

39.7 The Hydrogen Spectrum

Our analysis of the hydrogen atom has revealed stationary states, but how do we know whether the results make any sense? The most important experimental evidence that we have about the hydrogen atom is its spectrum, so the primary test of the Bohr hydrogen atom is whether it correctly predicts the spectrum.

The Hydrogen Energy-Level Diagram

FIGURE 39.24 The energy-level diagram of the hydrogen atom.

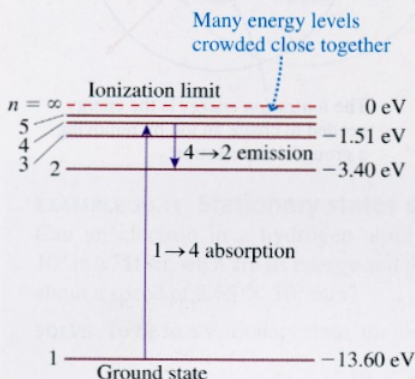


FIGURE 39.24 is an energy-level diagram for the hydrogen atom. As we noted earlier, the energies are like the rungs of a ladder. The lowest rung is the ground state, with $E_1 = -13.60$ eV. The top rung, with $E = 0$ eV, corresponds to a hydrogen ion in the limit $n \rightarrow \infty$. This top rung is called the **ionization limit**. In principle there are an infinite number of rungs, but only the lowest few are shown. The higher values of n are all crowded together just below the ionization limit at $n = \infty$.

The figure shows a $1 \rightarrow 4$ transition in which a photon is absorbed and a $4 \rightarrow 2$ transition in which a photon is emitted. For two quantum states m and n , where $n > m$ and E_n is the higher energy state, an atom can *emit* a photon in an $n \rightarrow m$ transition or *absorb* a photon in an $m \rightarrow n$ transition.

The Emission Spectrum

According to the fifth assumption of Bohr's model of atomic quantization, the frequency of the photon emitted in an $n \rightarrow m$ transition is

$$f = \frac{\Delta E_{\text{atom}}}{h} = \frac{E_n - E_m}{h} \quad (39.33)$$

We can use Equation 39.29 for the energies E_n and E_m to predict that the emitted photon has frequency

$$\begin{aligned} f &= \frac{1}{h} \left\{ \left[-\frac{1}{n^2} \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} \right) \right] - \left[-\frac{1}{m^2} \left(\frac{1}{4\pi\epsilon_0} \frac{e^2}{2a_B} \right) \right] \right\} \\ &= \frac{1}{4\pi\epsilon_0} \frac{e^2}{2ha_B} \left(\frac{1}{m^2} - \frac{1}{n^2} \right) \end{aligned} \quad (39.34)$$

The frequency is a positive number because $m < n$ and thus $1/m^2 > 1/n^2$.

We are more interested in wavelength than frequency, because wavelengths are the quantity measured by experiment. The wavelength of the photon emitted in an $n \rightarrow m$ quantum jump is

$$\lambda_{n \rightarrow m} = \frac{c}{f} = \frac{8\pi\epsilon_0 h c a_B / e^2}{\left(\frac{1}{m^2} - \frac{1}{n^2} \right)} \quad (39.35)$$

This looks rather gruesome, but notice that the numerator is simply a collection of various constants. The value of the numerator, which we can call λ_0 , is

$$\lambda_0 = \frac{8\pi\epsilon_0 h c a_B}{e^2} = 9.112 \times 10^{-8} \text{ m} = 91.12 \text{ nm}$$

With this definition, our prediction for the wavelengths in the hydrogen emission spectrum is

$$\lambda_{n \rightarrow m} = \frac{\lambda_0}{\left(\frac{1}{m^2} - \frac{1}{n^2} \right)} \quad m = 1, 2, 3, \dots \quad n = m + 1, m + 2, \dots \quad (39.36)$$

This should look familiar. It is the Balmer formula from Chapter 38! However, there is one *slight* difference: Bohr's analysis of the hydrogen atom has predicted

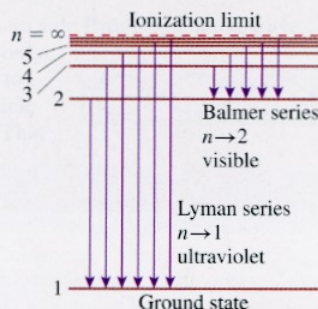
$\lambda_0 = 91.12 \text{ nm}$, whereas Balmer found, from experiment, that $\lambda_0 = 91.18 \text{ nm}$. Could Bohr have come this close but then fail to predict the Balmer formula correctly?

The problem, it turns out, is in our assumption that the proton remains at rest while the electron orbits it. In fact, *both* particles rotate about their common center of mass, rather like a dumbbell with a big end and a small end. The center of mass is very close to the proton, which is far more massive than the electron, but the proton is not entirely motionless. The good news is that a more advanced analysis can account for the proton's motion. It changes the energies of the stationary states ever so slightly—about 1 part in 2000—but that is precisely what is needed to give a revised value:

$$\lambda_0 = 91.18 \text{ nm when corrected for the nuclear motion}$$

It works! Unlike all previous atomic models, the **Bohr hydrogen atom correctly predicts the discrete spectrum of the hydrogen atom**. FIGURE 39.25 shows the *Balmer series* and the *Lyman series* transitions on an energy-level diagram. Only the Balmer series, consisting of transitions ending on the $m = 2$ state, gives visible wavelengths, and this is the series that Balmer initially analyzed. The Lyman series, ending on the $m = 1$ ground state, is in the ultraviolet region of the spectrum and was not measured until later. These series, as well as others in the infrared, are observed in a discharge tube where collisions with electrons excite the atoms upward from the ground state to state n . They then decay downward by emitting photons. Only the Lyman series is observed in the absorption spectrum because, as noted previously, essentially all the atoms in a quiescent gas are in the ground state.

