19.1 The Bohr Atom

SECTION OUTCOMES

- Describe and explain the Bohr model of the hydrogen atom.
- Explain the Bohr atomic model as a synthesis of classical and quantum physics.

KEY TERMS

- nuclear model
- Balmer series
- Rydberg constant
- Bohr radius
- principal quantum number

The new discoveries in quantum theory revealed phenomena that can be observed on the scale of subatomic particles, but are undetectable on a larger scale. These discoveries gave physicists the tools they needed to probe the structure of atoms in much more detail than ever before. The refinement of atomic theory grew side by side with the development of quantum theory.

Atomic Theory before Bohr

As you have learned in previous science courses, the first significant theory of the atom was proposed by John Dalton (1766–1844) in 1808. Dalton's model could be called the "billiard ball model" because he pictured atoms as solid, indivisible spheres. According to Dalton's model, atoms of each element are identical to each other in mass and all other properties, while atoms of one element differed from atoms of each other element. Dalton's model could explain most of what was known about the chemistry of atoms and molecules for nearly a hundred years.

Figure 19.1 Dalton proposed that atoms were the smallest particles that make up matter and that they were indestructible. With his model, Dalton could predict most of what was known about chemistry at the time.

The Dalton model of the atom was replaced when J.J. Thomson established in 1897 that the atom was divisible. He discovered that the "cathode rays" in gas discharge tubes (see Figure 19.2) were negatively charged particles with a mass nearly 2000 times smaller than a hydrogen atom, the smallest known atom. These negatively charged particles, later named "electrons," appeared to have come off the metal atoms in one of the electrodes in the gas discharge tubes. Based on this new information, Thomson developed another model of the atom, which consisted of a positively charged sphere with the negatively charged electrons imbedded in it, as illustrated in Figure 19.3.

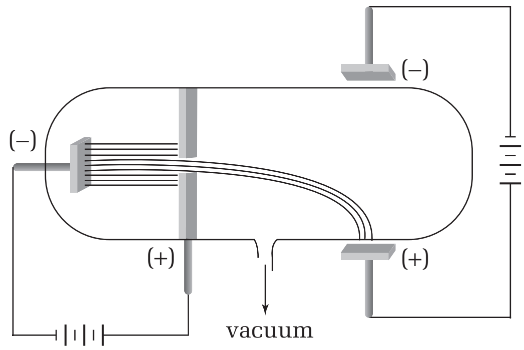


Figure 19.2 Metal electrodes were sealed in a glass tube that had been evacuated of all but a trace of a gas. A potential difference was created between the two electrodes. "Cathode rays" emanated from the negative electrode and a few passed through a hole in the positive electrode. Thomson showed that these "cathode rays" carried a negative charge by placing another set of electrodes outside the tube. The positive plate attracted the "rays."

Even as Thomson was developing his model of the atom, Ernest Rutherford (1871–1937) was beginning a series of experiments that would lead to replacement of Thomson's model. Rutherford was born and educated in New Zealand. In 1895, he went to England to continue his studies in the laboratory of J.J. Thomson. While there, he became interested in radioactivity and characterized the "rays" emitted by uranium, naming them "alpha rays" and "beta rays." He discovered that alpha rays were actually positively charged particles.

In 1898, Rutherford accepted a position in physics at McGill University in Montréal, where he continued his studies of alpha particles and published 80 scientific papers. Nine years later, Rutherford returned to England, where he accepted a position at the University of Manchester.

While in Manchester, Rutherford and his research assistant Hans Geiger (1882–1945) designed an apparatus (see Figure 19.4) to study the bombardment of very thin gold foils by highly energetic alpha particles. If Thomson's model of the atom was correct, the alpha particles would pass straight through, with little or no deflection. In their preliminary observations, most of the alpha particles did, in fact, pass straight through the gold foil. However, in a matter of days, Geiger excitedly went to Rutherford with the news that they had observed some alpha particles scatter at an angle greater than 90˚. Rutherford's famous response was, "It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15 inch shell at a piece of tissue paper and it came back and hit you!" The observations were consistent: Approximately 1 in every 20 000 alpha particles was deflected more than 90˚. These results could not be explained by Thomson's model of the atom.

