

The Energy Levels of Hydrogen

As early as the middle of the nineteenth century, it was known that hydrogen was the lightest and simplest atom and thus an ideal candidate for the study of atomic structure. Its emission spectrum was of particular interest. The spacing of spectral lines in the visible region formed a regular pattern. In 1885, this pattern attracted the attention of J.J. Balmer, a Swiss teacher who devised a simple empirical equation from which all of the lines in the visible spectrum of hydrogen could be computed. He found that the wavelengths of the spectral lines obeyed the equation

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

where R is a constant, later called the Rydberg constant, whose value Balmer found to be $1.097 \times 10^7 \text{ m}^{-1}$, and n is a whole number greater than 2. Each successive value of n (3, 4, 5, ...) yields a value for the wavelength of a line in the spectrum.

Further studies of the hydrogen spectrum carried out over the next three or four decades, using ultraviolet and infrared detection techniques, revealed that the entire hydrogen spectrum obeyed a relationship generalizing the one devised by Balmer. By replacing the 2^2 term in Balmer's expression with the squares of other integers, a more general expression was devised to predict the wavelengths of all possible lines in the hydrogen spectrum:

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

where n_l is any whole number 1, 2, 3, 4, ... , and n_u is any whole number greater than n_l . The choice of subscripts l for "lower" and u for "upper" reflects the idea of a transition between energy levels.

This expression can be related to the energy of the emitted photons by isolating $\frac{1}{\lambda}$ from $E_p = \frac{hc}{\lambda}$ and substituting. Also, the energy of the emitted photon E_p is determined from the difference in energy of the energy levels involved in the transition producing the photon, that is $E_p = E_u - E_l$. This yields

$$\frac{1}{\lambda} = \frac{E_p}{hc}$$

$$\frac{1}{\lambda} = \frac{E_u - E_l}{hc}$$

$$\frac{E_u - E_l}{hc} = R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

$$E_u - E_l = Rhc \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

$$E_l - E_u = Rhc \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$$

Now, when n_u becomes very large, E_u approaches the ionization state. If we choose the ionization state to have zero energy, then $E_u \rightarrow 0$ and $\frac{1}{n_u^2} \rightarrow 0$ and the formula for the energy levels becomes

$$E_l = \frac{-Rhc}{n_l^2}$$

LEARNING TIP

Abbreviations

Note that l stands for lower, but I , as in E_I , stands for ionization.

Rutherford's planetary model proposed that the hydrogen atom consists of a single proton nucleus (the Sun) and a single orbiting electron (a planet). In this model, the Coulomb force of attraction binds the electron to its nucleus in much the way Earth is bound to the Sun by the gravitational force. When we studied such a gravitational system earlier (Section 6.3), we found it useful to choose the zero level of energy as the point where the two masses are no longer bound to each other. This zero level of energy denotes the borderline between the bound and the free condition of the system. If an object has a total energy greater than zero, it can reach an essentially infinite distance, where its potential energy is near zero, without coming to rest. For the hydrogen atom, this situation corresponds to ionization: the electron is no longer bound to its nucleus, as part of the atom, but is liberated. Thus, if we choose $E_I = 0$ when n approaches infinity, then the expression for the energy levels of hydrogen becomes even simpler:

$$\begin{aligned} E_n &= E_I - \frac{Rhc}{n^2} \\ &= 0 - \frac{(1.097 \times 10^7 \text{ m}^{-1})(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{n^2} \\ E_n &= -\frac{2.18 \times 10^{-18} \text{ J}}{n^2} \end{aligned}$$

Then, converting from joules to electron volts, we have


$$E_n = -\frac{13.6}{n^2} \text{ eV} \quad \text{where } n = 1, 2, 3, \dots$$

INVESTIGATION 12.5.1

The Energy Levels of Hydrogen (p. 656)

You can measure the wavelengths and calculate the energies for the first four lines in the Balmer series, then compare your results with the theoretical values.

Using this equation, we can calculate the values of all the energy levels of the hydrogen atom, as in **Table 1**. The values can be represented graphically on an energy-level diagram (**Figure 1**), showing both the energy above the ground state (on the right) and the energy below ionization (on the left).

By performing Investigation 12.5.1 in the Lab Activities section at the end of this chapter, you can measure the line spectra in hydrogen. 

