4

The Particle Nature of Matter

Chapter Outline

In Chapter 3 we reviewed the evidence for the wave nature of electromagnetic radiation and dealt with major experimental puzzles of the first quarter of the 20th century, which required a particle-like behavior of radiation for their solution. In particular, we discussed Planck's revolutionary idea of energy quantization of oscillators in the walls of a perfect radiator, Einstein's extension of energy quantization to light in the photoelectric effect, and Compton's further confirmation of the existence of the photon as a particle carrying momentum in x-ray scattering experiments.

In this chapter we shall examine the evidence for the particle nature of matter. We only mention briefly the early atomists and concentrate instead on the developments from 1800 onward that dealt with the composition of atoms. In particular, we review the ingenious and fascinating experiments that led to the discoveries of the electron, the proton, the nucleus, and the important Rutherford–Bohr planetary model of the atom.

4.1 THE ATOMIC NATURE OF MATTER

To say that the world is made up of atoms is, today, commonplace. Because the atomic picture of reality is often accepted without question, students can miss out on the rich and fascinating story of how atoms were shown to be real. The discovery and proof of the graininess of the world seem especially fascinating for two reasons. First, because of the size of individual atoms, measurements of atomic properties are usually indirect and necessarily involve clever manipulations of large-scale measurements to infer properties of microscopic particles. Second, the historical evolution of ideas about atomicity shows clearly the real way in which science progresses. This progression is often nonlinear and involves an interdependence of physics, chemistry, and mathematics, and the convergence of many different lines of investigation.

There is also an exalted romance in honoring the great atomists who were able to pick out organizing principles from the confusing barrage of marketplace ideas of their time: Democritus and Leucippus, who speculated that the unchanging substratum of the world was atoms in motion; the debonair French chemist Lavoisier and his wife (see Fig. 4.1), who established the conservation of matter in many careful chemical experiments; Dalton, who perceived the atomicity of nature in the law of multiple proportions of compounds; Avogadro, who in a most obscure and little-appreciated paper, postulated that all pure gases at the same temperature and pressure have the same number of molecules per unit volume; and Maxwell,[1] who showed with his molecular-kinetic theory of gases how macroscopic quantities, such as pressure and temperature, could be derived from averages over distributions

Figure 4.1 Antoine Lavoisier (French chemist, 1743–1794) and Madame Lavoisier who together established the principle of conservation of mass in chemical reactions. In this painting they appear to have matters other than chemistry on the mind. (© *Bettmann/CORBIS*)

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[1] Maxwell was a genius twice over. Either his theory of electricity and magnetism or his kinetic theory of gases would qualify him for that rank.

of molecular properties. The list could run on and on. We abbreviate it by naming Jean Perrin and the ubiquitous Albert Einstein,[2] who carried on very important theoretical and experimental work concerning Brownian motion, the zigzag movement of small suspended particles caused by molecular impacts. Their work produced additional confirmation of the atomic-molecular hypothesis and resulted in improved values of Avogadro's number as late as the early 1900s.

4.2 THE COMPOSITION OF ATOMS

We now turn our attention to answering the rather dangerous question, "If matter is primarily composed of atoms, what are atoms composed of?" Again, we can point to some primary discoveries that showed that atoms are composed of light, negatively charged particles orbiting a heavy, positively charged nucleus. These were

- *The discovery of the law of electrolysis in 1833 by Michael Faraday*. Through careful experimental work on electrolysis, Faraday showed that the mass of an element liberated at an electrode is directly proportional to the charge transferred and to the atomic weight of the liberated material but is inversely proportional to the valence of the freed material.
- *The identification of cathode rays as electrons and the measurement of the charge-to-mass ratio (e/m_e) of these particles by Joseph John (J. J.) Thomson in 1897*. Thomson measured the properties of negative particles emitted from different metals and found that the value of e/m_e was always the same. He thus came to the conclusion that the electron is a constituent of all matter!
- *The precise measurement of the electronic charge (e) by Robert Millikan in 1909*. By combining his result for (e) with Thomson's e/m_e value, Millikan showed unequivocally that particles about 1000 times less massive than the hydrogen atom exist.
- *The establishment of the nuclear model of the atom by Ernest Rutherford and coworkers Hans Geiger and Ernest Marsden in 1913*. By scattering fast-moving α particles (charged nuclei of helium atoms emitted spontaneously in radioactive decay processes) from metal foil targets, Rutherford established that atoms consist of a compact positively charged nucleus (diameter $\approx 10^{-14}$ m) surrounded by a swarm of orbiting electrons (electron cloud diameter $\approx 10^{-10}$ m).

Let us describe these developments in more detail. We start with a brief example of Faraday's experiments, in particular the electrolysis of molten common salt (NaCl). Faraday found that if 96,500 C of charge (1 faraday) is passed through such a molten solution, 23.0 g of Na will deposit on the cathode and 35.5 g of chlorine gas will bubble off the anode (Fig. 4.2). In this case, exactly 1 gram atomic weight or mole of each element is released because both are monovalent. For divalent and trivalent elements, exactly $\frac{1}{2}$ and $\frac{1}{3}$ of a mole, respectively, would be released. As expected, doubling the

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[2] Much of Einstein's earliest work was concerned with the molecular analysis of solutions and determinations of molecular radii and Avogadro's number. See A. Pais, "*Subtle is the Lord . . .*" *The Science and the Life of Albert Einstein*, New York, Oxford University Press, 1982, Chapter 5.

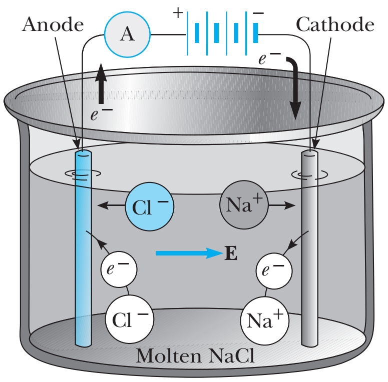

Figure 4.2 Electrolysis of molten NaCl.

quantity of charge passed doubles the mass of the neutral element liberated. Faraday's results may be given in equation form as

$$m = \frac{(q)\,(\text{molar mass})}{(96{,}500\ \text{C})\,(\text{valence})} \tag{4.1}$$

Faraday's law of electrolysis

where m is the mass of the liberated substance in grams, q is the total charge passed in coulombs, the molar mass is in grams, and the valence is dimensionless.

EXAMPLE 4.1 The Electrolysis of $BaCl_2$

How many grams of barium and chlorine (cough!) will you get if you pass a current of 10.0 A through molten $BaCl_2$ for 1 h? Barium has a molar weight of 137 g and a valence of 2. Chlorine has a molar weight of 35.5 g and a valence of 1.

Solution Using Equation 4.1 and $q = It$, where I is the current and t is the time, we have

$$m_{\text{Ba}} = \frac{(q)\,(\text{molar mass})}{(96{,}500\ \text{C})\,(\text{valence})}$$

$$= \frac{(10.0\ \text{C/s})\,(3600\ \text{s})\,(137\ \text{g})}{(96{,}500\ \text{C})\,(2)} = 25.6\ \text{g}$$

$$m_{\text{Cl}} = \frac{(10.0\ \text{C/s})\,(3600\ \text{s})\,(35.5\ \text{g})}{(96{,}500\ \text{C})\,(1)} = 13.2\ \text{g}$$

Faraday's law of electrolysis is explained in terms of an atomic picture shown in Figure 4.2. Charge passes through the molten solution in the form of ions, which possess an excess or deficiency of one or more electrons. Under the influence of the electric field produced by the battery, these ions move to the anode or cathode, where they respectively lose or gain electrons and are liberated as neutral atoms.

Although it was far from clear in 1833, Faraday's law of electrolysis confirmed three important parts of the atomic picture. First, it offered proof that matter consists of molecules and that molecules consist of atoms. Second, it showed that charge is quantized, because only integral numbers of charges are transferred at the electrodes. Third, it showed that the subatomic parts of atoms are positive and negative charges, although the mass and the size of the charge of these subatomic particles remained unknown.

Figure 4.3 J. J. Thomson. (*AIP Emilio Segrè Visual Archives/W. F. Meggers Collection*)

The next major step explaining the composition of atoms was taken by Joseph John (J. J.) Thomson (see Figure 4.3). His discovery in 1897[3] that the "rays" seen in low-pressure gas discharges were actually caused by negative particles (electrons) ended a debate dating back nearly 30 years: Were cathode rays material particles or waves? Contrary to our rather blasé present acceptance of the electron, many of Thomson's distinguished contemporaries responded with utter disbelief to the idea that electrons were a constituent of all matter. Much of the opposition to Thomson's discovery stemmed from the fact that it required the abandonment of the recently established concept of the atom as an indivisible entity. Thomson's discovery of the electron disturbed this newly established order in atomic theory and provoked startling new developments—Rutherford's nuclear model and the first satisfactory theory of the emission of light by atomic systems, the Bohr model of the atom.

Figure 4.4 shows the original vacuum tube used by Thomson in his e/m_e experiments. Figure 4.5 shows the various parts of the Thomson apparatus for easy reference. Electrons are accelerated from the cathode to the anode, collimated by slits in the anodes, and then allowed to drift into a region of crossed (perpendicular) electric and magnetic fields. The simultaneously applied $\mathbf{E}$ and $\mathbf{B}$ fields are first adjusted to produce an undeflected beam. If the $\mathbf{B}$ field is then turned off, the $\mathbf{E}$ field alone produces a measurable beam deflection on the phosphorescent screen. From the size of the deflection and the measured values of $\mathbf{E}$ and $\mathbf{B}$, the charge-to-mass ratio, e/m_e, may be determined. The truly ingenious feature of this experiment is the manner in which Thomson measured v_x, the horizontal velocity component of the beam. He did this by balancing the magnetic and electric forces. In effect, he created a *velocity selector*, which could select out of the beam those particles having a velocity within a narrow range of values. This device was extensively used in the first quarter

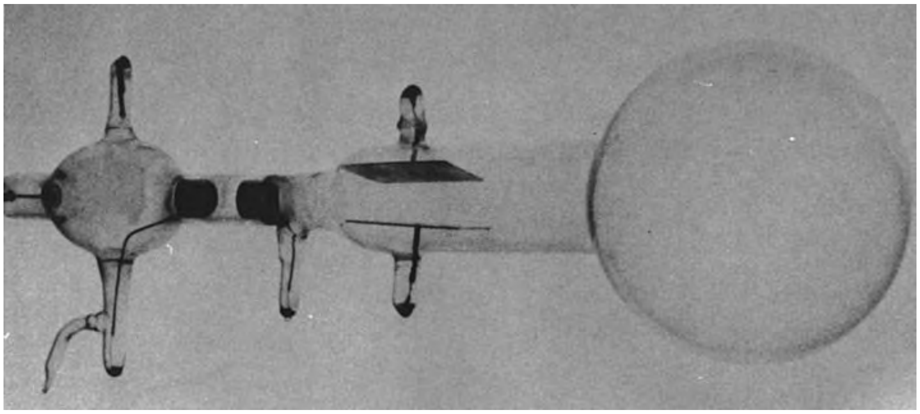

Figure 4.4 The original e/m_e tube used by J. J. Thomson. (*After Figure 1.3, p. 7, R. L. Sproull and W. A. Phillips,* Modern Physics, *3rd ed., New York, John Wiley & Sons, 1980*).

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[3] J. J. Thomson, *Phil. Mag.* 44:269, 1897.

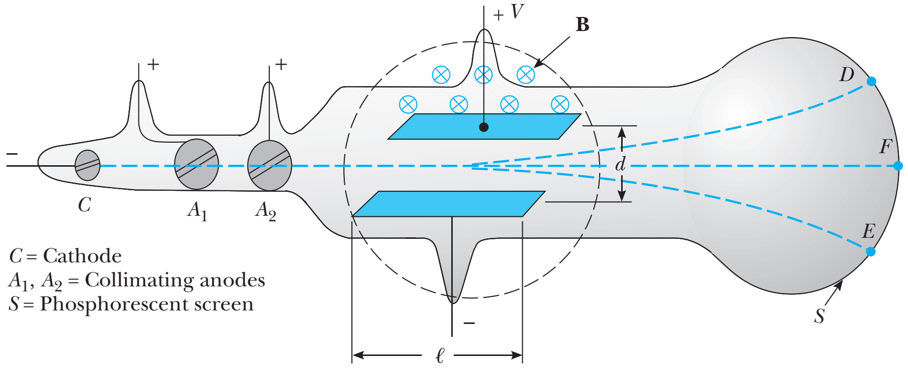

Figure 4.5 A diagram of Thomson's e/m_e tube (patterned after J. J. Thomson, *Philosophical Magazine* (5)44:293, 1897). Electrons subjected to an electric field alone land at *D*, while those subjected to a magnetic field alone land at *E*. When both electric and magnetic fields are present and properly adjusted, the electrons experience no net deflection and land at *F*.

of the 20th century in charge-to-mass measurements (q/m) on many particles and in early mass spectrometers.

