

30.3 Bohr's Theory of the Hydrogen Atom

Learning Objectives

By the end of this section, you will be able to:

- Describe the mysteries of atomic spectra.
- Explain Bohr's theory of the hydrogen atom.
- Explain Bohr's planetary model of the atom.
- Illustrate energy state using the energy-level diagram.
- Describe the triumphs and limits of Bohr's theory.

The great Danish physicist Niels Bohr (1885–1962) made immediate use of Rutherford's planetary model of the atom. (Figure 30.13). Bohr became convinced of its validity and spent part of 1912 at Rutherford's laboratory. In 1913, after returning to Copenhagen, he began publishing his theory of the simplest atom, hydrogen, based on the planetary model of the atom. For decades, many questions had been asked about atomic characteristics. From their sizes to their spectra, much was known about atoms, but little had been explained in terms of the laws of physics. Bohr's theory explained the atomic spectrum of hydrogen and established new and broadly applicable principles in quantum mechanics.

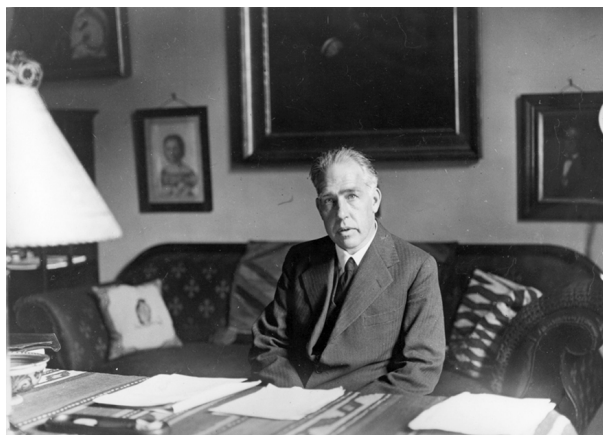


Figure 30.13 Niels Bohr, Danish physicist, used the planetary model of the atom to explain the atomic spectrum and size of the hydrogen atom. His many contributions to the development of atomic physics and quantum mechanics, his personal influence on many students and colleagues, and his personal integrity, especially in the face of Nazi oppression, earned him a prominent place in history. (credit: Unknown Author, via Wikimedia Commons)

Mysteries of Atomic Spectra

As noted in Quantization of Energy, the energies of some small systems are quantized. Atomic and molecular emission and absorption spectra have been known for over a century to be discrete (or quantized). (See Figure 30.14.)

Maxwell and others had realized that there must be a connection between the spectrum of an atom and its structure, something like the resonant frequencies of musical instruments. But, in spite of years of efforts by many great minds, no one had a workable theory. (It was a running joke that any theory of atomic and molecular spectra could be destroyed by throwing a book of data at it, so complex were the spectra.) Following Einstein's proposal of photons with quantized energies directly proportional to their wavelengths, it became even more evident that electrons in atoms can exist only in discrete orbits.

