

similarity of the two patterns shows that both X-rays and electrons do indeed behave analogously in these experiments.

The wavelike property of electrons is used in electron microscopes. The wavelengths of the electrons can be controlled through an applied voltage, and the small de Broglie wavelengths attainable offer a more precise probe than an ordinary light microscope. In addition, in contrast to electromagnetic radiation of similar wavelengths (X-rays and ultraviolet), the electron beam can be readily focused by using electric and magnetic fields, generating sharper images. Electron microscopes are used routinely in chemistry and biology to investigate atomic and molecular structures.

An interesting historical aside in the concept of the wave-particle duality of matter is that the first person to show that the electron was a subatomic particle was the English physicist Sir Joseph J. Thomson in 1895 and then his son Sir George P. Thomson was among the first to show experimentally in 1926 that the electron could act as a wave. The father won a Nobel Prize in 1906 for showing that the electron is a particle and the son won a Nobel Prize in 1937 for showing that it is a wave.

### 1–8. The Bohr Theory of the Hydrogen Atom Can Be Used to Derive the Rydberg Formula

In 1911, the Danish physicist Niels Bohr presented a theory of the hydrogen atom that gave a beautifully simple explanation of the hydrogen atomic spectrum. We present here a brief discussion of the Bohr theory.

According to the nuclear model of the atom, the hydrogen atom can be pictured as a central, rather massive nucleus with one associated electron. Because the nucleus is so much more massive than the electron, we can consider the nucleus to be fixed and the electron to be revolving about it. The force holding the electron in a circular orbit is supplied by the coulombic force of attraction between the proton and the electron (Coulomb's law):

$$f = \frac{e^2}{4\pi\epsilon_0 r^2}$$

where  $r$  is the radius of the orbit,  $e$  is the charge on the electron, and  $\epsilon_0 = 8.85419 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$  is the permittivity of free space. The occurrence of the factor  $4\pi\epsilon_0$  in Coulomb's law is a result of using SI units. The coulombic force is balanced by the centrifugal force (see Problem 1–41)

$$f = \frac{m_e v^2}{r} \quad (1.13)$$

where  $m_e$  and  $v$  are the mass and the speed of the electron, respectively. If we equate the coulombic force and the centrifugal force, then we obtain

$$\frac{e^2}{4\pi\epsilon_0 r^2} = \frac{m_e v^2}{r} \quad (1.14)$$

We are tacitly assuming here that the electron is revolving around the fixed nucleus in a circular orbit of radius  $r$ . Classically, however, because the electron is constantly being accelerated according to Equation 1.13 (Problem 1-41), it should emit electromagnetic radiation and lose energy. Consequently, classical physics predicts that an electron revolving around a nucleus will lose energy and spiral into the nucleus, and so a stable orbit for the electron is classically forbidden. Bohr's great contribution was to make two nonclassical assumptions. The first was to assume the existence of stationary electron orbits, in defiance of classical physics. He then specified these orbits by the equivalent of assuming that the de Broglie waves of the orbiting electron must "match" or be in phase, as the electron makes one complete revolution. Without such matching, cancellation of some amplitude occurs during each revolution, and the wave will disappear (see Figure 1.9). For the wave pattern around an orbit to be stable, we are led to the condition that an integral number of complete wavelengths must fit around the circumference of the orbit. Because the circumference of a circle is  $2\pi r$ , we have the quantum condition

$$2\pi r = n\lambda \quad n = 1, 2, 3, \dots \quad (1.15)$$

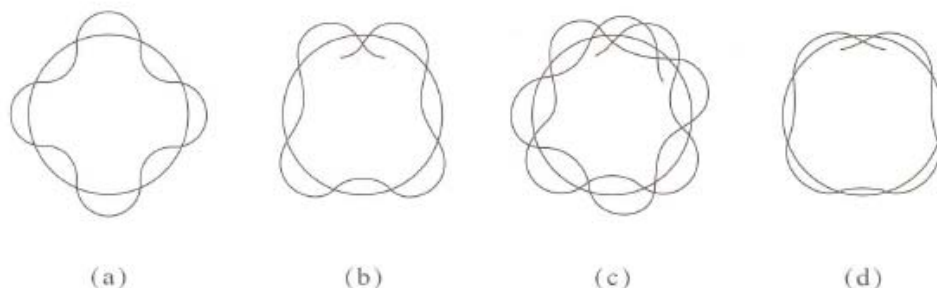
If we substitute the de Broglie wavelength formula (Equation 1.12) into Equation 1.15, we obtain

