CHAPTER 14

The Quantum Model of the Atom

14.1 SPECTRA OF GASES

One of the first important clues to understanding atomic structure involved the study of the emission and absorption of light by the atoms of different elements. Physicists knew from Maxwell's theory that light is emitted and absorbed only by accelerating charges. This suggested that the atom might contain moving charges. Patterns and regularities in the properties of the light emitted we expected to provide valuable clues about the precise nature of the motions of the moving charges. The results of this study were so important to the unraveling of atomic structure that we review their development here in some detail.

Emission Spectra

It has long been known that light is emitted by gases or vapors when they are excited in any one of several ways:

(1) by heating the gas to a high temperature, as when a volatile substance is put into a flame;
(2) by an electric discharge through gas in the space between the terminals of an electric arc; or
(3) by a continuous electric current in a gas at low pressure, as in the now familiar "neon sign."

The Scottish physicist Thomas Melvill made the pioneering experiments on light emitted by various excited gases in 1752. He put one substance after another in a flame, "having placed a pasteboard with a circular hole in it between my eye and the flame . . . , I examined the constitution of these different lights with a prism." Melvill found that the spectrum of visible light from a hot gas of a single element was different from the well-known rainbow-colored spectrum of a glowing solid or liquid. Melvill's spectrum was not an unbroken stretch of color continuously graded from violet to red. Rather, it consisted of individual patches, each having the color of that part of the spectrum in which it was located. There were dark gaps—missing colors—between the patches. Later, more general use was made of a narrow slit through which to pass the light. Now the spectrum of a gas was seen as a set of bright lines (see Figure 14.1). The bright lines are in fact colored images of the slit. Such spectra show that light from a gas is a mixture of only a few definite colors or narrow wavelength regions of light. These types of spectra are called *emission spectra* or *bright-line spectra*, and their study is known as *spectroscopy*.

Melvill also noted that the colors and locations of the bright lines were different when different substances were put into the flame. For example, with ordinary table salt in the flame, the dominant color was "bright yellow" (now known to be characteristic of the element sodium). In fact, the bright-line spectrum is markedly different for each chemically different gas because each chemical element emits its own characteristic set of wavelengths. In looking at a gaseous source without the aid of a prism or a grating, the eye combines the separate colors. It perceives the mixture as reddish for glowing neon, pale blue for nitrogen, yellow for sodium vapor, and so on.

Some gases have relatively simple emission spectra. Thus, the most prominent part of the visible spectrum of sodium vapor is a pair of bright yellow lines. This is why, for example, the flame in a gas stove turns yellow when soup, or any liquid containing salt, boils over. Sodium-vapor

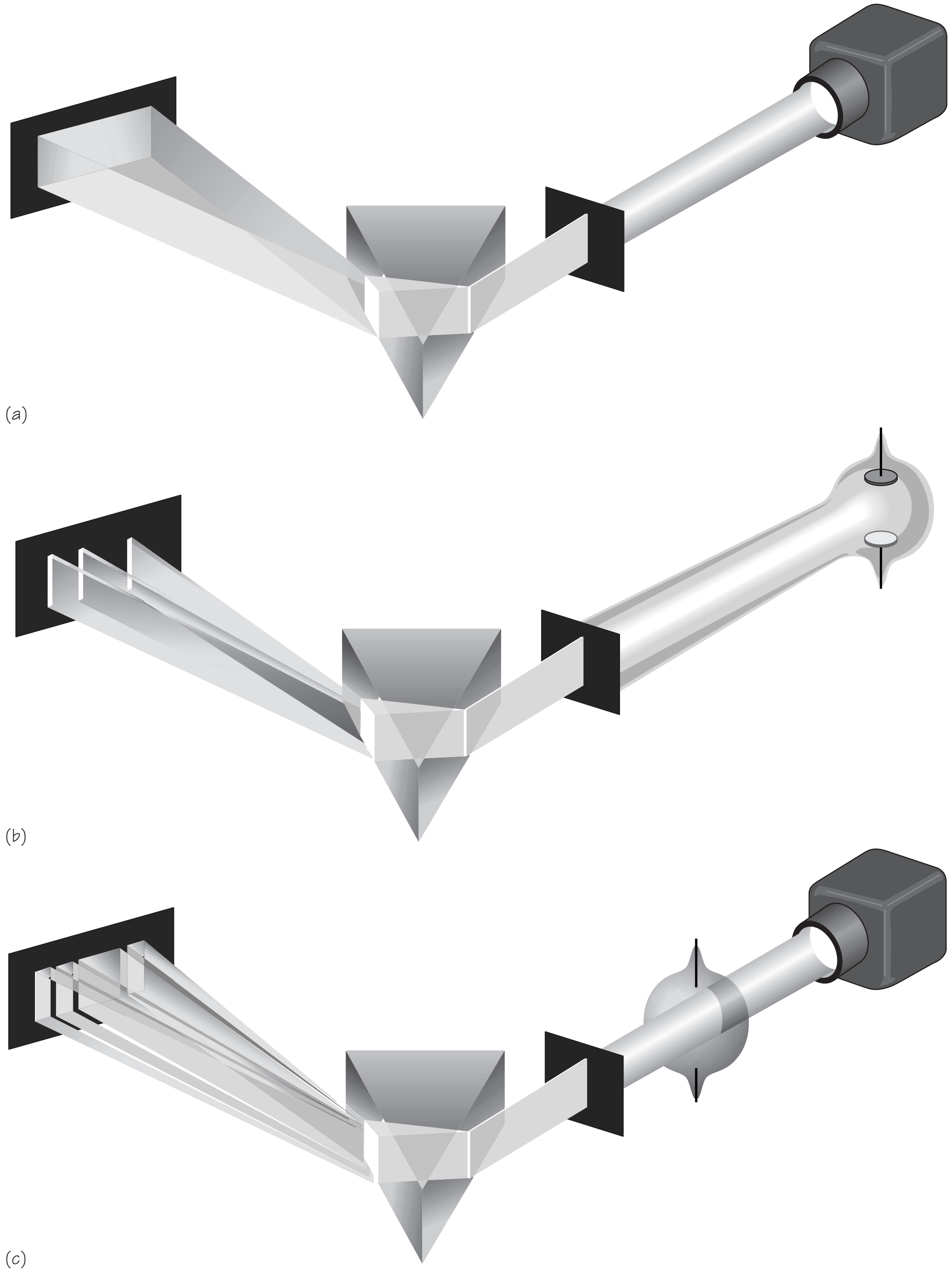


FIGURE 14.1 (a) Hot solids emit all wavelengths of light, producing a continuous spectrum on the screen at left. The shorter-wavelength portions of light are refracted more by the prism than are long wavelengths. (b) Hot gases emit only certain wavelengths of light, producing a bright line spectrum. If the slit had a different shape, so would the bright lines on the screen. (c) Cool gases absorb only certain wavelengths of light, producing a dark line spectrum when "white" light from a hot solid is passed through the cool gas.

lamps are now used in many places as street lights at night. Some gases or vapors have very complex spectra. Iron vapor, for example, has some 6000 bright lines in the visible range alone.

In 1823, the British astronomer John Herschel suggested that each gas could be identified by its unique line spectrum. By the early 1860s, the physicist Gustav R. Kirchhoff and the chemist Robert W. Bunsen, in Germany, had jointly discovered two new elements (rubidium and cesium) by noting previously unreported emission lines in the spectrum of the vapor of a mineral water. This was the first of a series of such discoveries. It started the development of a technique for speedy chemical analysis of small amounts of materials by *spectrum analysis*. The "flame test" you may have performed in a chemistry class is a simple application of this analysis.

Absorption Spectra

In 1802, the English scientist William Wollaston saw in the spectrum of sunlight something that had been overlooked before. Wollaston noticed a set of seven sharp, irregularly spaced *dark* lines, or spaces, across the continuous solar spectrum. He did not understand why they were there and did not investigate further. A dozen years later, the German physicist Joseph von Fraunhofer, using better instruments, detected many hundreds of such dark lines. To the most prominent dark lines von Fraunhofer assigned the letters A, B, C, etc. These dark lines can be easily seen in the Sun's spectrum with even quite simple modern spectroscopes. The letters A, B, C, . . . are still used to identify them. In the spectra of several other bright stars, von Fraunhofer found similar dark lines. Many, but not all, of these lines were in the same positions as those in the solar spectrum. All such spectra are known as *dark-line spectra* or *absorption spectra*.

Spectrometer or *spectrograph*: A device for measuring the wavelength of the spectrum and for recording the spectra (e.g., on film).

In 1859, Kirchhoff made some key observations that led to better understanding of both the dark-line and bright-line spectra of gases. It was

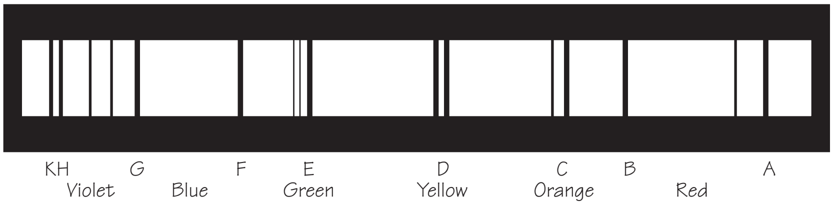


FIGURE 14.2 The Fraunhofer dark lines in the visible part of the solar spectrum. Only a few of the most prominent lines are represented here.

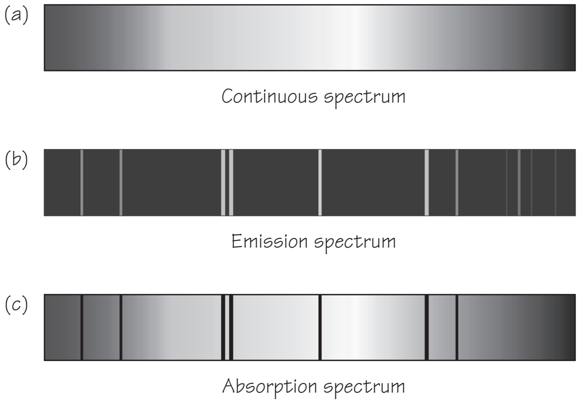


FIGURE 14.3 Emission, absorption, and continuous spectra (see Color Plate 5 for emission spectra of selected elements).

already known that the two prominent yellow lines in the emission spectrum of heated sodium vapor had the same wavelengths as two neighboring prominent dark lines in the solar spectrum. (The solar spectrum lines were the ones to which von Fraunhofer had assigned the letter D.) It was also known that the light emitted by a glowing solid forms a perfectly continuous spectrum that shows no dark lines. Kirchhoff now experimented with light from a glowing solid, as shown in Figure 14.1c. The white light was first passed through cooler sodium vapor and then dispersed by a prism. The spectrum produced showed the expected rainbow pattern, but it had two prominent dark lines at the same place in the spectrum as the D lines of the Sun's spectrum. It was therefore reasonable to conclude that the light from the Sun, too, was passing through a mass of sodium gas. This was the first evidence of the chemical composition of the gas envelope around the Sun.

