12.7: Bohr’s Theory of the Hydrogen Atom

Learning Objectives

- Describe early atomic models.
- Explain Bohr’s theory of the hydrogen atom.
- Distinguish between correct and incorrect features of the Bohr model, in light of modern quantum mechanics.

The great Danish physicist Niels Bohr (1885–1962) made immediate use of Rutherford’s planetary model of the atom. (Figure $12.7.1$). 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.

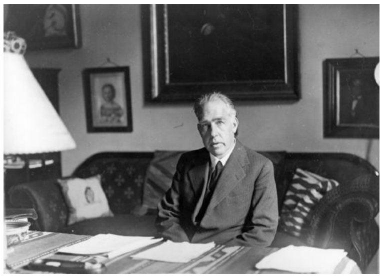

Figure 12.7.1: Niels Bohr, Danish physicist, used the planetary model of the atom to explain the atomic spectrum and size of the hydrogen atom. His many contributions to the development of atomic physics and quantum mechanics, his personal influence on many students and colleagues, and his personal integrity, especially in the face of Nazi oppression, earned him a prominent place in history. (credit: Unknown Author, via Wikimedia Commons)

Atomic Spectra

Atomic and molecular emission and absorption spectra have been known for over a century to be discrete (or quantized). Well before they were understood from first principles, chemists have been using the emission and absorption spectra for identification of elements. Figure $12.7.2$ shows iron emission spectrum, for example. No other elements emit the exactly the same set of frequencies of light. With the discovery of substructure of the atom and the discovery of photon (or more precisely, refined understanding of the particle nature of electromagnetic waves where the particle energy is proportional to the frequency of electromagnetic waves), these resonant frequencies of light emitted by atoms could be used to infer an atomic model.

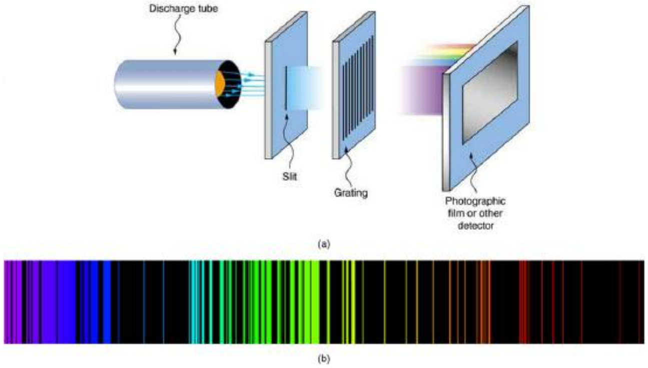

Figure 12.7.2: Part (a) shows, from left to right, a discharge tube, slit, and diffraction grating producing a line spectrum. Part (b) shows the emission line spectrum for iron. The discrete lines imply quantized energy states for the atoms that produce them. The line spectrum for each element is unique, 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)

For the hydrogen atom, the lightest element with the simplest atom, a pattern for its line spectrum was noticed by experimentalists (see Figure $12.7.3$). All wavelengths of the line spectrum could be described by a following formula, for the suitable choice of two integers n_i and n_f:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right), \tag{12.7.1}$$

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

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

The n_f is a positive integer associated with a specific series, which are named after their discoverers. 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 n_i is a positive integer greater than n_f. So for example, for the Balmer series, $n_f = 2$ and $n_i = 3, 4, 5, 6, \ldots$.

So, before Bohr's model of the hydrogen atom, such was the picture of atomic theory—full of suggestive (and even well-organized) data and no unifying explanation. Ernest Rutherford is quoted as saying, "All science is either physics or stamp-collecting." What he meant is, there are branches of science whose practitioners would be satisfied with a collection of interesting facts (i.e. "stamp-collecting"). But what makes physics *physics* is the search for the theoretical framework providing explanations based on fundamental principles, not idiosyncratic descriptions. Bohr's model brought the science of spectroscopy into physics.

