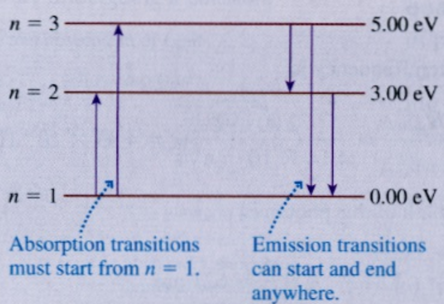
EXAMPLE 39.10 Emission and absorption

An atom has stationary states $E_1 = 0.00$ eV, $E_2 = 3.00$ eV, and $E_3 = 5.00$ eV. What wavelengths are observed in the absorption spectrum and in the emission spectrum of this atom?

MODEL Photons are emitted when an atom undergoes a quantum jump from a higher energy level to a lower energy level. Photons are absorbed in a quantum jump from a lower energy level to a higher energy level. But most of the atoms are in the $n = 1$ ground state, so the only quantum jumps seen in the absorption spectrum start from the $n = 1$ state.

VISUALIZE FIGURE 39.19 shows an energy-level diagram for the atom.

FIGURE 39.19 The atom's energy-level diagram.



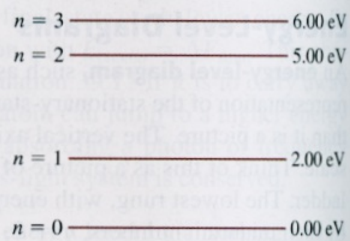
SOLVE This atom will absorb photons on the $1 \rightarrow 2$ and $1 \rightarrow 3$ transitions, with $\Delta E_{1\rightarrow 2} = 3.00$ eV and $\Delta E_{1\rightarrow 3} = 5.00$ eV. From $f = \Delta E_{atom}/h$ and $\lambda = c/f$, we find that the wavelengths in the absorption spectrum are

$$1 \rightarrow 2 \qquad f = 3.00 \text{ eV}/h = 7.25 \times 10^{14} \text{ Hz}$$
$$\lambda = 414 \text{ nm (blue)}$$
$$1 \rightarrow 3 \qquad f = 5.00 \text{ eV}/h = 1.21 \times 10^{15} \text{ Hz}$$
$$\lambda = 248 \text{ nm (ultraviolet)}$$

The emission spectrum will also have the 414 nm and 248 nm wavelengths due to the $2 \rightarrow 1$ and $3 \rightarrow 1$ quantum jumps from excited states 2 and 3 to the ground state. In addition, the emission spectrum will contain the $3 \rightarrow 2$ quantum jump with $\Delta E_{3\rightarrow 2} = -2.00$ eV that is *not* seen in absorption because there are too few atoms in the $n = 2$ state to absorb. We found in Example 39.9 that a 2.00 eV transition corresponds to a wavelength of 621 nm. Thus the emission wavelengths are

$$2 \rightarrow 1 \qquad \lambda = 414 \text{ nm (blue)}$$
$$3 \rightarrow 1 \qquad \lambda = 248 \text{ nm (ultraviolet)}$$
$$3 \rightarrow 2 \qquad \lambda = 621 \text{ nm (orange)}$$

STOP TO THINK 39.4 A photon with a wavelength of 414 nm has energy $E_{photon} = 3.00$ eV. Do you expect to see a spectral line with $\lambda = 414$ nm in the emission spectrum of the atom represented by this energy-level diagram? If so, what transition or transitions will emit it? Do you expect to see a spectral line with $\lambda = 414$ nm in the absorption spectrum? If so, what transition or transitions will absorb it?



39.6 The Bohr Hydrogen Atom

Bohr's hypothesis was a bold new idea, yet there was still one enormous stumbling block: What *are* the stationary states of an atom? Everything in Bohr's model hinges on the existence of these stationary states, of there being only certain electron orbits that are allowed. But nothing in classical physics provides any basis for such orbits. And Bohr's model describes only the *consequences* of having stationary states, not how to find them. If such states really exist, we will have to go beyond classical physics to find them.