Kirchhoff's experiment was repeated with various other relatively cool gases, placed between a glowing solid and the prism. Each gas produced its own characteristic set of dark lines. Evidently, each gas in some way absorbs light of certain wavelengths from the passing light. In addition, Kirchhoff showed that the wavelength of each absorption line matches the wavelength of a bright line in the emission spectrum of the same gas. *The conclusion is that a gas can absorb only light of those wavelengths which, when excited, it can emit*. (Note that not every emission line is represented in the absorption spectrum. Soon you will see why.)

Each of the various von Fraunhofer lines across the spectra of the Sun and other stars has now been identified with the action of some gas as tested in the laboratory. In this way, the whole chemical composition of the outer region of the Sun and other stars has been determined. This is really quite breathtaking from several points of view. First, it is surprising that scientists can learn the chemical composition of immensely distant objects—something which earlier thinkers had thought to be, almost by definition, an impossibility. It is even more surprising that chemical materials out there are, as Newton had earlier assumed, the same as those on Earth. (That this is true is clearly shown by the fact that even very complex absorption spectra are reproduced exactly in star spectra.) Finally, this result leads to a striking conclusion: *The physical processes that cause light absorption in the atom must be the same among the distant stars as on Earth*.

In these facts you can see a hint of how *universal* physical laws really are. Even at the farthest edges of the cosmos from which the Earth receives light, the laws of physics appear to be the same as for common materials close at hand in the laboratory! This is just what Galileo and Newton had intuited when they proposed that there is no difference between terrestrial and celestial physics.

14.2 REGULARITIES IN THE HYDROGEN SPECTRUM

Of all the spectra, the emission spectrum of hydrogen is especially interesting for both historical and theoretical reasons. In the visible and near-ultraviolet regions, the emission spectrum consists of an apparently systematic or orderly series of lines (see Figure 14.4). In 1885, Johann Jakob Balmer (1825–1898), a teacher at a girls' school in Switzerland, who was interested in number puzzles and numerology, found a simple formula—an empirical relation—which gave the wavelengths λ of the lines known at the time. The formula is

$$\lambda = b\left(\frac{n^2}{n^2 - 2^2}\right).$$

The quantity b is a constant which Balmer determined empirically and found to be equal to 364.56×10^{-9} m; n is a whole number, different for each line. Specifically, for the equation to yield the observed value for the respective wavelengths, n must be 3 for the first visible (red) line of the hydrogen emission spectrum (named H_α); $n = 4$ for the second (green) line (H_β); $n = 5$ for the third (blue) line (H_γ); and $n = 6$ for the fourth (violet)

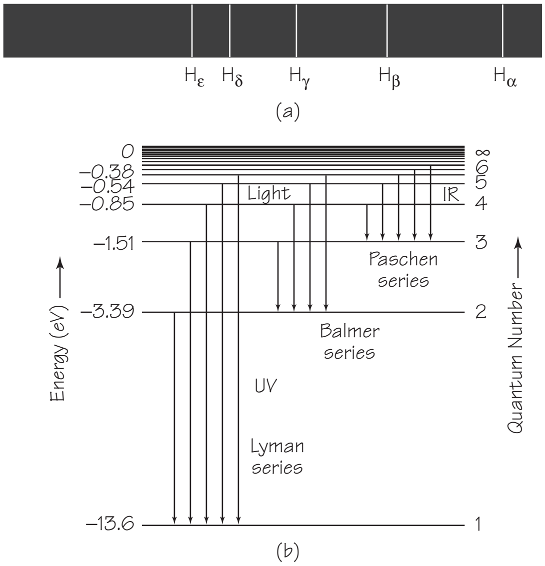


FIGURE 14.4 (a) The Balmer lines of hydrogen as they would appear in a photograph made with film sensitive to some ultraviolet as well as visible light. The lines get more crowded as they approach the series limit in the ultraviolet. (b) In Section 14.8, this scheme will explain the existence of all hydrogen emission lines.

line (H_δ). The table below shows excellent agreement (within 0.02%) between Balmer's calculations from his empirical formula and previously measured values.

Wavelength λ, in nanometers (10^{-9} m), for hydrogen emission spectrum.*

Name of line	n	*From Balmer's formula*	*By Ångström's measurement*	*Difference*
H_α	3	656.208	656.210	+0.002
H_β	4	486.08	486.074	−0.006
H_γ	5	434.00	434.01	+0.01
H_δ	6	410.13	410.12	−0.01

* Data for hydrogen spectrum (Balmer, 1885).

Not until 30 years later did scientists understand why Balmer's empirical formula worked so well, why the hydrogen atom emitted light whose wavelengths made such a simple sequence. But this did not keep Balmer from speculating that there might be other series of unsuspected lines in the hydrogen spectrum. Their wavelengths, he suggested, could be found by replacing the 2^2 in his equation with numbers such as 1^2, 3^2, 4^2, and so on. This suggestion stimulated many scientists to search for such additional spectral series. The search turned out to be fruitful, as you will see shortly.

In order to use modern notation, we rewrite Balmer's formula in a form that will be more useful:

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

In this equation, which can be derived from the previous one, R_H is a constant, equal to $4/b$. It is called the Rydberg constant for hydrogen, in honor of the Swedish spectroscopist J.R. Rydberg. Following Balmer, Rydberg made great progress in the search for various spectral series. The series of lines described by Balmer's formula are called the *Balmer series*. Balmer constructed his formula from the known wavelengths of only four lines in the visible part of the spectrum. The formula could be used to predict that there should be many more lines in the same series (indeed, infinitely many such lines, as n takes on values such as $n = 3, 4, 5, 6, 7, 8, \ldots \infty$). Moreover, every one of the lines is correctly predicted by Balmer's formula with considerable accuracy.

Following Balmer's speculative suggestion of replacing 2^2 by other numbers gives the following possibilities:

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

$$\frac{1}{\lambda} = R_H\left(\frac{1}{3^2} - \frac{1}{n^2}\right),$$

$$\frac{1}{\lambda} = R_H\left(\frac{1}{4^2} - \frac{1}{n^2}\right),$$

and so on. Each of these equations describes a possible series of emission lines. All these hypothetical series of lines can then be summarized by one overall formula

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

where n_f is a whole number that is fixed for any one series for which wavelengths are to be found. (For example, $n_f = 2$ for all lines in the Balmer series.) The letter n_i stands for integers that take on the values $n_f + 1$, $n_f + 2$, $n_f + 3$, . . . for the successive individual lines in a given series. (Thus, for the first two lines of the Balmer series, n_i is 3 and 4.) The constant R_H should have the same value for all of these hydrogen series.

So far, this discussion has been merely speculative. No series, no single line fitting the general formula, *need* exist, except for the observed Balmer series, where $n_f = 2$. But when physicists began to look for these hypothetical lines with good spectrometers, they found that they do, in fact, exist!

In 1908, F. Paschen in Germany found two hydrogen lines in the infrared. Their wavelengths were correctly given by setting $n_f = 3$ and $n_i = 4$ and 5 in the general formula. Many other lines in this "Paschen series" have since been identified. With improved experimental apparatus and techniques, new regions of the spectrum could be explored. Thus, other series gradually were added to the Balmer and Paschen series. In the table below, the name of each series listed is that of the discoverer.

Series of lines in the hydrogen spectrum.

Name of series	*Date of discovery*	*Region of spectrum*	*Values in Balmer equation*
Lyman	1906–1914	Ultraviolet	$n_f = 1$, $n_i = 2, 3, 4, \ldots$
Balmer	1885	Ultraviolet-visible	$n_f = 2$, $n_i = 3, 4, 5, \ldots$
Paschen	1908	Infrared	$n_f = 3$, $n_i = 4, 5, 6, \ldots$
Brackett	1922	Infrared	$n_f = 4$, $n_i = 5, 6, 7, \ldots$
Pfund	1924	Infrared	$n_f = 5$, $n_i = 6, 7, 8, \ldots$

Balmer hoped that his formula for the hydrogen spectra might be a pattern for finding series relationships in the spectra of other gases. This suggestion also bore fruit. Balmer's formula itself did not work directly in describing spectra of gases other than hydrogen. But it did inspire formulas of similar mathematical form that successfully described order in portions of many complex spectra. The Rydberg constant R_H also reappeared in such empirical formulas.

However, no model based on classical mechanics and electromagnetism could be constructed that would explain the spectra described by these formulas. What you have already learned in Chapter 13 about quantum theory suggests one line of attack. Obviously, the emission and absorption of light from an atom must correspond to a decrease and an increase of the atom's energy. If atoms of an element emit light of only certain frequencies, then the energy of the atoms must be able to change only by certain amounts. These changes of energy must involve rearrangement of the parts of the atom.

14.3 RUTHERFORD'S NUCLEAR MODEL OF THE ATOM

As so often, the next step arose from completely unrelated research. Ernest Rutherford, an outstanding physicist in the Cavendish Laboratory at Cambridge, provided a new basis for atomic models during the period 1909–1911. Rutherford was interested in the rays emitted by radioactive substances, especially α (alpha) rays. As you will see in Chapter 17, α rays consist of positively charged particles. These particles are positively charged helium ions with masses about 7500 times greater than the electron mass. Some radioactive substances emit α particles at very high rates and energies. Such particles are often used as projectiles in bombarding samples of elements. The experiments that Rutherford and his colleagues did with α particles are examples of a highly important kind of experiment in atomic and nuclear physics: the scattering experiment.

In a scattering experiment, a narrow, parallel beam of "projectiles" (e.g., α particles, electrons, X rays) is aimed at a target. The target is usually a thin foil or film of some material. As the beam strikes the target, some of the projectiles are deflected, or scattered, from their original direction. The scattering is the result of the interaction between the particles in the beam and the atoms of the material. A careful study of the projectiles after scattering can yield information about the projectiles, the atoms, and the interaction between them. If you know the mass, energy, and direction of the projectiles and see how they are scattered, you can deduce properties of the atoms that scattered the projectiles.