To gain a clearer picture of the Thomson experiment, let us analyze the electron's motion in his apparatus. Figure 4.6 shows the trajectory of a beam of negative particles entering the **E** and **B** field regions with horizontal velocity v_x. Consider first only an **E** field between the plates. For this case, v_x remains constant throughout the motion because there is no force acting in the x direction. The y component of velocity, v_y, is constant everywhere except between the plates, where the electron experiences a constant upward acceleration due to the electric force and follows a parabolic path. To solve for the deflection angle, θ, we must solve for v_x and v_y. Because v_y

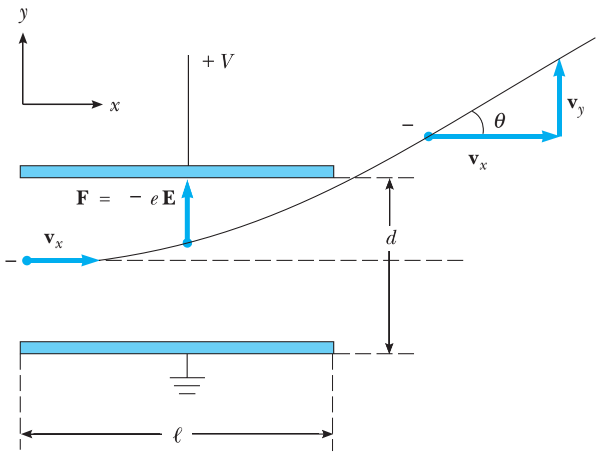

Figure 4.6 Deflection of negative particles by an electric field.

initially is zero, the electron leaves the plates with a y component of velocity given by

$$v_y = a_y t \tag{4.2}$$

Because $a_y = F/m_e = Ee/m_e = Ve/m_e d$, and $t = \ell/v_x$, where d and ℓ are the dimensions of the region between the plates and V is the applied potential, we obtain

$$v_y = \frac{V\ell e}{m_e v_x d} \tag{4.3}$$

From Figure 4.6, $\tan\theta = v_y/v_x$, so using Equation 4.3 we obtain

$$\tan\theta = \frac{V\ell}{v_x^2 d}\left(\frac{e}{m_e}\right) \tag{4.4}$$

Assuming small deflections, $\tan\theta \approx \theta$, so we have

$$\theta \approx \frac{V\ell}{v_x^2 d}\left(\frac{e}{m_e}\right) \tag{4.5}$$

Note that θ, the beam deflection, V, the voltage applied to the horizontal deflecting plates, and d and ℓ, the spacing and length, respectively, of the horizontal deflecting plates can all be measured. Hence, one only needs to measure v_x to determine e/m_e. Thomson determined v_x by applying a **B** field and adjusting its magnitude to just balance the deflection of the still present **E** field. Equating the magnitudes of the electric and magnetic forces gives

$$qE = qv_x B$$

or

$$v_x = \frac{E}{B} = \frac{V}{Bd} \tag{4.6}$$

Substituting Equation 4.6 into Equation 4.5 immediately yields a formula for e/m_e entirely in terms of measurable quantities:

$$\frac{e}{m_e} = \frac{V\theta}{B^2 \ell d} \tag{4.7}$$

The currently accepted value of e/m_e is 1.758803×10^{11} C/kg. Although Thomson's original value was only about 1.0×10^{11} C/kg, prior experiments on the electrolysis of hydrogen ions had given q/m values for hydrogen of about 10^8 C/kg. It was clear that Thomson had discovered a particle with a mass about 1000 times smaller than the smallest atom! In his observations, Thomson noted that the e/m_e ratio was independent of the discharge gas and the cathode metal. Furthermore, the particles emitted when electrical discharges were passed through different gases were found to be the same as those observed in the photoelectric effect. Based on these observations, Thomson concluded that these particles must be a universal constituent of all matter. Humanity had achieved its first glimpse into the subatomic world!

EXAMPLE 4.2 Deflection of an Electron Beam by E and B Fields

Using the accepted e/m_e value, calculate the magnetic field required to produce a deflection of 0.20 rad in Thomson's experiment, assuming the values $V = 200$ V, $\ell = 5.0$ cm, and $d = 1.5$ cm (the approximate values used by Thomson). Compare this value of B to the Earth's magnetic field.

Solution Because $e/m_e = V\theta/B^2\ell d$, solving for B gives

$$B = \sqrt{\frac{V\theta}{\ell d(e/m_e)}}$$

so

$$\begin{aligned} B &= \left[\frac{(200 \text{ V})(0.20 \text{ rad})}{(0.050 \text{ m})(0.015 \text{ m})(1.76 \times 10^{11} \text{ C/kg})}\right]^{1/2} \\ &= [3.03 \times 10^{-7} \text{ V}\cdot\text{kg/m}^2 \text{ C}]^{1/2} \\ &= [3.03 \times 10^{-7} \text{ N}^2/(\text{m/s})^2 \text{ C}^2]^{1/2} \\ &= 5.5 \times 10^{-4} \text{ N/(m/s)}\cdot\text{C} = 5.5 \times 10^{-4} \text{ T} \end{aligned}$$

As the Earth's magnetic field has a magnitude of about 0.5×10^{-4} T, we require a field 11 times as strong as the Earth's field.

Exercise 1 Find the horizontal speed v_x for this case.

Answer 2.4×10^7 m/s $= 0.080c$, where c is the speed of light.

Millikan's Value of the Elementary Charge

In 1897, Thomson had been unable to determine e or m_e separately. However, about two years later this great British experimentalist had bracketed the accepted value of e (1.602×10^{-19} C) with values of 2.3×10^{-19} C for charges emitted from zinc illuminated by ultraviolet light and 1.1×10^{-19} C for charges produced by ionizing x rays and radium emissions. He was also able to conclude that "e is the same in magnitude as the charge carried by the hydrogen atom in the electrolysis of solutions." The technique used by Thomson and his students to measure e is especially interesting because it represents the first use of the cloud chamber technique in physics and also formed the starting point for the famous Millikan oil-drop experiment. Charles Wilson, one of Thomson's students, had discovered that ions act as condensation centers for water droplets when damp air is cooled by a rapid expansion. Thomson used this idea to form charged clouds by using the apparatus shown in Figure 4.7a. Here Q is the measured total charge of the cloud, W is the measured weight of the cloud, and v is the rate of fall or terminal speed. Thomson assumed that the cloud was composed of spherical droplets having a constant mass (no evaporation) and that the magnitude of the drag force D on a single falling droplet was given by Stokes's law,

$$D = 6\pi a\eta v \tag{4.8}$$

where a is the droplet radius, η is the viscosity of air, and v is the terminal speed of the droplet. The following procedure was used to find a and w, the weight of a single drop. Because v is constant, the droplet is in equilibrium under the combined action of its weight, w, and the drag force, D, as shown in Figure 4.7b. Hence, we require that $w = D$, or

$$w = \tfrac{4}{3}\pi a^3\rho g = D = 6\pi a\eta v$$

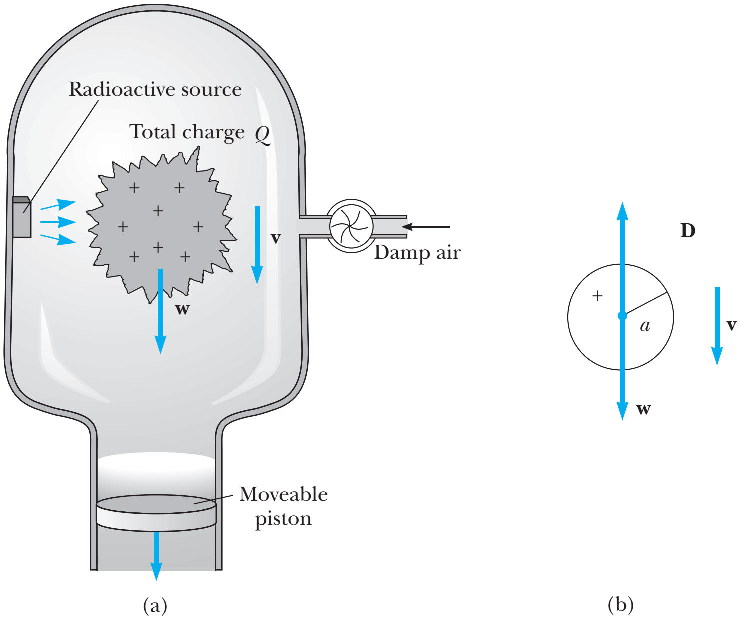

Figure 4.7 (a) A diagram of Thomson's apparatus for determining e. (b) A single droplet in the cloud.

so

$$a = \sqrt{\frac{9\eta v}{2\rho g}} \tag{4.9}$$

where ρ is the mass density of the droplet and g is the free-fall acceleration. From the droplet radius and the known density we can find w, the weight. Once w is obtained, the number of drops n (or number of ions) is given by W/w and the electronic charge e is equal to Q/n, assuming that each droplet carries only one electronic charge. Although ingenious, this method is inaccurate because the theory applies only to a single particle and the particles are all assumed to be identical in order to compare the theory to experiments performed on a cloud.

The tremendous advance of Millikan was made possible by his clever idea of making the experiment "fit" the theory. By observing single droplets he eliminated the problems of assuming all particles to be identical and of making uncertain measurements on a cloud. Millikan's basic idea was to measure the rate of fall of a single drop acted on by gravity and drag forces, apply Stokes's law to determine the drop radius and mass, then to measure its upward velocity in an opposing electric field, and hence determine the total charge on an individual drop.[4] A schematic of the Millikan apparatus is shown in Figure 4.8. Oil droplets charged by an atomizer are allowed to pass through a small hole in the upper plate of a parallel-plate capacitor. If these droplets are illuminated from the side, they appear as brilliant stars against a dark background, and the rate of fall of

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[4] Actually, the idea of allowing charges to "fall" under a combined gravitational and electric field was first applied to charged clouds of water vapor by H. A. Wilson in 1903. Millikan switched from water to oil to avoid the problems of a changing droplet mass and radius caused by water evaporation.

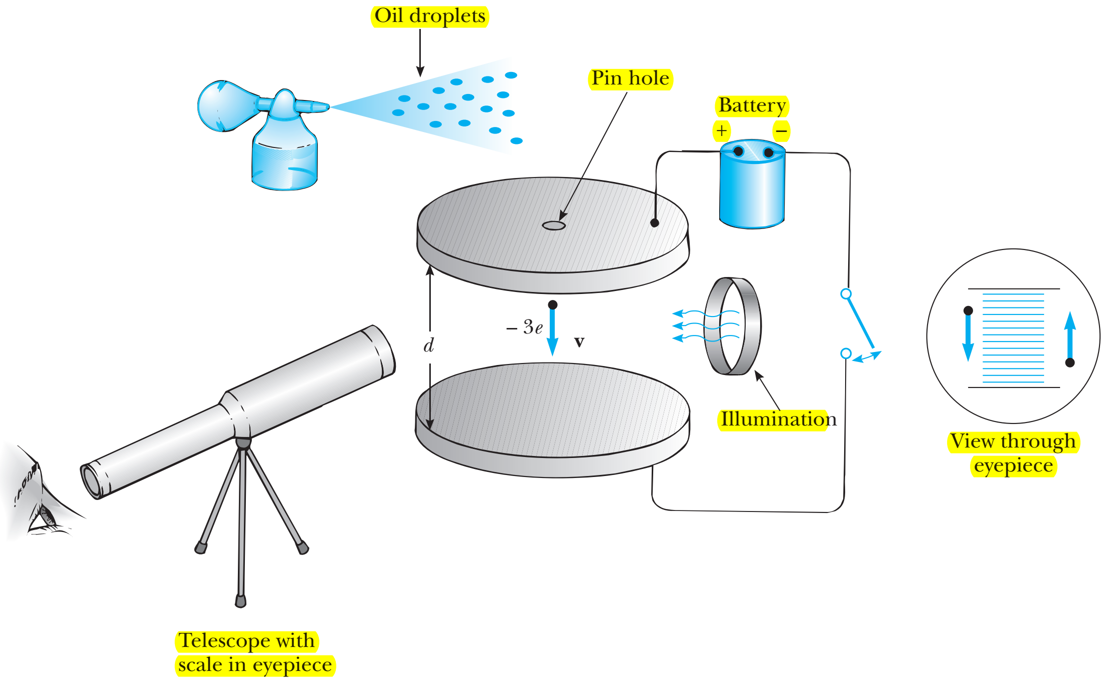

Figure 4.8 A schematic view of the Millikan oil-drop apparatus.

individual drops may be determined.[5] If an electrostatic field of several thousand volts per meter is applied to the capacitor plates, the drop may move slowly upward, typically at rates of *hundredths* of a centimeter per second. Because the rate of fall is comparable, a single droplet with constant mass and radius may be followed for hours, alternately rising and falling, by simply turning the electric field on and off. The atomicity of charge is shown directly by the observation that after a long series of measurements of constant upward velocities one observes a discontinuous change or jump to a different *upward* velocity (higher or lower). This discontinuous change is caused by the attraction of an ion to the charged droplet and a consequent change in droplet charge. Such changes become more frequent when a source of ionizing radiation is placed between the plates.

Millikan's determination of the electronic charge

The quantitative analysis of the Millikan experiment starts with Newton's second law applied to the oil drop, $\Sigma F_y = ma_y$. Because the drag force D is large, a constant velocity of fall is quickly achieved, and all measurements are made for the case $a_y = 0$, or $\Sigma F_y = 0$. If we assume that the magnitude of the drag force is proportional to the speed ($D = Cv$), and refer to Figure 4.9, we find

$$Cv - mg = 0 \qquad \text{(field off)}$$

$$q_1E - mg - Cv_1' = 0 \qquad \text{(field on)}$$

Eliminating C from these expressions gives

$$q_1 = \frac{mg}{E}\left(\frac{v + v_1'}{v}\right) \tag{4.10}$$

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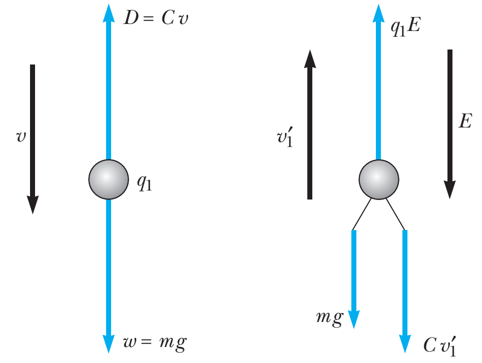
[5] Perhaps the reason for the failure of "Millikan's Shining Stars" as a poetic and romantic image has something to do with the generations of physics students who have experienced hallucinations, near blindness, migraine attacks, etc. while repeating his experiment!



(a) Field off (b) Field on

Figure 4.9 The forces on a charged oil droplet in the Millikan experiment.

