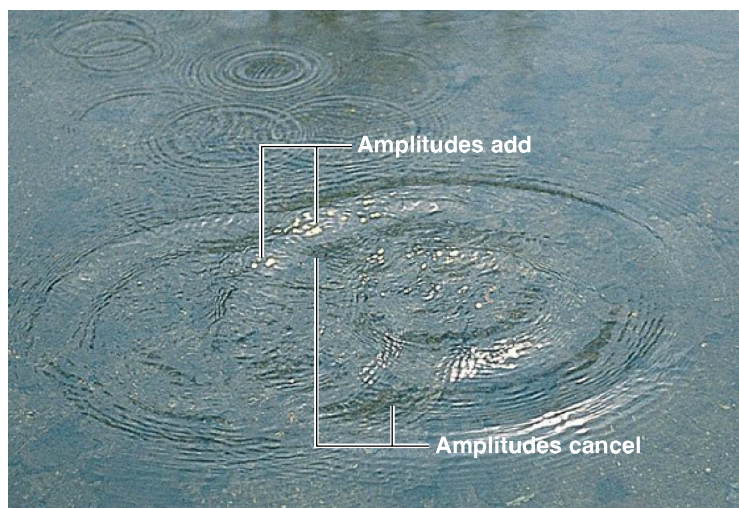


FIGURE 8.11 *Diffraction of water waves on the surface of a pond.* As the waves cross, the amplitudes increase where the waves are in phase and cancel where they are out of phase.

properties, mass and velocity. We may describe the electron either as a particle or a wave, and the de Broglie relationship provides a link between the two descriptions.

When first encountered, the concept of a particle of matter behaving as a wave rather than as a solid object is difficult to comprehend. This book certainly seems solid enough, especially if you drop it on your toe! The reason for the book's apparent solidity is that in de Broglie's equation (Equation 8.4) the mass appears in the denominator. This means that heavy objects have extremely short wavelengths. The peaks of the matter waves for heavy objects are so close together that the wave properties go unnoticed and can't even be measured experimentally. But tiny particles with very small masses have much longer wavelengths, so their wave properties become an important part of their overall behavior.

Perhaps by now you've begun to wonder if there is any way to *prove* that matter has wave properties. Actually, these properties can be demonstrated by a phenomenon that you have probably witnessed. When raindrops fall on a quiet pond, ripples spread out from where the drops strike the water, as shown in Figure 8.11. When two sets of ripples cross, there are places where the waves are *in phase*,

Gigantic waves, called *rogue waves*, with heights up to 100 ft have been observed in the ocean and are believed to be formed when a number of wave sets moving across the sea become in phase simultaneously.

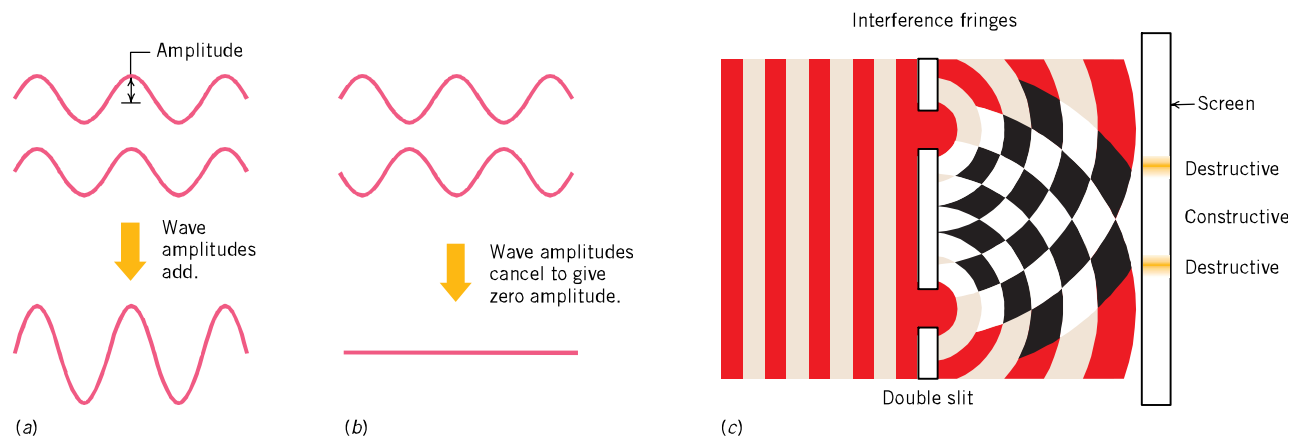


FIGURE 8.12 *Constructive and destructive interference.* (a) Waves in phase produce constructive interference and an increase in intensity. (b) Waves out of phase produce destructive interference and yield cancellation of intensity. (c) Light waves passing through two pinholes fan out and interfere with each other, producing an interference pattern characteristic of waves.