Rutherford noticed that when a beam of α particles passed through a thin metal foil, the beam spread out. This scattering may be thought of as caused by electrostatic forces between the positively charged α particles and the charges that make up atoms. Atoms contain both positive and negative charges. Therefore, an α particle undergoes both repelling and attracting forces as it passes through matter. The magnitude and direction of these forces depend on how closely the particle approaches the centers of the atoms among which it moves. When a particular atomic model is proposed, the extent of the expected scattering can be calculated and compared with experiment. For example, the Thomson model of the atom predicted al-

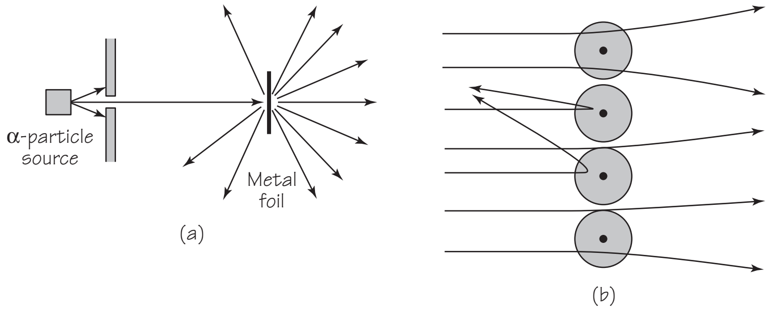


FIGURE 14.5 Alpha particle scattering showing deflection by the nuclei of the metal atoms. In somewhat the same way, you could (in principle) use a scattering experiment to discover the size and shape of an object hidden in a cloud or fog by directing a series of projectiles at the unseen object and tracing their paths back after deflection.

most no chance that an α particle would be deflected by an angle of more than a few degrees.

The breakthrough which led to the modern model of the atom followed a discovery by one of Rutherford's assistants, Hans Geiger. Geiger found that the number of particles scattered through angles of 10° or more was much greater than the number predicted by the Thomson model. In fact, a significant number were scattered through an angle greater than 90°, that is, many α particles virtually bounced right back from the foil. This result was entirely unexpected. According to Thomson's model, the atom should have acted only slightly on the projectile, rather like a cloud in which fine dust is suspended. Some years later, Rutherford wrote:

> . . . 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 [kinetic] energy, and you could show that if the scattering was due to the accumualted effect of a number of small scatterings, the chance of an α-particle's being scattered backward 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 backward . . ."

FIGURE 14.6 Ernest Rutherford (1871–1937) was born, grew up, and received most of his education in New Zealand. At age 24 he went to Cambridge, England, to work at the Cavendish Laboratory under J.J. Thomson. From there he went to McGill University in Canada, then home to be married and back to England again, to Manchester University. At these universities, and later at the Cavendish Laboratory where he succeeded J.J. Thomson as director, Rutherford performed important experiments on radioactivity, the nuclear nature of the atom, and the structure of the nucleus. Rutherford introduced the concepts "alpha," "beta," and "gamma" rays, "protons," and "half-life."

> 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 backward 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 centre, carrying a charge.

These experiments and Rutherford's interpretation marked the origin of the modern concept of the *nuclear atom*. Look at the experiments and Rutherford's conclusion more closely. Why must the atom have its mass and positive charge concentrated in a tiny nucleus at the center about which the electrons are clustered?

He writes that a possible explanation of the observed scattering is that the foil contains concentrations of mass and charge, that is, positively charged *nuclei*. These nuclei are much more dense than anything in Thomson's atoms. An α particle heading directly toward one of them is stopped and turned back. In the same way, a ball would bounce back from a rock but not from a cloud of dust particles. The drawing in Figure 14.7 is based

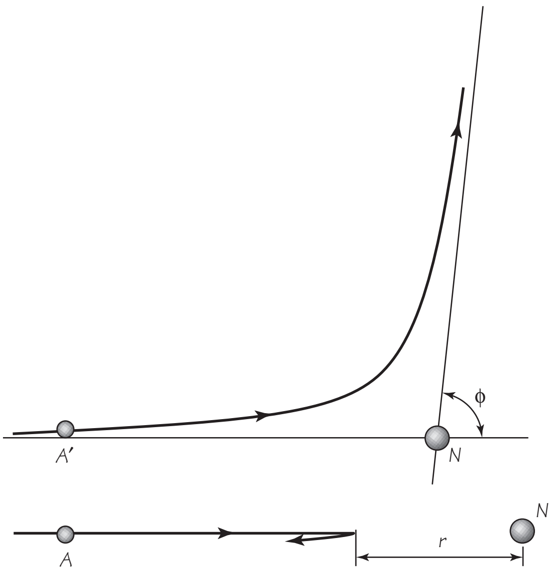


FIGURE 14.7 Paths of two alpha particles A and A′ approaching a nucleus *N*.

on one of Rutherford's diagrams in his paper of 1911, which laid the foundation for the modern theory of atomic structure. It shows two positively charged α particles, A and A′. The α particle A is heading directly toward a massive nucleus N. If the nucleus has a positive electric charge, it will repel the positive α particle. Because of this electrical repulsive force, A will slow to a stop at some distance r from N and then move directly back. A′ is an α particle that is *not* headed directly toward the nucleus N. It is repelled by N along a path which calculation shows must be a hyperbola. The deflection of A′ from its original path is indicated by the angle ϕ.

Rutherford considered the effects on the α particle's path of the important variables: the particle's speed, the foil thickness, and the quantity of charge Q on each nucleus. According to Rutherford's model, most of the α particles should be scattered through small angles, because the chance of approaching a very small nucleus nearly head-on is so small. But a significant number of α particles should be scattered through large angles.

Geiger and Marsden tested these predictions with the apparatus sketched in Figure 14.8. The lead box B contains a radioactive substance (radon) that emits α particles. The particles emerging from the small hole in the box are deflected through various angles ϕ in passing through the thin metal foil F. The number of particles deflected through each angle ϕ is found by letting the particles strike a zinc sulfide screen S. Each α particle that strikes the screen produces a scintillation (a momentary pinpoint of fluorescence). These scintillations can be observed and counted by looking through the

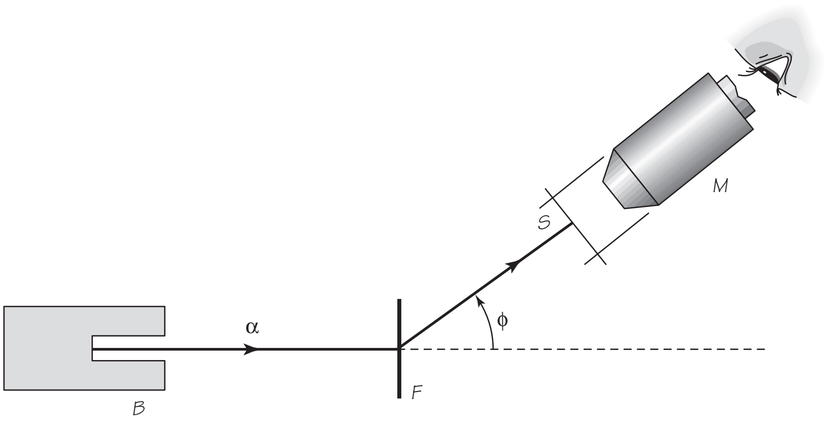


FIGURE 14.8 Rutherford's scintillation apparatus was placed in an evacuated chamber so that the alpha particles would not be slowed down by collisions with air molecules.

microscope M. The microscope and screen can be moved together along the arc of a circle. In later experiments, the number of α particles at any angle ϕ was counted more conveniently by a counter invented by Geiger (see Figure 14.9). The Geiger counter, in its more recent versions, is now a standard laboratory item.

Geiger and Marsden found that the number of α particles counted depended on the scattering angle, the speed of the particles, and the thickness of the foil. These findings agreed with Rutherford's predictions and

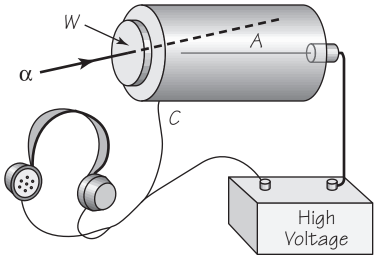


FIGURE 14.9 A Geiger counter that consists of a metal cylinder C containing a gas and a thin wire *A* that is insulated from the cylinder. A potential difference slightly less than that needed to produce a discharge through the gas is maintained between the wire (anode *A*) and cylinder (cathode *C*). When an alpha particle enters through the thin mica window (*W*), it frees a few electrons from the gas molecules. The electrons are accelerated toward the anode, freeing more electrons along the way by collisions with gas molecules. The avalanche of electrons constitutes a sudden surge of current that can be amplified to produce a click in the headphones or to operate a register

supported a new atomic model, in which most of the mass and all positive charge occupy a very small region at the center of the atom.

14.4 NUCLEAR CHARGE AND SIZE

Despite the success of Rutherford's model in dealing with α-scattering data, a problem remained. There still was no way to measure independently the charge Q on the nucleus. However, the scattering experiments had confirmed Rutherford's predictions about the effect of the speed of the α particle and the thickness of the foil on the angle of scattering. As often happens when part of a theory is confirmed, it is reasonable to proceed temporarily as if the whole theory were justified; that is, pending further proof, one could assume that the value of Q needed to explain the observed scattering data was the correct value of Q for the actual nucleus, as determined by Coulomb's law and the motion of the α particles. On this basis, Rutherford compiled scattering data for several different elements, among them carbon, aluminum, and gold. The following positive nuclear charges yielded the best agreement with experiments: for carbon, $Q = 6e$; for aluminum, $Q = 13e$ or $14e$; and for gold, $Q = 78e$ or $79e$, where e is the magnitude of the charge of one electron ($e = 1.6 \times 10^{-19}$ C). Similarly, values were found for other elements.

The magnitude of the positive charge of the nucleus was an important and welcome piece of information about the atom. The atom as a whole is of course electrically neutral. So if the nucleus has a positive charge of $6e$,

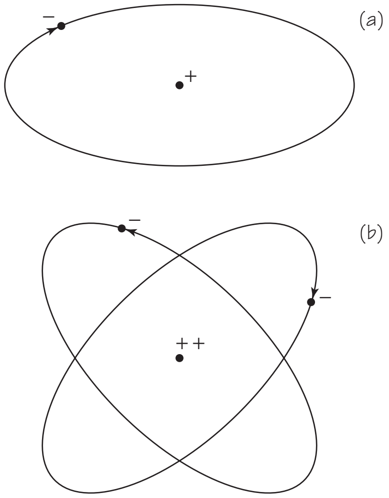


FIGURE 14.10 Sketch of simple atomic structure: (a) hydrogen, (b) helium.

13*e*, 14*e*, etc., the number of negatively charged electrons surrounding the nucleus must be 6 for carbon, 13 or 14 for aluminum, etc. Thus, for the first time, scientists had a good idea of just how many electrons an atom may have.

An even more important fact was soon noticed. For each element, the value for the nuclear charge, in multiples of *e*, was close to the atomic number Z, the place number of that element in the periodic table! The results of scattering experiments with α particles were not yet precise enough to make this conclusion with certainty. But the data indicated that *each nucleus has a positive charge* Q *numerically equal to* Z*e*.