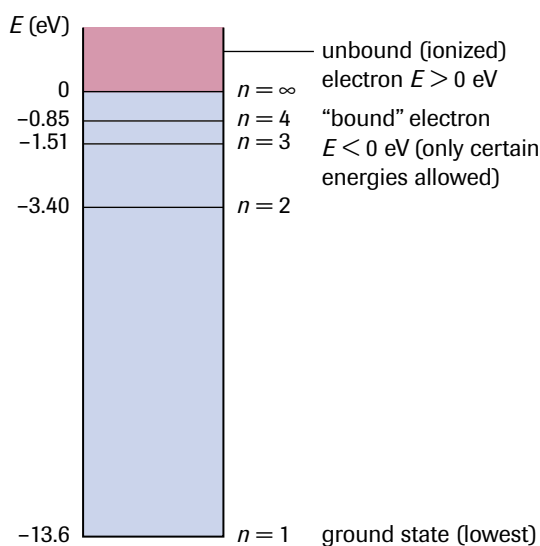


Figure 1
Energy levels of hydrogen

Table 1 Energy Levels of Hydrogen

Level	Value of n	Energy	Energy Above Ground State
ground state	1	-13.6 eV	0
1st excited state	2	-3.4 eV	10.2 eV
2nd excited state	3	-1.51 eV	12.1 eV
3rd excited state	4	-0.85 eV	12.8 eV
4th excited state	5	-0.54 eV	13.1 eV
⋮			
ionization state	∞	0	13.6 eV

▶ SAMPLE problem 1

Calculate the energy of the $n = 6$ state for hydrogen, and state it with respect to the ground state.

Solution

$$n = 6$$

$$E = ?$$

$$E = -\frac{13.6 \text{ eV}}{n^2}$$

$$= -\frac{13.6 \text{ eV}}{6^2}$$

$$E = -0.38 \text{ eV}$$

The $n = 6$ energy level is -0.38 eV , or $-13.6 \text{ eV} - (-0.38 \text{ eV}) = 13.2 \text{ eV}$, above the ground state.

▶ SAMPLE problem 2

If an electron in a hydrogen atom moves from the $n = 6$ to the $n = 4$ state, what is the wavelength of the emitted photon? In what region of the electromagnetic spectrum does it reside?

Solution

$$\lambda = ?$$

From Sample Problem 1, the energy of the $n = 6$ state is -0.38 eV .

The energy of the $n = 4$ state is

$$E = -\frac{13.6 \text{ eV}}{4^2}$$

$$E = -0.85 \text{ eV}$$

$$\text{energy change} = -0.38 \text{ eV} - (-0.85 \text{ eV})$$

$$\text{energy change} = 0.47 \text{ eV}$$

$$0.47 \text{ eV} = (0.47 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV}) = 7.5 \times 10^{-20} \text{ J}$$

The wavelength is calculated from the relationship

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{7.52 \times 10^{-20} \text{ J}}$$

$$\lambda = 2.6 \times 10^{-6} \text{ m, or } 2.6 \times 10^2 \text{ nm}$$

The wavelength of the emitted photon is $2.6 \times 10^2 \text{ nm}$, in the ultraviolet region of the spectrum.

Answers

- $n = 8$ to $n = 2$
- (a) 13.6 eV
(b) 1.51 eV
- $n = 3$ and $n = 2$
- (a) 0.97 eV
(b) 0.26 eV

Practice

Understanding Concepts

- What values of n are involved in the transition that gives rise to the emission of a 388-nm photon from hydrogen gas?
- How much energy is required to ionize hydrogen when it is in
(a) the ground state?
(b) the state for $n = 3$?
- A hydrogen atom emits a photon of wavelength 656 nm. Between what levels did the transition occur?
- What is the energy of the photon that, when absorbed by a hydrogen atom, could cause
(a) an electron transition from the $n = 3$ state to the $n = 5$ state?
(b) an electron transition from the $n = 5$ state to the $n = 7$ state?

DID YOU KNOW?

Collapse Time

Detailed calculations beyond the scope of this text suggest that the collapse of an atom would occur within 10^{-8} s.