When the droplet undergoes a discontinuous change in its *upward speed* from v_1' to v_2' (m, g, E, and v remaining constant), its new charge q_2 is given by

$$q_2 = \frac{mg}{E}\left(\frac{v + v_2'}{v}\right) \tag{4.11}$$

Dividing Equation 4.10 by Equation 4.11 gives

$$\frac{q_1}{q_2} = \frac{v + v_1'}{v + v_2'} \tag{4.12}$$

Robert Millikan (1868–1953). Although Millikan *(left)* studied Greek as an undergraduate at Oberlin College, he fell in love with physics during his graduate training after teaching school for a few years. He was the first student to receive a Ph.D. in physics from Columbia University in 1895. Following postdoctoral work in Germany under Planck and Nernst, Millikan obtained an academic appointment at the University of Chicago in 1910, where he worked with Michelson. He received the Nobel prize in 1923 for his famous experimental determination of the electronic charge. He is also remembered for his careful experimental work to verify the theory of the photoelectric effect deduced by Einstein. Following World War I, he transferred to the California Institute of Technology, where he worked in atmospheric physics and remained until his retirement. (*Courtesy AIP Emìlio Segrè Visual Archives*)

Equation 4.12 constitutes a remarkably direct and powerful proof of the quantization of charge, because if successive speed ratios are ratios of whole numbers, successive charges on the drop must be multiples of the same elementary charge! Millikan's experimental measurements of speed ratios beautifully confirmed this quantization of charge to within about 1% accuracy.[6]

Up to this point our arguments have been quite general and have assumed only that the drag force on the droplet is proportional to its velocity. To determine the actual value of the electronic charge, e, the mass of the drop must be determined, as can be seen from Equation 4.10. As noted earlier, the droplet radius a may be determined from the application of Stokes's law. This value of a, in turn, can be used to find m from the oil density, ρ. In this procedure, a is

$$a = \sqrt{\frac{9\eta v}{2\rho g}} \tag{4.9}$$

and the mass of the droplet can be expressed as

$$m = \rho \cdot \text{volume} = \rho \tfrac{4}{3}\pi a^3 \tag{4.13}$$

An example of this technique for determining e using Stokes's law is given in Example 4.3.

EXAMPLE 4.3 Experimental Determination of *e*

In a Millikan experiment the distance of rise or fall of a droplet is 0.600 cm and the average time of fall (field off) is 21.0 s. The observed successive rise times are 46.0, 15.5, 28.1, 12.9, 45.3, and 20.0 s.

(a) Prove that charge is quantized.

Solution Charge is quantized if q_1/q_2, q_2/q_3, q_3/q_4, and so on are ratios of small whole numbers. Because

$$\frac{q_1}{q_2} = \frac{v + v_1'}{v + v_2'}, \quad \frac{q_2}{q_3} = \frac{v + v_2'}{v + v_3'}, \quad \text{etc.}$$

we must find the speeds. Thus,

$$v = \frac{\Delta y}{\Delta t} = \frac{0.600\ \text{cm}}{21.0\ \text{s}} = 0.0286\ \text{cm/s}$$

$$v_1' = \frac{\Delta y}{\Delta t} = \frac{0.600\ \text{cm}}{46.0\ \text{s}} = 0.0130\ \text{cm/s}$$

$$v_2' = 0.600/15.5 = 0.0387\ \text{cm/s}$$

$$v_3' = 0.600/28.1 = 0.0214\ \text{cm/s}$$

$$v_4' = 0.600/12.9 = 0.0465\ \text{cm/s}$$

$$v_5' = 0.600/45.3 = 0.0132\ \text{cm/s}$$

$$v_6' = 0.600/20.0 = 0.0300\ \text{cm/s}$$

so

$$\frac{q_1}{q_2} = \frac{v + v_1'}{v + v_2'} = \frac{0.0286 + 0.0130}{0.0286 + 0.0387} = 0.618 \approx \frac{3}{5}$$

$$\frac{q_2}{q_3} = \frac{v + v_2'}{v + v_3'} = \frac{0.0286 + 0.0387}{0.0286 + 0.0214} = 1.35 \approx \frac{4}{3}$$

$$\frac{q_3}{q_4} = \frac{v + v_3'}{v + v_4'} = \frac{0.0286 + 0.0214}{0.0286 + 0.0465} = 0.666 \approx \frac{2}{3}$$

$$\frac{q_4}{q_5} = \frac{v + v_4'}{v + v_5'} = \frac{0.0286 + 0.0465}{0.0286 + 0.0132} = 1.80 \approx \frac{9}{5}$$

$$\frac{q_5}{q_6} = \frac{v + v_5'}{v + v_6'} = \frac{0.0286 + 0.0132}{0.0286 + 0.0300} = 0.713 \approx 8/11 \quad \text{or } 7/10$$

(b) If the oil density is 858 kg/m^3 and the viscosity of air is 1.83×10^{-5} kg/m·s, find the radius, volume, and mass of the drop used in this experiment.

Solution The radius of the drop is

$$a = \sqrt{\frac{9\eta v}{2\rho g}}$$

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[6] R. A. Millikan, *Phys. Rev.* 1911, p. 349.

$$= \left[\frac{9(1.83 \times 10^{-5}\ \text{kg/m}\cdot\text{s})(0.0286 \times 10^{-2}\ \text{m/s})}{2(858\ \text{kg/m}^3)(9.81\ \text{m/s}^2)}\right]^{1/2}$$

$$= [2.80 \times 10^{-12}\ \text{m}^2]^{1/2}$$

$$= 1.67 \times 10^{-6}\ \text{m} \quad \text{or } 1.67\ \mu\text{m}$$

The volume is

$$V = \tfrac{4}{3}\pi a^3 = 1.95 \times 10^{-17}\ \text{m}^3$$

The mass is

$$m = \rho V = (858\ \text{kg/m}^3)(1.95 \times 10^{-17}\ \text{m}^3)$$

$$= 1.67 \times 10^{-14}\ \text{kg}$$

(c) Calculate the successive charges on the drop, and from these results determine the electronic charge. Assume a plate separation of 1.60 cm and a potential difference of 4550 V for the parallel-plate capacitor.

Solution To calculate the charge on each drop using Equation 4.10, we must first calculate the magnitude of the electric field, E. Thus,

$$E = \frac{V}{d} = \frac{4550\ \text{V}}{0.0160\ \text{m}} = 2.84 \times 10^5\ \text{V/m}$$

Now we can find the charges on the drop:

$$q_1 = \left(\frac{mg}{E}\right)\left(\frac{v + v_1'}{v}\right)$$

$$= \frac{(1.67 \times 10^{-14}\ \text{kg})(9.81\ \text{m/s}^2)}{(2.84 \times 10^5\ \text{V/m})}\left(\frac{0.0286 + 0.0130}{0.0286}\right)$$

$$= 8.39 \times 10^{-19}\ \text{C}$$

Likewise, $q_2 = 13.6 \times 10^{-19}$ C, $q_3 = 10.1 \times 10^{-19}$ C, $q_4 = 15.2 \times 10^{-19}$ C, $q_5 = 8.43 \times 10^{-19}$ C, and $q_6 = 11.8 \times 10^{-19}$ C.

To find the average value of e, we shall use the fact that at the time of Millikan's work e was known to be between 1.5×10^{-19} C and 2.0×10^{-19} C. Dividing q_1 through q_6 by these values gives the range of integral charges on each drop. Thus, the range of q_1 is 8.39/1.5 = 5.6 electronic charges to 8.39/2.0 = 4.2 electronic charges. Similarly, q_2 has 9.1 to 5.8 charges, q_3 has 6.7 to 5.1 charges, q_4 has 10.1 to 7.6 charges, q_5 has 5.6 to 4.2 charges, and q_6 has 7.9 to 5.9 charges. Because there must be an integral number of charges on each drop, we pick an integer in the middle of the allowed range. Therefore, in terms of the electronic charge e, we conclude that $q_1 = 5e$, $q_2 = 8e$, $q_3 = 6e$, $q_4 = 9e$, $q_5 = 5e$, and $q_6 = 7e$. Using the preceding values, we find

$$e_1 = q/5 = 1.68 \times 10^{-19}\ \text{C}$$

$$e_2 = q_1/8 = 1.70 \times 10^{-19}\ \text{C}$$

$$e_3 = q_2/6 = 1.68 \times 10^{-19}\ \text{C}$$

$$e_4 = q_3/9 = 1.69 \times 10^{-19}\ \text{C}$$

$$e_5 = q_4/5 = 1.69 \times 10^{-19}\ \text{C}$$

$$e_6 = q_5/7 = 1.69 \times 10^{-19}\ \text{C}$$

Taking the average of these values, we find the value of the electronic charge to be $e = 1.688 \times 10^{-19}$ C for this data set.

Stokes's law, as Millikan was aware, is only approximately correct for tiny spheres moving through a gas. The expression $D = 6\pi a\eta v$ holds quite accurately for a 0.1-cm radius sphere moving through a liquid or for any case where the moving-object radius, a, is large compared with the mean free path, L, of the surrounding molecules. (The mean free path is essentially the average distance between molecules.) In the Millikan experiment, however, a is of the same order of magnitude as the mean free path of air at STP. Consequently, Stokes's law overestimates the drag force, because the droplet actually moves for appreciable times through a frictionless "vacuum." Millikan corrected Stokes's law by using a drag force whose magnitude is

$$D = \frac{6\pi a\eta v}{1 + \alpha(L/a)} \tag{4.14}$$

and found that $\alpha = 0.81$ gave the most consistent values of e for drops of different radii. Further corrections to Stokes's law were made by Perrin and Roux, and corrections to Stokes's law and the correct value of e remained a controversial issue for more than 20 years. The currently accepted value of the magnitude of the electronic charge is

$$e = 1.60217733 \times 10^{-19}\ \text{C}$$

Electronic charge

Rutherford's Model of the Atom

The early years of the 20th century were generally a period of incredible ferment and change in physics, including the advent of relativity, quantum theory, and atomic and subatomic physics. Hardly had the reality of pristine, indivisible atoms been established ("They are the only material things which still remain in the precise condition in which they first began to exist" wrote Maxwell in 1872), when Thomson announced their divisibility in 1899: "Electrification essentially involves the splitting of the atom, a part of the mass of the atom getting free and becoming detached from the original atom." Further daring assaults on the indivisibility of the chemical atom came from the experimental work on radioactivity by Marie Curie (1867–1934, a Polish physicist–chemist), and by Ernest Rutherford (1871–1937, New Zealand physicist), and Frederick Soddy, a British physicist, who explained radioactive transformations of elements in terms of the emission of subatomic particles. The porosity of atoms was also known before 1910 from Lenard's experiments, which showed that electrons are easily transmitted through thin metal and mica foils. All these discoveries, plus the suspicion that the intricate atomic spectral lines (light emitted at a discrete set of frequencies characteristic of each element) must be produced by charge rattling around inside the atom, led to various proposals concerning the internal structure of atoms. The most famous of these early atomic models was the Thomson "plum-pudding" model (1898). This proposal viewed the atom as a homogeneous sphere of uniformly distributed mass and positive charge in which were embedded, like raisins in a plum pudding, negatively charged electrons, which just balanced the positive charge to produce electrically neutral atoms. Although such models possessed electrical stability against collapse or explosion of the atom, they failed to explain the rich line spectra of even the simplest atom, hydrogen.

The key to understanding the mysterious line spectra and the correct model of the atom were both furnished by Ernest Rutherford and his students Hans Geiger (1882–1945, German physicist) and Ernest Marsden (1899–1970, British physicist) through a series of experiments conducted from 1909 to 1914. Noticing that a beam of collimated α particles broadened on passing through a metal foil yet easily penetrated the thin film of metal, they embarked on experiments to probe the distribution of mass within the atom by observing in detail the scattering of α particles from foils. These experiments ultimately led Rutherford to the discovery that most of the atomic mass and all of the positive charge lie in a minute central nucleus of the atom. The accidental chain of events and the clever capitalization on the accidental discoveries leading up to Rutherford's monumental nuclear theory of the atom are nowhere better described than in Rutherford's own essay summarizing the development of the theory of atomic structure:

Rutherford's nuclear model

> . . . I would like to use this example to show how you often stumble upon facts by accident. In the early days I had observed the scattering of α-particles, and Dr. Geiger in my laboratory had examined it in detail. He found, in thin pieces of heavy metal, that the scattering was usually small, of the order of one degree. One

> day Geiger came to me and said, "Don't you think that young Marsden, whom I am training in radioactive methods, ought to begin a small research?" Now I had thought that, too, so I said, "Why not let him see if any α-particles can be scattered through a large angle?" I may tell you in confidence that I did not believe that they would be, since we knew that the α-particle was a very fast, massive particle, with a great deal of energy, and you could show that if the scattering was due to the accumulated effect of a number of small scatterings the chance of an α-particle's being scattered backwards was very small. Then I remember two or three days later Geiger coming to me in great excitement and saying, "We have been able to get some of the α-particles coming backwards. . . ." 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. On consideration, I realized that this scattering backwards must be the result of a single collision, and when I made calculations I saw that it was impossible to get anything of that order of magnitude unless you took a system in which the greater part of the mass of the atom was concentrated in a minute nucleus. It was then that I had the idea of an atom with a minute massive center carrying a charge. I worked out mathematically what laws the scattering should obey, and I found that the number of particles scattered through a given angle should be proportional to the thickness of the scattering foil, the square of the nuclear charge, and inversely proportional to the fourth power of the velocity. These deductions were later verified by Geiger and Marsden in a series of beautiful experiments.[7]

The essential experimental features of Rutherford's apparatus are shown in Figure 4.10. A finely collimated beam of α particles emitted with speeds of about 2×10^7 m/s struck a thin gold foil several thousand atomic layers thick. Most of the α's passed straight through the foil along the line DD' (again showing the porosity of the atom), but some were scattered at an angle ϕ. The number of scattered α's at each angle per unit detector area and per unit time

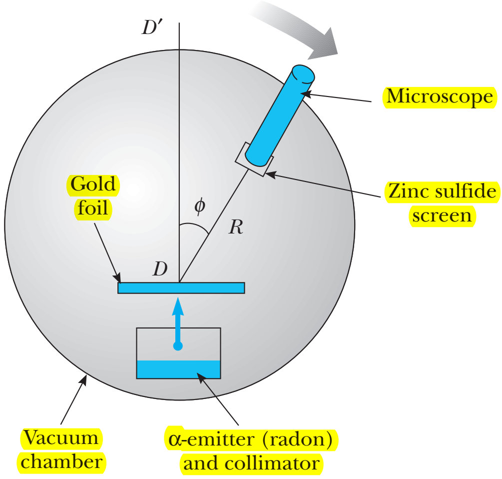

Figure 4.10 A schematic view of Rutherford's α scattering apparatus.