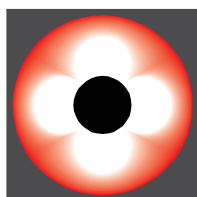
FIGURE 8.13 *Diffraction of light from a compact disc.* Colored interference fringes are produced by the diffraction of reflected light from the closely spaced grooves on the surface of a compact disc.

which means that the peak of one wave coincides with the peak of the other. At these points the intensities of the waves add and the height of the water is equal to the sum of the heights of the two crossing waves. At other places the crossing waves are *out of phase*, which means the peak of one wave occurs at the trough of the other. In these places the intensities of the waves cancel. This reinforcement and cancellation of wave intensities, referred to, respectively, as *constructive* and *destructive interference*, is a phenomenon called **diffraction**. It is examined more closely in Figure 8.12. Note how diffraction creates characteristic **interference fringes** when waves pass through adjacent pinholes or reflect off closely spaced grooves. You have seen interference fringes yourself if you've ever noticed the rainbow of colors that shine from the surface of a compact disc (Figure 8.13). When white light that contains radiations of all wavelengths is reflected from the closely spaced "grooves" on the CD, it is divided into many individual light beams. The light waves in these beams experience interference with each other, and for a given angle between the incoming and reflected light, all colors cancel except for one, which reinforces. Because we only see colors that reinforce, as the angle changes, so do the colors of the light we see.

Diffraction is a phenomenon that can only be explained as a property of waves, and we have seen how it can be demonstrated with water waves and light waves. Experiments can also be done to show that electrons, protons, and neutrons experience diffraction, which demonstrates their wave nature (see Figure 8.14). In fact, electron diffraction is the principle on which the electron microscope is based.

Bound electrons have quantized energies because they behave like standing waves

Before we can discuss how electron waves behave in atoms, we need to know a little more about waves in general. There are basically two kinds of waves, *traveling waves* and *standing waves*. On a lake or ocean the wind produces waves whose



(a)

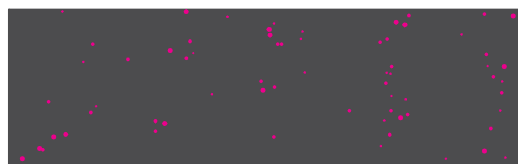
FIGURE 8.14 *Experimental evidence of the wave behavior of electrons.* (a) An electron diffraction pattern collected by reflecting a beam of electrons from crystalline silicon (Semiconductor Surface Physics Group, Queens University). (b) Electrons passing one at a time through a double slit. As more and more electrons are passed through the slits, interference fringes are observed.

Electrons passing through double slit:

1000



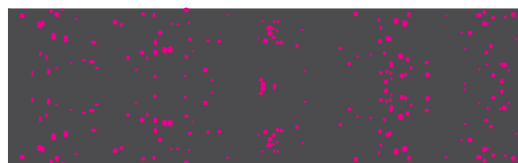
3000



20,000



70,000



(b)

crests and troughs move across the water's surface, as shown in Figure 8.15. The water moves up and down while the crests and troughs travel horizontally in the direction of the wind. These are examples of **traveling waves**.

A more important kind of wave for us is the standing wave. An example is the vibrating string of a guitar. When the string is plucked, its center vibrates up and down while the ends, of course, remain fixed. The crest, or point of maximum amplitude of the wave, occurs at one position. At the ends of the string are points of zero amplitude, called **nodes**, and their positions are also fixed. A **standing wave**, then, is one in which the crests and nodes do not change position. One of the interesting things about standing waves is that they lead naturally to "quantum numbers." Let's see how this works using the guitar as an example.

As you know, many notes can be played on a guitar string by shortening its effective length with a finger placed at frets along the neck of the instrument. But even without shortening the string, we can play a variety of notes. For instance, if the string is touched momentarily at its midpoint at the same time it is plucked, the string vibrates as shown in Figure 8.16 and produces a tone an octave higher. The wave that produces this higher tone has a wavelength exactly half of that formed when the untouched string is plucked. In Figure 8.16 we see that other wavelengths are possible, too, and each gives a different note.