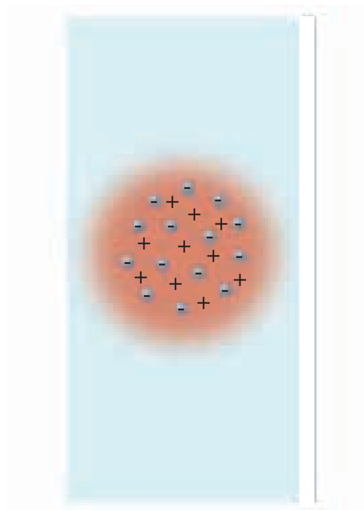


Figure 19.3 Thomson named his model the "plum pudding model" because it resembled a pudding with raisins distributed throughout.

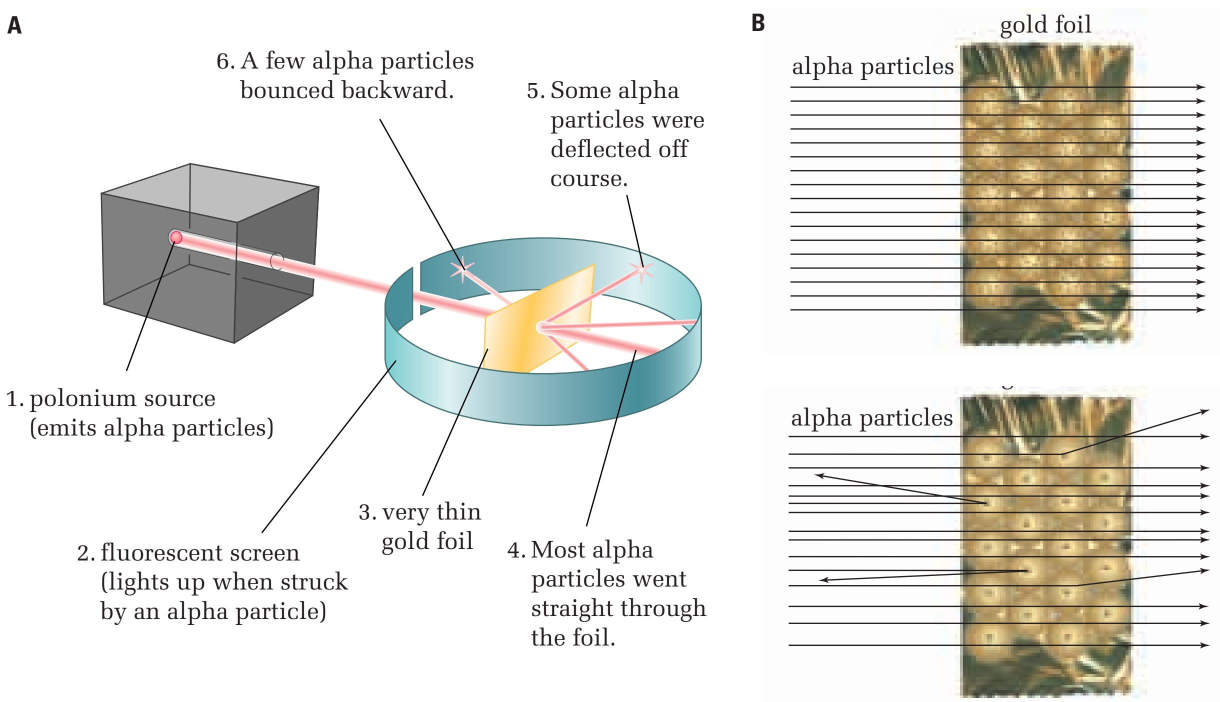


Figure 19.4 **(A)** A fine beam of alpha particles was directed at a very thin gold foil. The circular screen around the foil was coated with zinc sulfide, which emitted a flash of light when hit by an alpha particle. **(B)** If positive and negative charges were equally distributed throughout the foil, they would have little effect on the direction of the alpha particles. **(C)** If all of the positive charge in each atom was concentrated in a very tiny point, it would create a large electric field close to the point. The field would deflect alpha particles that are moving directly toward or very close to the tiny area where the positive charge is located.