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[7] An essay on "The Development of the Theory of Atomic Structure," 1936, Lord Rutherford, published in *Background to Modern Science*, New York, Macmillan Company, 1940.

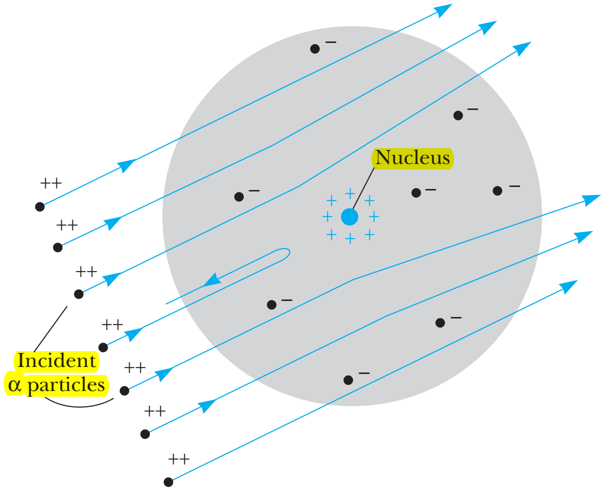

Figure 4.11 Scattering of α particles by a dense, positively charged nucleus.

was measured by counting the scintillations produced by scattered α's on the ZnS screen. These scintillations were counted with the aid of the microscope. The distance from the point where α particles strike the foil to the zinc sulfide screen is denoted R in Figure 4.10.

Rutherford's basic insight was that because the mass and kinetic energy of the α's are large, even a nearly head-on collision with a particle with the mass of a hydrogen atom would deflect the α particle only slightly and knock the hydrogen atom straight ahead. Multiple scattering of the α particles in the foil accounted for the small broadening (about 1°) originally observed by Rutherford, but it could not account for the occasional large-scale deflections. On the other hand,[8] if all of the positive charge in an atom is assumed to be concentrated at a single central point and not spread out throughout the atom, the electric repulsion experienced by an incident α particle in a head-on collision becomes much greater. Because the charge and mass of the gold atom are concentrated at the nucleus, large deflections of the α particle could be experienced in a *single* collision with the massive nucleus. This situation is shown in Figure 4.11.

EXAMPLE 4.4 Collision of an α Particle with a Proton

(a) An α particle of mass m_α and speed v_α strikes a stationary proton with mass m_p. If the collision is elastic and head-on, show that the speed of the proton after the collision, v_p, and the speed of the α particle after the collision, v'_α, are given by

$$v_\mathrm{p} = \left(\frac{2m_\alpha}{m_\alpha + m_\mathrm{p}}\right) v_\alpha$$

and

$$v'_\alpha = \left(\frac{m_\alpha - m_\mathrm{p}}{m_\alpha + m_\mathrm{p}}\right) v_\alpha$$

(b) Calculate the percent change in velocity for an α particle colliding with a proton.

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[8] A dangerous expression that never fails to bring to mind President Truman's infamous request: "If you know of any one-handed economists, bring them to me."

Solution (a) Because the collision is elastic, the total kinetic energy is conserved; therefore,

$$\tfrac{1}{2}m_\alpha v_\alpha^2 = \tfrac{1}{2}m_\alpha v_\alpha'^2 + \tfrac{1}{2}m_\mathrm{p}v_\mathrm{p}^2 \tag{1}$$

Conservation of momentum for this one-dimensional collision yields

$$m_\alpha v_\alpha = m_\mathrm{p}v_\mathrm{p} + m_\alpha v_\alpha' \tag{2}$$

Solving Equation 1 for $(m_\alpha v_\alpha')^2$ yields

$$(m_\alpha v_\alpha')^2 = m_\alpha(m_\alpha v_\alpha^2 - m_\mathrm{p}v_\mathrm{p}^2) \tag{3}$$

Solving Equation 2 for $(m_\alpha v_\alpha')^2$ and equating this to Equation 3 gives

$$(m_\alpha v_\alpha)^2 + (m_\mathrm{p}v_\mathrm{p})^2 - 2m_\alpha m_\mathrm{p}v_\alpha v_\mathrm{p} = (m_\alpha v_\alpha)^2 - m_\alpha m_\mathrm{p}v_\mathrm{p}^2$$

or

$$(m_\mathrm{p}v_\mathrm{p})(m_\mathrm{p}v_\mathrm{p} - 2m_\alpha v_\alpha + m_\alpha v_\mathrm{p}) = 0$$

The solutions to this equation are

$$v_\mathrm{p} = 0$$

and

$$v_\mathrm{p} = \left(\frac{2m_\alpha}{m_\alpha + m_\mathrm{p}}\right)v_\alpha \tag{4}$$

Because the proton must move when struck by the heavy α particle, Equation 4 is the only physically reasonable solution for v_p. The solution for v_α' follows immediately from the substitution of Equation 4 into Equation 2.

Solution (b) Because an α particle consists of two protons and two neutrons, $m_\alpha = 4m_\mathrm{p}$. Thus,

$$v_\mathrm{p} = \left(\frac{2m_\alpha}{m_\alpha + m_\mathrm{p}}\right)v_\alpha = \left(\frac{8m_\mathrm{p}}{5m_\mathrm{p}}\right)v_\alpha = 1.60v_\alpha$$

$$v_\alpha' = \left(\frac{m_\alpha - m_\mathrm{p}}{m_\alpha + m_\mathrm{p}}\right)v_\alpha = \left(\frac{3m_\mathrm{p}}{5m_\mathrm{p}}\right)v_\alpha = 0.60v_\alpha$$

The percent change in velocity of the α particle is

$$\%\text{ change in } v_\alpha = \left(\frac{v_\alpha' - v_\alpha}{v_\alpha}\right) \times 100\% = -40\%$$

Exercise 2 An α particle with initial velocity v_α undergoes an elastic, head-on collision with an electron initially at rest. Using the fact that an electron's mass is about 1/2000 of the proton mass, calculate the final velocities of the electron and α particle and the percent change in velocity of the α particle.

Answers $v_e = 1.998v_\alpha$, $v_\alpha' = 0.9998v_\alpha$, and the percent change in $v_\alpha = -0.02\%$.

In his analysis, Rutherford assumed that large-angle scattering is produced by a single nuclear collision and that the repulsive force between an α particle and a nucleus separated by a distance r is given by Coulomb's law,

$$F = k\frac{(2e)(Ze)}{r^2} \tag{4.15}$$

where $+2e$ is the charge on the α, $+Ze$ is the nuclear charge, and k is the Coulomb constant. With this assumption, Rutherford was able to show that the number of α particles entering the detector per unit time, Δn, at an angle ϕ is given by

$$\Delta n = \frac{k^2Z^2e^4NnA}{4R^2(\frac{1}{2}m_\alpha v_\alpha^2)^2\sin^4(\phi/2)} \tag{4.16}$$

Here R and ϕ are defined in Figure 4.10, N is the number of nuclei per unit area of the foil (and is thus proportional to the foil thickness), n is the total number of α particles incident on the target per unit time, and A is the area of the detector. The dependence of scattering on foil thickness, α particle speed, and scattering angle was confirmed experimentally by Geiger and Marsden.[9]

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[9] H. Geiger and E. Marsden, "Deflection of α-Particles through Large Angles," *Phil. Mag.* (6)25:605, 1913.

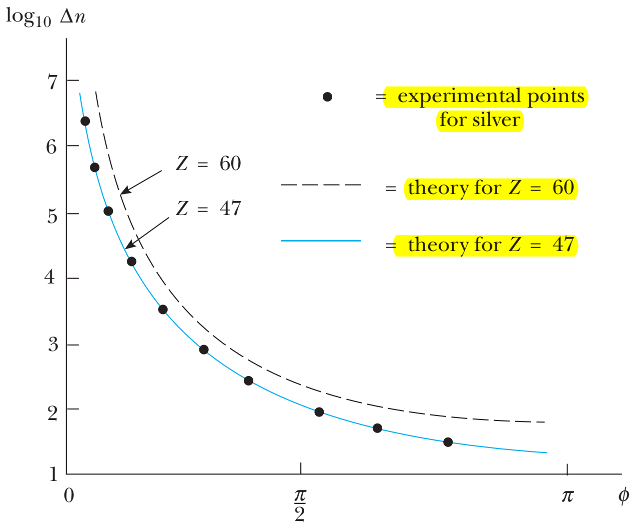

Figure 4.12 Comparison of theory and experiment for α particle scattering from a silver foil. (*From E. Rutherford, J. Chadwick, and J. Ellis,* Radiations from Radioactive Substances, *Cambridge, Cambridge University Press, 1951.*)

Because the values of atomic number (Z) were uncertain at the time, the scattering dependence on Z could not be directly checked. Turning the argument around, however, and assuming the correctness of Equation 4.16, one could find the value of Z that gave the best fit of this equation to the experimental data points. An illustration of this sensitive technique for determining Z for a silver foil is shown in Figure 4.12. Note that changing Z produces only a vertical shift in the graph and not a change in shape.

Much of the remarkable experimental work of the ingenious Lord Rutherford can be credited to an ability to use his current discoveries to probe even deeper into nature's mysteries. For example, he turned his studies of the transmission of radioactive particles through matter into a sensitive and delicate technique for probing the atom. Another example was his clever technique for measuring the size of the nucleus. Realizing that Equation 4.15 would hold only if the α particle did not have enough energy to deform or penetrate the scattering nucleus, he systematically looked for the threshold α energy at which departures from his scattering equation occurred, the idea being that at this threshold energy the α should be just penetrating the nuclear radius at its distance of closest approach. Following Rutherford, we set the kinetic energy of the α at infinity equal to the potential energy of the system (α + target nucleus) at the distance of closest approach, d_{min}, or

$$\frac{1}{2} m_\alpha v_\alpha^2 = k \frac{(Ze)(2e)}{d_{\text{min}}} \tag{4.17}$$

Equation 4.17 may then be solved for d_{min} to determine the distance of closest approach. In the case when the kinetic energy of the α is so high that Equation 4.16 begins to fail, this distance of closest approach is approximately equal to the nuclear radius.

Rutherford was confronted with the experimental dilemma that no failures of Equations 4.15 or 4.16 were found for heavy metal foils with the most energetic naturally occurring α particles available to him ($\approx$ 8 MeV). Showing characteristic economy, instead of embarking on a particle accelerator program, he made use of metals like aluminum with lower Z's and hence lower Coulomb barriers to α penetration.[10] Thus, in 1919, he was able to determine the nuclear radius of aluminum to be about 5×10^{-15} m.

EXAMPLE 4.5 Estimate of the Radius of the Aluminum Nucleus

In 1919, Rutherford was able to show a breakdown in Equation 4.16 for 7.7-MeV α particles scattered at large angles from aluminum nuclei ($Z = 13$). Estimate the radius of the aluminum nucleus from these facts.

Solution Rutherford's scattering formula is no longer valid when α particles begin to penetrate or touch the nucleus. When the α particle is very far from the aluminum nucleus, its kinetic energy is 7.7 MeV. This is also the total energy of the system (α particle plus aluminum nucleus), because the aluminum nucleus is at rest and the potential energy is zero for an infinite separation of particles. When the α particle is at the point of closest approach to the aluminum nucleus in a head-on collision, its kinetic energy is zero and it is at a distance $d_{\min}$, which we may take to be the radius of the aluminum nucleus. At this point, the kinetic energy of the system is zero and the total energy is just the potential energy of the system. Applying conservation of energy gives

$$K_\alpha = \text{potential energy at closest approach} = \frac{k(Ze)(2e)}{d_{\min}}$$

or

$$\begin{aligned} d_{\min} &= k\frac{2Ze^2}{K_\alpha} \\ &= \frac{2(13)(1.60 \times 10^{-19}\ \text{C})^2\,(8.99 \times 10^9\ \text{N}\cdot\text{m}^2/\text{C}^2)}{(7.7 \times 10^6\ \text{eV})(1.60 \times 10^{-19}\ \text{J/eV})} \\ &= 4.9 \times 10^{-15}\ \text{m} \end{aligned}$$

The overall success of the Rutherford nuclear model was striking. Rutherford and his students had shown that all the mass and positive charge Ze were concentrated in a minute nucleus of the atom of diameter 10^{-14} m and that Z electrons must circle the nucleus in some way. As with all great discoveries, however, the idea of the nuclear atom raised a swarm of questions at the next deeper level: (1) If there are only Z protons in the nucleus, what composes the other half of the nuclear mass? (2) What provides the cohesive force to keep many protons confined in the incredibly small distance of 10^{-14} m? (3) How do the electrons move around the nucleus to form a stable atom, and how does their motion account for the observed spectral lines?

Rutherford had no precise answer to the first question. He speculated that the difference between the mass of Z protons and the total nuclear mass could be accounted for by additional groupings of neutral particles, each consisting of a bound electron–proton pair. This conjecture seemed especially satisfying because it built the atom out of the most fundamental particles then known to exist.

In answer to the second question, Rutherford cautiously held that electrical forces provided the cement to hold the nucleus together. He wrote, "The nucleus, though of minute dimensions, is in itself a very complex system

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[10] Rutherford was famous for the remark to his graduate students, "There is no money for apparatus—we shall have to use our heads" (A. Keller, *Infancy of Atomic Physics: Hercules in His Cradle,* Oxford, Clarendon Press, 1983, p. 215).