If you examine Figure 8.16, you will see that there are some restrictions on the wavelengths that can exist. Not just any wavelength is possible because the nodes at either end of the string are in fixed positions. The only waves that can occur are those for which a half-wavelength is repeated *exactly* a whole number of times. Expressed another way, the length of the string is a whole-number multiple of half-wavelengths. In a mathematical form we could write this as

$$L = n \left(\frac{\lambda}{2} \right)$$

where L is the length of the string, λ is a wavelength (therefore, $\lambda/2$ is half the wavelength), and n is an integer. Rearranging this to solve for the wavelength gives

$$\lambda = \frac{2L}{n} \quad (8.5)$$

We see that the waves that are possible are determined quite naturally by a set of whole numbers (similar to quantum numbers).

We are now in a position to demonstrate how quantum theory unites wave and particle descriptions to build a simple but accurate model of a bound electron. Let's look at an electron that is confined to a wire of length L . To keep things simple, let's assume that the wire is infinitely thin, so that the electron can only move in straight lines along the wire. The wire is clamped in place at either end, and its ends cannot move up or down.

First, let's consider a classical particle model: the "bead on a wire" model shown in Figure 8.17a. The bead can slide in either direction along the wire, like a bead on an abacus. If the electron's mass is m and its velocity is v , its kinetic energy is given by

$$E = \frac{1}{2} mv^2$$

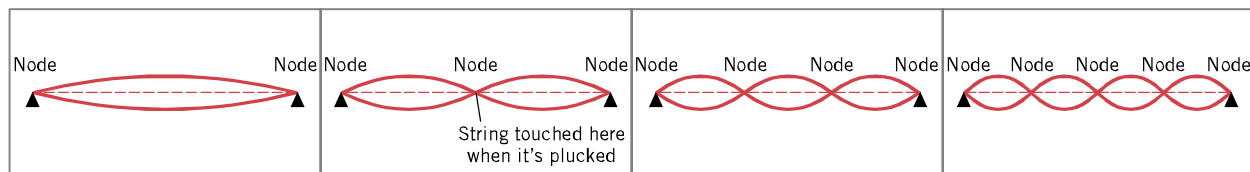


FIGURE 8.16 Standing waves on a guitar string.

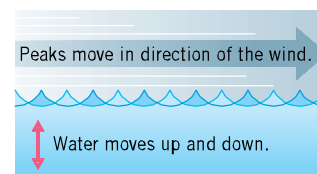


FIGURE 8.15 Traveling waves.

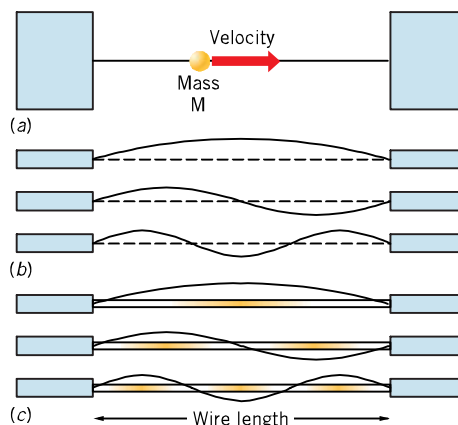
The wavelength of this wave is actually twice the length of the string.



Notes played on a guitar rely on standing waves. The ends of the strings correspond to nodes of the standing waves. Different notes can be played by shortening the effective lengths of the strings with fingers placed along the neck of the instrument.

Notes played this way are called *harmonics*.

FIGURE 8.17 Three models of an electron on an infinitely thin wire of length L . (a) a classical model of the electron as a bead that can slide along the wire. Any energy is possible, even zero, and the exact position and velocity of the bead can be known simultaneously. (b) a classical model of the electron as a standing wave on a wire. An integer number of peaks and troughs (n) is required. The wavelength is restricted to values given by Equation 8.5. (c) a quantum mechanical model of the electron on a wire obtained by uniting model (a) with model (b), using the de Broglie relationship (Equation 8.4). The dark areas indicate most probable positions for the electron. Energy is quantized and never zero.



The bead can have any velocity, even zero, so the energy E can have any value, even zero. No position on the wire is any more favorable than any other, and the bead is equally likely to be found anywhere on the wire. There is no reason why the bead's position and velocity cannot be known simultaneously.

Now consider a classical wave along the wire, Figure 8.17b. It is exactly like the guitar string we looked at in Figure 8.16. The ends of the wire are clamped in place, so there *must* be a whole number of peaks and troughs along the wire. The wavelength is restricted to values calculated by Equation 8.5. We can see that the quantum number, n , is just the number of peaks and troughs along the wave. It has integer values (1, 2, 3, . . .) because you can't have half a peak or half a trough.