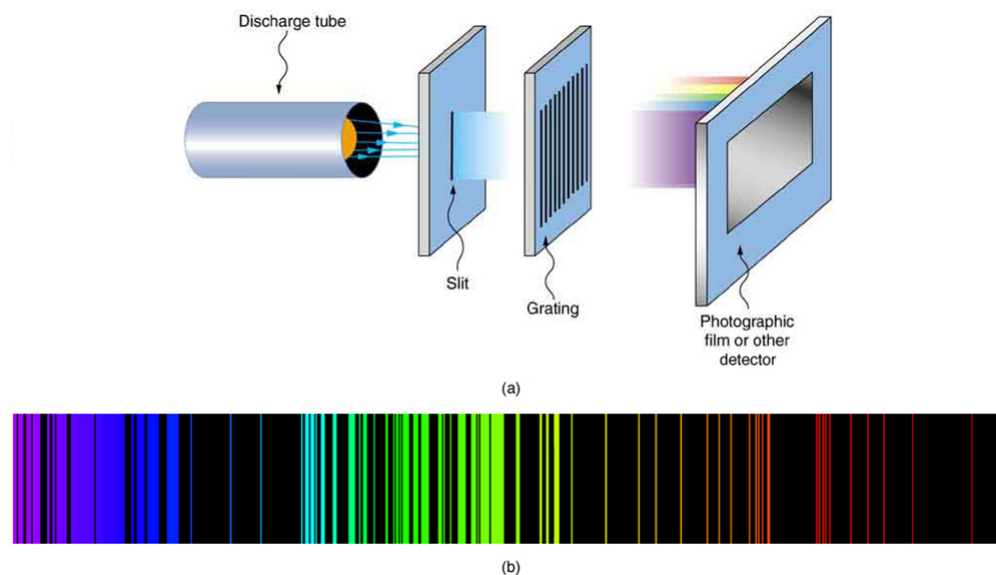


Figure 30.14 Part (a) shows, from left to right, a discharge tube, slit, and diffraction grating producing a line spectrum. Part (b) shows the emission line spectrum for iron. The discrete lines imply quantized energy states for the atoms that produce them. The line spectrum for each element is unique, providing a powerful and much used analytical tool, and many line spectra were well known for many years before they could be explained with physics. (credit for (b): Yttrium91, Wikimedia Commons)

In some cases, it had been possible to devise formulas that described the emission spectra. As you might expect, the simplest atom—hydrogen, with its single electron—has a relatively simple spectrum. The hydrogen spectrum had been observed in the infrared (IR), visible, and ultraviolet (UV), and several series of spectral lines had been observed. (See Figure 30.15.) These series are named after early researchers who studied them in particular depth.

The observed hydrogen-spectrum wavelengths can be calculated using the following formula:

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right),$$

30.13

where λ is the wavelength of the emitted EM radiation and R is the Rydberg constant, determined by the experiment to be

$$R = 1.097 \times 10^7 / \text{m} \text{ (or } \text{m}^{-1}\text{)}.$$

30.14

The constant n_f is a positive integer associated with a specific series. For the Lyman series, $n_f = 1$; for the Balmer series, $n_f = 2$; for the Paschen series, $n_f = 3$; and so on. The Lyman series is entirely in the UV, while part of the Balmer series is visible with the remainder UV. The Paschen series and all the rest are entirely IR. There are apparently an unlimited number of series, although they lie progressively farther into the infrared and become difficult to observe as n_f increases. The constant n_i is a positive integer, but it must be greater than n_f . Thus, for the Balmer series, $n_f = 2$ and $n_i = 3, 4, 5, 6, \dots$. Note that n_i can approach infinity. While the formula in the wavelengths equation was just a recipe designed to fit data and was not based on physical principles, it did imply a deeper meaning. Balmer first devised the formula for his series alone, and it was later found to describe all the other series by using different values of n_f . Bohr was the first to comprehend the deeper meaning. Again, we see the interplay between experiment and theory in physics. Experimentally, the spectra were well established, an equation was found to fit the experimental data, but the theoretical foundation was missing.

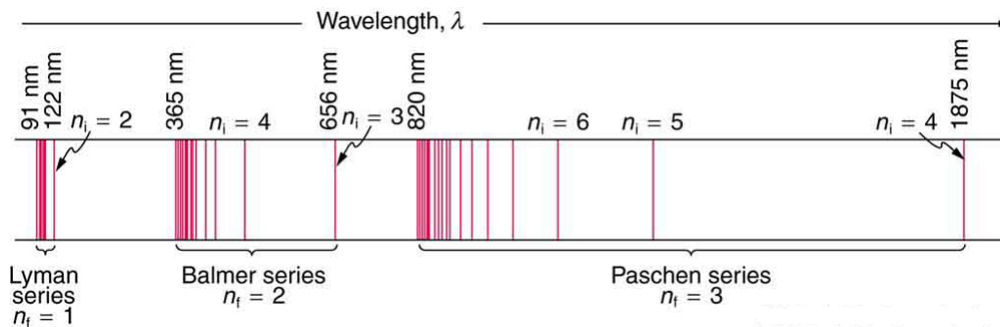


Figure 30.15 A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines.

Example 30.1

Calculating Wave Interference of a Hydrogen Line What is the distance between the slits of a grating that produces a first-order maximum for the second Balmer line at an angle of 15° ?

Strategy and Concept For an Integrated Concept problem, we must first identify the physical principles involved. In this example, we need to know (a) the wavelength of light as well as (b) conditions for an interference maximum for the pattern from a double slit. Part (a) deals with a topic of the present chapter, while part (b) considers the wave interference material of Wave Optics.

Solution for (a) Hydrogen spectrum wavelength. The Balmer series requires that $n_f = 2$. The first line in the series is taken to be for $n_i = 3$, and so the second would have $n_i = 4$.