$$m_e v r = \frac{nh}{2\pi}$$

or

$$m_e v r = n\hbar \quad n = 1, 2, 3, \dots \quad (1.16)$$

where we introduce the symbol  $\hbar$  for  $h/2\pi$ . The short-hand notation is introduced because  $\hbar$  appears in many of the equations of quantum chemistry. The quantity on the left side of Equation 1.16 is the angular momentum of the electron. Thus, another



**FIGURE 1.9**

An illustration of matching and mismatching de Broglie waves travelling in Bohr orbits. If the wavelengths of the de Broglie waves are such that an integral number of them fit around the circle, then they match after a complete revolution (a). If a wave does not match after a complete revolution (b), cancellation will result and the wave will progressively disappear (c, d).

interpretation of Equation 1.15, and one more commonly attributed to Bohr, is that the angular momentum of the electron about the proton must be quantized; in other words, it can have only certain discrete values that satisfy Equation 1.16 for  $n = 1, 2, 3, \dots$

If we solve Equation 1.16 for  $v$  and substitute it into Equation 1.14, we find that the radii of the orbits must satisfy

$$r = \frac{\epsilon_0 \hbar^2 n^2}{\pi m_e e^2} = \frac{4\pi \epsilon_0 \hbar^2 n^2}{m_e e^2} \quad (1.17)$$

Thus, we see that the radii of the allowed orbits, or Bohr orbits, are quantized. According to this picture, the electron can move around the nucleus in circular orbits only with radii given by Equation 1.17. The orbit with the smallest radius is the one with  $n = 1$ , for which

$$\begin{aligned} r &= \frac{4\pi(8.85419 \times 10^{-12} \text{ C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2})(1.055 \times 10^{-34} \text{ J} \cdot \text{s})^2}{(9.109 \times 10^{-31} \text{ kg})(1.6022 \times 10^{-19} \text{ C})^2} \\ &= 5.292 \times 10^{-11} \text{ m} = 52.92 \text{ pm} \end{aligned} \quad (1.18)$$

The radius of the first Bohr orbit is often denoted by  $a_0$ .

The total energy of the electron in an atom is equal to the sum of its kinetic energy and potential energy. The potential energy of an electron and a proton separated by a distance  $r$  is given by Coulomb's law

$$V(r) = -\frac{e^2}{4\pi \epsilon_0 r} \quad (1.19)$$

The negative sign here indicates that the proton and electron attract each other; their energy is less than it is when they are infinitely separated [ $V(\infty) = 0$ ]. The total energy of the electron in a hydrogen atom is

$$E = \text{KE} + V(r) = \frac{1}{2} m_e v^2 - \frac{e^2}{4\pi \epsilon_0 r} \quad (1.20)$$

Using Equation 1.14 to eliminate the  $m_e v^2$  in the kinetic energy term, Equation 1.20 becomes

$$E = \frac{1}{2} \left( \frac{e^2}{4\pi \epsilon_0 r} \right) - \frac{e^2}{4\pi \epsilon_0 r} = -\frac{e^2}{8\pi \epsilon_0 r} \quad (1.21)$$

The only allowed values of  $r$  are those given by Equation 1.17, and so if we substitute Equation 1.17 into Equation 1.21, we find that the only allowed energies are

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 \hbar^2} \frac{1}{n^2} \quad n = 1, 2, \dots \quad (1.22)$$

The negative sign in this equation indicates that the energy states are bound states; the energies given by Equation 1.22 are less than when the proton and electron are infinitely separated. Note that  $n = 1$  in Equation 1.22 corresponds to the state of lowest energy.