Now let's use the de Broglie relation, Equation 8.4, to unite these two classical models. Our goal is to derive an expression for the energy of an electron trapped on the wire. Notice that to calculate the kinetic energy of the bead on a wire, we need to know its velocity, a particle property. The de Broglie relation lets us relate particle velocities with wavelengths. Rearranging Equation 8.4, we have

$$v = \frac{h}{m\lambda}$$

and inserting this equation for kinetic energy gives

$$\begin{aligned} E &= \frac{1}{2}m\left(\frac{h}{m\lambda}\right)^2 \\ &= \frac{h^2}{2m\lambda^2} \end{aligned}$$

This equation will give us the energy of the electron from its wavelength. If we substitute in Equation 8.5, which gives the wavelength of the standing wave in terms of the wire length L and the quantum number n , we have

$$E = \frac{n^2h^2}{8mL^2} \quad (8.6)$$

This equation has a number of profound implications. The fact that the electron's energy depends on an integer, n , means that *only certain energy states are allowed*. The allowed states are plotted on the energy-level diagram shown in Figure 8.18. The lowest value of n is 1, so the lowest energy level (the ground state) is $E = h^2/8mL^2$. Energies lower than this are not allowed, so the energy cannot be zero! This indicates that the electron will always have some residual kinetic energy. The electron is never at rest. This is true for the electron trapped in a wire and it is also

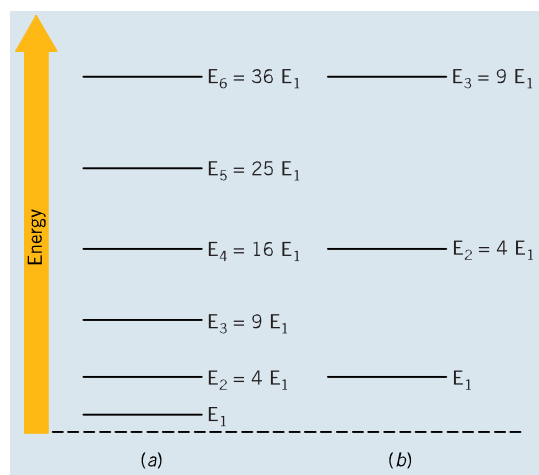


FIGURE 8.18 Energy-level diagram for the electron-on-a-wire model. (a) A long wire, with $L = 2$ nm. (b) A short wire, with $L = 1$ nm. Notice how the energy levels become more closely spaced when the electron has more room to move. Also notice that the energy in the ground state is not zero.

true for an electron trapped in an atom. Thus, *quantum theory resolves the collapsing atom paradox*.

Note that the spacing between energy levels is proportional to $1/L^2$. This means that when the wire is made longer, the energy levels become more closely spaced. In general, *the more room an electron has to move in, the smaller the spacings between its energy levels*. Chemical reactions sometimes change the way that electrons are confined in molecules. This causes changes in the wavelengths of light the reacting mixture absorbs. This is why color changes sometimes occur during chemical change.

The wave that corresponds to the electron is called a **wave function**. The wave function is usually represented by the symbol ψ (Greek letter *psi*). The wave function can be used to describe the shape of the electron wave and its energy. The wave function is not an oscillation of the wire, like a guitar wave, nor is it an electromagnetic wave. The wave's amplitude at any given point can be related to the probability of finding the electron there.

The electron waves shown in Figure 8.17c show that unlike the bead-on-a-wire model, the electron is more likely to be found at some places on the wire than others. For the ground state, with $n = 1$, the electron is most likely to be found in the center of the wire. Where the amplitude is zero—for example, at the ends of the wire or the center of the wire in the $n = 2$ state—there is a zero probability of finding the electron! Points where the amplitude of the electron wave is zero are called *nodes*. Notice that the higher the quantum number n , the more nodes the electron wave has, and from Equation 8.6, the more energy the electron has. It is generally true that *the more nodes an electron wave has, the higher its energy*.

The probability of finding an electron at a given point is proportional to the amplitude of the electron wave squared. Thus, peaks and troughs in the electron wave indicate places where there is the greatest buildup of negative charge.

Electron waves in atoms are called orbitals

In 1926 Erwin Schrödinger (1887–1961), an Austrian physicist, became the first scientist to successfully apply the concept of the wave nature of matter to an explanation of electronic structure. His work and the theory that developed from it are highly mathematical. Fortunately, we need only a qualitative understanding of electronic structure, and the main points of the theory can be understood without all the math.