What force could possibly be strong enough to repel such a highly energetic alpha particle? Rutherford searched his mind and performed many calculations. He concluded that the only force great enough to repel the alpha particles would be an extremely strong electrostatic field. The only way that a field this strong could exist was if all of the positive charge was confined in an extremely small space at the centre of the atom. Thus, Rutherford proposed his **nuclear model** of the atom. All of the positive charge and nearly all of the mass of an atom is concentrated in a very small area at the centre of the atom, while the negatively charged electrons circulate around this "nucleus," somewhat like planets around the Sun, as illustrated in Figure 19.5.

In the following Quick Lab, you will apply some of the same concepts that Rutherford used to estimate the size of the atomic nucleus.

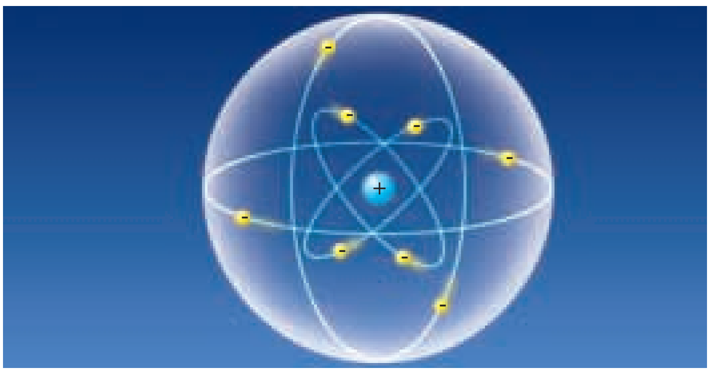


Figure 19.5 Rutherford's nuclear model resembles a solar system in which the positively charged nucleus could be likened to the Sun and the electrons are like planets orbiting the Sun.

QUICK LAB

Estimating the Size of the Nucleus

TARGET SKILLS

- Hypothesizing
- Analyzing and interpreting

Method 1

At the time that Rutherford was performing his experiments, physicists knew that the diameter of the entire atom was about 10^{-10} m.

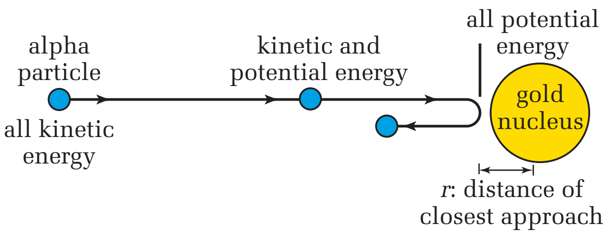
- Calculate the cross-sectional area of the atom, assuming that its diameter is 10^{-10} m.

Rutherford's students observed that about 1 in every 20 000 alpha particles scattered backward from the foil. If they were all headed toward the atom but only 1 in 20 000 was headed directly toward the nucleus, what must be the cross-sectional area of the nucleus?

- Calculate the cross-sectional area of the nucleus based on the above information.
- Using your cross-sectional area of the nucleus, calculate the diameter of the nucleus.

Method 2

Make a second estimate of the size of the nucleus based on the conservation of mechanical energy of the alpha particle. As shown in the diagram, at a large distance from the nucleus, the energy of the alpha particle is all kinetic energy. As it approaches the nucleus, its kinetic energy is converted into electric potential energy. When all of its kinetic energy is converted into electric potential energy, the alpha particle will stop. At this point, called the "distance of closest approach," the repulsive Coulomb forces will drive the alpha particle directly backward. If the alpha particle penetrated the nucleus, it would be trapped and would not scatter backward.



- The equation below states that the kinetic energy of the alpha particle at a large distance from the nucleus is equal to the electric potential energy of the alpha particle at the distance of closest approach. Substitute into the equality the mathematical expressions for kinetic energy and electric potential energy between two point charges a distance, r, apart.