The calculation is a straightforward application of the wavelength equation. Entering the determined values for n_f and n_i yields

$$\begin{aligned}\frac{1}{\lambda} &= R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \\ &= (1.097 \times 10^7 \text{ m}^{-1})\left(\frac{1}{2^2} - \frac{1}{4^2}\right) \\ &= 2.057 \times 10^6 \text{ m}^{-1}.\end{aligned}$$

30.15

Inverting to find λ gives

$$\begin{aligned}\lambda &= \frac{1}{2.057 \times 10^6 \text{ m}^{-1}} = 486 \times 10^{-9} \text{ m} \\ &= 486 \text{ nm}.\end{aligned}$$

30.16

Discussion for (a) This is indeed the experimentally observed wavelength, corresponding to the second (blue-green) line in the Balmer series. More impressive is the fact that the same simple recipe predicts *all* of the hydrogen spectrum lines, including new ones observed in subsequent experiments. What is nature telling us?

Solution for (b) Double-slit interference (Wave Optics). To obtain constructive interference for a double slit, the path length difference from two slits must be an integral multiple of the wavelength. This condition was expressed by the equation

$$d \sin \theta = m\lambda,$$

30.17

where d is the distance between slits and θ is the angle from the original direction of the beam. The number m is the order of the interference; $m = 1$ in this example. Solving for d and entering known values yields

$$d = \frac{(1)(486 \text{ nm})}{\sin 15^\circ} = 1.88 \times 10^{-6} \text{ m}.$$

30.18

Discussion for (b) This number is similar to those used in the interference examples of Introduction to Quantum Physics (and is close to the spacing between slits in commonly used diffraction glasses).

Bohr's Solution for Hydrogen

Bohr was able to derive the formula for the hydrogen spectrum using basic physics, the planetary model of the atom, and some very important new proposals. His first proposal is that only certain orbits are allowed: we say that *the orbits of electrons in atoms are quantized*. Each orbit has a different energy, and electrons can move to a higher orbit by absorbing energy and drop to a lower orbit by emitting energy. If the orbits are quantized, the amount of energy absorbed or emitted is also quantized, producing discrete spectra. Photon absorption and emission are among the primary methods of transferring energy into and out of atoms. The energies of the photons are quantized, and their energy is explained as being equal to the change in energy of the electron when it moves from one orbit to another. In equation form, this is

$$\Delta E = hf = E_i - E_f.$$

30.19

Here, ΔE is the change in energy between the initial and final orbits, and hf is the energy of the absorbed or emitted photon. It is quite logical (that is, expected from our everyday experience) that energy is involved in changing orbits. A blast of energy is required for the space shuttle, for example, to climb to a higher orbit. What is not expected is that atomic orbits should be quantized. This is not observed for satellites or planets, which can have any orbit given the proper energy. (See Figure 30.16.)

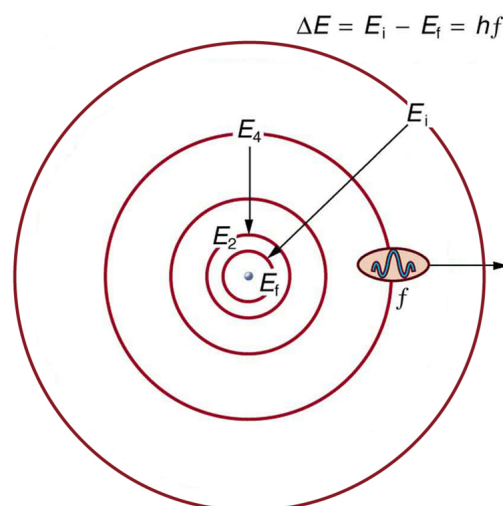


Figure 30.16 The planetary model of the atom, as modified by Bohr, has the

orbits of the electrons quantized. Only certain orbits are allowed, explaining why atomic spectra are discrete (quantized). The energy carried away from an atom by a photon comes from the electron dropping from one allowed orbit to another and is thus quantized. This is likewise true for atomic absorption of photons.

Figure 30.17 shows an energy-level diagram, a convenient way to display energy states. In the present discussion, we take these to be the allowed energy levels of the electron. Energy is plotted vertically with the lowest or ground state at the bottom and with excited states above. Given the energies of the lines in an atomic spectrum, it is possible (although sometimes very difficult) to determine the energy levels of an atom. Energy-level diagrams are used for many systems, including molecules and nuclei. A theory of the atom or any other system must predict its energies based on the physics of the system.