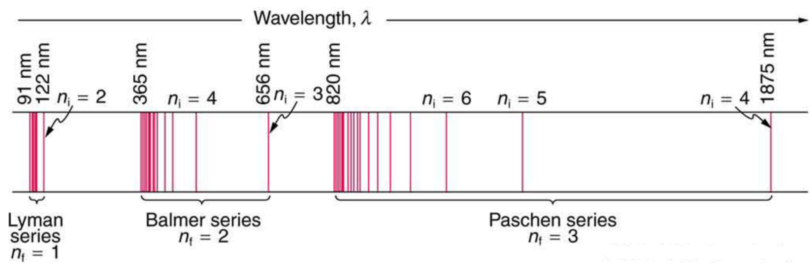

Figure 12.7.3: A schematic of the hydrogen spectrum shows several series named for those who contributed most to their determination. Part of the Balmer series is in the visible spectrum, while the Lyman series is entirely in the UV, and the Paschen series and others are in the IR. Values of n_f and n_i are shown for some of the lines.

Bohr's Model for Hydrogen

The planetary model of the atom suggested by Rutherford was in trouble. While the model provided a possible picture of how the very small atomic nucleus might be arranged with the electrons in a stable arrangement, it did not provide for the size of electron orbits (which would be related to the size of the atom), and the arrangement was not actually stable—an orbiting electron is an oscillating charge; an oscillating charge emits electromagnetic waves; electromagnetic waves carry away energy; so as the electron loses energy, it would fall into the proton. By some estimates, this would occur in as short a time as 10^{-7} s!

Bohr's starting point for his successful model was this: he proposed that *the orbits of electrons in atoms are quantized*. To fully understand this statement, we can compare the orbits of electrons in atoms to the orbits of planets in the solar system. The orbits of planets are not quantized. While laws of physics govern how planets move in the solar system (see for example, Kepler's laws, or their derivation by Newton starting with the inverse-square law of gravitation), there is no law of physics dictating how far each body in the solar system must be from the Sun. So the orbits of planets are not quantized.

So what Bohr was proposing was an entirely *new* law of physics no one had known before. In one sense, it was not completely new (Planck and Einstein already enjoyed some successes from suggesting quantization of energy in thermal oscillators and EM radiation); in another sense, it was a big break from centuries of classical mechanics. This was Bohr's quantization rule: **angular momentum of an electron in its orbit is quantized**. In mathematical form,

$$L = n\hbar,$$

where nn could take on any positive integer value ($n = 1, 2, 3, \ldots$), and $\hbar$ is known as the reduced Planck constant ($\hbar = h/2\pi$). And angular momentum, L, as you might remember from earlier chapter, is given by the following for a particle in a uniform circular orbit: $L = mvr$, where m is the mass of the particle, v is the speed of the particle in orbit, and rr is the radius of circular orbit. Using this as the starting point, semiclassical analysis of orbital motion yields a whole array of quantized (i.e. allowed) values of orbital distance (r_n), orbital speed (v_n), and orbital energy (E_n), among others (see: Table 12.7.1 for a summary).

With the quantized orbital energies for the electron, we have a ready explanation for the features of atomic spectra. EM radiation is emitted when an electron transitions from a higher energy level (E_i) to a lower energy level (E_f), with the photon carrying away the energy difference,

$$hf = \Delta E = E_i - E_f, \tag{12.7.2}$$

where f is the frequency of the photon. Figure $12.7.4$ shows a schematic representation of this relationship. With only discrete values of energy E_n allowed, there are only discrete values of frequency (f) and wavelength (λ) allowed also, as shown in the line spectra.

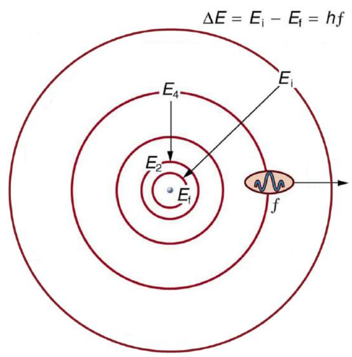

Figure $12.7.4$: The planetary model of the atom, as modified by Bohr, has the orbits of the electrons quantized. Only certain orbits are allowed, explaining why atomic spectra are discrete (quantized). The energy carried away from an atom by a photon comes from the electron dropping from one allowed orbit to another and is thus quantized. This is likewise true for atomic absorption of photons.