  E_k (very far from nucleus)
  $= E_Q$ (distance of closest approach)

- The mass of an alpha particle is about 6.6×10^{-27} kg and those that Rutherford used had an initial velocity of 1.5×10^7 m/s. Calculate the kinetic energy of the alpha particle.
- An alpha particle has 2 positive charges and a gold nucleus has 79 positive charges. Using the magnitude of one elementary charge (1.6×10^{-19} C), calculate the magnitude of the charges needed for the determination of the electric potential energy.
- Substitute all of the known values into the equation above. You will find that r is the only unknown variable. Solve the equation for r, the distance of closest approach.

Analyze and Conclude

1. Comment on the validity of each of the two methods. What types of errors might affect the results?
2. How well do your two methods agree?
3. The accepted size of an average nucleus is in the order of magnitude of 10^{-14} m. How well do your calculations agree with the accepted value?

The Bohr Model of the Atom

Rutherford's model of the atom was based on solid experimental data, but it had one nagging problem that he did not address. According to classical electromagnetism, an accelerating charge should radiate electromagnetic waves and lose energy. If electrons are orbiting around a nucleus, then they are accelerating and they should be radiating electromagnetic waves. If the electrons lost energy through radiation, they would spiral into the nucleus. According to Rutherford's model, electrons remain permanently in orbit.

Niels Henrik David Bohr (1885–1962) addressed the problem of electrons that do not obey classical electromagnetic theory. Bohr was born and educated in Denmark, and in 1912, went to study in Rutherford's laboratory in Manchester. (Rutherford said of Bohr, "This young Dane is the most intelligent chap I've ever met.") Convinced that Rutherford was on the right track with the nuclear atom, Bohr returned home to Copenhagen, where he continued his search for an explanation for the inconsistency of the nuclear atom with classical theory.

Bohr was very aware of the recent publications of Planck and Einstein on blackbody radiation and the photoelectric effect, and that these phenomena did not appear to obey the laws of classical physics. He realized that some phenomena that are unobservable on the macroscopic level become apparent on the level of the atom. Thus, he did not hesitate to propose characteristics for the atom that appeared to contradict classical laws.

Bohr had another, very significant piece of evidence available to him — atomic spectra. When Kirchhoff defined blackbodies, he was studying very low-pressure gases in gas discharge tubes. Kirchhoff discovered that when gases of individual elements were sealed in gas discharge tubes and bombarded with "cathode rays," each element produced a unique spectrum of light. The spectrum of hydrogen is shown in Figure 19.6.

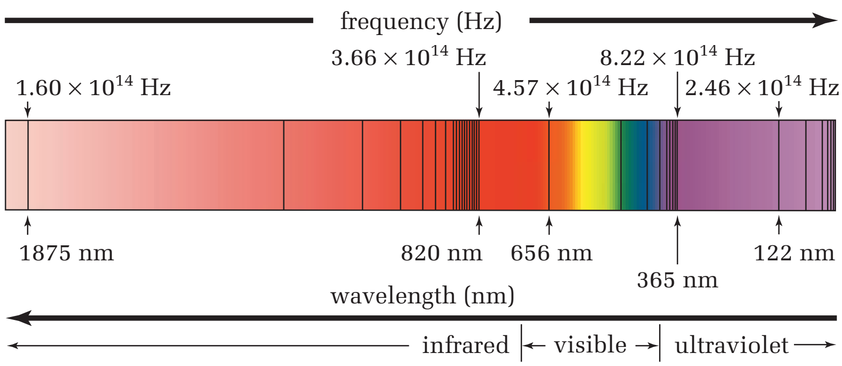


Figure 19.6 When bombarded by high-energy electrons, hydrogen atoms emit a very precise set of frequencies of electromagnetic radiation, extending from the infrared region, through the visible region, and well into the ultraviolet region of the spectrum.