This suggestion made the picture of the nuclear atom much clearer and simpler. On this basis, the hydrogen atom ($Z = 1$) has one electron outside the nucleus. A helium atom ($Z = 2$) has in its neutral state two electrons outside the nucleus. A uranium atom ($Z = 92$) has 92 electrons. Additional experiments further supported this simple scheme. The experiments showed that it was possible to produce singly ionized hydrogen atoms, H^+, and doubly ionized helium atoms, He^{++}, but neither H^{++} nor He^{+++}. Evidently, a hydrogen atom has only one electron to lose, and a helium atom only two. Unexpectedly, the concept of the nuclear atom thus provided new insight into the periodic table of the elements. The nuclear concept suggested that *the periodic table is really a listing of the elements according to the number of electrons around the nucleus, or equally well according to the number of positive units of charge on the nucleus.*

These results cleared up some of the difficulties in Mendeleev's periodic table. For example, the elements tellurium and iodine had been assigned positions $Z = 52$ and $Z = 53$ on the basis of their chemical properties. This positioning contradicted the order of their atomic weights. But now Z was seen to correspond to a fundamental fact about the nucleus. Thus, the reversed order of atomic weights was understood to be not a basic fault in the scheme.

As an important additional result of these scattering experiments, Rutherford could estimate the size of the nucleus. Suppose an α particle is moving directly toward a nucleus. Its kinetic energy on approach is transformed into electrical potential energy. It slows down and eventually stops, like a ball rolling up a hill. The distance of closest approach can be computed from the known original kinetic energy of the α particle and the charges of α particle and nucleus. The value calculated for the closest approach is approximately 3×10^{-14} m. If the α particle does not penetrate the nucleus, this distance must be at least as great as the sum of the radii of α particles and nucleus; thus, the radius of the nucleus could not be larger than about 10^{-14} m. But 10^{-14} m is only about 1/1000 of the known radius of an atom. Furthermore, the total volume of the atom is proportional to the cube of its radius. So it is clear that *the atom is mostly empty,* *with the nucleus occupying only one-billionth of the space!* This explains how α particles or electrons can penetrate thousands of layers of atoms in metal foils or in gases, with only an occasional large deflection backward.

Successful as this model of the nuclear atom was in explaining scattering phenomena, it raised many new questions: What is the arrangement of electrons about the nucleus? What keeps the negative electron from falling into a positive nucleus by electrical attraction? Of what is the nucleus composed? What keeps it from exploding on account of the repulsion of its positive charges? Rutherford realized the problems raised by these questions and the failure of his model to answer them. But he rightly said that one should not expect one model, made on the basis of one set of puzzling results which it explains well, also to handle all other puzzles. Additional assumptions were needed to complete the model and answer the additional questions about the details of atomic structure. The remainder of this chapter will deal with the theory proposed by Niels Bohr, a young Danish physicist who joined Rutherford's group just as the nuclear model was being announced.

14.5 BOHR'S THEORY: THE POSTULATES

Assume, as Rutherford did, that an atom consists of a positively charged nucleus surrounded by a number of negatively charged electrons. What, then, keeps the electrons from falling into the nucleus, pulled in by the electric force of attraction? One possible answer is that an atom may be like a planetary system, with the electrons revolving in orbits around the nucleus. As you may know (see Section 3.12), a ball whirling on a string or a planet orbiting the Sun must be subject to an attractive force toward the center. Otherwise, the ball or planet would fly away on a straight line, according to Newton's first Law of Motion. This force toward the center is often called a *centripetal force*. For planets, this force arises from the gravitational attraction of the Sun on the planet. For electrons in atoms, Rutherford suggested that, instead of the gravitational force, the electric attractive force between the nucleus and an electron would supply a centripetal force. This centripetal force would tend to keep the moving electron in orbit.

This idea seems to be a good start toward a theory of atomic structure. But a serious problem arises concerning the stability of a "planetary" atom. According to Maxwell's theory of electromagnetism, a charged particle radiates energy when it is accelerated. An electron moving in an orbit around a nucleus continually changes its direction, hence also its velocity vector. In other words, it is *always being accelerated* by the centripetal electric force.


(a) (b) (c)

FIGURE 14.11 Niels Bohr (1885–1962): (a) pictured with his wife, Margrethe, on their wedding day; (b) ca. 1917; (c) in his later years. Bohr was born in Copenhagen, Denmark, and became a professor at the university there. He received the Nobel Prize in physics in 1922 for his work described in this chapter. He helped found the new quantum mechanics, was a leading contributor to theories of nuclear structure and nuclear fission, and helped press for peaceful uses of nuclear energy.

The electron, therefore, should lose energy by emitting radiation and thus being drawn steadily closer to the nucleus. (Somewhat similarly, an artificial satellite loses energy, because of friction in the upper atmosphere, and gradually spirals toward the Earth.) Within a very short time, the energy-radiating electron should actually be pulled into the nucleus. According to classical physics, mechanics, and electromagnetism, a planetary atom would not be stable for more than a very small fraction of a second.

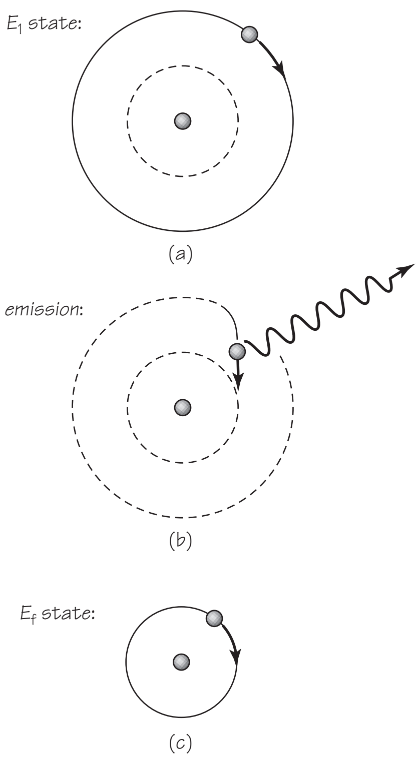
The idea of a planetary atom was nevertheless appealing. Physicists continued to look for a theory that would include a stable planetary structure and predict separate line spectra for the elements. Niels Bohr, then an unknown Danish physicist who had just received his doctorate, succeeded in constructing such a theory in 1912–1913. This theory was called the Bohr model or quantum model of the atom, because it incorporated the quantum idea of Einstein and Planck. It was widely recognized as a major victory. Although it had to be modified later to account for many more phenomena, it showed how to attack atomic problems by using quantum theory. Today, it seems a rather naive way of thinking about the atom, compared with more recent quantum-mechanical theories. But in fact, considering what it was designed to do, Bohr's theory is an impressive example of a successful physical model. Since Bohr incorporated Rutherford's idea of the nucleus, the model that Bohr's theory discusses is often called the Rutherford–Bohr model.

Bohr introduced two bold new postulates specifically to account for the existence of stable electron orbits and for separate emission spectra for each element. These postulates may be stated as follows:

1. Contrary to the predictions of classical physics—which after all had been tested only for relatively large-scale circumstances—there are states for an atomic system in which electromagnetic radiation simply does not occur, despite any acceleration of the charged particles (electrons). These states are called the *stationary states* of the atom.
2. Any emission or absorption of radiation, either as visible light or other electromagnetic radiation, corresponds to a sudden transition of the charge between two such stationary states. The radiation emitted or absorbed has a frequency f determined by the relation $hf = E_i - E_f$. (In this equation, h is Planck's constant, and E_i and E_f are the energies of the atom in the initial and final stationary states, respectively.)

Quantum theory had begun with Planck's idea that atoms emit light only in definite amounts of energy. This concept was extended by Einstein's idea that light travels only as definite parcels, quanta, of energy. Now it was extended further by Bohr's idea that atoms exist in a stable condition only in

FIGURE 14.12 An electron changing orbital states with the emission of a photon.



definite, “quantized” energy states. But Bohr also used the quantum concept in deciding which of all the conceivable stationary states were actually possible. An example of how Bohr did this is given in the next section.

For simplicity, the hydrogen atom, with a single electron revolving around the nucleus, is used. Following Bohr, we assume that the possible electron orbits are simply circular. Light is emitted by the atom when it changes from one state to another (see Figure 14.12). (The details of some additional assumptions and calculations are worked out in the *Student Guide*.) Bohr’s result for the possible stable orbit radii r_n was $r_n = a \cdot n^2$, where a is a constant $(h^2/4\pi^2 mkq_e^2)$ that can be calculated from known physical values, and n stands for any whole number, 1, 2, 3. . . .

14.6 THE SIZE OF THE HYDROGEN ATOM

Bohr’s result is remarkable. In hydrogen atoms, the possible orbital radii of the electrons are whole multiples of a constant which can at once be evaluated; that is, n^2 takes on values of 1^2, 2^2, 3^2, . . . , and all factors to the left of n^2 are quantities known previously by independent measurement! Calculating the value ($h^2/4\pi^2mkq_e^2$) gives 5.3×10^{-11} m. Therefore, according to Bohr's model, the radii of stable electron orbits should be $r_n = 5.3 \times 10^{-11}\ \text{m} \times n^2$, that is, 5.3×10^{-11} m when $n = 1$ (first allowed orbit), $4 \times 5.3 \times 10^{-11}$ m when $n = 2$ (second allowed orbit), $9 \times 5.3 \times 10^{-11}$ m when $n = 3$, etc. *In between these values, there are no allowed radii.* In short, the separate allowed electron orbits are spaced around the nucleus in a regular way, with the allowed radii quantized in a regular manner. Emission and absorption of light should therefore correspond to the transition of the electron from one allowed orbit to another. Emission of light occurs when the electron "drops" from a higher energy state to a lower state; absorption of light occurs when the electron "jumps" from a lower-energy state up to a higher-energy state.

This is just the kind of result hoped for. It tells which radii are possible and where they lie. But so far, it had all been model building. Do the orbits in a real hydrogen atom actually correspond to this model? In his first paper of 1913, Bohr was able to give at least a partial "yes" as an answer. It had long been known that the normal "unexcited" hydrogen atom has a radius of about 5×10^{-11} m (i.e., the size of the atom obtained, for example, by interpreting measured characteristics of gases in terms of the kinetic theory). This known value of about 5×10^{-11} m corresponds excellently to the prediction from the equation for orbital radius r if n has the lowest value, namely 1. Now there was a way to understand the size of the neutral, unexcited hydrogen atom. For every such atom, the size corresponds to the size of the innermost allowed electron orbit.

14.7 OTHER CONSEQUENCES OF THE BOHR MODEL

With his two postulates, Bohr could calculate the radius of each permitted orbit. In addition, he could calculate the total energy of the electron in each orbit, i.e., the energy of the stationary state.

The results that Bohr obtained may be summarized in two simple formulas. As you saw, the radius of an orbit with quantum number n is given by the expression

$$r_n = n^2 r_1,$$

where r_1 is the radius of the first orbit (the orbit for $n = 1$) and has the value 5.3×10^{-9} cm or 5.3×10^{-11} m.