1-8. The Bohr Theory of the Hydrogen Atom Can Be Used to Derive the Rydberg Formula

This energy is called the *ground-state energy*. At ordinary temperatures, hydrogen atoms, as well as most other atoms and molecules, are found almost exclusively in their ground electronic states. The states of higher energy are called *excited states* and are generally unstable with respect to the ground state. An atom or a molecule in an excited state will usually relax back to the ground state and give off the energy as electromagnetic radiation.

We can display the energies given by Equation 1.22 in an energy-level diagram such as that in Figure 1.10. Note that the energy levels merge as  $n \rightarrow \infty$ . Bohr assumed that the observed spectrum of the hydrogen atom is due to transitions from one allowed energy state to another, and using Equation 1.22, he predicted that the allowed energy differences are given by

$$\Delta E = \frac{m_e e^4}{8\epsilon_0^2 h^2} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) = h\nu \quad (1.23)$$

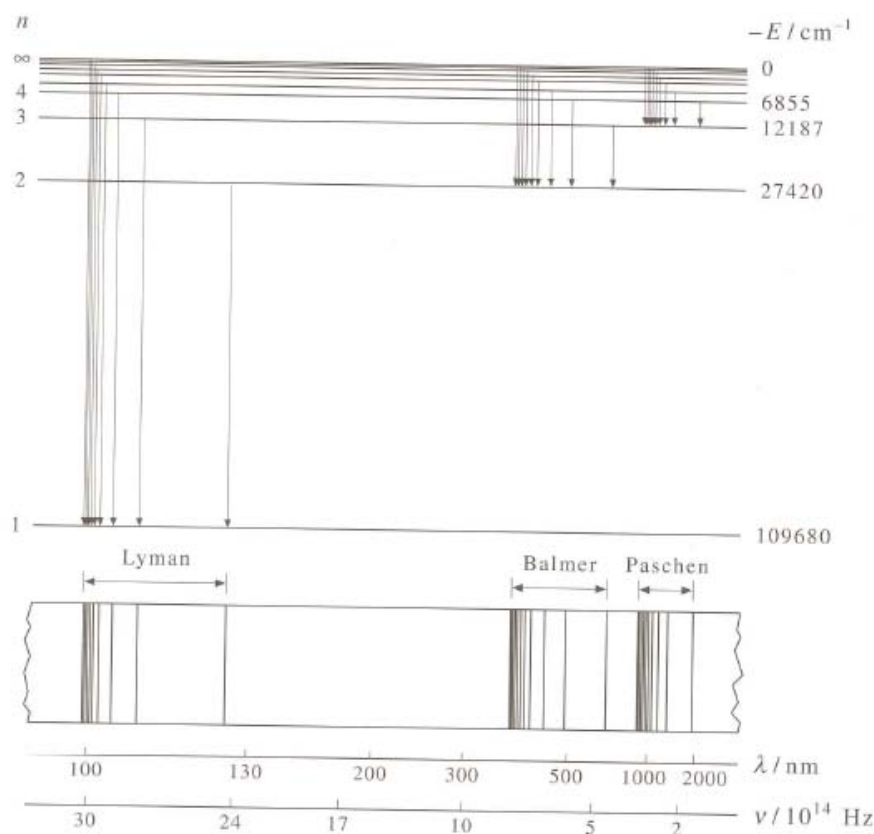


FIGURE 1.10

The energy-level diagram for the hydrogen atom, showing how transitions from higher states into some particular state lead to the observed spectral series for hydrogen.

The equation  $\Delta E = h\nu$  is called the *Bohr frequency condition*. Bohr assumed that as the electron falls from one level to another, the energy evolved is given off as a photon of energy  $E = h\nu$ . Figure 1.10 groups the various transitions that occur according to the final state into which the electron falls. We can see, then, that the various observed spectral series arise in a natural way from the Bohr model. The Lyman series occurs when electrons that are excited to higher levels relax to the  $n = 1$  state; the Balmer series occurs when excited electrons fall back into the  $n = 2$  state, and so on.