Since emission spectra did not have an immediately obvious pattern, Bohr thought them too complex to be useful. However, a friend who had studied spectroscopy directed Bohr to a pattern that had been determined in 1885 by Swiss secondary school teacher Johann Jakob Balmer (1825–1898). Balmer had studied the visible range of the hydrogen spectrum and found an empirical expression that could produce the wavelength of any line in that region of the spectrum. Balmer's formula is given below. Remember that empirical equations are developed from experimental data and are not associated with any theory. Balmer could not explain why his formula had the form that it did. He could demonstrate only that it worked.

$$\frac{1}{\lambda} = R\left[\frac{1}{2^2} - \frac{1}{n^2}\right], \quad \text{where } n = 3, 4, 5, \ldots \text{ and } R = 1.097\ 373\ 15 \times 10^7\ \text{m}^{-1}$$

The spectral lines of hydrogen that lie in the visible range are now known as the **Balmer series**. As spectroscopists developed methods to observe lines in the infrared and ultraviolet regions of the spectrum, they found more series of lines. Swedish physicist Johannes Robert Rydberg (1854–1919) modified Balmer's formula, as shown below, to incorporate all possible lines in the hydrogen spectrum. The constant R is known as the **Rydberg constant**.

$$\frac{1}{\lambda} = R\left[\frac{1}{m^2} - \frac{1}{n^2}\right], \quad \text{where } m \text{ and } n \text{ are integers; } 1, 2, 3, 4, \ldots \text{ and } n > m$$

Bohr Postulates

When Bohr saw these mathematical patterns, he said, "As soon as I saw Balmer's formula, the whole thing was immediately clear to me." Bohr was ready to develop his model of the atom. Bohr's model, illustrated in Figure 19.7, was based on the following postulates.

- Electrons exist in circular orbits, much like planetary orbits. However, the central force that holds them in orbit is the electrostatic force between the positive nucleus and the negative charge on the electrons, rather than a gravitational force.
- Electrons can exist only in a series of "allowed" orbits. Electrons, much like planets, have different amounts of total energy (kinetic plus potential) in each orbit, so these orbits can also be described as "energy levels." Since only certain orbits are allowed, then only certain energy levels are allowed, meaning that the energy of electrons in atoms is quantized.
- Contrary to classical theory, while an electron remains in one orbit, it does not radiate energy.
- Electrons can "jump" between orbits, or energy levels, by absorbing or emitting an amount of energy that is equal to the *difference* in the energy levels.

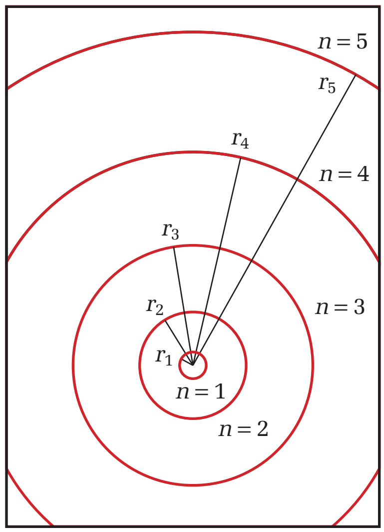


Figure 19.7 According to Bohr's model of the atom, electrons can exist in specific, allowed energy levels and can jump from one level to another by absorbing or emitting energy.

PHYSICS FILE

Johann Balmer's life was a contrast to that of most other contributors to the theory of the atom. Balmer taught mathematics in a secondary school for girls and lectured at the University of Basel in Switzerland. He published only two scientific papers in his career, one when he was 60 years old and one when he was 72. Balmer died 15 years before Niels Bohr provided an explanation for Balmer's now famous formula for the emission spectrum of hydrogen.

Electrons can "jump" to higher energy levels by absorbing thermal energy (collision with an energetic atom or molecule), by bombardment with an energetic electron (as in gas discharge tubes), or by absorbing photons of radiant energy with energies that exactly match the difference in energy levels of the electrons in the atom. Likewise, electrons can "drop" to a lower energy level by emitting a photon that has an energy equal to the *difference* between the energy levels. Since the energy of a photon is directly related to the frequency of the electromagnetic waves, you could express this relationship between energy levels and photons as follows.

$$|E_\mathrm{f} - E_\mathrm{i}| = hf$$

E_f is the energy of the final energy level, E_i is the energy of the initial energy level, and hf is the photon energy. This concept gives meaning to the "2" and the "n" in Balmer's formula, because the "2" represents the second energy level and "n" is any energy level above the second one. In Rydberg's more general formula, m is the final energy level, which can be any level. Likewise, n is the initial level and must therefore be higher than the final level.