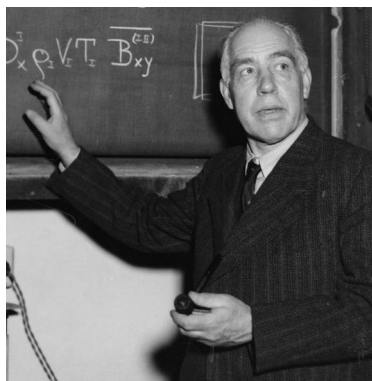


Figure 2

Niels Bohr (1885–1962) received his Ph.D. from the University of Copenhagen in 1911 but worked at Manchester University with Rutherford until 1916, when he returned to Copenhagen to take up a professorial chair in physics. He was awarded the 1922 Nobel Prize in physics for his development of the atomic model. An avid supporter of the peaceful uses of atomic energy, Bohr organized the first Atoms for Peace Conference in 1955 and in 1957 was honoured with the first Atoms for Peace Award.

The Bohr Model

The Rutherford planetary model of the atom had negatively charged electrons moving in orbits around a small, dense, positive nucleus, held there by the force of Coulomb attraction between unlike charges. It was very appealing, although it did have two major shortcomings. First, according to Maxwell's well-established theories of electrodynamics, any accelerating electric charge would continuously emit energy in the form of electromagnetic waves. An electron orbiting a nucleus in Rutherford's model would be accelerating centripetally and, hence, continuously giving off energy in the form of electromagnetic radiation. The electron would be expected to spiral in toward the nucleus in an orbit of ever-decreasing radius, as its total energy decreased. Eventually, with all its energy spent, it would be captured by the nucleus, and the atom would be considered to have collapsed. On the basis of classical mechanics and electromagnetic theory, atoms should remain stable for only a relatively short time. This is, of course, in direct contradiction to the evidence that atoms exist on a seemingly permanent basis and show no such tendency to collapse.

Second, under certain conditions, atoms do emit radiation in the form of visible and invisible light, but only at specific, discrete frequencies. The spiralling electron described above would emit radiation in a continuous spectrum, with a gradually increasing frequency until the instant of arrival at the nucleus. Furthermore, the work of Franck and Hertz plus the analysis of emission and absorption spectra had virtually confirmed the notion of discrete, well-defined internal energy levels within the atom, a feature that Rutherford's model lacked.

Shortly after the publication of Rutherford's proposals, the young Danish physicist Niels Bohr (**Figure 2**), a post-doctoral student in Rutherford's laboratory, became intrigued with these problems inherent in the model. He realized that the laws of classical mechanics and electrodynamics might fail to apply within the confines of the atom. Inspired by the Planck–Einstein introduction of quanta into the theory of electromagnetic radiation, Bohr proposed a quantum approach to the motion of electrons within the atom.

His paper, released in 1913 after two years of formulation, sent shock waves through the scientific community. In making the following three postulates about the motion of electrons within atoms, he defied the well-established classical laws of mechanics and electromagnetism:

- Of all the possible circular and elliptical orbits for electrons around a nucleus, only a very special few orbits are physically “allowed.” Each allowed orbit is characterized by a different specific amount of electron energy.
- When moving in an allowed orbit, an electron is exempt from the classical laws of electromagnetism and, in particular, does not radiate energy as it moves along its orbital path. Each such orbit is consequently called a **stationary state**.
- Electrons “jump” from a higher energy orbit to a lower energy orbit, with the energy difference between these two stationary states given off in the form of a single photon of electromagnetic radiation. Similarly, an atom can only absorb energy if that amount of energy is equal to the energy difference between a lower stationary state and some higher one.

stationary state the orbit of an electron in which it does not radiate energy

To summarize: Bohr’s idea was that atoms only exist in certain stationary states characterized by certain allowed orbits for their electrons, which move in these orbits with only certain amounts of total energy, the so-called energy levels of the atom. But what made these allowed orbits different from all the other disallowed orbits?

Bohr believed, drawing on the work of Planck, that something in the model of the atom must be quantized. Although he actually chose angular momentum, the picture is clearer if we leap ahead a decade and borrow the concept of wave–particle duality from de Broglie. Let us suppose that electrons can only exist in stable orbits if the length of the orbital path is a whole number of de Broglie electron wavelengths. Recall that an electron of mass m and speed v has a de Broglie wavelength given by

$$\lambda = \frac{h}{mv}$$

where h is Planck’s constant (6.63×10^{-34} J·s).