The energy (the sum of kinetic energy and electric potential energy) of the electron in the orbit with quantum number n can also be computed from Bohr's postulates. As pointed out in Chapter 6, it makes no sense to assign an absolute value to potential energy. In this case, only *changes* in energy have physical meaning. Therefore, any convenient zero level can be chosen. For an electron orbiting in an electric field, the mathematics is particularly simple if, as a zero level for energy, the state $n = \infty$ is chosen. At this level, the electron would be infinitely far from the nucleus (and therefore free of it). The energy for any other state E_n is then the *difference* from this free state. The possible energy states for the hydrogen atom are therefore

$$E_n = \frac{1}{n^2} E_1,$$

where E_1 is the total energy of the atom when the electron is in the first orbit ($n = 1$). E_1 is the lowest energy possible for an electron in a hydrogen atom. Its value is -13.6 eV (the negative value means only that the energy is 13.6 eV less than the free state value E_∞). This is called the *ground state*. In that state, the electron is most tightly "bound" to the nucleus. The value of E_2, the first "excited state" above the ground state, is, according to the above equation,

$$E_2 = \frac{1}{2^2} \times (-13.6 \text{ eV}) = -3.4 \text{ eV}.$$

This state is only 3.4 eV less than in the free state.

According to the formula for r_n, the first stationary orbit, defined by $n = 1$, has the smallest radius. Higher values of n correspond to orbits that have larger radii. The higher orbits are spaced further and further apart, and the force field of the nucleus falls off even more rapidly. So the work required to move out to the next larger orbit actually becomes smaller and smaller. Also, the jumps in energy from one level of allowed energy E to the next become smaller and smaller.

14.8 BOHR ACCOUNTS FOR THE SERIES SPECTRA OF HYDROGEN

The most spectacular success of Bohr's model was that it could be used to explain all emission (and absorption) lines in the hydrogen spectrum; that is, Bohr could use his model to derive, and so to explain, the Balmer formula for the series spectra of hydrogen!

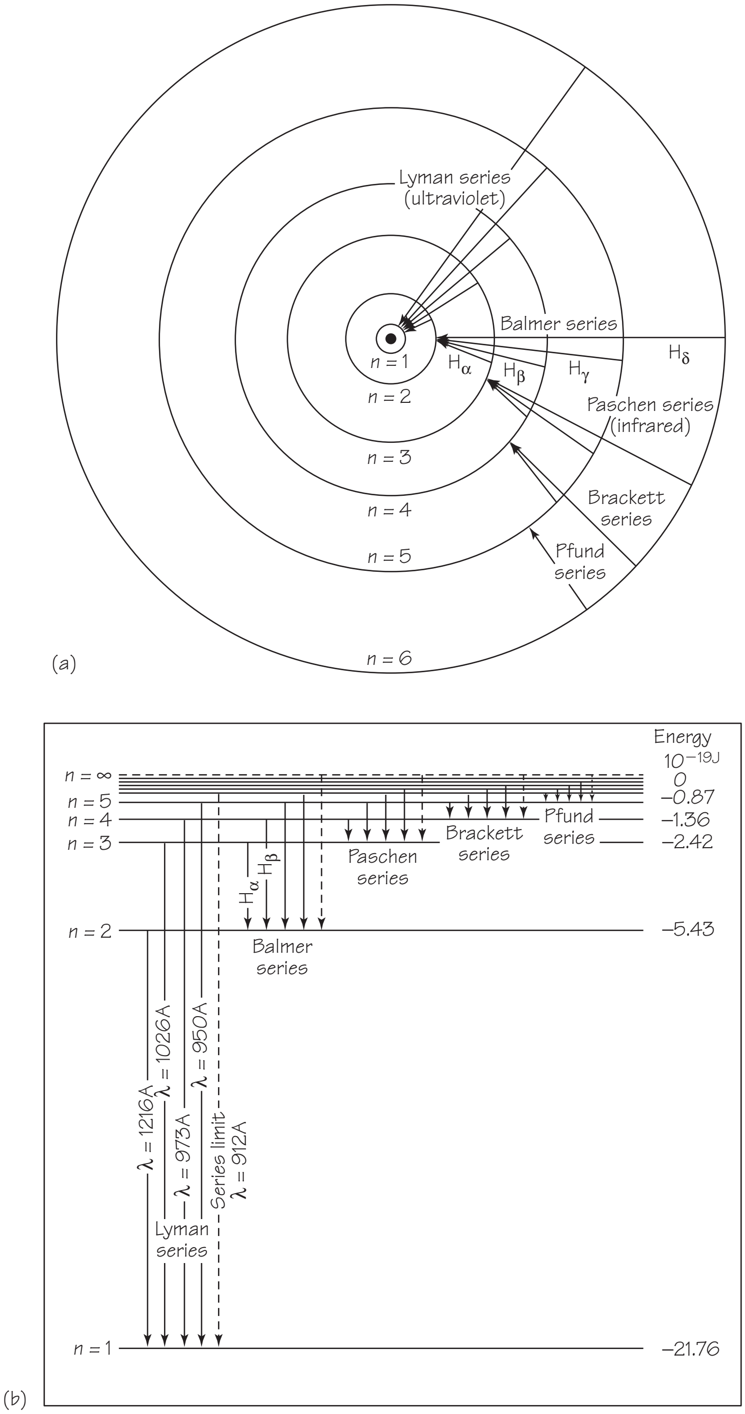


FIGURE 14.13 (a) A schematic diagram of transitions between stationary states of electrons in hydrogen atom, giving rise to five of the series of emission spectra lines. (b) Energy-level diagram for the hydrogen atom. Possible transitions between energy states are shown for the first few levels (from n = 2 to n = 3 to n = 2 or n = 1, etc.). The dotted arrow for each series indicates the series limit, a transition from the state where the electron is completely free from the nucleus.

By Bohr's second postulate, the radiation emitted or absorbed in a transition in an atom should have a frequency determined by

$$hf = E_1 - E_2.$$

If n_f is the quantum number of the final state and n_i is the quantum number of the initial state, then according to the result for E_n:

$$E_f = \frac{1}{n_f^2}E_1 \qquad \text{and} \qquad E_i = \frac{1}{n_i^2}E_1.$$

The frequency of radiation emitted or absorbed when the atom goes from the initial state to the final state is therefore determined by the equation

$$hf = \frac{E_1}{n_i^2} - \frac{E_1}{n_f^2} \qquad \text{or} \qquad hf = E_1\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right).$$

In order to deal with wavelength λ (as in Balmer's formula) rather than frequency, we use the relationship between frequency and wavelength given in Chapter 8. The frequency of a line in the spectrum is equal to the speed of the light wave divided by its wavelength: $f = c/\lambda$. Substituting c/λ for f in the last equation and then dividing both sides by the constant hc (Planck's constant times the speed of light), gives

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right).$$

According to Bohr's model, then, this equation gives the wavelength λ of the radiation emitted or absorbed when a hydrogen atom changes from one stationary state with quantum number n_i to another with n_f.

How does this prediction from Bohr's model compare with the long-established *empirical* Balmer formula for the Balmer series? This, of course, is the crucial question. The Balmer formula, given in Section 14.2, in modern terms is

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

You can see at once that the equation for the wavelength λ of emitted (or absorbed) light derived from the Bohr model is exactly the same as Balmer's formula, if $n_f = 2$ and $R_H = -E_1/hc$.

The Rydberg constant R_H was long known from spectroscopic measurements to have the value of $1.097 \times 10^7\ \text{m}^{-1}$. Now it could be compared with the value for $-E_1/hc$. (Remember that E_1 is negative, so $-E_1$ is positive.) Remarkably, there was fine agreement. R_H, previously regarded as just an experimentally determined constant, was now shown to be a number that could be calculated from known fundamental constants of nature, namely, the mass and charge of the electron, Planck's constant, and the speed of light.

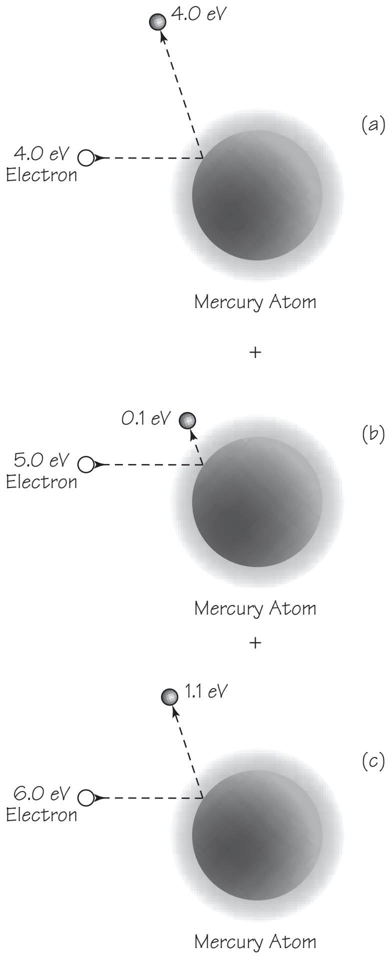
More important, you can now see the *meaning*, in physical terms, of the old empirical formula for the lines (H_α, H_β, . . .) in the Balmer series. All the lines in the Balmer series simply correspond to transitions from various initial states (various values of n_i larger than 2) to the same final state, for which $n_f = 2$. Thus, photons having the frequency or wavelength of the line H_α are emitted when electrons in a gas of hydrogen atoms "jump" from the state $n = 3$ to the state $n = 2$, as shown in the diagrams in Figure 14.14. The H_β line corresponds to "jumps" from $n = 4$ to $n = 2$, and so forth.

When Bohr proposed his theory in 1913, emission lines in only the Balmer and Paschen series for hydrogen were known definitely. Balmer had suggested, and the Bohr model agreed, that additional series should exist. Further experiments revealed the Lyman series in the ultraviolet portion of the spectrum (1904–1914), the Brackett series (1922), and the Pfund series (1924), both of the latter series being in the infrared region of the spectrum. In each series, the measured frequencies of every one of the lines were found to be those predicted by Bohr's theory, and (equally important) no lines existed that were *not* given by the theory. Similarly, Bohr's model could explain the general formula that Balmer guessed might apply for all spectral lines of hydrogen. As described in empirical terms in Section 14.2, the lines of the Lyman series correspond to transitions from various initial states to the final state $n_f = 1$; the lines of the Paschen series correspond to transitions from various initial states to the final state $n_f = 3$; and so on, as indicated by the equation on page 644 from Bohr's model:

$$\frac{1}{\lambda} = \frac{E_1}{hc}\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right) \qquad \text{or} \qquad \frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right).$$

The general scheme of possible transitions among the first six orbits is shown in Figure 14.14a. Thus, the theory not only related known information about the hydrogen spectrum, but also predicted correctly the wavelengths of previously unknown series of lines in the spectrum. Moreover, it provided a reasonable physical model; Balmer's general formula had provided no physical reason for the empirical relationship among the lines of each series.

FIGURE 14.14 Diagrams of an atom of mercury undergoing impacts by electrons of energies of 4.0 eV, 5.0 eV, 6.0 eV.