To find the exact energies of these "allowed energy levels," Bohr had to determine exactly what property of the electron was quantized. An important clue comes from the units of Planck's constant — joule · seconds. First, simplify joules to base units.

$$\mathrm{J \cdot s = N \cdot m \cdot s} = \frac{\mathrm{kg \cdot m}}{\mathrm{s}^{\cancel{2}}} \cdot \mathrm{m} \cdot \cancel{\mathrm{s}} = \mathrm{kg} \cdot \frac{\mathrm{m}}{\mathrm{s}} \cdot \mathrm{m}$$

The final units, $\mathrm{kg} \cdot \frac{\mathrm{m}}{\mathrm{s}} \cdot \mathrm{m}$, are the units for the quantities of mass, speed, and distance, or mvd. At one time in physics, this combination was called "action." In fact, Planck called his constant, h, the "quantum of action." If you apply these quantities to the electron in an orbit of radius r, you will get $m_\mathrm{e}v_\mathrm{n}2\pi r$, where $2\pi r$ is the distance that the electron travels during one orbit around the nucleus. If this value is quantized, you would have the following.

$$2\pi m_\mathrm{e} v_\mathrm{n} r_\mathrm{n} = nh$$

You might recognize the expression $m_\mathrm{e}v_\mathrm{n}r_\mathrm{n}$ as the angular momentum of the electron in the n^{th} orbit. Following a similar logic, Bohr proposed that the angular momentum was quantized and then tested that hypothesis. The angular momentum of the n^{th} orbit can be written as follows.

$$m_\mathrm{e} v_\mathrm{n} r_\mathrm{n} = n\frac{h}{2\pi}$$

You can test the theory by using the equation for the quantized angular momentum to find allowed radii and allowed energies of electrons. Then, you can compare these differences between energy levels to Balmer's formula and the Rydberg constant. Since you have two unknown quantities, r and v, you will need more relationships to find values for either r or v in terms of known constants. Because Bohr based his concept on circular orbits, you can use the fact that the electrostatic force between the electron and the nucleus provides the centripetal force that keeps the electron in a circular orbit. The following steps will lead you through the procedure.

Deriving the Bohr Radius

- Write Coulomb's law. $$F = k\frac{q_1 q_2}{r^2}$$
- Let Z be the number of positive charges in the nucleus. Therefore, Ze is the charge of the nucleus. The charge on an electron is, of course, e. Let r_n be the radius of the n^{th} orbit. Substitute these values into Coulomb's law. $$F = k\frac{Ze^2}{{r_n}^2}$$
- Set the coulomb force equal to the centripetal force. $$k\frac{Ze^2}{r_n^2} = \frac{m_e v_n^2}{r_n}$$
- Multiply both sides by r_n^2. $$kZe^2 = m_e v_n^2 r_n$$
- Divide both sides by $m_e v_n^2$. $$r_n = \frac{kZe^2}{m_e v_n^2}$$
- Write Bohr's condition for quantization of angular momentum. $$m_e v_n r_n = n\frac{h}{2\pi}$$
- Solve for v_n. $$v_n = \frac{nh}{2\pi m_e r_n}$$
- Substitute this expression for v_n into the equation for r_n. $$r_n = \frac{kZe^2}{m_e\left(\frac{nh}{2\pi m_e r_n}\right)^2}$$
- Start the simplification by inverting the fraction in the denominator in brackets and then multiplying by the inverted fraction. $$r_n = \frac{kZe^2}{m_e} \cdot \frac{4\pi^2 m_e^2 r_n^2}{n^2 h^2}$$
- Divide both sides of the equation by r_n. $$1 = \left(\frac{4\pi^2 kZe^2 m_e^{\cancel{2}}}{\cancel{m_e} n^2 h^2}\right) r_n$$
- Invert and multiply by the expression in brackets. $$r_n = \frac{n^2 h^2}{4\pi^2 kZe^2 m_e}$$

The expression, $\frac{h}{2\pi}$, occurs so frequently in quantum theory that the symbol $\hbar$ is often used in place of $\frac{h}{2\pi}$. The final expression is usually written as follows.

$$r_n = n^2\frac{\hbar^2}{m_e kZe^2}$$

For the first allowed radius of the electron in a hydrogen atom, $Z = 1$ and $n = 1$. All of the other values in the equation are constants and if you substitute them into the equation and simplify, you will obtain $r_1 = 0.052\ 917\ 7\ \text{nm}$. This value is known as the **Bohr radius**.