Figure 4.13 Bohr (on the right) and Rutherford (on the left) were literal as well as intellectual supports for each other. This photograph of Bohr and Rutherford sitting back to back was taken at a rowing regatta in June, 1923 at Cambridge University. (*AIP Niels Bohr Library, and* Physics Today *October 1985, an issue devoted to Bohr.*)

consisting of positively and negatively charged bodies bound closely together by intense electrical forces." In fact, it was not until 1921 that it was clearly recognized that the Coulomb force did not hold the nucleus together and that a completely new and very strong type of force binds protons together. Interestingly it was James Chadwick, the discoverer of the neutron, who first recognized that a new force of much more than electric intensity was at work in the nucleus.[11] Perhaps Rutherford's magnificent achievement of explaining α scattering with the Coulomb law blinded him to the possibility that this was not the ultimate law at work within the nucleus.

The answer to the third question was not to be given by Rutherford. That was to be the masterwork of Niels Bohr (Fig. 4.13). Even so, with characteristic insight, Rutherford mentioned a planetary model of the atom or, more precisely, that negative charges revolved around the dense positive core as the planets revolved around the Sun.[12]

4.3 THE BOHR ATOM

> Bohr's original quantum theory of spectra was one of the most revolutionary, I suppose, that was ever given to science, and I do not know of any theory that has been more successful . . . . I consider the work of Bohr one of the greatest triumphs of the human mind. (Lord Rutherford)

> Then it is one of the greatest discoveries. (Albert Einstein, on hearing of Bohr's theoretical calculation of the Rydberg constants for hydrogen and singly ionized helium)

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[11] J. Chadwick and E. S. Biele, *Phil. Mag.* 42:923, 1921.

[12] Thomson and Hantaro Nagaoka, a Japanese physicist, had worked even earlier with planetary atomic models in 1904.

Spectral Series

Before looking in detail at the first successful theory of atomic dynamics, we review the experimental work on line spectra that served as the impetus for and the clear confirmation of the first quantum theory of the atom. As already pointed out in Chapter 3, glowing solids and liquids (and even gases at the high densities found in stars) emit a continuous distribution of wavelengths. This distribution exhibits a common shape for the intensity-versus-wavelength curve, and the peak in this curve shifts toward shorter wavelengths with increasing temperature. This universal “blackbody” curve is shown in Figure 4.14.

In sharp contrast to this continuous spectrum is the discrete line spectrum emitted by a low-pressure gas subject to an electric discharge. When the light from such a low-pressure gas discharge is examined with a spectroscope, it is found to consist of a few bright lines of pure color on a dark background. This contrasts sharply with the continuous rainbow of colors seen when a glowing solid is viewed through a spectroscope. Furthermore, as can be seen from Figure 4.15, the wavelengths contained in a given line spectrum are characteristic of the particular element emitting the light. (Also see the inside front cover.) The simplest line spectrum is observed for atomic hydrogen, and we shall describe this spectrum in detail. Other atoms, such as mercury, helium, and neon, give completely different line spectra. Because no two elements emit the same line spectrum, this phenomenon represents a practical and sensitive technique for identifying the elements present in unknown samples. In fact, by 1860 spectroscopy had advanced so far in the hands of Gustav Robert Kirchhoff (Fig. 4.16) and Robert Wilhelm von Bunsen (Fig. 4.17) at the University of Heidelberg that they were able to discover two new elements, rubidium and cesium, by observing new sequences of spectral lines in mineral samples. Improvements in instruments and techniques resulted in an enormous growth in spectral analysis in Europe from 1860 to 1900. Even the European public imagination was captured by spectroscopy when spectroscopic techniques showed that “celestial” meteorites consisted only of known Earth elements after all.

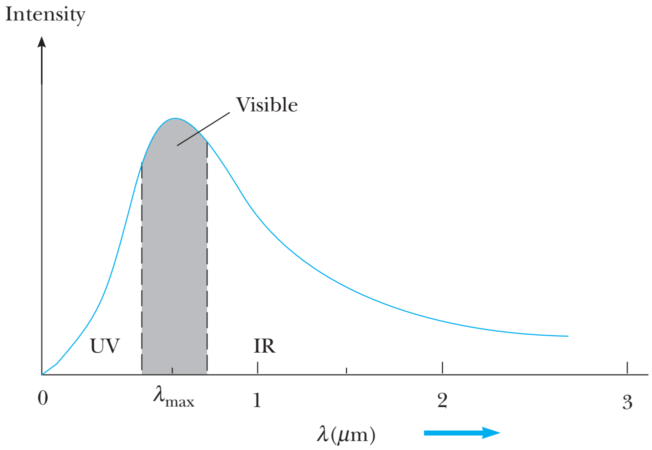

Figure 4.14 Intensity versus wavelength for a body heated to 6000 K.

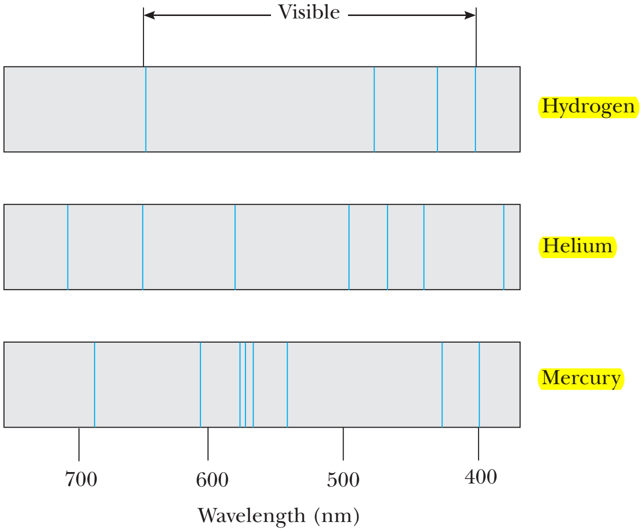

Figure 4.15 Emission line spectra of a few representative elements.

Figure 4.16 Gustav Robert Kirchhoff (1824–1887). Yes, this is the same fellow who brought us the circuit loop theorem and established the connection between the absorption and emission of an object (see Section 3.2). (*AIP Emilio Segrè Visual Archives, W. F. Meggers Collection*)

Kirchhoff's immense contribution to spectroscopy is also shown by another advance he made in 1859—the foundation of **absorption spectroscopy** and the explanation of Fraunhofer's dark D-lines in the solar spectrum.[13] In 1814, Joseph Fraunhofer had passed the continuous spectrum from the Sun through a narrow slit and then through a prism. He observed the surprising result of nearly 1000 fine dark lines, or gaps, in the continuous rainbow spectrum of the Sun, and he assigned the letters A, B, C, D . . . to the most

Figure 4.17 Robert Wilhelm von Bunsen (1811–1899). Bunsen is pictured with his most famous invention, the gas laboratory burner named for him. The greatest achievement of this fine chemist, however, was the development, with Kirchhoff, of the powerful analytical method of spectral analysis. (*AIP Emilio Segrè Visual Archives, E. Scott Barr Collection*)

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[13] G. Kirchhoff, *Monatsber.*, Berlin, 1859, p. 662.

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prominent dark lines. These lines and many more are shown in Figure 4.18. Kirchhoff correctly deduced that the mysterious dark lines are produced by a cloud of vaporized atoms in the Sun's outer, cooler layers, which absorb at discrete frequencies the intense continuous radiation from the center of the Sun. Further, he showed that the Fraunhofer D-lines were produced by vaporized sodium and that they had the same wavelengths as the strong yellow lines in the emission spectrum of sodium. Kirchhoff also correctly deduced that all of Fraunhofer's dark lines should be attributable to absorption by different elements present in the Sun. In a single stroke he opened the way to determining the elemental composition of stars trillions of miles from the Earth. His elegant yet simple method for demonstrating the presence of sodium vapor in the solar atmosphere is shown in schematic form in Figure 4.19.

Today, absorption spectroscopy is certainly as important as emission spectroscopy for qualitative and quantitative analyses of elements and molecular groups. In general, one obtains an absorption spectrum by passing light from a continuous source [whether in the ultraviolet (uv), visible (vis), or infrared (IR) regions] through a gas of the element being analyzed. The absorption spectrum consists of a series of dark lines superimposed on the otherwise continuous spectrum emitted by the source. Each line in the absorption spectrum of an element coincides with a line in the emission spectrum of that same element; however, not all of the emission lines are present in an absorption spectrum. The differences between emission and absorption spectra are complicated in general and depend on the temperature of the absorbing vapor.

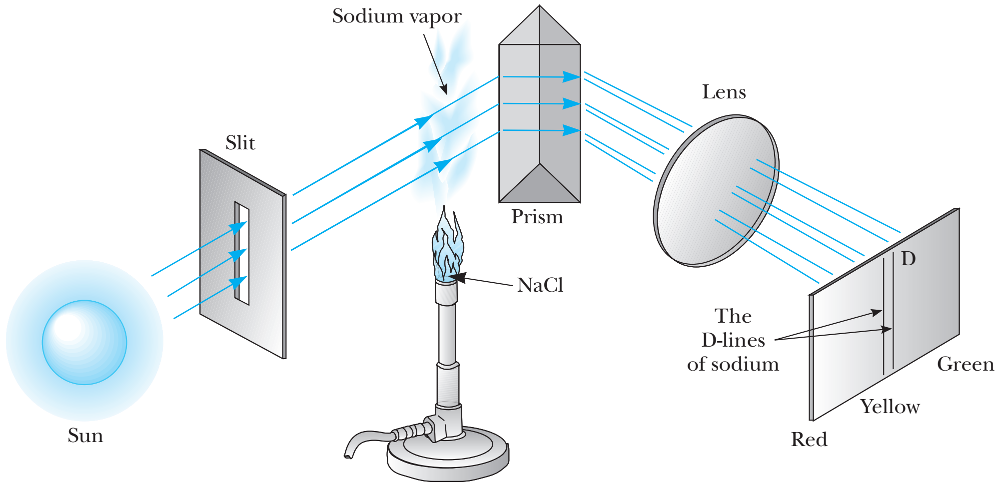

Figure 4.19 Kirchhoff's experiment explaining the Fraunhofer D-lines. The D-lines darken noticeably when sodium vapor is introduced between the slit and the prism.

An interesting use of the coincidence of absorption and emission lines is made in the atomic absorption spectrometer. This device is routinely used to measure parts per million (ppm) of metals in unknowns. For example, if sodium is to be measured, a sodium lamp emitting a line spectrum is chosen as the light source. The unknown is heated in a hot flame (usually oxyacetylene) to vaporize the sample, to break the chemical bonds of sodium to other elements, and to produce a gas of elemental sodium. The spectrometer is then tuned to a wavelength for which both absorption and emission lines exist (say, one of the D-lines at 588.99 or 589.59 nm), and the amount of darkening or decrease in intensity is measured with a sensitive photomultiplier. The decrease in intensity is a measure of the sodium concentration. With proper calibration, concentrations of 0.1 ppm can be measured with this extremely selective technique. Atomic absorption spectroscopy has been a useful technique in analyzing heavy-metal contamination of the food chain. For example, the first determinations of high levels of mercury in tuna fish were made with atomic absorption.

From 1860 to 1885 spectroscopic measurements accumulated voluminously, burying frenzied theoreticians under a mountain of data. Accurate measurements of four visible emission lines of hydrogen had recently been made by Anders Ångström, a Swedish physicist, when in 1885 a Swiss schoolteacher, Johann Jakob Balmer, published a paper with the unpretentious title "Notice Concerning the Spectral Lines of Hydrogen." By trial and error Balmer had found a formula that correctly predicted the wavelengths of Ångström's four visible lines: H_α (red), H_β (green), H_γ (blue), and H_δ (violet). Figure 4.20 shows these and other lines in the emission spectrum of hydrogen. Balmer gave his formula in the form

$$\lambda(\text{cm}) = C_2\left(\frac{n^2}{n^2 - 2^2}\right) \qquad n = 3, 4, 5, \ldots \tag{4.18}$$

where λ is the wavelength emitted in cm and $C_2 = 3645.6 \times 10^{-8}$ cm, a constant called the **convergence limit** because it gave the wavelength of

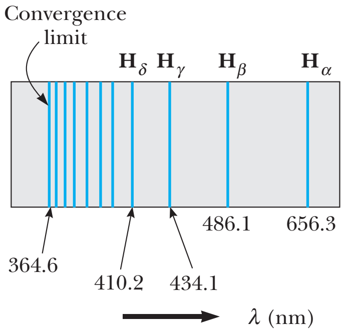

Figure 4.20 The Balmer series of spectral lines for hydrogen (emission spectrum).

the line with the largest n value ($n = \infty$). Also, note that $n = 3, 4, 5, \ldots$, where H_α has $n = 3$, H_β has $n = 4$, and so forth. Although only four lines were known to Balmer when he started his paper, by the time he had finished, ten more lines in the violet and ultraviolet had been measured. Much to his delight and satisfaction, these lines agreed with his empirical formula to within 0.1%! Encouraged by his success and because he was a bit of a numerologist, Balmer suggested that other hydrogen series might exist of the form

$$\lambda = C_3\left(\frac{n^2}{n^2 - 3^2}\right) \qquad n = 4, 5, 6, \ldots \tag{4.19}$$

$$\lambda = C_4\left(\frac{n^2}{n^2 - 4^2}\right) \qquad n = 5, 6, 7, \ldots \tag{4.20}$$

As we now know, his speculations were correct, and these series do indeed exist. In today's notation, all of these series are given by a single formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right) \tag{4.21}$$

where n_f and n_i are *integers*. The Rydberg constant, R, is the same for all series and has the value

$$R = 1.0973732 \times 10^7 \ \mathrm{m}^{-1} \tag{4.22}$$

Note that for a given series, n_f has a constant value. Furthermore, for a given series $n_\mathrm{i} = n_\mathrm{f} + 1, n_\mathrm{f} + 2, \ldots$. Table 4.1 lists the name of each series (named after their discoverers) and the integers that define the series.

Bohr's Quantum Model of the Atom

In April of 1913, a young Danish physicist, Niels Bohr (who had recently been working with both Thomson and Rutherford), published a three-part paper that shook the world of physics to its foundations.[14] Not only did this young rebel give the first successful theory of atomic line spectra but in the process he overthrew some of the most cherished principles of the reigning king of electromagnetism, James Clerk Maxwell.