To address this problem, Bohr did an explicit analysis of the hydrogen atom. The hydrogen atom, with only a single electron, was known to be the simplest atom. Furthermore, as we discussed in Chapters 25 and 38, Balmer had discovered a fairly simple formula that characterized the wavelengths in the hydrogen emission spectrum. Anyone with a successful model of an atom was going to have to *derive* Balmer's formula for the hydrogen atom.

Bohr's paper followed a rather circuitous line of reasoning. That is not surprising because he had little to go on at the time. But our goal is a clear explanation of the ideas, not a historical study of Bohr's methods, so we are going to follow a different analysis using de Broglie's matter waves. De Broglie did not propose matter waves until 1924, 11 years after Bohr's paper, but with the clarity of hindsight we can see that treating the electron as a wave provides a more straightforward analysis of the hydrogen atom. Although our route will be different from Bohr's, we will arrive at the same point, and, in addition, we will be in a much better position to understand the work that came after Bohr.

NOTE ▶ Bohr's analysis of the hydrogen atom is sometimes called the *Bohr atom.* It's important not to confuse this analysis, which applies only to hydrogen, with the more general postulates of the *Bohr model of the atom.* Those postulates, which we looked at in Section 39.5, apply to any atom. To make the distinction clear, we'll call Bohr's analysis of hydrogen the *Bohr hydrogen atom.* ◀

The Stationary States of the Hydrogen Atom

FIGURE 39.20 shows a Rutherford hydrogen atom, with a single electron orbiting a nucleus that consists of a single proton. We will assume a circular orbit of radius r and speed v. We will also assume, to keep the analysis manageable, that the proton remains stationary while the electron revolves around it. This is a reasonable assumption because the proton is roughly 1800 times as massive as the electron. With these assumptions, the atom's energy is the kinetic energy of the electron plus the potential energy of the electron-proton interaction. This is

$$E = K + U = \frac{1}{2}mv^2 + \frac{1}{4\pi\epsilon_0}\frac{q_{\text{elec}}q_{\text{proton}}}{r} = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \qquad (39.18)$$

where we used $q_{\text{elec}} = -e$ and $q_{\text{proton}} = +e$.

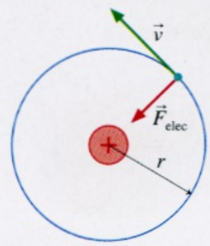


FIGURE 39.20 A Rutherford hydrogen atom. The size of the nucleus is greatly exaggerated.

NOTE ▶ m is the mass of the electron, *not* the mass of the entire atom. ◀

Now, the electron, as we are coming to understand it, has both particle-like and wave-like properties. First, let us treat the electron as a charged particle. The proton exerts a Coulomb electric force on the electron:

$$\vec{F}_{\text{elec}} = \left(\frac{1}{4\pi\epsilon_0}\frac{e^2}{r^2}, \text{toward center}\right) \qquad (39.19)$$

This force gives the electron an acceleration $\vec{a}_{\text{elec}} = \vec{F}_{\text{elec}}/m$ that also points to the center. This is a centripetal acceleration, causing the particle to move in its circular orbit. The centripetal acceleration of a particle moving in a circle of radius r at speed v *must* be v^2/r, thus

$$a_{\text{elec}} = \frac{F_{\text{elec}}}{m} = \frac{e^2}{4\pi\epsilon_0 mr^2} = \frac{v^2}{r} \qquad (39.20)$$

Rearranging, we find

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} \qquad (39.21)$$

Equation 39.21 is a *constraint* on the motion. The speed v and radius r must obey Equation 39.21 if the electron is to move in a circular orbit. This constraint is not unique to atoms. We earlier found a similar relationship between v and r for orbiting satellites.

Now let's treat the electron as a de Broglie wave. In Section 39.4 we found that a particle confined to a one-dimensional box sets up a standing wave as it reflects back and forth. A standing wave, you will recall, consists of two traveling waves moving in

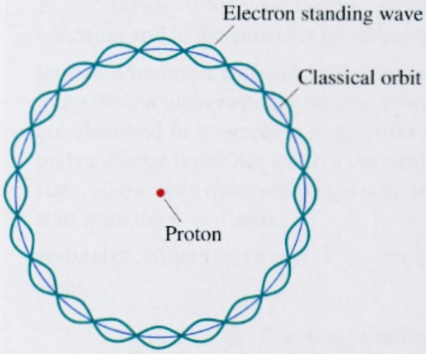


FIGURE 39.21 An $n = 10$ electron standing wave around the orbit's circumference.

opposite directions. When the round-trip distance in the box is equal to an integer number of wavelengths ($2L = n\lambda$), the two oppositely traveling waves interfere constructively to set up the standing wave.