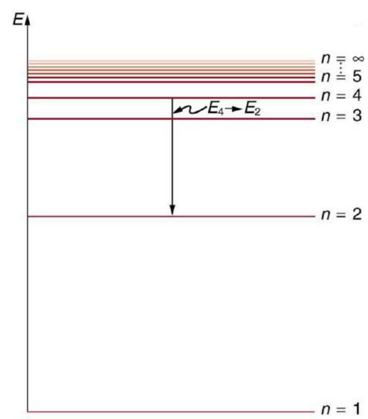

Figure $12.7.5$: An energy-level diagram plots energy vertically and is useful in visualizing the energy states of a system and the transitions between them. This diagram is for the hydrogen-atom electrons, showing a transition between two orbits having energies E_4 and E_2.

Energy-level diagram, shown in Figure $12.7.5$, is another convenient way to illustrate these relationships. Allowed energy levels for the atom are plotted vertically with the lowest state (or **ground state**) at the bottom and with excited states above that. The energies of the lines in an atomic spectrum correspond to the *differences* in energy levels in the level diagram (figure illustrates a transition from E_4 to E_2, which would show up in the atomic spectrum as one line).

Table $12.7.1$: Summary of quantized quantities in the Bohr model of the hydrogen atom. The full derivations take some bit of algebra, and they use: (1) centripetal force due to the Coulomb force, (2) relationship between quantized orbital radius and quantized orbital speed through quantization of angular momentum, and (3) expression for the total energy, including orbital kinetic energy and the Coulomb potential energy.

Quantized quantity	Dependence on quantum number n	Full expression
angular momentum: L_n	proportional to n	$L_n = n\hbar$
orbital radius: r_n	proportional to n^2	$r_n = \frac{n^2\hbar^2}{mke^2}$
orbital speed: v_n	proportional to $\frac{1}{n}$	$v_n = \frac{ke^2}{n\hbar}$
orbital energy: E_n	proportional to $\frac{1}{n^2}$	$E_n = -\frac{mk^2e^4}{2n^2\hbar^2} = -\frac{13.6}{n^2}\,\mathrm{eV}$

Two key results are worth highlighting. The first is the **Bohr radius**, or the smallest orbital radius a, given for $n=1$,

$$\begin{aligned} a &= r_1 = \hbar^2/mke^2 \\ &= 0.529 \times 10^{-10}\ \mathrm{m}. \end{aligned}$$

This is the Bohr model's prediction for the size of the atom, made with nothing more than electric constants, mass of the electron, and the Planck's constant, and this theoretical prediction matches experimentally measured sizes of atoms fairly well.

The second is the derivation of the Rydberg formula, first given in Equation (12.7.1). To derive this, we start out with Equation (12.7.2) and substitute in expressions for hydrogen energies from Table 12.7.1:

$$\begin{aligned} hf &= -\frac{mk^2e^4}{2n_i^2\hbar^2} - \left(-\frac{mk^2e^4}{2n_f^2\hbar^2}\right) \\ &= \frac{mk^2e^4}{2\hbar^2}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) \end{aligned}$$

Frequency f is equal to c/λ. Plugging this in and solving for $1/\lambda$ while also replacing all instances of $\hbar$ with $h/2\pi$, we get,

$$\frac{1}{\lambda} = \frac{2\pi^2mk^2e^4}{h^3c}\left(\frac{1}{n_f} - \frac{1}{n_i}\right),$$

which yields an analytical expression for the Rydberg constant,

$$R = \frac{2\pi^2mk^2e^4}{h^3c} = 1.097 \times 10^7\ \mathrm{m}^{-1}.$$

Figure 12.7.6 shows an energy-level diagram for hydrogen that also illustrates how the various spectral series for hydrogen are related to transitions between energy levels.