Table 4.1 Some Spectral Series for the Hydrogen Atom

Lyman Series (uv)	$n_\mathrm{f} = 1$	$n_\mathrm{i} = 2, 3, 4, \ldots$
Balmer Series (vis–uv)	$n_\mathrm{f} = 2$	$n_\mathrm{i} = 3, 4, 5, \ldots$
Paschen Series (IR)	$n_\mathrm{f} = 3$	$n_\mathrm{i} = 4, 5, 6, \ldots$
Brackett Series IR)	$n_\mathrm{f} = 4$	$n_\mathrm{i} = 5, 6, 7, \ldots$
Pfund Series (IR)	$n_\mathrm{f} = 5$	$n_\mathrm{i} = 6, 7, 8, \ldots$

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[14] N. Bohr, "On the Constitution of Atoms and Molecules," *Phil. Mag.* 26:1, 1913. Also, N. Bohr, *Nature* 92:231, 1913.

From our point of view, Bohr's model may seem only a reasonable next step, but it appeared astounding, confounding, and incredibly bold to his contemporaries. As mentioned earlier, both Thomson and Rutherford realized that the electrons must revolve about the nucleus in order to avoid falling into it. They, along with Bohr, realized that according to Maxwell's theory, accelerated charges revolving with orbital frequency f should radiate light waves of frequency f. Unfortunately, pushed to its logical conclusion, this classical model leads to disaster. As the electron radiates energy, its orbit radius steadily decreases and its frequency of revolution increases. This leads to an ever-increasing frequency of emitted radiation and an ultimate catastrophic collapse of the atom as the electron plunges into the nucleus (Fig. 4.21).

These deductions of electrons falling into the nucleus and a continuous emission spectrum from elements were boldly circumvented by Bohr. He simply postulated that classical radiation theory, which had been confirmed by Hertz's detection of radio waves using large circuits, did not hold for atomic-sized systems. Moreover, he drew on the work of Planck and Einstein as sources of the correct theory of atomic systems. He overcame the problem of a classical electron that continually lost energy by applying Planck's ideas of quantized energy levels to orbiting atomic electrons. Thus he postulated that electrons in atoms are generally confined to certain stable, nonradiating energy levels and orbits known as **stationary states.**[15] He applied Einstein's concept of the photon to arrive at an expression for the frequency of the light emitted when the electron jumps from one stationary state to another. Thus, if ΔE is the separation of two possible electronic stationary states, then $\Delta E = hf$, where h is Planck's constant and f is the frequency of the emitted light regardless of the frequency of the electron's orbital motion. In this way, by combining certain principles of classical mechanics with new quantum principles of light emission, Bohr arrived at a theory of the atom that agreed remarkably with experiment.

Stationary states

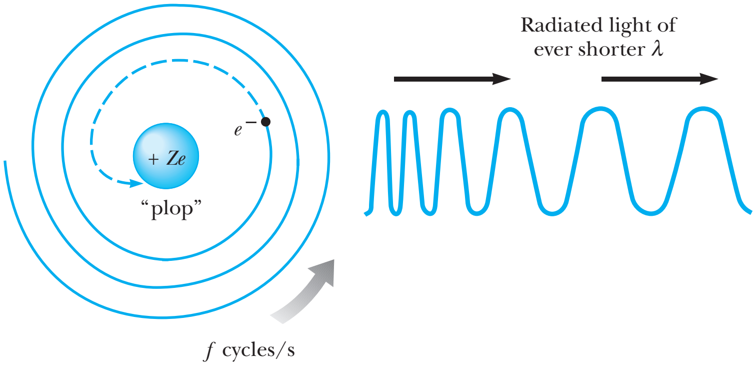

Figure 4.21 The classical model of the nuclear atom.

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[15] *Stationary state* was a term used by Bohr to mean a state of an atom that was stable, nonradiating, and had an energy constant with time. It does not mean "fixed in position" or "without motion," since electrons in stationary orbits move with high speed.

Assumptions of the Bohr theory

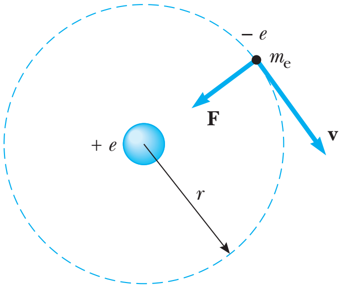

Figure 4.22 Diagram representing Bohr's model of the hydrogen atom.

Now that we have looked at the general principles of Bohr's model of hydrogen and at the detailed experimental spectra already discovered by 1913, let us examine Bohr's quantum theory in detail. The basic ideas of the Bohr theory as it applies to an atom of hydrogen are as follows:

- The electron moves in circular orbits about the proton under the influence of the Coulomb force of attraction, as in Figure 4.22. So far nothing new!
- Only certain orbits are stable. These stable orbits are ones in which the electron does not radiate. Hence the energy is fixed or stationary in time, and ordinary classical mechanics may be used to describe the electron's motion in these stable orbits.
- Radiation is emitted by the atom when the electron "jumps" from a more energetic initial stationary state to a less energetic lower state. This "jump" cannot be visualized or treated classically. In particular, **the frequency *f* of the photon emitted in the jump is independent of the frequency of the electron's orbital motion.** Instead, the frequency of the light emitted is related to the change in the atom's energy and is given by the Planck–Einstein formula

$$E_i - E_f = hf \tag{4.23}$$

where E_i is the energy of the initial state, E_f is the energy of the final state, and $E_i > E_f$.

- The size of the allowed electron orbits is determined by an additional quantum condition imposed on the electron's orbital angular momentum. Namely, the allowed orbits are those for which the electron's orbital angular momentum about the nucleus is an integral multiple of $\hbar = h/2\pi$,

$$m_e vr = n\hbar \qquad n = 1, 2, 3, \ldots \tag{4.24}$$

Using these four assumptions, we can now calculate the allowed energy levels and emission wavelengths of the hydrogen atom. Recall that the electrical potential energy of the system shown in Figure 4.22 is given by $U = qV = -ke^2/r$, where k (the Coulomb constant) has the value $1/4\pi\epsilon_0$. Thus, the total energy of the atom, which contains both kinetic and potential energy terms, is

$$E = K + U = \tfrac{1}{2}m_e v^2 - k\frac{e^2}{r} \tag{4.25}$$

Applying Newton's second law to this system, we see that the Coulomb attractive force on the electron, ke^2/r^2, must equal the mass times the centripetal acceleration of the electron, or

$$\frac{ke^2}{r^2} = \frac{m_e v^2}{r}$$

From this expression, we immediately find the kinetic energy to be

$$K = \frac{m_e v^2}{2} = \frac{ke^2}{2r} \tag{4.26}$$

Substituting this value of K into Equation 4.25 gives the total energy of the atom as

$$E = -\frac{ke^2}{2r} \tag{4.27}$$

Note that the total energy is negative, indicating a *bound* electron–proton system. This means that energy in the amount of $ke^2/2r$ must be added to the atom to remove the electron to infinity and leave it motionless. An expression for r, the radius of the electron orbit, may be obtained by eliminating v between Equations 4.24 and 4.26:

Radii of Bohr orbits in hydrogen

$$r_n = \frac{n^2\hbar^2}{m_e ke^2} \qquad n = 1, 2, 3, \ldots \tag{4.28}$$

Equation 4.28 shows that only certain orbits are allowed and that these preferred orbits follow from the nonclassical step of requiring the electron's angular momentum to be an integral multiple of $\hbar$. The smallest radius occurs for $n = 1$, is called the **Bohr radius,** and is denoted a_0. The value for the Bohr radius is

$$a_0 = \frac{\hbar^2}{m_e ke^2} = 0.529\ \text{Å} = 0.0529\ \text{nm} \tag{4.29}$$

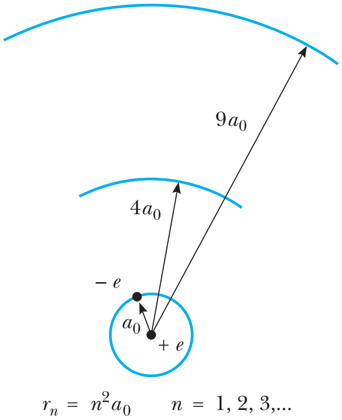

Figure 4.23 The first three Bohr orbits for hydrogen.

The fact that Bohr's theory gave a value for a_0 in good agreement with the experimental size of hydrogen without any empirical calibration of orbit size was considered a striking triumph for this theory. The first three Bohr orbits are shown to scale in Figure 4.23.

The quantization of the orbit radii immediately leads to energy quantization. This can be seen by substituting $r_n = n^2a_0$ into Equation 4.27, giving for the allowed energy levels

Energy levels of hydrogen

$$E_n = -\frac{ke^2}{2a_0}\left(\frac{1}{n^2}\right) \qquad n = 1, 2, 3, \ldots \tag{4.30}$$

Inserting numerical values into Equation 4.30 gives

$$E_n = -\frac{13.6}{n^2}\ \text{eV} \qquad n = 1, 2, 3, \ldots \tag{4.31}$$

Quantum numbers

The integers n corresponding to the discrete, or quantized, values of the atom's energy have the special name **quantum numbers.** Quantum numbers are central to quantum theory and in general refer to the set of integers that label the discrete values of important atomic quantities, such as energy and angular momentum. The lowest stationary, or nonradiating, state is called the **ground state,** has $n = 1$, and has an energy $E_1 = -13.6$ eV. The next state, or **first excited state,** has $n = 2$ and an energy $E_2 = E_1/2^2 = -3.4$ eV. An energy-level diagram showing the energies of these discrete energy states and the corresponding quantum numbers is shown in Figure 4.24. The uppermost level, corresponding to $n = \infty$ (or $r = \infty$) and $E = 0$, represents the state for which the electron is removed from the atom and is motionless. The minimum energy required to ionize the atom (that is, to completely remove an electron in the ground state from the proton's influence) is called the **ionization energy.** As can be seen from Figure 4.24, the ionization energy for hydrogen based on Bohr's calculation is 13.6 eV. This constituted another major achievement for the Bohr theory, because the ionization energy for hydrogen had already been measured to be precisely 13.6 eV.

Equation 4.30 together with Bohr's third postulate can be used to calculate the frequency of the photon emitted when the electron jumps from an outer orbit to an inner orbit:

$$f = \frac{E_\mathrm{i} - E_\mathrm{f}}{h} = \frac{ke^2}{2a_0 h}\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right) \tag{4.32}$$

Because the quantity actually measured is wavelength, it is convenient to convert frequency to wavelength using $c = f\lambda$ to get

Emission wavelengths of hydrogen

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{ke^2}{2a_0 hc}\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right) \tag{4.33}$$

The remarkable fact is that the *theoretical* expression, Equation 4.33, is identical to Balmer's *empirical* relation

$$\frac{1}{\lambda} = R\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right) \tag{4.34}$$

provided that the combination of constants $ke^2/2a_0hc$ is equal to the experimentally determined Rydberg constant, $R = 1.0973732 \times 10^7\ \mathrm{m}^{-1}$. When Bohr demonstrated the agreement of these two quantities to a precision of about 1% late in 1913, it was recognized as the crowning achievement of his quantum theory of hydrogen. Furthermore, Bohr showed that all of the observed spectral series for hydrogen mentioned previously in this section have a natural interpretation in his theory. These spectral series are shown as transitions between energy levels in Figure 4.24.

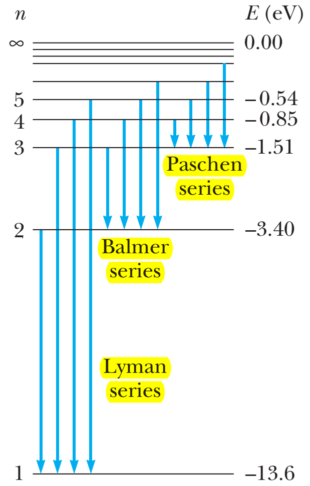

Figure 4.24 An energy-level diagram for hydrogen. In such diagrams the allowed energies are plotted on the vertical axis. Nothing is plotted on the horizontal axis, but the horizontal extent of the diagram is made large enough to show allowed transitions. Note that the quantum numbers are given on the left.

Bohr immediately extended his model for hydrogen to other elements in which all but one electron had been removed. Ionized elements such as He$^+$, Li^{2+}, and Be^{3+} were suspected to exist in hot stellar atmospheres, where frequent atomic collisions occurred with enough energy to completely remove one or more atomic electrons. Bohr showed that several mysterious lines observed in the Sun and stars could not be due to hydrogen, but were correctly predicted by his theory if attributed to singly ionized helium. In general, to describe a single electron orbiting a fixed nucleus of charge $+Ze$, Bohr's theory gives

$$r_n = (n^2)\frac{a_0}{Z} \tag{4.35}$$

and

$$E_n = -\frac{ke^2}{2a_0}\left(\frac{Z^2}{n^2}\right) \qquad n = 1, 2, 3, \ldots \tag{4.36}$$

EXAMPLE 4.6 Spectral Lines from the Star ζ-Puppis

The mysterious lines observed by the American astronomer Edward Charles Pickering in 1896 in the spectrum of the star ζ-Puppis fit the empirical formula

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

where R is, again, the Rydberg constant. Show that these lines can be explained by the Bohr theory as originating from He$^+$.

Solution He$^+$ has $Z = 2$. Thus, the allowed energy levels are given by Equation 4.36 as

$$E_n = \frac{ke^2}{2a_0}\left(\frac{4}{n^2}\right)$$

Using $hf = E_\mathrm{i} - E_\mathrm{f}$ we find

$$\begin{aligned} f &= \frac{E_\mathrm{i} - E_\mathrm{f}}{h} = \frac{ke^2}{2a_0 h}\left(\frac{4}{n_\mathrm{f}^2} - \frac{4}{n_\mathrm{i}^2}\right) \\ &= \frac{ke^2}{2a_0 h}\left(\frac{1}{(n_\mathrm{f}/2)^2} - \frac{1}{(n_\mathrm{i}/2)^2}\right) \end{aligned}$$

or

$$\frac{1}{\lambda} = \frac{f}{c} = \frac{ke^2}{2a_0 hc}\left(\frac{1}{(n_\mathrm{f}/2)^2} - \frac{1}{(n_\mathrm{i}/2)^2}\right)$$

This is the desired solution, because $R \equiv ke^2/2a_0hc$.