We can write the theoretical formula (Equation 1.23) in the form of the empirical Rydberg formula by writing  $h\nu = hc\tilde{\nu}$ :

$$\tilde{\nu} = \frac{m_e e^4}{8\epsilon_0^2 ch^3} \left( \frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \quad (1.24)$$

If we compare Equations 1.11 and 1.24, we conclude that

$$R_\infty = \frac{m_e e^4}{8\epsilon_0^2 ch^3} \quad (1.25)$$

should be equal to the Rydberg constant, Equation 1.11.

#### EXAMPLE 1-8

Using the values of the physical constants given inside the front cover of this book, calculate  $R_\infty$  and compare the result to its experimental value,  $109\,677.6\text{ cm}^{-1}$ .

SOLUTION:

$$\begin{aligned} R_\infty &= \frac{(9.10939 \times 10^{-31}\text{ kg})(1.602177 \times 10^{-19}\text{ C})^4}{(8)(8.85419 \times 10^{-12}\text{ C}^2\cdot\text{N}^{-1}\cdot\text{m}^{-2})^2(2.99792 \times 10^8\text{ m}\cdot\text{s}^{-1})(6.626076 \times 10^{-34}\text{ J}\cdot\text{s})^3} \\ &= 1.09737 \times 10^7\text{ m}^{-1} = 109\,737\text{ cm}^{-1} \end{aligned}$$

which is within 0.05% of the experimental value of  $109\,677.6\text{ cm}^{-1}$ , surely a remarkable agreement.

#### EXAMPLE 1-9

Calculate the ionization energy of the hydrogen atom.

SOLUTION: The ionization energy  $IE$  is the energy required to take the electron from the ground state to the first unbound state, which is obtained by letting  $n_2 = \infty$  in Equation 1.24. Thus, we write

$$IE = R_\infty \left( \frac{1}{1^2} - \frac{1}{\infty^2} \right)$$

or

$$\begin{aligned} IE = R_{\infty} &= 109\,737\text{ cm}^{-1} \\ &= 2.1787 \times 10^{-18}\text{ J} \\ &= 13.598\text{ eV} = 1312.0\text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

Note that we have expressed the energy in units of wave numbers ( $\text{cm}^{-1}$ ). This unit is not strictly a unit of energy, but because of the simple relation between wave number and energy,  $E = hc\tilde{\nu}$ , energy is often expressed in this way (cf. Problem 1-1).

Despite a number of successes and the beautiful simplicity of the Bohr theory, the theory could not be extended successfully even to a two-electron system such as helium. Furthermore, even for a simple system such as hydrogen, it could not explain the spectra that arise when a magnetic field is applied to the system, nor could it predict the intensities of the spectral lines.

### 1-9. The Heisenberg Uncertainty Principle States That the Position and the Momentum of a Particle Cannot Be Specified Simultaneously with Unlimited Precision

We now know that we must consider light and matter as having the characteristics of both waves and particles. Let's consider a measurement of the position of an electron. If we wish to locate the electron within a distance  $\Delta x$ , then we must use a measuring device that has a spatial resolution less than  $\Delta x$ . One way to achieve this resolution is to use light with a wavelength on the order of  $\lambda \approx \Delta x$ . For the electron to be "seen", a photon must interact or collide in some way with the electron, for otherwise the photon will just pass right by and the electron will appear transparent. The photon has a momentum  $p = h/\lambda$ , and during the collision, some of this momentum will be transferred to the electron. The very act of locating the electron leads to a change in its momentum. If we wish to locate the electron more accurately, we must use light with a smaller wavelength. Consequently, the photons in the light beam will have greater momentum because of the relation  $p = h/\lambda$ . Because some of the photon's momentum must be transferred to the electron in the process of locating it, the momentum change of the electron becomes greater. A careful analysis of this process was carried out in the mid-1920s by the German physicist Werner Heisenberg, who showed that it is not possible to determine exactly how much momentum is transferred to the electron. This difficulty means that if we wish to locate an electron to within a region  $\Delta x$ , there will be an uncertainty in the momentum of the electron. Heisenberg was able to show that if  $\Delta p$  is the uncertainty in the momentum of the electron, then

$$\Delta x \Delta p \geq h \quad (1.26)$$