Deriving Allowed Energy Levels

You can use the equation for the radius of the n^{th} orbit of an electron to find the energy for an electron in the n^{th} energy level in an atom as shown in the following steps.

- Write the expression for the total energy (kinetic plus potential) of a charge a distance, r, from another charge.
$$E = \frac{1}{2}mv^2 - k\frac{q_1q_2}{r}$$
- Substitute in the values for an electron at a distance, r_n, from a nucleus.
$$E_n = \frac{1}{2}m_e v_n^2 - k\frac{Ze^2}{r_n}$$
- To eliminate the variable, v, from the equation, go back to the expression you wrote when you set the Coulomb force equal to the centripetal force.
$$k\frac{Ze^2}{r_n^2} = \frac{m_e v^2}{r_n}$$
- Multiply both sides of the expression by $\frac{r_n}{2}$ and simplify.
$$\left(k\frac{Ze^2}{r_n^2}\right)\left(\frac{r_n}{2}\right) = \left(\frac{m_e v^2}{r_n}\right)\left(\frac{r_n}{2}\right)$$
$$\frac{kZe^2}{2r_n} = \frac{1}{2}m_e v_n^2$$
- Substitute this value found in the last step for kinetic energy, $\frac{1}{2}m_e v_n^2$, in the second equation and then simplify.
$$E_n = \frac{kZe^2}{2r_n} - k\frac{Ze^2}{r_n}$$
$$E_n = -\frac{kZe^2}{2r_n}$$
- Substitute the value for r_n into the expression for energy.
$$E_n = -\frac{kZe^2}{2\left(n^2\frac{\hbar^2}{m_e kZe^2}\right)}$$
- To simplify, invert the fraction in the denominator and multiply.
$$E_n = -\frac{kZe^2}{2(n^2)} \cdot \frac{m_e kZe^2}{\hbar^2}$$
$$E_n = -\frac{k^2e^4m_e}{2\hbar^2} \cdot \frac{Z^2}{n^2}$$

Once again, you can write a general formula for the total energy of an electron in the n^{th} level of a hydrogen atom ($Z = 1$) by substituting the correct values for the constants. You will discover that $E_n = -\frac{13.6\text{ eV}}{n^2}$. The integer, n, is now known as the **principal quantum number**.

Recalling Bohr's hypothesis that the difference in the energy levels would be the energies of the photons emitted from an atom, you can now use this formula to compare Bohr's model of the atom with the observed frequencies of the spectral lines for hydrogen atoms. For example, you should be able to calculate the frequency of the first line in the Balmer series by doing the following.

$$hf = E_3 - E_2$$

$$hf = \frac{-13.6\ \text{eV}}{3^2} - \left(-\frac{13.6\ \text{eV}}{2^2}\right)$$

$$hf = -1.511\ \text{eV} + 3.40\ \text{eV}$$

$$hf = 1.89\ \text{eV}$$

$$f = \left(\frac{1.89\ \cancel{\text{eV}}}{h}\right)\left(\frac{1.6 \times 10^{-19}\ \text{J}}{\cancel{\text{eV}}}\right)$$

$$f = \frac{3.0222 \times 10^{-19}\ \cancel{\text{J}}}{6.63 \times 10^{-34}\ \cancel{\text{J}} \cdot \text{s}}$$

$$f = 4.56 \times 10^{14}\ \text{Hz}$$

This value is in excellent agreement with the observed frequency of the first line in the Balmer series. If you performed similar calculations for the other lines in the Balmer series, you would find the same excellent agreement with observations.

Spectroscopists continued to find series of lines that were matched with electrons falling from higher levels of the hydrogen atom down into the first five energy levels. These series are named and illustrated in Figure 19.8.