Suppose that, instead of traveling back and forth along a line, our wave-like particle travels around the circumference of a circle. The particle will set up a standing wave, just like the particle in the box, if there are waves traveling in both directions and if the round-trip distance is an integer number of wavelengths. This is the idea we want to carry over from the particle in a box. As an example, **FIGURE 39.21** shows a standing wave around a circle with $n = 10$ wavelengths.

The mathematical condition for a circular standing wave is found by replacing the round-trip distance $2L$ in a box with the round-trip distance $2\pi r$ on a circle. Thus a circular standing wave will occur when

$$2\pi r = n\lambda \qquad n = 1, 2, 3, \ldots \tag{39.22}$$

But the de Broglie wavelength for a particle *has* to be $\lambda = h/p = h/mv$. Thus the standing-wave condition for a de Broglie wave is

$$2\pi r = n\frac{h}{mv}$$

This condition is true only if the electron's speed is

$$v_n = \frac{nh}{2\pi mr} \qquad n = 1, 2, 3, \ldots \tag{39.23}$$

The quantity $h/2\pi$ occurs so often in quantum physics that it is customary to give it a special name. We define the quantity $\hbar$, pronounced "h bar," as

$$\hbar \equiv \frac{h}{2\pi} = 1.055 \times 10^{-34}\ \text{J s} = 6.58 \times 10^{-16}\ \text{eV s}$$

With this definition, we can write Equation 39.23 as

$$v_n = \frac{n\hbar}{mr} \qquad n = 1, 2, 3, \ldots \tag{39.24}$$

This, like Equation 39.21, is another relationship between v and r. This is the constraint that arises from treating the electron as a wave.

Now if the electron can act as both a particle *and* a wave, then both the Equation 39.21 *and* Equation 39.24 constraints have to be obeyed. That is, v^2 as given by the Equation 39.21 particle constraint has to equal v^2 of the Equation 39.24 wave constraint. Equating these gives

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} = \frac{n^2\hbar^2}{m^2r^2}$$

We can solve this equation to find that the radius r is

$$r_n = n^2\frac{4\pi\epsilon_0\hbar^2}{me^2} \qquad n = 1, 2, 3, \ldots \tag{39.25}$$

where we have added a subscript n to the radius r to indicate that it depends on the integer n.

The right-hand side of Equation 39.25, except for the n^2, is just a collection of constants. Let's group them all together and define the **Bohr radius** a_B as

$$a_B = \text{Bohr radius} \equiv \frac{4\pi\epsilon_0\hbar^2}{me^2} = 5.29 \times 10^{-11}\ \text{m} = 0.0529\ \text{nm}$$

With this definition, Equation 39.25 for the radius of the electron's orbit becomes

$$r_n = n^2 a_B \qquad n = 1, 2, 3, \ldots \tag{39.26}$$

The first few allowed values of r_n are

$$r_n = \begin{cases} 0.053 \text{ nm} & n = 1 \\ 0.212 \text{ nm} & n = 2 \\ 0.476 \text{ nm} & n = 3 \\ \vdots & \vdots \end{cases}$$

We have discovered stationary states! That is, **a hydrogen atom can exist *only* if the radius of the electron's orbit is one of the values given by Equation 39.26.** Intermediate values of the radius, such as $r = 0.100$ nm, cannot exist because the electron cannot set up a standing wave around the circumference. The possible orbits are *quantized,* with only certain orbits allowed.

The key step leading to Equation 39.26 was the requirement that the electron have wave-like properties in addition to particle-like properties. This requirement leads to quantized orbits, or what Bohr called stationary states. The integer n is thus the *quantum number* that numbers the various stationary states.