FIGURE 39.25 Transitions producing the Lyman series and the Balmer series of lines in the hydrogen spectrum.



EXAMPLE 39.12 Hydrogen absorption

Whenever astronomers look at distant galaxies, they find that the light has been strongly absorbed at the wavelength of the $1 \rightarrow 2$ transition in the Lyman series of hydrogen. This absorption tells us that interstellar space is filled with vast clouds of hydrogen left over from the Big Bang. What is the wavelength of the $1 \rightarrow 2$ absorption in hydrogen?

SOLVE Equation 39.36 predicts the *absorption* spectrum of hydrogen if we let $m = 1$. The absorption seen by astronomers is from the ground state of hydrogen ($m = 1$) to its first excited state ($n = 2$). The wavelength is

$$\lambda_{1 \rightarrow 2} = \frac{91.18 \text{ nm}}{\left(\frac{1}{1^2} - \frac{1}{2^2}\right)} = 121.6 \text{ nm}$$

ASSESS This wavelength is far into the ultraviolet. Ground-based astronomy cannot observe this region of the spectrum because the wavelengths are strongly absorbed by the atmosphere, but with space-based telescopes, first widely used in the 1970s, astronomers see 121.6 nm absorption in nearly every direction they look.

Hydrogen-Like Ions

An ion with a *single* electron orbiting Z protons in the nucleus is called a **hydrogen-like ion**. Z is the atomic number and describes the number of protons in the nucleus. He^+ , with one electron circling a $Z = 2$ nucleus, and Li^{++} , with one electron and a $Z = 3$ nucleus, are hydrogen-like ions. So is U^{91+} , with one lonely electron orbiting a $Z = 92$ uranium nucleus.

Any hydrogen-like ion is simply a variation on the Bohr hydrogen atom. The only difference between a hydrogen-like ion and neutral hydrogen is that the potential energy $-e^2/4\pi\epsilon_0 r$ becomes, instead, $-Ze^2/4\pi\epsilon_0 r$. Hydrogen itself is the $Z = 1$ case. If we repeat the analysis of the previous sections with this one change, we find:

$$\begin{aligned} r_n &= \frac{n^2 a_B}{Z} \\ v_n &= Z \frac{v_1}{n} \\ E_n &= -\frac{13.60 Z^2 \text{ eV}}{n^2} \\ \lambda_0 &= \frac{91.18 \text{ nm}}{Z^2} \end{aligned} \quad (39.37)$$

As the nuclear charge increases, the electron moves into a smaller-diameter, higher-speed orbit. Its ionization energy $|E_1|$ increases significantly, and its spectrum shifts to shorter wavelengths. Table 39.3 compares the ground-state atomic diameter $2r_1$, the ionization energy $|E_1|$, and the first wavelength $3 \rightarrow 2$ in the Balmer series for hydrogen and the first two hydrogen-like ions.

TABLE 39.3 Comparison of hydrogen-like ions with $Z = 1, 2$, and 3

Ion	Diameter $2r_1$	Ionization energy $ E_1 $	Wavelength of $3 \rightarrow 2$
H ($Z = 1$)	0.106 nm	13.6 eV	656 nm
He ⁺ ($Z = 2$)	0.053 nm	54.4 eV	164 nm
Li ²⁺ ($Z = 3$)	0.035 nm	125.1 eV	73 nm

Success and Failure

Bohr's analysis of the hydrogen atom seemed to be a resounding success. By introducing Einstein's ideas about light quanta, Bohr was able to provide the first understanding of discrete spectra and to predict the Balmer formula for the wavelengths in the hydrogen spectrum. And the Bohr hydrogen atom, unlike Rutherford's model, was stable. There was clearly some validity to the idea of stationary states.

But Bohr was completely unsuccessful at explaining the spectra of any other neutral atom. His method did not work even for helium, the second element in the periodic table with a mere two electrons. Something inherent in Bohr's assumptions seemed to work correctly for a single electron but not in situations with two or more electrons.

It is important to make a distinction between the Bohr model of atomic quantization, described in Section 39.5, and the Bohr hydrogen atom. The Bohr model assumes that stationary states exist, but it does not say how to find them. We found the stationary states of a hydrogen atom by requiring that an integer number of de Broglie waves fit around the circumference of the orbit, setting up standing waves. The difficulty with more complex atoms is not the Bohr model but the method of finding the stationary states. Bohr's model of the atomic quantization remains valid, and we will continue to use it, but the procedure of fitting standing waves to a circle is just too simple to find the stationary states of complex atoms. We need to find a better procedure.

Einstein, de Broglie, and Bohr carried physics into uncharted waters. Their successes made it clear that the microscopic realm of light and atoms is governed by quantization, discreteness, and a blurring of the distinction between particles and waves. Although Bohr was clearly on the right track, his inability to extend the Bohr hydrogen atom to more complex atoms made it equally clear that the complete and correct theory remained to be discovered. Bohr's theory was what we now call "semi-classical," a hybrid of classical Newtonian mechanics with the new ideas of quanta. Still missing was a complete theory of motion and dynamics in a quantized universe—a *quantum mechanics*.