Schrödinger developed an equation that can be solved to give wave functions and energy levels for electrons trapped inside atoms. Wave functions for electrons in atoms are called **orbitals**. Not all of the energies of the waves are different, but most are. *Energy changes within an atom are simply the result of an*

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Schrödinger won a Nobel Prize in 1933 for his work. The equation he developed that gives electronic wave functions and energies is known as *Schrödinger's equation*. The equation is extremely difficult to solve. Even an approximate solution of the equation for large molecules can require hours or days of supercomputer time.

Electron waves are described by the term *orbital* to differentiate them from the notion of *orbits*, which was part of the Bohr model of the atom.

“Most stable” almost always means “lowest energy.”

The term *shell* comes from an early notion that atoms could be thought of as similar to onions, with the electrons being arranged in layers around the nucleus.

Bohr was fortunate to have used the element hydrogen to develop his model of the atom. If he had chosen a different element, his model would not have worked.

ℓ is also called the *azimuthal quantum number* and the *orbital angular momentum number*.

Relationship between n and ℓ

Value of n	Values of ℓ
1	0
2	0, 1
3	0, 1, 2
4	0, 1, 2, 3
5	0, 1, 2, 3, 4
n	0, 1, 2, . . . , $(n - 1)$

The number of subshells in a given shell equals the value of n for that shell. For example, when $n = 3$, there are three subshells.

electron changing from a wave pattern with one energy to a wave pattern with a different energy.

We will be interested in two properties of orbitals, their energies and their shapes. Their energies are important because when an atom is in its most stable state (its **ground state**), the atom's electrons have waveforms with the lowest possible energies. The shapes of the wave patterns (i.e., where their amplitudes are large and where they are small) are important because the theory tells us that the amplitude of a wave at any particular place is related to the likelihood of finding the electron there. This will be important when we study how and why atoms form chemical bonds to each other.

In much the same way that the characteristics of a wave on a one-dimensional guitar string can be related to a single integer, wave mechanics tells us that the three-dimensional electron waves (orbitals) can be characterized by a set of *three* integer quantum numbers, n , ℓ , and m_ℓ . In discussing the energies of the orbitals, it is usually most convenient to sort the orbitals into groups according to these quantum numbers.

The principal quantum number, n

The quantum number n is called the **principal quantum number**, and all orbitals that have the same value of n are said to be in the same **shell**. The values of n can range from $n = 1$ to $n = \infty$. The shell with $n = 1$ is called the *first shell*, the shell with $n = 2$ is the *second shell*, and so forth. The various shells are also sometimes identified by letters, beginning (for no significant reason) with **K** for the first shell ($n = 1$), **L** for the second shell ($n = 2$), and so on.

The principal quantum number is related to the size of the electron wave (i.e., how far the wave effectively extends from the nucleus). The higher the value of n , the larger is the electron's average distance from the nucleus. This quantum number is also related to the energy of the orbital. As n increases, the energies of the orbitals also increase.

Bohr's theory took into account only the principal quantum number n . His theory worked fine for hydrogen because hydrogen just happens to be the one element in which all orbitals having the same value of n also have the same energy. Bohr's theory failed for atoms other than hydrogen, however, because when the atom has more than one electron, orbitals with the same value of n can have different energies.

The secondary quantum number, ℓ

The **secondary quantum number**, ℓ , divides the shells into smaller groups of orbitals called **subshells**. The value of n determines which values of ℓ are allowed. For a given n , ℓ can range from $\ell = 0$ to $\ell = (n - 1)$. Thus, when $n = 1$, $(n - 1) = 0$, so the only value of ℓ that's allowed is zero. This means that when $n = 1$, there is only one subshell (the shell and subshell are really identical). When $n = 2$, ℓ can have values of 0 or 1. (The maximum value of $\ell = n - 1 = 2 - 1 = 1$.) This means that when $n = 2$, there are two subshells. One has $n = 2$ and $\ell = 0$, and the other has $n = 2$ and $\ell = 1$. The relationship between n and the allowed values of ℓ are summarized in the table in the margin.

Subshells could be identified by their value of ℓ . However, to avoid confusing numerical values of n with those of ℓ , a letter code is normally used to specify the value of ℓ .

Value of ℓ	0	1	2	3	4	5	. . .
Letter designation	<i>s</i>	<i>p</i>	<i>d</i>	<i>f</i>	<i>g</i>	<i>h</i>	. . .

To designate a particular subshell, we write the value of its principal quantum number followed by the letter code for the subshell. For example, the subshell with $n = 2$ and $\ell = 1$ is the $2p$ subshell; the subshell with $n = 4$ and $\ell = 0$ is the $4s$