Hydrogen Atom Energy Levels

Now we can make progress quickly. Knowing the possible radii, we can return to Equation 39.23 and find the possible electron speeds to be

$$v_n = \frac{n\hbar}{mr_n} = \frac{1}{n}\frac{\hbar}{ma_B} = \frac{v_1}{n} \qquad n = 1, 2, 3, \ldots \tag{39.27}$$

where $v_1 = \hbar/ma_B = 2.19 \times 10^6$ m/s is the electron's speed in the $n = 1$ orbit. The speed decreases as n increases.

Finally, we can determine the energies of the stationary states. From Equation 39.18 for the energy, with Equations 39.26 and 39.27 for r and v, we have

$$E_n = \frac{1}{2}mv_n^2 - \frac{e^2}{4\pi\epsilon_0 r_n} = \frac{1}{2}m\left(\frac{\hbar^2}{m^2 a_B^2 n^2}\right) - \frac{e^2}{4\pi\epsilon_0 n^2 a_B} \tag{39.28}$$

As a homework problem, you can show that this rather messy expression simplifies to

$$E_n = -\frac{1}{n^2}\left(\frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_B}\right) \tag{39.29}$$

Let's define

$$E_1 \equiv \frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_B} = 13.60 \text{ eV}$$

We can then write the energy levels of the stationary states of the hydrogen atom as

$$E_n = -\frac{E_1}{n^2} = -\frac{13.60 \text{ eV}}{n^2} \qquad n = 1, 2, 3, \ldots \tag{39.30}$$

This has been a lot of math, so we need to see where we are and what we have learned. Table 39.2 on the next page shows values of r_n, v_n, and E_n evaluated for quantum number values $n = 1$ to 5. We do indeed seem to have discovered stationary states of the hydrogen atom. Each state, characterized by its quantum number n, has a unique radius, speed, and energy. These are displayed graphically in **FIGURE 39.22**, on the next page, in which the orbits are drawn to scale. Notice how the atom's diameter increases very rapidly as n increases. At the same time, the electron's speed decreases.

FIGURE 39.22 The first four stationary states, or allowed orbits, of the Bohr hydrogen atom drawn to scale.

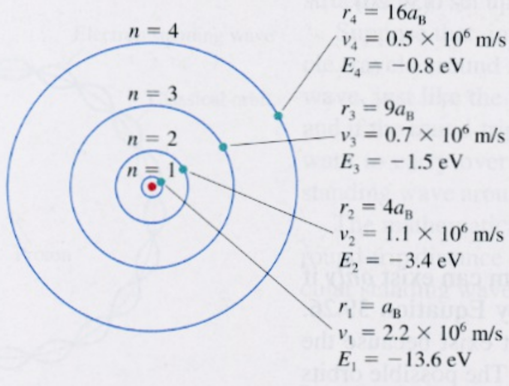


TABLE 39.2 Radii, speeds, and energies for the first five states of the Bohr hydrogen atom

n	r_n (nm)	v_n (m/s)	E_n (eV)
1	0.053	2.19×10^6	−13.60
2	0.212	1.09×10^6	−3.40
3	0.476	0.73×10^6	−1.51
4	0.846	0.55×10^6	−0.85
5	1.322	0.44×10^6	−0.54

EXAMPLE 39.11 Stationary states of the hydrogen atom

Can an electron in a hydrogen atom have a speed of 3.60×10^5 m/s? If so, what are its energy and the radius of its orbit? What about a speed of 3.65×10^5 m/s?

SOLVE To be in a stationary state, the electron must have speed

$$v_n = \frac{v_1}{n} = \frac{2.19 \times 10^6 \text{ m/s}}{n}$$

where n is an integer. A speed of 3.60×10^5 m/s would require quantum number

$$n = \frac{2.19 \times 10^6 \text{ m/s}}{3.60 \times 10^5 \text{ m/s}} = 6.08$$

This is not an integer, so the electron can *not* have this speed. But if $v = 3.65 \times 10^5$ m/s, then

$$n = \frac{2.19 \times 10^6 \text{ m/s}}{3.65 \times 10^5 \text{ m/s}} = 6$$

This is the speed of an electron in the $n = 6$ excited state. An electron in this state has energy

$$E_6 = -\frac{13.60 \text{ eV}}{6^2} = -0.38 \text{ eV}$$

and the radius of its orbit is

$$r_6 = 6^2(5.29 \times 10^{-11} \text{ nm}) = 1.90 \times 10^{-9} \text{ m} = 1.90 \text{ nm}$$