The standing-wave pattern for an electron in a stable orbit might then, for example, be three wavelengths, as in **Figure 3(a)**. Similar conditions hold for the standing-wave interference pattern for a string fixed at both ends (**Figure 3(b)**).

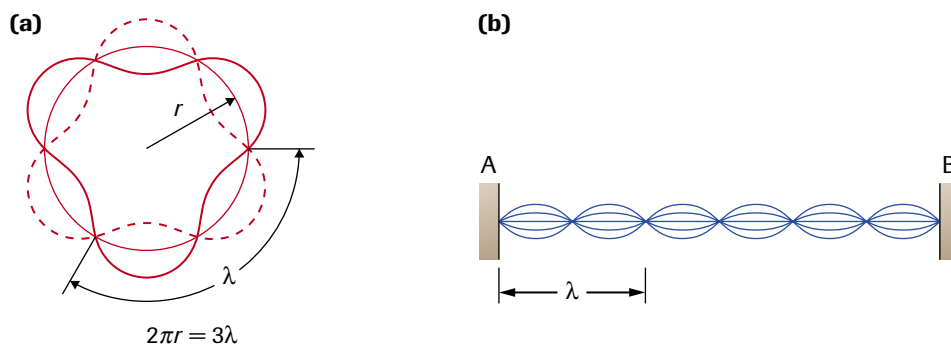


Figure 3

- (a)** The standing-wave pattern for an electron wave in a stable orbit of hydrogen, here chosen to have exactly three wavelengths
- (b)** The standing-wave pattern for a string fixed at both ends

If the orbits are essentially circular, and if the first allowed orbit has a radius r_1 and is occupied by an electron moving with a speed v_1 , the length of the orbital path will be one wavelength:

$$2\pi r_1 = \lambda$$

$$2\pi r_1 = \frac{h}{mv_1}$$

Similarly, for the second allowed orbit,

$$2\pi r_2 = 2\lambda$$

DID YOU KNOW?

Symbols

The expression mv_0r_0 represents the angular momentum of a mass m , moving in a circle of radius r_0 , at a constant speed v_0 . The quantity $\frac{h}{2\pi}$ appears so frequently in quantum physics that it is often abbreviated to \hbar (“ h bar”).

More generally, for the n th allowed orbit,

$$2\pi r_n = n\lambda = n\left(\frac{h}{mv_n}\right)$$

Thus, according to Bohr, the allowed orbits are those determined by the relationship

$$mv_n r_n = n\left(\frac{h}{2\pi}\right) \quad (n = 1, 2, \dots)$$

The whole number n appearing in this equation, which represents the number of de Broglie wavelengths in the orbital path, is called the “quantum number” for the allowed orbit (**Figure 4**). The equation itself, named “Bohr’s quantum condition,” provides the key to an explanation of atomic structure more complete than Rutherford’s.

The Wave-Mechanical Model of the Hydrogen Atom

With the formulation of Bohr’s quantum hypothesis about the special nature of the allowed orbits, it became possible to combine classical mechanics with quantum wave mechanics to produce an elegant model of atomic structure, satisfactory for hydrogen (but overhauled a few years later to generalize the electron orbits of all elements).

A hydrogen atom consists of a stationary proton of mass m_p and charge $+1e$ and a moving electron of mass m_e and charge $-1e$. The electron moves in a circular orbit of radius r_n at a constant speed v_n in such a way that n complete de Broglie wavelengths fit exactly into each orbital path. The Coulomb force of electrical attraction between the proton and the electron provides the force necessary to sustain the circular orbit; that is,

$$F_c = F_e$$

$$\frac{m_e v_n^2}{r_n} = \frac{ke^2}{r_n^2}$$

or more simply,

$$m_e v_n^2 = \frac{ke^2}{r_n} \quad \text{Equation (1)}$$

Applying Bohr’s quantum hypothesis,

$$mv_n r_n = n\left(\frac{h}{2\pi}\right) \quad \text{Equation (2)}$$

Solving Equation (2) for v_n , we have

$$v_n = \frac{nh}{2\pi m_e r_n} \quad \text{Equation (2a)}$$

Substituting this value for v_n into Equation (1), we have

$$m_e \left(\frac{nh}{2\pi m_e r_n}\right)^2 = \frac{ke^2}{r_n}$$

$$\frac{n^2 h^2}{4\pi^2 m_e r_n^2} = \frac{ke^2}{r_n}$$

$$r_n = \frac{n^2 h^2}{4\pi^2 m_e ke^2} \quad \text{Equation (3)}$$

as an expression for the radius of the n th circular allowed orbit in the hydrogen atom.