The schematic diagram shown on page 643 is useful as an aid for the imagination. But it has the danger of being too specific. For instance, it may lead one to think of the emission of radiation as actual "jumps" of electrons between orbits. In Chapter 15 you will see why it is impossible to detect an electron moving in such orbits. A second way of presenting the results of Bohr's theory yields the same facts but does not adhere as closely to a picture of orbits. This scheme is shown in Figure 14.13b. It focuses not on orbits but on the corresponding possible energy states. These energy states are all given by the formula $E_n = 1/n^2 \times E_1$. In terms of this *mathematical model*, the atom is normally unexcited, with an energy E_1 about -13.6 eV (or -22×10^{-19} J).

Absorption of energy can place the atoms in an excited state, with a correspondingly higher energy. The excited atom is then ready to emit light, with a consequent reduction in energy. The energy absorbed or emitted always shifts the total energy of the atom to one of the values specified by the formula for E_n. Thus, the hydrogen atom may also be represented, not by orbits, but by means of an energy-level diagram.

14.9 DO STATIONARY STATES REALLY EXIST?

The success of Bohr's theory in accounting for the spectrum of hydrogen left this question: *Could experiments show directly that atoms do have only certain, separate energy states?* In other words, are there really gaps between the energies that an atom can have? A famous experiment in 1914, by the German physicists James Franck and Gustav Hertz (a nephew of Heinrich Hertz), showed that these separate energy states do indeed exist.

Franck and Hertz bombarded atoms with electrons from an "electron gun," a hot wire that emitted electrons which were then accelerated through a hole leading into an evacuated region where they were aimed at a target. (A similar type of electron gun is used today in TV tubes and computer monitors.) Franck and Hertz were able to measure the energy lost by the electrons in collisions with the target atoms. They could also determine the energy gained by the atoms in these collisions.

In their first experiment, Franck and Hertz bombarded mercury vapor contained in a chamber at very low pressure. The procedure was equivalent to measuring the kinetic energy of electrons on leaving the electron gun, and again after they had passed through the mercury vapor. The only way electrons could lose energy was in collisions with the mercury atoms. Franck and Hertz found that when the kinetic energy of the electrons leaving the gun was small (up to several electron volts), the electrons still had almost exactly the same energy after passage through the mercury vapor as they had on leaving the gun. This result could be explained in the following way. A mercury atom is several hundred thousand times more massive than an electron. When it has low kinetic energy, the electron just bounces off a mercury atom, much as a golf ball thrown at a bowling ball would bounce off. A collision of this kind is called an "elastic" collision (discussed in Chapter 6). In an elastic collision, the mercury atom (bowling ball) takes up only a negligible part of the kinetic energy of the electron (golf ball), so that the electron loses practically none of its kinetic energy.

But when the kinetic energy of the electrons was raised to 5 eV, the experimental results changed dramatically. When an electron collided with a mercury atom, the electron lost almost exactly 4.9 eV of energy. When the energy was increased to 6.0 eV, the electron still lost just 4.9 eV of energy

Physicists now know two ways of "exciting" an atom: by absorption and by collision. In absorption, an atom absorbs a photon with just the right energy to cause a transition from the lowest energy level to a higher one. Collision may involve collision with an electron from an electron gun or collisions among agitated atoms (as in a heated enclosure or a discharge tube).

in collision, being left with 1.1 eV of energy. These results indicated that a mercury atom cannot accept less than 4.9 eV of energy. Furthermore, when the mercury atom is offered somewhat more energy, for example, 5 eV or 6 eV, it still accepts only 4.9 eV. The accepted amount of energy cannot go into kinetic energy of the mercury because the atom is so much more massive than the electron. Therefore, Franck and Hertz concluded that the 4.9 eV is added to the internal energy of the mercury atom; that is, the mercury atom enters a stationary state with enemy 4.9 eV greater than that of the lowest energy state, with no allowed energy level in between.

What happens to this extra 4.9 eV of internal energy? According to the Bohr model, this amount of energy should be emitted as electromagnetic radiation when the atom returns to its lowest state. Franck and Hertz looked for this radiation, and they found it! They observed that the mercury vapor, after having been bombarded with electrons, emitted light at a wavelength of 253.5 nm. This wavelength was known to exist in the emission spectrum of hot mercury vapor. The wavelength corresponds to a frequency f for which the photon's energy, hf, is just 4.9 eV (as you can calculate). This result showed that mercury atoms had indeed gained (and then radiated away) 4.9 eV of energy in collisions with electrons.

Later experiments showed that mercury atoms bombarded by electrons could also gain other sharply defined amounts of energy, for example, 6.7 eV and 10.4 eV. In each case, the subsequently emitted radiation corresponded to known lines in the emission spectrum of mercury. In each case, similar results were obtained: the electrons always lost energy, and the atoms always gained energy, both only in sharply defined amounts. Each type of atom studied was found to have separate energy states. The amounts of energy gained by the atoms in collisions with electrons always corresponded to the energy of photons in known spectrum lines. Thus, this direct experiment confirmed the existence of separate stationary states of atoms as predicted by Bohr's theory of atomic spectra. This result provided strong evidence of the validity of the Bohr theory.

14.10 CONSTRUCTING THE PERIODIC TABLE

In the Bohr model, atoms of the different elements differ in the charge and mass of their nuclei and in the number and arrangement of the electrons. Bohr, along with the German physicist Arnold Sommerfeld, came to picture the electronic orbits, not only as circular but also as elliptical orbits, and not as a series of concentric rings in one plane, but as patterns in three dimensions.

How does the Bohr model of atoms help to explain chemical properties? Recall that the elements hydrogen (atomic number $Z = 1$) and lithium ($Z = 3$) are somewhat alike chemically. (Refer to the periodic table on the color plate in this book.) Both have valences of 1. Both enter into compounds of similar types, for example, hydrogen chloride (HCl) and lithium chloride (LiCl). There are also some similarities in their spectra. All this suggests that the lithium atom resembles the hydrogen atom in some important respects. Bohr speculated that two of the three electrons of the lithium atom are relatively close to the nucleus, in orbits resembling those of the helium atom ($Z = 2$), forming, as one may call it, a "shell" around the nucleus. But the third electron is in a circular or elliptical orbit outside the inner system. Since this inner system consists of a nucleus of charge $+3e$ and two electrons each of the charge $-e$, its net charge is $+e$. Thus, the lithium atom may be roughly pictured as having a central core of charge $+e$. Around this core one electron revolves, somewhat as for a hydrogen atom. This similar physical structure, then, is the reason for the similar chemical behavior.

Referring to the periodic table, you will see that helium ($Z = 2$) is a chemically inert noble gas. These properties indicate that the helium atom is highly stable, having both of its electrons closely bound to the nucleus. It seems sensible, then, to regard both electrons as moving in the same *innermost "shell"* group or on orbits around the nucleus when the atom is unexcited. Moreover, because the helium atom is so stable and chemically inert, we may reasonably assume that this shell cannot hold more than two electrons. This shell is called the K-shell. The single electron of hydrogen is also said to be in the K-shell when the atom is unexcited. Lithium has two electrons in the K-shell, filling it to capacity; the third electron starts a new shell, called the L-shell. This single outlying and loosely bound electron is the reason why lithium combines so readily with oxygen, chlorine, and many other elements.

Sodium ($Z = 11$) is the next element in the periodic table that has chemical properties similar to those of hydrogen and lithium. This similarity suggests that the sodium atom is also hydrogen-like in having a central core about which one electron revolves. Moreover, just as lithium follows helium in the periodic table, sodium follows the noble gas neon ($Z = 10$). You may assume that two of neon's 10 electrons are in the first (K) shell, while the remaining eight electrons are in the second (L) shell. Because of the chemical inertness and stability of neon, we may further assume that these eight electrons fill the L-shell to capacity. For sodium, then, the eleventh electron must be in a third shell, called the M-shell.

LASERS

An atom in an excited state gives off energy by emitting a photon, a quantum of electromagnetic radiation, according to Bohr's second postulate. Although Bohr's specific model of the atom has been vastly extended and incorporated into models based on a different approach (see Chapter 15), this postulate is still valid.

As you have seen, atoms can acquire internal energy, that is, be brought to an excited state, in many ways. In the Franck–Hertz experiment, inelastic collisions provided the energy; in a cool gas displaying a dark-line spectrum, it is the absorption of photons; in a spark or discharge tube, it is collisions between electrons and atoms. There are other mechanisms as well.

Once an atom has acquired internal energy, it can also get rid of it in several ways. An atom can give up energy in inelastic collisions, or (as discussed above) it can emit energy as electromagnetic radiation. There are many different kinds of inelastic collisions; which one an atom undergoes depends as much on its surroundings as on the atom itself.

There are also two different ways an atom can emit radiation. Spontaneous radiation is the kind considered elsewhere in this chapter. At some random (unpredictable) moment, the previously excited atom emits a photon (of frequency ν) and changes its state to one of lower energy (by an amount ΔE). If, however, there are other photons of the appropriate frequency ($f = \Delta E/h$) in the vicinity, the atom may be *stimulated* to emit its energy. The radiation emitted is at exactly the same frequency, polarization, and phase as the stimulating radiation. That is, it is exactly in step with the existing radiation. In the wave model of light, you can think of the emission simply increasing the amplitude of the oscillations of the existing electromagnetic field within which the emitting atom finds itself.

Stimulated emission behaves very much like the classical emission of radiation discussed in Chapter 12. A collection of atoms stimulating one another to emit radiation behaves much like an antenna. You can think of the electrons in the different atoms as simply vibrating in step just as they do in an ordinary radio antenna, although much, much faster.

Usually atoms emit their energy spontaneously long before another photon comes along to stimulate them. Most light sources therefore emit incoherent light, that is, light made up of many different contributions, differing slightly in frequency, out of step with each other, and randomly polarized.

Usually, most of the atoms in a group are in the ground state. Light that illuminates the group is more likely to be absorbed than to stimulate any emission, since it is more likely to encounter an atom in the ground state than in the appropriate excited state. But suppose conditions are arranged so that more atoms are in one of the excited states than are in the ground state. (Such a group of atoms is said to be inverted.) In that case, light of the appropriate frequency is more likely to stimulate emission than to be absorbed. Then an interesting phenomenon takes over. Stimulated emission becomes more probable the more light there is around. The stimulated emission from some atoms therefore leads to a chain reaction, as more and more atoms give up some of their internal energy to the energy of the radiation. The incident light pulse has been amplified. Such an arrangement is called a *laser* (*light amplification* by *stimulated emission* of *radiation*).

Physicists and engineers have developed many tricks for producing "inverted" groups of atoms, on which laser operation depends. Exactly what the tricks are is not important for the action of the laser itself, although without them the laser would be impossible. Sometimes it is possible to maintain the inversion even while the laser is working; that is, it is possible to supply enough energy by the mechanisms that excite the atoms (inelastic collisions with other kinds of atoms, for example) to compensate for the energy emitted as radiation. These lasers can therefore operate continuously.