Binding Energy and Ionization Energy

It is important to understand why the energies of the stationary states are negative. Because the potential energy of two charged particles is $U = q_1q_2/4\pi\epsilon_0 r$, the zero of potential energy occurs at $r = \infty$ where the particles are infinitely far apart. The state of zero total energy corresponds to having the electron at rest ($K = 0$) and infinitely far from the proton ($U = 0$). This situation, which is the case of two "free particles," occurs in the limit $n \to \infty$, for which $r_n \to \infty$ and $v_n \to 0$.

An electron and a proton bound into an atom have *less* energy than two free particles. We know this because we would have to do work (i.e., add energy) to pull the electron and proton apart. If the bound atom has less energy than two free particles, and if the total energy of two free particles is zero, then it must be the case that the atom has a *negative* amount of energy.

Thus $|E_n|$ is the **binding energy** of the electron in stationary state n. In the ground state, where $E_1 = -13.60$ eV, we would have to add 13.60 eV to the electron to free it from the proton and reach the zero energy state of two free particles. We can say that the electron in the ground state is "bound by 13.60 eV." An electron in an $n = 3$ orbit, where it is farther from the proton and moving more slowly, is bound by only 1.51 eV. That is the amount of energy you would have to supply to remove the electron from an $n = 3$ orbit.

Removing the electron entirely leaves behind a positive ion, H^+ in the case of a hydrogen atom. (The fact that H^+ happens to be a proton does not alter the fact that it is also an atomic ion.) Because nearly all atoms are in their ground state, the binding energy $|E_1|$ of the ground state is called the **ionization energy** of an atom. Bohr's analysis predicts that the ionization energy of hydrogen is 13.60 eV. **FIGURE 39.23** illustrates the ideas of binding energy and ionization energy.

We can test this prediction by shooting a beam of electrons at hydrogen atoms. A projectile electron can knock out an atomic electron if its kinetic energy K is greater than the atom's ionization energy, leaving an ion behind. But a projectile electron will be unable to cause ionization if its kinetic energy is less than the atom's ionization energy. This is a fairly straightforward experiment to carry out, and the evidence shows that the ionization energy of hydrogen is, indeed, 13.60 eV.

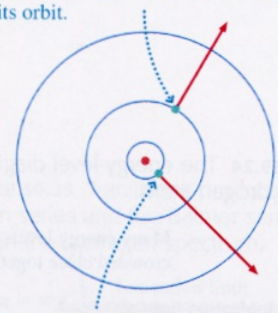


FIGURE 39.23 Binding energy and ionization energy.

Quantization of Angular Momentum

The angular momentum of a particle in circular motion, whether it is a planet or an electron, is

$$L = mvr$$

You will recall that angular momentum is conserved in orbital motion because a force directed toward a central point exerts no torque on the particle. Bohr used conservation of energy explicitly in his analysis of the hydrogen atom, but what role does conservation of angular momentum play?

The condition that a de Broglie wave for the electron set up a standing wave around the circumference was given, in Equation 39.22, as

$$2\pi r = n\lambda = n\frac{h}{mv}$$

We can rewrite this equation as

$$mvr = n\frac{h}{2\pi} = n\hbar \tag{39.31}$$

But mvr is the angular momentum L for a particle in a circular orbit. It appears that the angular momentum of an orbiting electron cannot have just any value. Instead, it must satisfy

$$L = n\hbar \qquad n = 1, 2, 3, \ldots \tag{39.32}$$

Thus angular momentum also is quantized! The electron's angular momentum must be an integer multiple of Planck's constant $\hbar$.

The quantization of angular momentum is a direct consequence of this wave-like nature of the electron. We will find that the quantization of angular momentum plays a major role in the behavior of more complex atoms, leading to the idea of electron shells that you likely have studied in chemistry.

STOP TO THINK 39.5 What is the quantum number of this hydrogen atom?