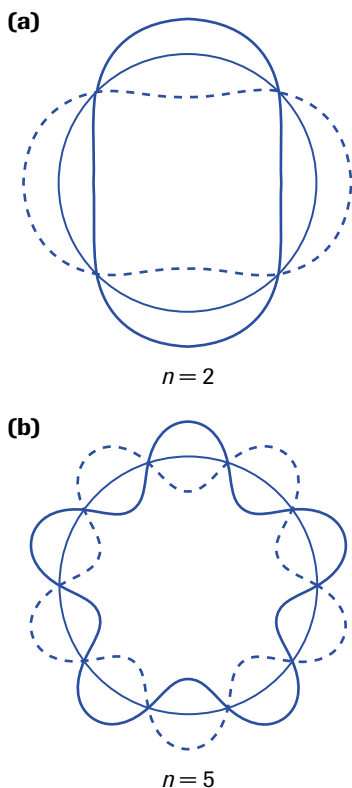


Figure 4

Standing circular waves for **(a)** two and **(b)** five de Broglie wavelengths. The number of wavelengths n is also the quantum number.

By substituting known values for the constants, we can evaluate this radius:

$$r_n = n^2 \left[\frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2}{4\pi^2 (9.1 \times 10^{-31} \text{ kg})(9.0 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2} \right]$$

$$r_n = 5.3 \times 10^{-11} n^2 \text{ m}$$

The radius of the smallest orbit in hydrogen (when $n = 1$) is $5.3 \times 10^{-11} \text{ m}$, sometimes called the Bohr radius. It is a good estimate of the normal size of a hydrogen atom. The radii of other orbits, given by the equation above, are

$$r_2 = 2^2 r_1 = 4r_1 = 4(5.3 \times 10^{-11} \text{ m}) = 2.1 \times 10^{-10} \text{ m}$$

$$r_3 = 3^2 r_1 = 9r_1 = 4.8 \times 10^{-10} \text{ m} \quad (\text{and so on})$$

Recall that, according to Bohr, an electron can only exist in one of these allowed orbits, with no other orbital radius being physically possible.

To find the speed v_n with which the electron moves in its orbit, we rearrange Equation (2a) to get

$$v_n = \frac{nh}{2\pi m_e \left(\frac{n^2 h^2}{4\pi^2 k m_e e^2} \right)}$$

$$v_n = \frac{2\pi k e^2}{nh} \quad \text{Equation (4)}$$

Again substituting known values, we have

$$v_n = \frac{1}{n} \left[\frac{2\pi(9.0 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2)(1.6 \times 10^{-19} \text{ C})^2}{6.63 \times 10^{-34} \text{ J}\cdot\text{s}} \right]$$

$$v_n = \frac{1}{n} (2.2 \times 10^6) \text{ m/s}$$

so that

$$v_1 = 2.2 \times 10^6 \text{ m/s}$$

$$v_2 = \frac{1}{2} v_1 = 1.1 \times 10^6 \text{ m/s}$$

$$v_3 = \frac{1}{3} v_1 = 7.3 \times 10^5 \text{ m/s} \quad (\text{and so on})$$

Just as with a satellite orbiting Earth, the electron has a definite, characteristic energy, given by the sum of its kinetic and electrical-potential energies. Thus, in its n th orbit the total energy of the electron is

$$E_n = E_K + E_e$$

$$E_n = \frac{1}{2} m_e v_n^2 + \left(-\frac{ke^2}{r_n} \right)$$

Substituting values for v_n from Equation (4) and for r_n from Equation (3), we have

$$E_n = \frac{1}{2} m_e \left(\frac{2\pi k e^2}{nh} \right)^2 - \frac{ke^2}{\left(\frac{n^2 h^2}{4\pi^2 k m_e e^2} \right)}$$

$$= \frac{2\pi^2 m_e k^2 e^4}{n^2 h^2} - \frac{4\pi^2 m_e k^2 e^4}{n^2 h^2}$$

$$E_n = -\frac{2\pi^2 m_e k^2 e^4}{n^2 h^2}$$

DID YOU KNOW?