There are two reasons laser light is very desirable for certain applications. First, it can be extreme *intense*; some lasers can emit millions of joules in minute fractions of a second, as all their atoms emit their stored energy at once. Second, it is *coherent*; the light waves are all in step with each other. Incoherent light waves are somewhat like the waves crisscrossing the surface of a pond in a gale. But coherent waves are like those in a ripple tank, or at a beach where tall breakers arrive rhythmically.

The high intensity of some lasers can be used for applications in which a large amount of energy must be focused on a small spot. Such lasers are used in industries for cutting and welding delicate parts. In medicine, they are used, for example, to reattach the retina (essentially by searing a very small spot) in the eye.

The coherence of lasers is used in applications that require a stable light source emitting light of a precisely given frequency and polarization in one precise direction. Surveyors can use lasers to lay out straight lines, since the coherent beam spreads out very little with distance. Telephone companies can use them to carry signals in the same way they now use radio and microwaves.

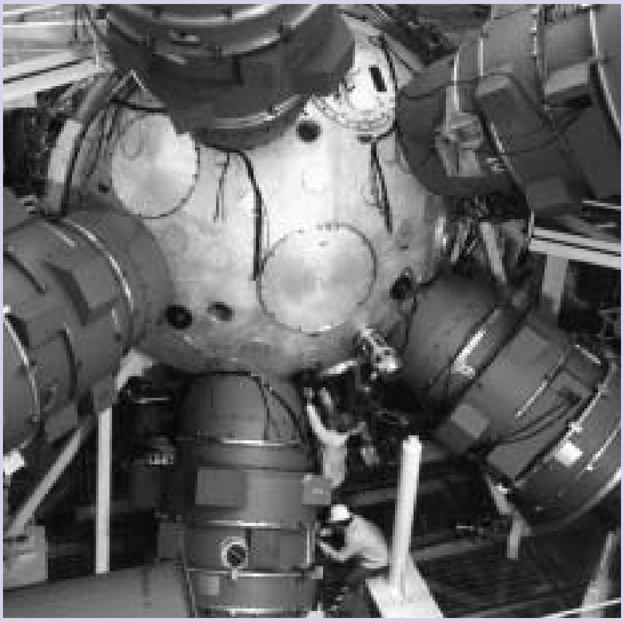


FIGURE 14.15 NOVA laser at Lawrence Livermore National Laboratory. The five tubes are lasers focused on a single point.

Passing on to potassium ($Z = 19$), the next alkali metal in the periodic table, you may again picture an inner core and a single electron outside it. The core consists of a nucleus with charge $+19e$. There are two, eight, and eight electrons occupying the K-, L-, and M-shells, respectively. The nineteenth electron revolves around the core in a fourth shell, called the N-shell. The atom of the noble gas argon, with $Z = 18$, comes just before potassium in the periodic table. Argon again represents a tight and stable electron pattern, with two in the K-shell, eight in the L-shell, and eight in the M-shell.

These qualitative considerations lead to a consistent picture of electrons distributed in groups, or shells, around the nucleus. The arrangement of electrons in the noble gases may be considered particularly stable. For each new alkali metal in Group IA of the periodic table, a new shell is started. Each alkali metal atom has a single electron around a core that resembles the pattern for the preceding noble gas. You may expect this outlying electron to be easily "loosened" by the action of neighboring atoms, and this agrees with the facts. The elements lithium, sodium, and potassium are alkali metals. In compounds or in solution (as in electrolysis), they may be considered to be in the form of ions such as Li^+, Na^+, and K^+. Each ion lacks one electron and so has one positive net charge $+e$. In the neutral atoms of these elements, the outer electron is relatively free to move about. This property has been used as the basis of a theory of electrical conductivity. According to this theory, a good conductor has many "free" electrons that can form a current under appropriate conditions. A poor conductor has relatively few "free" electrons. The alkali metals are all good conductors. Elements whose electron shells are all filled are very poor conductors; they have no "free" electrons. In Chapter 10, you saw how electrical conduction takes place in metals. It is because metals have many "free" electrons that they are conductors. We will return to this in Chapter 16.

In Group II of the periodic table, you would expect those elements that follow immediately after the alkali metals to have atoms with two outlying electrons. For example, beryllium ($Z = 4$) should have two electrons in the K-shell, thus filling it, and two in the L-shell. If the atoms of all these elements have two outlying electrons, they should be chemically similar, as indeed they are. Thus, calcium and magnesium, which belong to this group, should easily form ions such as Ca^{++} and Mg^{++}, each with a positive net charge of $+2e$. This is also found to be true.

As a final example, consider those elements that immediately precede the noble gases in the periodic table. For example, fluorine atoms ($Z = 9$) should have two electrons filling the K-shell but only seven electrons in the L-shell, one less than enough to fill it. If a fluorine atom captures an additional electron, it should become an F^- ion with one negative net charge. The L-shell would then be filled, as it is for neutral neon ($Z = 10$), and you would expect the F^- ion to be relatively stable. This prediction agrees with observation. Indeed, all the elements immediately preceding the inert gases tend to form stable, singly charged negative ions in solution. In the solid state, you would expect these elements to lack free electrons. In fact, all of them are poor conductors of electricity.

As indicated in Figure 14.16, based on an illustration from Bohr's work in 1922, the seven main shells, K, L, M, . . . , Q, divide naturally into orbits or subshells. The shells fill with electrons so that the total energy of the atom is minimized. The periodicity results from the completion of the subshells.

Bohr's table, still useful, was the result of physical theory and offered a fundamental *physical basis* for understanding chemistry. For example, it showed how the structure of the periodic table follows from the shell structure of atoms. This was another triumph of the Bohr theory.

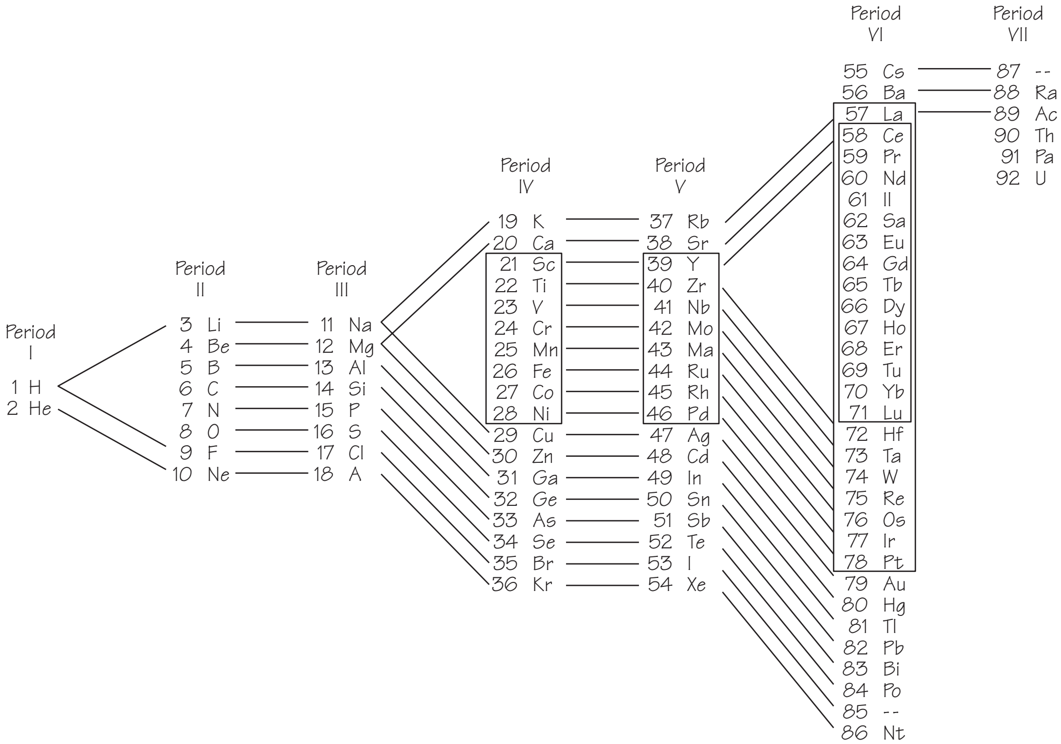


FIGURE 14.16 Bohr's periodic table of the elements (1921). Some of the element names and symbols have since been changed. Masurium (43) had been falsely identified at the time. The place is taken by technetium (43).

14.11 EVALUATING THE BOHR MODEL

In March 1913, Bohr wrote to his mentor Rutherford, enclosing a draft of his first paper on the quantum theory of atomic constitution. Rutherford replied in a letter, the first part of which is quoted here:

> Dear Dr. Bohr:
>
> I have received your paper and read it with great interest, but I want to look it over again carefully when I have more leisure. Your ideas as to the mode of origin of spectra in hydrogen are very ingenious and seem to work out well; but the mixture of Planck's ideas with the old mechanics make it very difficult to form a physical idea of what is the basis of it. There appears to me one grave difficulty in your hypothesis, which I have no doubt you fully realize, namely, how does an electron decide what frequency it is going to vibrate at when it passes from one stationary state to the other? It seems to me that you would have to assume that the electron knows beforehand where it is going to stop. . . .

Every Model and Every Theory Has Its Limits

The Bohr theory achieved great successes in the years between 1913 and 1924. But it also contained unanswered questions and unresolved problems, as Rutherford so keenly observed. As time progressed, further problems arose for which the theory proved inadequate.

Bohr's theory accounted very well for the spectra of atoms with a single electron in the outermost shell. However, serious differences between theory and experiment appeared in the spectra of atoms with two or more electrons in the outermost shell. Experiments also revealed that when a sample of an element is placed in an electric or magnetic field, its emission spectrum shows additional lines. For example, in a magnetic field each line is split into several lines. The Bohr theory could not account, in a quantitative way, for some of the observed splittings. Furthermore, the theory supplied no method for predicting the relative brightness (intensity) of spectral lines. These relative intensities depend on the probabilities with which atoms in a sample undergo transitions among the stationary states—high probabilities resulting in more intense lines. Physicists wanted to be able to calculate the probability of a transition from one stationary state to another. They could not make such calculations with the Bohr theory.

By the early 1920s it was clear that the Bohr theory, despite its remarkable successes, was limited. To form a theory that would solve more problems, Bohr's theory would have to be revised or replaced—incidentally, a reminder that a main purpose of science today is always to prepare the ground for better science tomorrow. But the successes of Bohr's theory did show that a better theory of atomic structure would still have to account for the existence of stationary states, which are separate, distinct atomic energy levels. Therefore, such a theory would still have to be based on quantum concepts—a reminder that new theories tend to evolve by incorporating what was good in old ones, rather than by a revolutionary overthrow of the old theory.