EXAMPLE 4.7 An Electronic Transition in Hydrogen

The electron in a hydrogen atom at rest makes a transition from the $n = 2$ energy state to the $n = 1$ ground state.

(a) Find the wavelength, frequency, and energy (eV) of the emitted photon.

Solution We can use Equation 4.34 directly to obtain λ, with $n_\mathrm{i} = 2$ and $n_\mathrm{f} = 1$:

$$\frac{1}{\lambda} = R\left(\frac{1}{n_\mathrm{f}^2} - \frac{1}{n_\mathrm{i}^2}\right) = R\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3R}{4}$$

$$\begin{aligned} \lambda &= \frac{4}{3R} = \frac{4}{3(1.097 \times 10^7\ \mathrm{m}^{-1})} \\ &= 1.215 \times 10^{-7}\ \mathrm{m} = 121.5\ \mathrm{nm} \end{aligned}$$

This wavelength lies in the ultraviolet region.

Because $c = f\lambda$, the frequency of the photon is

$$f = \frac{c}{\lambda} = \frac{3.00 \times 10^8\ \mathrm{m/s}}{1.215 \times 10^{-7}\ \mathrm{m}} = 2.47 \times 10^{15}\ \mathrm{Hz}$$

The energy of the photon is given by $E = hf$, so

$$\begin{aligned} E &= hf \\ &= (4.136 \times 10^{-15}\ \mathrm{eV \cdot s})(2.47 \times 10^{15}\ \mathrm{Hz}) = 10.2\ \mathrm{eV} \end{aligned}$$

(b) The calculation of part (a) assumes that *all* of the $n = 2$ to $n = 1$ transition energy is carried off by the photon; however, this is technically incorrect because some of this energy must go into the recoil motion of the atom. Using conservation of momentum as it applies to the system (atom + photon), and assuming that the recoil energy of the atom is small compared with the $n = 2$ to $n = 1$ energy-level separation, find the momentum and energy of the recoiling hydrogen atom.

Solution Because momentum is conserved, and the total momentum before emission is zero, the total momentum after emission must also be zero. The photon and atom therefore move off in opposite directions, with

$$mv = \frac{E_\mathrm{photon}}{c}$$

where m and v are the mass and recoil speed of the hydrogen atom, E_photon is the actual energy of the photon (less than 10.2 eV), and c is the speed of light. Because the energy difference between the $n = 2$ and $n = 1$ levels, E, is the source of both the photon energy and the recoil kinetic energy of the atom, we can write

$$E = E_\mathrm{photon} + \tfrac{1}{2}mv^2$$

Because the atom is massive, we can assume that its recoil speed v and kinetic energy are so small that $E \approx E_\mathrm{photon}$. Substituting $E_\mathrm{photon} = 10.2$ eV into the expression for mv yields

$$mv = 10.2\ \mathrm{eV}/c$$

The (approximate) recoil kinetic energy of the hydrogen atom can now be calculated:

$$\begin{aligned} K &= \frac{1}{2}mv^2 = \frac{1}{2}\frac{(mv)^2}{m} = (0.5)\frac{(10.2\ \mathrm{eV})^2}{mc^2} \\ &= \frac{(0.5)(10.2\ \mathrm{eV})^2}{938.8 \times 10^6\ \mathrm{eV}} = 5.56 \times 10^{-8}\ \mathrm{eV} \end{aligned}$$

Thus the fraction of the energy difference between the $n = 2$ and $n = 1$ levels that goes into atomic recoil energy is *very* small, approximately 5 parts per billion:

$$\frac{K}{E} = \frac{5.56 \times 10^{-8}\ \mathrm{eV}}{10.2\ \mathrm{eV}} = 5.4 \times 10^{-9}$$

Evidently the process of simply equating the photon's energy to the atomic energy-level separation yields accurate answers because little energy is needed to conserve momentum.

Exercise 3 Check the approximation that $E \approx E_{\text{photon}}$ made in Example 4.7 by directly calculating the recoil kinetic energy of the hydrogen atom, $1/2mv^2$. (*Hint:* Solve $mv = E_{\text{photon}}/c$ and $E = E_{\text{photon}} + 1/2mv^2$ simultaneously to show $v \approx E/mc$, calculate the numerical value of $1/2mv^2$, and compare this answer to the result given in Example 4.7.)

Exercise 4 What is the wavelength of the photon emitted by hydrogen when the electron makes a transition from the $n = 3$ state to the $n = 1$ state?

Answer $\dfrac{9}{8R} = 102.6$ nm.

EXAMPLE 4.8 The Balmer Series for Hydrogen

The Balmer series for the hydrogen atom corresponds to electronic transitions that terminate in the state of quantum number $n = 2$, as shown in Figure 4.24.

(a) Find the longest-wavelength photon emitted and determine its energy.

Solution The longest-wavelength (least-energetic) photon in the Balmer series results from the transition from $n = 3$ to $n = 2$. Using Equation 4.34 gives

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

$$\frac{1}{\lambda_{\text{max}}} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = \frac{5}{36}R$$

$$\lambda_{\text{max}} = \frac{36}{5R} = \frac{36}{5(1.097 \times 10^7\ \text{m}^{-1})} = 656.3\ \text{nm}$$

This wavelength is in the red region of the visible spectrum.

The energy of this photon is

$$E_{\text{photon}} = hf = \frac{hc}{\lambda_{\text{max}}}$$

$$= \frac{(6.626 \times 10^{-34}\ \text{J}\cdot\text{s})(3.00 \times 10^8\ \text{m/s})}{656.3 \times 10^{-9}\ \text{m}}$$

$$= 3.03 \times 10^{-19}\ \text{J} = 1.89\ \text{eV}$$

We could also obtain the energy of the photon by using the expression $hf = E_3 - E_2$, where E_2 and E_3 are the energy levels of the hydrogen atom, which can be calculated from Equation 4.31. Note that this is the lowest-energy photon in this series because it involves the smallest energy change.

(b) Find the shortest-wavelength photon emitted in the Balmer series.

Solution The shortest-wavelength (most-energetic) photon in the Balmer series is emitted when the electron makes a transition from $n = \infty$ to $n = 2$. Therefore,

$$\frac{1}{\lambda_{\text{min}}} = R\left(\frac{1}{2^2} - \frac{1}{\infty}\right) = \frac{R}{4}$$

$$\lambda_{\text{min}} = \frac{4}{R} = \frac{4}{1.097 \times 10^7\ \text{m}^{-1}} = 364.6\ \text{nm}$$

This wavelength is in the ultraviolet region and corresponds to the series limit.

Exercise 5 Find the energy of the shortest-wavelength photon emitted in the Balmer series for hydrogen.

Answer 3.40 eV.

Although the theoretical derivation of the line spectrum was a remarkable feat in itself, the scope and impact of Bohr's monumental achievement is truly seen only when it is realized what else he treated in his three-part paper of 1913:

- He explained why fewer lines are seen in the absorption spectrum of hydrogen than in the emission spectrum.
- He explained the emission of x rays from atoms.
- He explained the nuclear origin of β particles.

- He explained the chemical properties of atoms in terms of the electron shell model.
- He explained how atoms associate to form molecules.

Two of these topics, the comparison of absorption and emission in hydrogen and the shell structure of atoms, are of such general importance that they deserve more explanation.

We have already pointed out that a gas will absorb at wavelengths that correspond exactly to some emission lines, but not every line present in emission is seen as a dark absorption line. Bohr explained absorption as the reverse of emission; that is, an electron in a given energy state can only absorb a photon of the exact frequency required to produce a "jump" from a lower energy state to a higher energy state. Ordinarily, hydrogen atoms are in the ground state ($n = 1$) and so only the high-energy Lyman series corresponding to transitions from the ground state to higher energy states is seen in absorption. The longer-wavelength Balmer series corresponding to transitions originating in the first excited state ($n = 2$) is not seen because the average thermal energy of each atom is insufficient to raise the electron to the first excited state. That is, the number of electrons in the first excited state is insufficient at ordinary temperatures to produce measurable absorption.

EXAMPLE 4.9 Hydrogen in Its First Excited State

Calculate the temperature at which many hydrogen atoms will be in the first excited state ($n = 2$). What series should be prominent in absorption at this temperature? (Calculate both from $N_2/N_1 = \exp(-\Delta E/k_B T)$ and from $\frac{3}{2}k_B T$ = average thermal energy.)

Solution At room temperature almost all hydrogen atoms are in the ground state with an energy of -13.6 eV. The first excited state ($n = 2$) has an energy equal to $E_2 = -3.4$ eV. Therefore, each hydrogen atom must gain an energy of 10.2 eV to reach the first excited state. If the atoms are to obtain this energy from heat, we must have

$$\tfrac{3}{2}k_B T = \frac{\text{average thermal energy}}{\text{atom}} \approx 10.2\ \text{eV}$$

or

$$T = \frac{10.2\ \text{eV}}{(3/2)k_B} = \frac{10.2\ \text{eV}}{(1.5)(8.62 \times 10^{-5}\ \text{eV/K})}$$
$$= 79{,}000\ \text{K}$$

Let us check this result by using the Boltzmann distribution. In Section 3.3 we saw that the probability of finding an atom with energy E at temperature T is

$$P(E) = P_0 e^{-(E-E_0)/k_B T}$$

where P_0 is the probability of finding the atom in the ground state of energy, E_0. From this expression, it follows that the ratio of the number of atoms in two different energy levels in thermal equilibrium at temperature T is

$$\frac{N_2}{N_1} = \frac{P(E_2)}{P(E_1)} = e^{-(E_2-E_1)/k_B T}$$

where N_2 is the number in the upper level, N_1 is the number in the lower level, and ΔE is the energy separation of the two levels. Let us use this equation to determine the temperature at which approximately 10% of the hydrogen atoms are in the $n = 2$ state.

$$\frac{N_2}{N_1} = 0.10 = e^{-(10.2\ \text{eV})/k_B T}$$

or

$$\ln(0.10) = -\frac{10.2\ \text{eV}}{k_B T}$$

Solving for T gives

$$T = -\frac{10.2\ \text{eV}}{k_B \ln(0.10)} = -\frac{10.2\ \text{eV}}{(8.62 \times 10^{-5}\ \text{eV/K})\ln(0.10)}$$
$$= 51{,}000\ \text{K}$$

Thus the two estimates agree in order of magnitude and show that the Balmer series will only be seen in absorption if the absorbing gas is quite hot, as in a stellar atmosphere.

The final comment on Bohr's work concerns his development of electronic shell theory to treat multielectron atoms. In part II of his paper he attempted to find stable electronic arrangements subject to the conditions that the total angular momentum of all the electrons is quantized and, simultaneously, that the total energy is a minimum. This is a difficult problem, and one that becomes more difficult as more electrons are introduced into a system. Nevertheless, Bohr had considerable success in explaining the chemical activity of multielectron atoms. For example, he was able to show that neutral hydrogen could add another electron to become H^-, and that neutral helium was particularly stable with a closed innermost shell of two electrons and a high ionization potential. He also proposed that lithium ($Z = 3$) had an electronic arrangement consisting of two electrons in one orbit near the nucleus and the third in a large, loosely bound outer orbit. This explains the tendency of lithium atoms to lose an electron and "take a positive charge in chemical combinations with other elements." Although we cannot afford the luxury of looking in detail at all of Bohr's predictions about multielectron atoms, his basic ideas of shell structure are as follows:

- Electrons of elements with higher atomic number form stable concentric rings, with definite numbers of electrons allowed for each ring or shell.
- The number of electrons in the outermost ring determines the valency.[16]

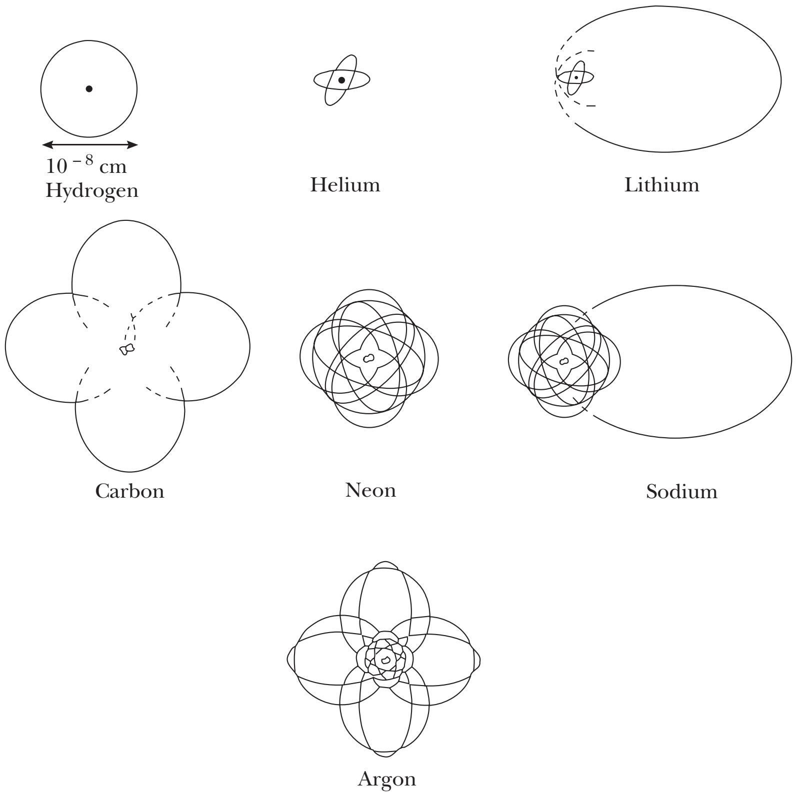

Figure 4.25 Bohr's sketches of electronic orbits.