Rydberg Constant

Spectroscopists had derived the same result for E_n by examining the Rydberg constant:

$$E_n = -\frac{Rhc}{n^2} = -\frac{13.6 \text{ eV}}{n^2}$$

This meant that the Rydberg constant, obtained empirically by fitting the data for the emission lines of hydrogen, agreed with Bohr's predicted value to 0.02%, one of the most accurate predictions then known in science.

Again substituting values for the constants, we have

$$E_n = -\frac{1}{n^2} \left[\frac{2\pi^2(9.1 \times 10^{-31} \text{ kg})(9.0 \times 10^9 \text{ N}\cdot\text{m}^2/\text{C}^2)^2(1.6 \times 10^{-19} \text{ C})^4}{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})^2} \right]$$

$$= -\frac{2.17 \times 10^{-18} \text{ J}}{n^2}$$

$$E_n = -\frac{13.6}{n^2} \text{ eV}$$

Thus, the energy levels for the allowed orbits of hydrogen are

$$E_1 = -\frac{13.6}{1^2} = -13.6 \text{ eV}$$

$$E_2 = -\frac{13.6}{2^2} = -3.40 \text{ eV}$$

$$E_3 = -\frac{13.6}{3^2} = -1.51 \text{ eV} \quad (\text{and so on})$$

This model verifies, exactly, the hydrogen atom energy levels previously established on the basis of the hydrogen emission spectrum. Although all the energy levels are negative, as is characteristic of a “bound” system, the energy of the outer orbits is less negative, and hence greater, than the energy of the inner orbits. The orbit closest to the nucleus ($n = 1$) has the lowest energy (-13.6 eV), the smallest radius ($0.53 \times 10^{-10} \text{ m}$), and the greatest electron speed ($2.2 \times 10^6 \text{ m/s}$).

It is now possible to draw a complete and detailed energy-level diagram for the hydrogen atom (**Figure 5**).