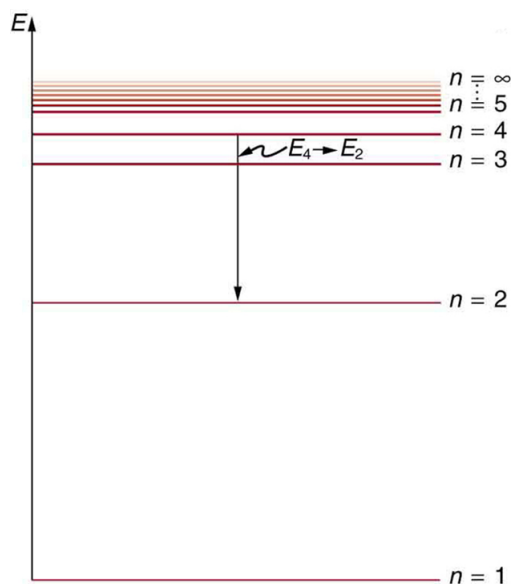


Figure 30.17 An energy-level diagram plots energy vertically and is useful in visualizing the energy states of a system and the transitions between them. This diagram is for the hydrogen-atom electrons, showing a transition between two orbits having energies E_4 and E_2 .

Bohr was clever enough to find a way to calculate the electron orbital energies in hydrogen. This was an important first step that has been improved upon, but it is well worth repeating here, because it does correctly describe many characteristics of hydrogen. Assuming circular orbits, Bohr proposed that the **angular momentum L of an electron in its orbit is quantized**, that is, it has only specific, discrete values. The value for L is given by the formula

$$L = m_e v r_n = n \frac{h}{2\pi} (n = 1, 2, 3, \dots),$$

30.20

where L is the angular momentum, m_e is the electron's mass, r_n is the radius of the n th orbit, and h is Planck's constant. Note that angular momentum is $L = I\omega$. For a small object at a radius r , $I = mr^2$ and $\omega = v/r$, so that $L = (mr^2)(v/r) = mvr$. Quantization says that this value of mvr can only be equal to $h/2$, $2h/2$, $3h/2$, etc. At the time, Bohr himself did not know why angular momentum should be quantized, but using this assumption he was able to calculate the energies in the hydrogen spectrum, something no one else had done at the time.

From Bohr's assumptions, we will now derive a number of important properties of the hydrogen atom from the classical physics we have covered in the text. We start by noting the centripetal force causing the electron to follow a circular path is supplied by the Coulomb force. To be more general, we note that this analysis is valid for any single-electron atom. So, if a nucleus has Z protons ($Z = 1$ for hydrogen, 2 for helium, etc.) and only one electron, that atom is called a hydrogen-like atom. The spectra of hydrogen-like ions are similar to hydrogen, but shifted to higher energy by the greater attractive force between the electron and nucleus. The magnitude of the centripetal force is $m_e v^2 / r_n$, while the Coulomb force is $k(Zq_e)(q_e) / r_n^2$. The tacit assumption here is that the nucleus is more massive than the stationary electron, and the electron orbits about it. This is consistent with the planetary model of the atom. Equating these,

$$k \frac{Zq_e^2}{r_n^2} = \frac{m_e v^2}{r_n} (\text{Coulomb} = \text{centripetal}).$$

30.21

Angular momentum quantization is stated in an earlier equation. We solve that equation for v , substitute it into the above, and rearrange the expression to obtain the radius of the orbit. This yields:

$$r_n = \frac{n^2}{Z} a_B, \text{ for allowed orbits } (n = 1, 2, 3, \dots),$$

30.22

where a_B is defined to be the Bohr radius, since for the lowest orbit ($n = 1$) and for hydrogen ($Z = 1$), $r_1 = a_B$. It is left for this chapter's Problems and Exercises to show that the Bohr radius is

$$a_B = \frac{h^2}{4\pi^2 m_e k q_e^2} = 0.529 \times 10^{-10} \text{ m}.$$

30.23

These last two equations can be used to calculate the **radii of the allowed (quantized) electron orbits in any hydrogen-like atom**. It is impressive that the formula gives the correct size of hydrogen, which is measured experimentally to be very close to the Bohr radius. The earlier equation also tells us that the orbital radius is proportional to n^2 , as illustrated in Figure 30.18.