Besides the inability to predict certain properties of atoms at all, the Bohr theory had two additional shortcomings. First, it predicted some results that did not agree with the experiment (such as incorrect spectra for elements with two or three electrons in the outermost electron shells). Second, it predicted results that could not be tested in any known way (such as the details of electron orbits). Although orbits were easy to draw on paper, they could not be observed directly. Nor could they be related to any observable properties of atoms. Planetary theory has very different significance when applied to a planet in an observable orbit than when applied to an electron in an atom. The precise position of a planet is important, especially in experiments such as photographing an eclipse, or a portion of the surface of Mars from a satellite. But the moment-to-moment position of an electron in its orbit has no such meaning because it has no relation to any experiment physicists have been able to devise. It thus became evident that the Bohr theory led to some questions that could not be answered experimentally.

In the early 1920s, physicists, especially Bohr himself, began to work seriously on revising the basic ideas of the theory. One fact that stood out was, as Rutherford had pointed out, that the theory started with a mixture of classical and quantum ideas. An atom was assumed to act according to the laws of classical physics up to the point where these laws did not work. Beyond this point, quantum ideas were introduced. The picture of the atom that emerged was an inconsistent mixture. It combined ideas from classical physics with concepts for which there was no place in classical physics. The orbits of the electrons were determined by the classical, Newtonian laws of motion, much like the orbits of planets around the Sun. But of the many theoretical orbits, only a small portion were regarded as possible. Even these few orbits were selected by rules for which there was no room in classical mechanics. Again, the frequency calculated for the orbital revolution of electrons was quite different from the frequency of light emitted or absorbed when the electron moved from or to this orbit. Also, the decision that the number n could never be zero seemed arbitrary but it was necessary to prevent the model from collapsing by letting the electron fall on the nucleus. It became evident that a better theory of atomic structure would need a more consistent foundation in quantum concepts.

The contribution of Bohr's theory may be summarized as follows. It provided some excellent answers to the questions raised about atomic structure in Chapter 13. Although the theory turned out to be inadequate, it drew attention to how quantum concepts can be used. It indicated the path that a new theory would have to take. A new theory would have to supply the right answers that the Bohr theory gave, but it would also have to supply the right answers for the problems the Bohr theory could not solve. One of the most fascinating aspects of Bohr's work was the proof that physical and chemical properties of matter can be traced back to the fundamental role of integers (quantum numbers such as $n = 1, 2, 3, \ldots$). As Bohr said, "The solution of one of the boldest dreams of natural science is to build up an understanding of the regularities of nature upon the consideration of pure number." You can catch here an echo of the hope of Pythagoras and Plato, of Kepler and Galileo.

Since the 1920s, a successful new theory of atomic structure has been developed and generally accepted by physicists. It is part of *quantum mechanics*, so called because it is a new mechanics built directly on quantum concepts. It goes far beyond understanding atomic structure. In fact, it is the basis of the modern conception of events on a submicroscopic scale. Some aspects of this theory will be discussed in the next chapter. Significantly, Bohr himself was again a leading contributor.

SOME NEW IDEAS AND CONCEPTS

absorption spectra
Balmer series
Bohr model
electron shells
emission spectra
ground state
nuclear model
nucleus
quantum mechanics
spectroscopy
stationary states

SOME IMPORTANT EQUATIONS

$$\frac{1}{\lambda} = R_H\left(\frac{1}{2^2} - \frac{1}{n^2}\right), \qquad n = 3, 4, 5, 6, \ldots$$

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

$$r_n = a \cdot n^2,$$

$$E_n = \left(\frac{1}{n^2}\right)E_1.$$

FURTHER READING

G. Holton and S.G. Brush, *Physics, The Human Adventure* (Piscataway, NJ: Rutgers University Press, 2001), Chapter 28.

C.H. Townes, *How the Laser Happened: Adventures of a Scientist* (New York: Oxford University Press, 1999).

STUDY GUIDE QUESTIONS

14.1 Spectral of Gases

1. How is the emission spectrum of an element related to its absorption spectrum?
2. What can you conclude about a source if its light gives a bright-line spectrum?
3. What can you conclude about a source if its light gives a dark-line spectrum?
4. What evidence is there that the physics and chemistry of materials at great distances from Earth are the same as those of matter close at hand? What does this fact say about the structure of the Universe?
5. An unknown gas is contained in a glass tube. Give two ways in which it could be identified using spectroscopy.

14.2 Regularities in the Hydrogen Spectrum

1. What is the Balmer series? How is it summarized by Balmer's formula?
2. What evidence did Balmer have that there were other series of lines in the hydrogen spectrum, with terms such as 3^2, 4^2, etc., instead of 2^2?
3. How are the other series summarized by the extension of Balmer's formula?
4. Often discoveries result from grand theories (like Newton's) or from a good intuitive grasp of phenomena (like Faraday's). What led Balmer to his relation for hydrogen spectra?
5. From the Balmer formula in the last form given, is there any upper limit to the wavelengths of light emitted by the hydrogen atom?

14.3 Rutherford's Nuclear Model of the Atom

1. Describe Rutherford's experiment and its "incredible" result. What did Rutherford conclude from this experiment?
2. Why was Rutherford as surprised with this result as he would have been if a 15-in shell fired at a piece of tissue paper "came back and hit you"?
3. Why are α particles scattered by atoms? Why is the angle of scattering mostly small but sometimes large?
4. What was the basic difference between Rutherford's and Thomson's models of the atom?

14.4 Nuclear Charge and Size

1. What does the "atomic number" of an element refer to, according to the Rutherford model of the atom?
2. What is the greatest positive charge that an ion of lithium (the next heaviest element after helium) could have?
3. How did the scattering of α rays help Rutherford estimate the size of the nucleus?
4. How big is the nucleus? How does this compare with the size of the atom? What does this say about the interior of the atom?
5. How does one find by experiment the size of the nucleus?

14.5 Bohr's Theory: The Postulates

1. State Bohr's two quantum postulates in your own words.
2. In what ways do these postulates contradict Newton's mechanics and Maxwell's electromagnetic theory?
3. What was the main evidence to support the fact that an atom could exist only in certain energy states?
4. How did Bohr deal with the idea that as long as an electron is steadily orbiting a nucleus, it does not radiate electromagnetic energy?

14.6 The Size of the Hydrogen Atom

1. According to Bohr, why do all unexcited hydrogen atoms have the same size?
2. Why does the hydrogen atom have just the size it has?

14.7 Other Consequences of the Bohr Model

1. What happens to the electron in the hydrogen atom as n goes to infinity?
2. How is the ground state defined?
3. What happens to the radii of the Bohr orbits as n increases?
4. What happens to the stationary-state energies as n increases?
5. Why do the energies of the stationary states have negative values?

14.8 Bohr Accounts for the Series Spectra of Hydrogen

1. In general terms, how did Bohr account for Balmer's formula?
2. Balmer had predicted accurately that there might be other spectral series of hydrogen 30 years before Bohr did. Why is Bohr's prediction considered more significant?

3. How does Bohr's model account for absorption spectra?
4. In Section 14.1 you saw that an absorption spectrum does not contain all the lines of the corresponding emission spectrum. Based on the Bohr model, why is this so?
5. Why is it correct to say that the hydrogen atom can have an infinity of emission lines?

14.9 Do Stationary States Really Exist?

1. Briefly describe the Franck–Hertz experiment and the conclusion Franck and Hertz obtained in answering the question in the title of this section.
2. How much kinetic energy will an electron have after a collision with a mercury atom if its kinetic energy before collision is:
   (a) 4.0 eV?
   (b) 5.0 eV?
   (c) 7.0 eV?

14.10 Constructing the Periodic Table

1. Describe in your own words what happens to the structure of the atoms of different elements as you progress through the periodic table.
2. Draw a sketch of the atoms in the first two rows of the periodic table and label everything in your picture. Include the nucleus, its charge, and the various electron shells.
3. Why do the next heavier elements after the noble gases easily become positively charged?
4. Why do the elements in the next to last column of the periodic table easily become negatively charged?
5. What is special about the noble-gas elements?
6. Why are there only two elements in Period I, eight in Period II, eight in Period III, etc.?

14.11 Evaluating the Bohr Theory

1. Evaluate Bohr's theory of the atom. Was it a good theory? What were some of its advantages? What were some of its problems?
2. Why did some physicists begin looking for a quantum mechanics?
3. How did they expect this theory to differ from Bohr's theory?

DISCOVERY QUESTIONS

1. (a) Suggest experiments to show which of the Fraunhofer lines in the spectrum of sunlight result from absorption in the Sun's atmosphere rather than from absorption by gases in the Earth's atmosphere.
   (b) How might one decide, from spectroscopic observations, whether the Moon and the planets shine by their own light or by reflected light from the Sun?

2. Theoretically, how many series of lines are there in the emission spectrum of hydrogen? In all these series, how many lines are in the visible region?
3. As indicated in the figure on page 643, the lines in one of hydrogen's spectral series are bunched closely at one end. Does the formula

$$\frac{1}{\lambda} = R_H\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right)$$

suggest that such bunching will occur?

4. Physicists generally suppose that the atom and the nucleus are each spherical. They assume that the diameter of the atom is of the order of 10^{-10} m and that the diameter of the nucleus is of the order of 10^{-14} m.
   (a) What are the evidences that these are reasonable suppositions?
   (b) What is the ratio of the diameter of the nucleus to that of the atom?
5. Make an energy-level diagram to represent the results of the Franck–Hertz experiment.
6. Many substances emit visible radiation when illuminated with ultraviolet light. This phenomenon is an example of fluorescence. Stokes, a British physicist of the nineteenth century, found that in fluorescence, the wavelength of the emitted light usually was the same or longer than the illuminating light. How would you account for this phenomenon on the basis of the Bohr theory?

   Sometimes in fluorescence the wavelength of the emitted light is *shorter* than the illuminating light. What may cause this?
7. Use the periodic table to predict the electron structure of element 19. Why does it have chemical properties similar to those of elements 1, 3, and 11?
8. Write an essay on the successes and failures of the Bohr model of atoms. Can it be called a good model? a simple model? a beautiful model?

Quantitative

1. What would be the radius of a hydrogen atom if its electron is orbiting in state: $n = 2$? $n = 5$? $n = 10$? Do you see a pattern in these results?
2. The constant R in the Balmer formula has the value 1.1×10^7 m. What are the wavelengths of the first two Balmer lines? What are the wavelengths of the lines for $n = 10$ and $n = 20$? Do you see a pattern to these results? Where does each of these lines lie in the electromagnetic spectrum?
3. The "Lyman series" for hydrogen involves a "jump" of the electron to the state $n = 1$. What are the wavelengths of the first two lines of the Lyman series? Why is the word "jump" only to be taken as a metaphor?
4. The nucleus of a hydrogen atom has a radius of about 1.5×10^{-15} m. Imagine the atom magnified so that the nucleus has a radius about the size of a grain of dust, or 0.1 mm. What would be the size of the corresponding hydrogen atom in the ground state? Attempt to construct a scale model of the radius of such a "hydrogen atom" on a long sidewalk or in a stadium.