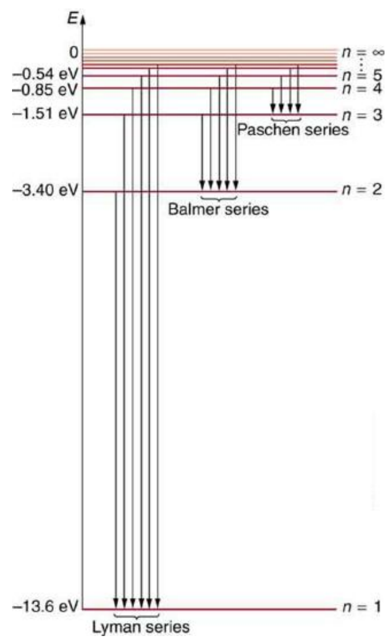

Figure 12.7.6: Energy-level diagram for hydrogen showing the Lyman, Balmer, and Paschen series of transitions. The orbital energies are calculated using the above equation, first derived by Bohr.

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, $n_\mathrm{f}=1$ — that is, all the transitions end in the ground state (see also Figure 12.7.6). For the Balmer series, $n_\mathrm{f}=2$, 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. 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 a *semiclassical* model. The orbits are quantized (quantum mechanical) 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. These deficiencies are addressed in later, fully-quantum-mechanical atomic models, 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.

Section Summary

- The planetary model of the atom pictures electrons orbiting the nucleus in the way that planets orbit the sun. Bohr used the planetary model to develop the first reasonable theory of hydrogen, the simplest atom. Atomic and molecular spectra are quantized, with hydrogen spectrum wavelengths given by the formula

$$\frac{1}{\lambda} = R\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2}\right),$$

  where λ is the wavelength of the emitted EM radiation and R is the Rydberg constant, which has the value

$$R = 1.097 \times 10^7 \ \mathrm{m}^{-1}.$$

- The constants n_{i} and n_{f} are positive integers, and n_{i} must be greater than n_{f}.
- Bohr correctly proposed that the energy and radii of the orbits of electrons in atoms are quantized, with energy for transitions between orbits given by

$$\Delta E = hf = E_{\mathrm{i}} - E_{\mathrm{f}},$$

- where ΔE is the change in energy between the initial and final orbits and hf is the energy of an absorbed or emitted photon. It is useful to plot orbital energies on a vertical graph called an energy-level diagram.
- Bohr proposed that the allowed orbits are circular and must have quantized orbital angular momentum given by

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

  where L is the angular momentum, r_n is the radius of the nth orbit, and h is Planck's constant.
- Additional quantized orbital quantities—orbital radius, orbital speed, and orbital energy—can be derived starting from Bohr's assumption, and they yield predictions consistent with the experimental Rydberg formula.
- While Bohr's semiclassical model of the atom does not account for all experimental facts about the atom, it is an important stepping stone to fully-quantum-mechanical models of the atom.

Glossary

hydrogen spectrum wavelengths

the wavelengths of visible light from hydrogen; can be calculated by $\frac{1}{\lambda} = R\left(\frac{1}{n_{\mathrm{f}}^2} - \frac{1}{n_{\mathrm{i}}^2}\right)$

Rydberg constant

a physical constant related to the atomic spectra with an established value of $1.097 \times 10^7 \ \mathrm{m}^{-1}$

double-slit interference

an experiment in which waves or particles from a single source impinge upon two slits so that the resulting interference pattern may be observed

energy-level diagram

a diagram used to analyze the energy level of electrons in the orbits of an atom

Bohr radius

the mean radius of the orbit of an electron around the nucleus of a hydrogen atom in its ground state

hydrogen-like atom

any atom with only a single electron

energies of hydrogen-like atoms

Bohr formula for energies of electron states in hydrogen-like atoms: $E_n = -\frac{Z^2}{n^2} E_0 (n = 1, 2, 3, \ldots)$