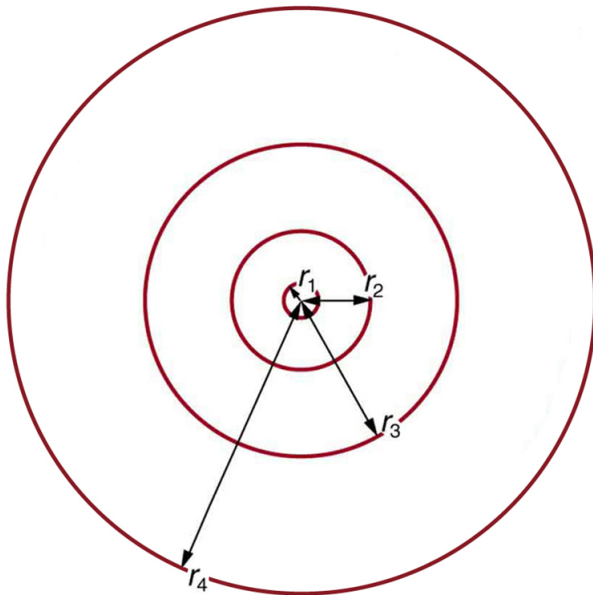


Figure 30.18 The allowed electron orbits in hydrogen have the radii shown. These radii were first calculated by Bohr and are given by the equation $r_n = \frac{n^2}{Z} a_B$. The lowest orbit has the experimentally verified diameter of a hydrogen atom.

To get the electron orbital energies, we start by noting that the electron energy is the sum of its kinetic and potential energy:

$$E_n = \text{KE} + \text{PE}.$$

30.24

Kinetic energy is the familiar $\text{KE} = (1/2)m_e v^2$, assuming the electron is not moving at relativistic speeds. Potential energy for the electron is electrical, or $\text{PE} = q_e V$, where V is the potential due to the nucleus, which looks like a point charge. The nucleus has a positive charge Zq_e ; thus, $V = kZq_e/r_n$, recalling an earlier equation for the potential due to a point charge. Since the electron's charge is negative, we see that $\text{PE} = -kZq_e/r_n$. Entering the expressions for KE and PE, we find

$$E_n = \frac{1}{2}m_e v^2 - k \frac{Zq_e^2}{r_n}.$$

30.25

Now we substitute r_n and v from earlier equations into the above expression for energy. Algebraic manipulation yields

$$E_n = -\frac{Z^2}{n^2} E_0 (n = 1, 2, 3, \dots)$$

30.26

for the orbital energies of hydrogen-like atoms. Here, E_0 is the **ground-state energy** ($n = 1$) for hydrogen ($Z = 1$) and is given by

$$E_0 = \frac{2\pi^2 q_e^4 m_e k^2}{h^2} = 13.6 \text{ eV}.$$

30.27

Thus, for hydrogen,

$$E_n = -\frac{13.6 \text{ eV}}{n^2} (n = 1, 2, 3, \dots).$$

30.28

Figure 30.19 shows an energy-level diagram for hydrogen that also illustrates how the various spectral series for hydrogen are related to transitions between energy levels.

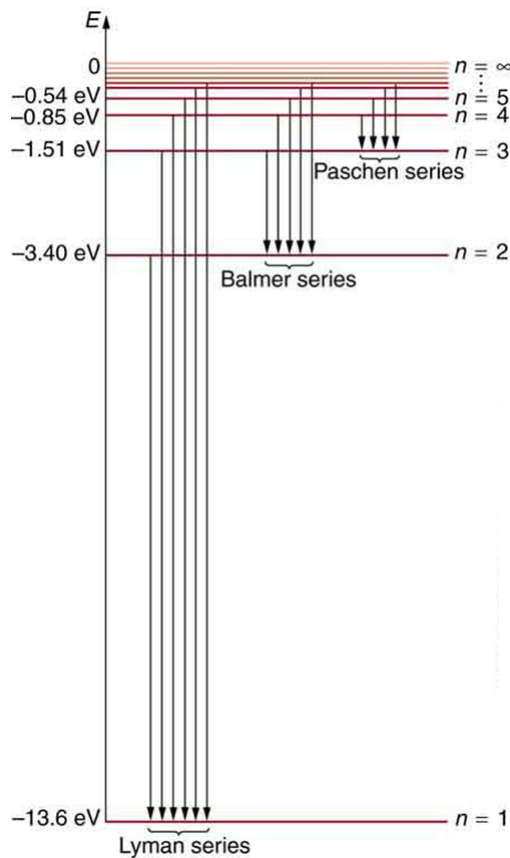


Figure 30.19 Energy-level diagram for hydrogen showing the Lyman, Balmer, and Paschen series of transitions. The orbital energies are calculated using the above equation, first derived by Bohr.