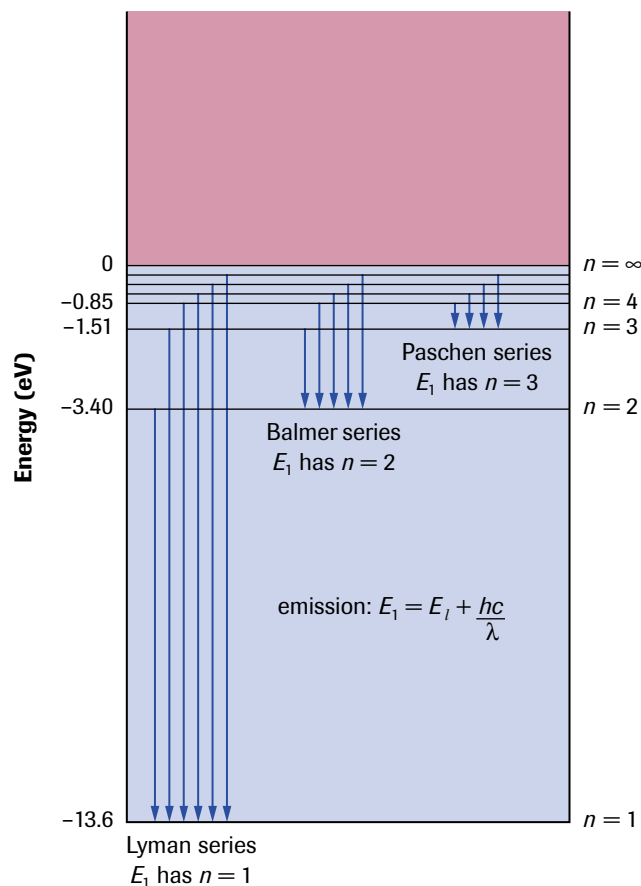


Figure 5

Energy-level diagram for the hydrogen atom

The lone electron of the hydrogen atom normally resides in the ground state ($n = 1$). However, in absorbing energy from photons or during collisions with high-speed particles, it may be boosted up to any of the excited states ($n = 2, 3, 4, \dots$). Once in an excited state, the electron will typically jump down to any lower energy state, giving off the excess energy by creating a photon. The arrows in **Figure 5** represent downward transitions giving rise to the various lines found in the hydrogen emission spectrum. They are grouped together in series, according to their common lower state; the series are named after famous spectroscopists whose work led to their discovery. The **Lyman series** is the set of transitions from higher energy levels to the ground state ($n = 1$); the **Balmer series** is the set of downward transitions to $n = 2$; and the **Paschen series** is the set of downward transitions to $n = 3$.

A sample problem illustrates how we can identify these spectral lines.

▶ **SAMPLE problem 3**

Determine, with the help of **Figure 5**, the wavelength of light emitted when a hydrogen atom makes a transition from the $n = 5$ orbit to the $n = 2$ orbit.

Solution

$\lambda = ?$

$$\text{For } n = 5, \quad E_5 = -\frac{13.6}{5^2} \text{ eV} = -0.54 \text{ eV}$$

$$\text{For } n = 2, \quad E_2 = -\frac{13.6}{2^2} \text{ eV} = -3.40 \text{ eV}$$

$$\begin{aligned} E_p &= E_5 - E_2 \\ &= -0.54 \text{ eV} - (-3.40 \text{ eV}) \end{aligned}$$

$$E_p = 2.86 \text{ eV}$$

Thus,

$$\begin{aligned} \lambda &= \frac{hc}{E_p} \\ &= \frac{(6.63 \times 10^{-34} \text{ J}\cdot\text{s})(3.00 \times 10^8 \text{ m/s})}{(2.86 \text{ eV})(1.60 \times 10^{-19} \text{ J/eV})} \end{aligned}$$

$$\lambda = 4.35 \times 10^{-7} \text{ m, or } 435 \text{ nm}$$

The wavelength of light emitted is 435 nm. (This is a violet line in the visible spectrum, the third line in the Balmer series.)

▶ **Practice**

Understanding Concepts

- How does the de Broglie wavelength of the electron compare with the circumference of the first orbit?
- Calculate the energies of all the photons that could possibly be emitted by a large sample of hydrogen atoms, all initially excited to the $n = 5$ state.
- In performing a Franck–Hertz type experiment, you accelerate electrons through hydrogen gas at room temperature over a potential difference of 12.3 V. What wavelengths of light could be emitted by the hydrogen?
- Calculate the wavelength of the line in the hydrogen Balmer series for which $n = 4$.

Lyman series series of wavelengths emitted in transitions of a photon from higher energy levels to the $n = 1$, or ground, state

Balmer series series of wavelengths emitted in transitions of a photon from higher energy levels to the $n = 2$ state

Paschen series series of wavelengths emitted in transitions of a photon from higher energy levels to the $n = 3$ state

Answers

- 0.31 eV; 0.65 eV; 0.96 eV; 1.9 eV; 2.6 eV; 2.86 eV; 10.2 eV; 12.1 eV; 12.8 eV; 13.1 eV
- 122 nm; 103 nm; 654 nm
- 488 nm

Answers

9. (a) 93 nm
(b) 1.2×10^4 nm
10. 10.2 eV; 122 nm
11. (a) 122 nm
(b) 1.89×10^3 nm
12. $n = 4.3 \times 10^3$;
 -7.4×10^{-7} eV

9. Calculate the wavelengths of (a) the most energetic and (b) the least energetic photon that can be emitted by a hydrogen atom in the $n = 7$ state.
10. Calculate the energy and wavelength of the least energetic photon that can be absorbed by a hydrogen atom at room temperature.
11. Calculate the longest wavelengths in (a) the hydrogen Lyman series ($n = 1$) and (b) the hydrogen Paschen series ($n = 3$).
12. What value of n would give a hydrogen atom a Bohr orbit of radius 1.0 mm? What would be the energy of an electron in that orbit?