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[16] G. N. Lewis, an American chemist, contributed much to our understanding of shell structure in 1916, building on Bohr's remarkable foundation.

With almost magical insight, Bohr ended part II of his classic paper with the explanation of the similar chemical properties of the iron group (Fe, Co, Ni) and the rare earths, which have atomic numbers that progressively increase by 1 and would not normally be expected to be chemically alike. The answer, according to Bohr, is that the configuration of electrons in the outermost ring of these elements is identical and that it is energetically more favorable to add electrons to inner rings. At the risk of encouraging some to take the idea of electronic orbits too seriously, Figure 4.25 shows some sketches of electronic orbits as drawn by Bohr in the early 1900s.

4.4 BOHR'S CORRESPONDENCE PRINCIPLE, OR WHY IS ANGULAR MOMENTUM QUANTIZED?

Correspondence principle

Where others might have left a wild and lawless gap between the revolutionary new laws that apply to atomic systems and those that hold for classical systems, Bohr provided a gentle and refined continuum in the form of the **correspondence principle.** This principle states that **predictions of quantum theory must correspond to the predictions of classical physics in the region of sizes where classical theory is known to hold.** These classical sizes for length, mass, and time are on the order of centimeters, grams, and seconds and typically involve very large quantum numbers, as can be seen by calculating n for a hydrogen atom with a radius of 1 cm. If the quantum number becomes large because of increased size or mass, we may state the correspondence principle symbolically as

$$\lim_{n\to\infty} [\text{quantum physics}] = [\text{classical physics}]$$

where n is a typical quantum number of the system such as the quantum number for hydrogen. In the hands of Bohr, the correspondence principle became a masterful tool to test new quantum results as well as a source of fundamental postulates about atomic systems. In fact, Bohr used reasoning of this type to arrive at the concept of the quantization of the electron's orbital angular momentum. Both Bohr's idea of discrete, nonradiating energy states and the emission postulate for atoms were foreshadowed by Planck's quantization of the energy of blackbody oscillators and by Einstein's treatment of the photoelectric effect. However, the concept of angular momentum quantization seems to have sprung full blown from Bohr's *Gedankenkuche* (thought kitchen), as so aptly expressed by Einstein. Indeed, in some of his later writings Bohr emphasized the point of view that the quantization of angular momentum was a postulate, underivable from any deeper law, and that its validity depended simply on the agreement of his model with experimental spectra.

What is most interesting is that in his 1913 paper Bohr ingeniously showed that the quantization of angular momentum is a consequence of the smooth and gradual emergence of classical results from quantum theory in the limit of large quantum number. In particular, Bohr argued that according to his correspondence principle, the quantum condition for emission ($\Delta E = hf$) and Maxwell's classical radiation theory (electronic charges with orbital frequency f radiate light waves of frequency f) *must simultaneously hold for the case of extremely large electronic orbits.* This case is

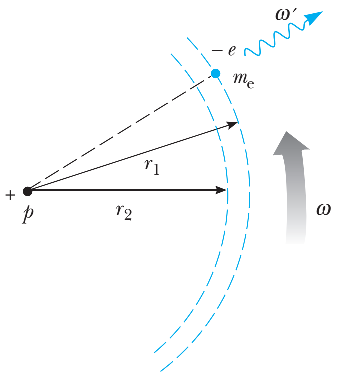

Figure 4.26 The classical limit of the Bohr atom. Note that r_1 and r_2 are the radii of the two adjacent quantum orbits, in which the electron has orbital angular frequencies of ω_1 and ω_2. We assume $r_1 \approx r_2 \approx r$ and $\omega_1 \approx \omega_2 \approx \omega$; ω' is the angular frequency of a photon emitted in a transition from r_1 to r_2.

shown in Figure 4.26. In this figure, r_1 and r_2 are the radii of two large adjacent orbits that are separated in energy by an amount dE and ω is the orbital angular frequency of the electron, where ω is approximately constant in a transition between large orbits. (The algebra is simpler if we use angular frequency instead of frequency. Recall that the connection is $\omega = 2\pi f$.) Because we want to determine the allowed values of the angular momentum from the known change in the atom's energy when light is emitted, we need the relation between the total energy of the atom, $E = -ke^2/2r$ (Equation 4.27) and the magnitude of the total angular momentum of the atom, $L = m_e vr = m_e \omega r^2$. Using the fact that the electron is kept in orbit by the Coulomb force, it is not difficult to show that $1/r = m_e ke^2/L^2$ (see Problem 30), so Equation 4.27 becomes

$$E = -\frac{1}{2}\frac{m_e k^2 e^4}{L^2} \tag{4.37}$$

Taking a derivative of Equation 4.37 gives the desired connection between the change in energy and the change in angular momentum for the Bohr atom.

$$\frac{dE}{dL} = \frac{m_e k^2 e^4}{L^3} \tag{4.38}$$

Finally, we obtain dE/dL in terms of ω, the electron orbital angular frequency, by using $L^3 = m_e k^2 e^4/\omega$ (see Problem 30). Thus,

$$\frac{dE}{dL} = \frac{m_e k^2 e^4}{(m_e k^2 e^4/\omega)} = \omega \tag{4.39}$$

Now consider the emission of a photon of energy $dE = \hbar\omega'$ when the electron makes a transition from r_1 to r_2. Equation 4.39 becomes

$$dE = \omega \, dL$$

or

$$\hbar\omega' = \omega \, dL \tag{4.40}$$

where ω' is the photon angular frequency and ω is the electron orbital angular frequency. Ordinarily, ω' and ω are not simply related. However, because we are dealing with large orbits in this situation, the correspondence principle tells us that the quantum theory must predict the same frequency for the emitted light as Maxwell's law of radiation. Because Maxwell's classical theory requires the electron to radiate light of the same frequency as its orbital motion frequency, $\omega' = \omega$, and Equation 4.40 becomes

$$\hbar\omega = \omega \, dL$$

or

$$dL = \hbar \tag{4.41}$$

Equation 4.41 shows that the change in electronic angular momentum for a transition between adjacent, large electronic orbits is *always* $\hbar$. This means that the magnitude of total angular momentum of the electron in a specific orbit may be taken to have a value equal to an integral multiple of $\hbar$, or

$$L = m_e vr = n\hbar \tag{4.42}$$

for n = large integers.

Bohr realized that although Equation 4.42 was derived for the case of large electron orbits, it was a universal quantum principle applicable to all systems and of wider applicability than Maxwell's law of radiation. Such a bold and far-seeing vision was characteristic of the man so aptly described by Einstein in the following quote: "That this insecure and contradictory foundation [physics from 1910 to 1920] was sufficient to enable a man of Bohr's unique instinct and tact to discover the major laws of the spectral lines and of the electron shells of the atoms together with their significance for chemistry appeared to me like a miracle—and appears to me as a miracle even today. This is the highest form of musicality in the sphere of thought."

4.5 DIRECT CONFIRMATION OF ATOMIC ENERGY LEVELS: THE FRANCK–HERTZ EXPERIMENT

In the preceding sections we have shown the involved trail of reasoning indirectly proving the existence of quantized energy levels in atoms from observations of the optical line spectra emitted by different elements. Now we turn to a simpler and more direct experimental proof of the existence of discrete energy levels in atoms involving their excitation by collision with low-energy electrons. The first experiment of this type was performed by German physicists James Franck and Gustav Hertz (a nephew of Heinrich Hertz) in 1914 on mercury (Hg) atoms. It provided clear experimental proof of the existence of quantized energy levels in atoms and showed that the levels deduced from electron bombardment agreed with those deduced from optical line spectra. Furthermore, it confirmed the universality of energy quantization in atoms, because the quite different physical processes of photon emission and electron bombardment yielded the same energy levels.

Figure 4.27 shows a schematic of a typical college laboratory device similar to the Franck–Hertz apparatus. Electrons emitted by the filament are accelerated over a relatively long region (≈ 1 cm) by the positive potential on the

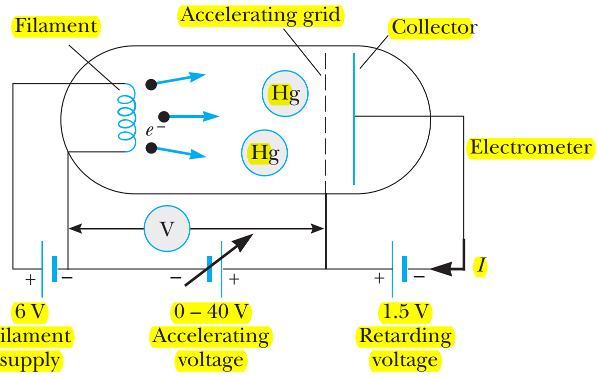

Figure 4.27 Franck–Hertz apparatus. A drop of pure mercury is sealed into an evacuated tube. The tube is heated to 185°C during measurements to provide a high-enough density of mercury to ensure many electron–atom collisions.

grid, V. The electrons can reach the collector and be registered on the electrometer (a sensitive ammeter) if they have sufficient energy to overcome the retarding potential of about 1.5 V set up over the short distance ($\approx$ 1 mm) between grid and collector. At low electron energies or accelerating voltages, perfectly elastic collisions occur between the electrons and Hg atoms in which the *sum* of the kinetic energies of both electron and atom are conserved. Because the Hg atom is much more massive than the electron, the electron transfers very little kinetic energy to the atom in a collision (see Problem 38). Even after multiple collisions the electron reaches the grid with a kinetic energy of approximately e times V and will be collected if the accelerating voltage V is greater than 1.5 V. When V is modestly increased, more electrons reach the collector and the current, I, rises.

As the accelerating voltage is increased further, a threshold voltage is reached at which inelastic collisions occur at the grid, where the electrons reach an energy of e times V. In these inelastic collisions, electrons can transfer almost all of their kinetic energy to the atom, raising it to its first excited state (see Problem 39 and Question 9). Electrons that have collided inelastically are unable to overcome the retarding potential and consequently I decreases for this threshold voltage. Figure 4.28 shows a typical plot of current versus accelerating voltage, with the first weak current dip (A) occurring at a threshold voltage of slightly more than 7 V. When the voltage is increased once again, the inelastic collision region moves closer to the filament and the electrons that were stopped by an inelastic collision are reaccelerated, reaching the collector and causing another rise in current (B). Another dip (C) occurs when V is increased enough for an electron to have two successive inelastic collisions: An electron excites an atom halfway between filament and grid, loses all its energy, and is then reaccelerated to excite another atom at the grid, finally ending up with insufficient energy to be collected. This process takes place periodically with increasing grid voltage, giving rise to equally spaced maxima and minima in the I–V curve, as shown in Figure 4.28.

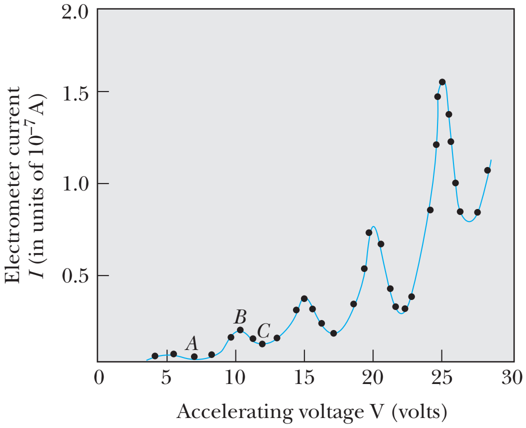

Figure 4.28 Current as a function of voltage in the Franck–Hertz experiment. To obtain these data, the filament voltage was set at 6.0 V and the tube heated to 185°C. (*Data taken by Bob Rodick, Utica College, class of 1992*)

If the adjacent maxima and minima separations of Figure 4.28 are carefully averaged, one finds an average of 4.9 ± 0.1 V, or a ground to first excited state separation of 4.9 ± 0.1 eV. Note, however, that the first minimum does not occur at 4.9 V but at about 7.1 V. The extra energy (7.1 − 4.9 = 2.2 eV) is required because the filament and collector are made of different metals with different work functions. (Recall that the work function is the energy needed to pull an electron out of a metal—see Chapter 3.) Although the filament, like all good emitters, has a low work function, the collector has a high work function, and this work function energy must be supplied to extract an electron from the collector so a current can flow in the circuit.

As we have seen Franck and Hertz used simple ammeter and voltmeter measurements to show that atoms can only accept discrete amounts of energy from an electron beam. In addition, they showed that the energy levels obtained from electron bombardment agreed with the spectroscopic results. Reasoning that an Hg atom actually excited to an energy level 4.9 eV above its ground state could return to its ground state by emitting a single photon (as Bohr had just postulated), they calculated the wavelength of such a photon to be

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

or

$$\lambda = \frac{hc}{\Delta E} = \frac{1240 \text{ eV}\cdot\text{nm}}{4.9 \text{ eV}} = 253 \text{ nm} \tag{4.43}$$

Because glass is not transparent to such ultraviolet radiation, they constructed a quartz apparatus and carefully measured the radiation emitted, finding radiation of wavelength 254 nm to be emitted as soon as the accelerating voltage exceeded 4.9 V. For this direct experimental confirmation of Bohr's basic ideas of discrete energy levels in atoms and the process of photon emission, Franck and Hertz were awarded the Nobel prize in 1925.

SUMMARY

The determination of the composition of atoms relies heavily on four classic experiments:

- **Faraday's law of electrolysis,** which may be stated as

  $$m = \frac{(q)\,(\text{molar mass})}{(96{,}500 \text{ C})\,(\text{valence})} \tag{4.1}$$

  where m is the mass liberated at an electrode and q is the total charge passed through the solution. Faraday's law shows that atoms are composed of positive and negative charges and that atomic charges always consist of multiples of some unit charge.
- **J. J. Thomson's determination of e/m_e** and that the electron is a part of all atoms. Thomson measured e/m_e of electrons from a variety of elements by measuring the deflection of an electron beam by an electric field. He then applied a magnetic field to just cancel the electric deflec-