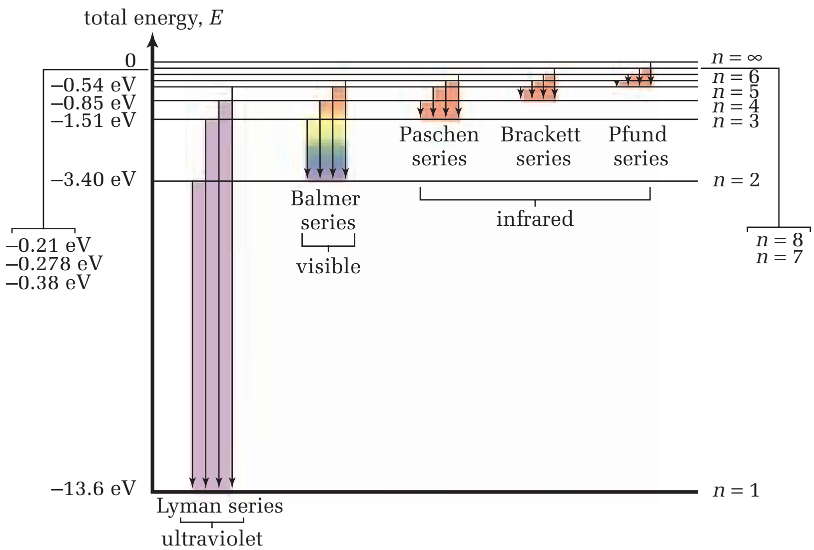


Figure 19.8 Photons from transitions that *end* at the same energy level have energies (and therefore frequencies) that are relatively close together. When inspecting a particular range of frequencies emitted by an element, therefore, an observer would find a set of spectral lines quite close together. Each set of lines is named after the person who observed and described them.

You could perform calculations such as the sample calculation of the frequency of the first line in the Balmer series for any combination of energy levels and find agreement with the corresponding line in the hydrogen spectrum. Bohr's model of the atom was thoroughly tested and was found to be in agreement with most of the data available at the time.

ELECTRONIC LEARNING PARTNER

Enhance your understanding of the Bohr atom, modelled as a wave or as a particle, by referring to your Electronic Learning Partner.

Conceptual Problems

- Start with the expression $hf = |E_f - E_i|$, then substitute the equation for the energy of the n^{th} level of an electron into E_f and E_i into the first expression. Finally, use the relationship $c = f\lambda$ to derive the following expression.

$$\frac{1}{\lambda} = \left|\frac{2\pi^2 k^2 e^4 m_e Z^2}{h^3 c}\left[\frac{1}{n_f^{\,2}} - \frac{1}{n_i^{\,2}}\right]\right|$$

- The equation above would be identical to the Rydberg equation if the combination of constants $\frac{2\pi^2 k^2 e^4 m_e}{h^3 c}$ was equal to the Rydberg constant for hydrogen atoms ($Z = 1$). Calculate the value of the constants and compare your answer with the Rydberg constant. What does this result tell you about Bohr's model of the atom?

19.1 Section Review

1. **C** Discuss the similarities and differences between Dalton's model of the atom and J.J. Thomson's model of the atom.
2. **K/U** What surprising observation did Rutherford and Geiger make that motivated Rutherford to define a totally new model of the atom?
3. **K/U** In what way did Rutherford's nuclear model of the atom conflict with classical theory?
4. **C** Explain how experimentally observed spectra of atomic hydrogen helped Bohr develop his model of the atom.
5. **K/U** According to Bohr's model of the atom, what property of electrons in atoms must be quantized?
6. **K/U** List the four postulates on which Bohr based his model of the atom.
7. **C** Explain how Coulomb's law played a role in the determination of the Bohr radius.
8. **C** Describe the two features of the emission spectrum of atomic hydrogen that revealed a flaw in Bohr's model of the atom.

UNIT PROJECT PREP

Inquisitive minds following unexpected results often lead to advances in our scientific understanding of the universe.

- Do you believe, and can you support, the idea that unexpected experimental results have contributed more to scientific discovery than any other means?
- Which theory, special relativity or quantum mechanics, was received with more skepticism by the general public of the time? Suggest reasons.