Electron total energies are negative, since the electron is bound to the nucleus,

analogous to being in a hole without enough kinetic energy to escape. As n approaches infinity, the total energy becomes zero. This corresponds to a free electron with no kinetic energy, since r_n gets very large for large n , and the electric potential energy thus becomes zero. Thus, 13.6 eV is needed to ionize hydrogen (to go from -13.6 eV to 0, or unbound), an experimentally verified number. Given more energy, the electron becomes unbound with some kinetic energy. For example, giving 15.0 eV to an electron in the ground state of hydrogen strips it from the atom and leaves it with 1.4 eV of kinetic energy.

Finally, let us consider the energy of a photon emitted in a downward transition, given by the equation to be

$$\Delta E = hf = E_i - E_f.$$

30.29

Substituting $E_n = (-13.6 \text{ eV}/n^2)$, we see that

$$hf = (13.6 \text{ eV}) \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

30.30

Dividing both sides of this equation by hc gives an expression for $1/\lambda$:

$$\frac{hf}{hc} = \frac{f}{c} = \frac{1}{\lambda} = \frac{(13.6 \text{ eV})}{hc} \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right).$$

30.31

It can be shown that

$$\left(\frac{13.6 \text{ eV}}{hc} \right) = \frac{(13.6 \text{ eV})(1.602 \times 10^{-19} \text{ J/eV})}{(6.626 \times 10^{-34} \text{ J} \cdot \text{s})(2.998 \times 10^8 \text{ m/s})} = 1.097 \times 10^7 \text{ m}^{-1} = R$$

30.32

is the Rydberg constant. Thus, we have used Bohr's assumptions to derive the formula first proposed by Balmer years earlier as a recipe to fit experimental data.

$$\frac{1}{\lambda} = R \left(\frac{1}{n_f^2} - \frac{1}{n_i^2} \right)$$

30.33

We see that Bohr's theory of the hydrogen atom answers the question as to why this previously known formula describes the hydrogen spectrum. It is because the energy levels are proportional to $1/n^2$, where n is a non-negative integer. A downward transition releases energy, and so n_i must be greater than n_f . The various series are those where the transitions end on a certain level. For the Lyman series, $n_f = 1$ — that is, all the transitions end in the ground state (see also Figure 30.19). For the Balmer series, $n_f = 2$, or all the transitions end in the first excited state; and so on. What was once a recipe is now based in physics, and something new is emerging—angular momentum is quantized.

Triumphs and Limits of the Bohr Theory

Bohr did what no one had been able to do before. Not only did he explain the spectrum of hydrogen, he correctly calculated the size of the atom from basic physics. Some of his ideas are broadly applicable. Electron orbital energies are quantized in all atoms and molecules. Angular momentum is quantized. The electrons do not spiral into the nucleus, as expected classically (accelerated charges radiate, so that the electron orbits classically would decay quickly, and the electrons would sit on the nucleus—matter would collapse). These are major triumphs.

But there are limits to Bohr's theory. It cannot be applied to multielectron atoms, even one as simple as a two-electron helium atom. Bohr's model is what we call *semiclassical*. The orbits are quantized (nonclassical) but are assumed to be simple circular paths (classical). As quantum mechanics was developed, it became clear that there are no well-defined orbits; rather, there are clouds of probability. Bohr's theory also did not explain that some spectral lines are doublets (split into two) when examined closely. We shall examine many of these aspects of quantum mechanics in more detail, but it should be kept in mind that Bohr did not fail. Rather, he made very important steps along the path to greater knowledge and laid the foundation for all of atomic physics that has since evolved.

PhET Explorations

Models of the Hydrogen Atom How did scientists figure out the structure of atoms without looking at them? Try out different models by shooting light at the atom. Check how the prediction of the model matches the experimental results.

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