Success of the Bohr Model

Although based on theoretical assumptions designed to fit the observations rather than on direct empirical evidence, Bohr's model was for many reasons quite successful:

- It provided a physical model of the atom whose internal energy levels matched those of the observed hydrogen spectrum.
- It accounted for the stability of atoms: Once an electron had descended to the ground state, there was no lower energy to which it could jump. Thus, it stayed there indefinitely, and the atom was stable.
- It applied equally well to other one-electron atoms, such as a singly ionized helium ion.

The model was incomplete, however, and failed to stand up to closer examination:

- It broke down when applied to many-electron atoms because it took no account of the interactions between electrons in orbit.
- With the development of more precise spectroscopic techniques, it became apparent that each of the excited states was not a unique, single energy level but a group of finely separated levels, near the Bohr level. To explain this splitting of levels, it was necessary to introduce modifications to the shape of the Bohr orbits as well as the concept that the electron was spinning on an axis as it moved.

Even though the Bohr model eventually had to be abandoned, it was a triumph of original thought and one whose basic features are still useful. It first incorporated the ideas of quantum mechanics into the inner structure of the atom and provided a basic physical model of the atom. In time, scientific thought would replace it by moving into the less tangible realm of electron waves and probability distributions, as discussed in the next section.

SUMMARY

The Bohr Model of the Atom

- Balmer devised a simple empirical equation from which all of the lines in the visible spectrum of hydrogen could be computed: $\frac{1}{\lambda} = R \left(\frac{1}{n_l^2} - \frac{1}{n_u^2} \right)$.

His equation allowed the energy levels for hydrogen to be predicted as

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

- The work of Franck and Hertz, and the analysis of emission and absorption spectra had confirmed that there are discrete, well-defined internal energy levels within the atom.

- Bohr proposed that atoms only exist in certain stationary states with certain allowed orbits for their electrons. Electrons move in these orbits with only certain amounts of total energy, called energy levels of the atom.
- Bohr made the following three postulates regarding the motion of electrons within atoms:
 1. There are a few special electron orbits that are “allowed,” each characterized by a different specific electron energy.
 2. When moving in an allowed stationary orbit, an electron does not radiate energy.
 3. Electrons may move from a higher-energy orbit to a lower-energy orbit, giving off a single photon. Similarly, an atom can only absorb energy if that energy is equal to the energy difference between a lower stationary state and some higher one.
- Bohr combined classical mechanics with quantum wave mechanics to produce a satisfactory model of the atomic structure of hydrogen.
- The lone electron of a hydrogen atom normally resides in the ground state ($n = 1$). By absorbing energy from photons, however, or from collisions with high-speed particles, it may be boosted up to any of the excited states ($n = 2, 3, 4, \dots$). Once in an excited state, the electron quickly moves to any lower state, creating a photon in the process.
- Bohr’s model was quite successful in that it provided a physical model of the hydrogen atom, matching the internal energy levels to those of the observed hydrogen spectrum, while also accounting for the stability of the hydrogen atom.
- Bohr’s model was incomplete in that it broke down when applied to many-electron atoms.

▶ Section 12.5 Questions

Understanding Concepts

1. In the hydrogen atom, the quantum number n can increase without limit. Does the frequency of possible spectral lines from hydrogen correspondingly increase without limit?
2. A hydrogen atom initially in its ground state ($n = 1$) absorbs a photon, ending up in the state for which $n = 3$.
 - (a) Calculate the energy of the absorbed photon.
 - (b) If the atom eventually returns to the ground state, what photon energies could the atom emit?
3. What energy is needed to ionize a hydrogen atom from the $n = 2$ state? How likely is such ionization to occur? Explain your answer.
4. Determine the wavelength and frequency of the fourth Balmer line (emitted in the transition from $n = 6$ to $n = 2$) for hydrogen.
5. For which excited state, according to the Bohr theory, can the hydrogen atom have a radius of 0.847 nm?
6. According to the Bohr theory of the atom, the speed of an electron in the first Bohr orbit of the hydrogen atom is 2.19×10^6 m/s.
 - (a) Calculate the de Broglie wavelength associated with this electron.
 - (b) Prove, using the de Broglie wavelength, that if the radius of the Bohr orbit is 4.8×10^{-10} m, then the quantum number is $n = 3$.
7. Calculate the Coulomb force of attraction on the electron when it is in the ground state of the Bohr hydrogen atom.