CHAPTER 4

Structure of the Atom

> *In the present first part of the paper the mechanism of the binding of electrons by a positive nucleus is discussed in relation to Planck's theory. It will be shown that it is possible from the point of view taken to account in a simple way for the law of the line spectrum of hydrogen.*
>
> ***Niels Bohr, 1913***

By the end of the 19th century most physicists and chemists (with a few notable exceptions) believed in an atomic theory of matter, even though no one had ever directly observed an atom. Moreover, there was good reason to believe that atoms themselves were composite structures and not the featureless hard spheres the Greek philosophers had imagined them to be. It may seem paradoxical that the scientists of the 19th century were able to determine that objects far too small for them to see possessed an internal structure. Because of the similarities between their situation and that of present-day "elementary particle" physics, we shall explain how they were able to do this.

First of all, there seemed to be too many kinds of atoms, each belonging to a distinct chemical element. The original Greek idea was that there were four types of atoms—earth, air, water, and fire—which combined together to make the various kinds of matter we observe. But the development of chemistry made plain that there were at least seventy kinds of atoms, far too many for them all to be the ultimate elementary constituents of matter.

Second, it was found experimentally that atoms and electromagnetic phenomena were intimately related. For example, molecules can be dissociated into their component atoms by electrolysis. Some kinds of atoms form magnetic materials, and others form electrical conductors and insulators. All kinds of atoms emit light (which was known to be electromagnetic in nature) when they are heated, as well as when an electrical discharge passes through them. The visible light emitted by free or nearly free atoms of the chemical elements is not a continuum of frequencies, but rather a discrete set of characteristic colors, so substances can be analyzed according to their chemical composition using their flame spectra. The existence of **characteristic spectra** pointed to an internal structure distinguishing the elements.

Third, there was the problem of **valence**—why certain elements combine with some elements but not with others, and when they do combine, they do so in varying proportions determined by the valences of the atoms. The laws of valence suggested that the forces between atoms were very specific in nature, a characteristic that hinted at an internal atomic structure.

Finally, there were the discoveries of radioactivity, of x rays, and of the electron, all of which were at variance with earlier ideas of indivisible and elementary atoms.

Because there were these tantalizing indirect hints that the atom had a structure, the most exciting frontier of physical science in the early part of the 20th century developed into an investigation of the atom and its internal composition. The subject of this chapter is the beginning of quantum physics and its relation to the first cohesive theories of atomic structure. Although we now have a more complete theoretical framework with which to understand the early experiments than was available to the scientists themselves, it is worth repeating some of their reasoning, both for its historical interest and because it illustrates how science progresses by trying to extend well-established ideas into unknown terrain.

In this chapter we will discuss the atomic models of Thomson and Rutherford and learn how Rutherford discerned the correct structure of the atom by performing alpha-particle scattering experiments. We will see that Bohr presented a model of the hydrogen atom based on the new quantum concept that correctly produced the Rydberg equation, and we will study the successes and failures of Bohr's theory. We will also learn the origin of characteristic x-ray spectra and the concept of atomic number. Finally, we will show that electron scattering (the Franck-Hertz experiment) also confirmed the quantized structure of the atom.

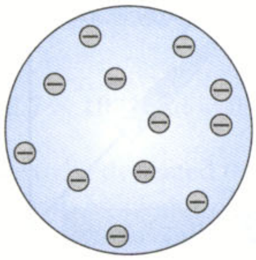

FIGURE 4.1 Schematic of J. J. Thomson's model of the atom (later proven to be incorrect). The electrons are imbedded in a homogeneous positively charged mass much like "raisins in plum pudding." The electric force on the electrons is zero, so the electrons do not move around rapidly. The oscillations of the electrons give rise to electromagnetic radiation.

4.1 The Atomic Models of Thomson and Rutherford

In the years immediately following J. J. Thomson's discovery of the electron, Thomson and others tried to unravel the mystery of the atomic structure. In just a few years it was learned that electrons were much less massive than atoms and that the number of electrons was equal to about half the number representing the atomic mass. The central question was, "How were the electrons arranged and where were the positive charges that made the atom electrically neutral?" (Remember that protons had not been discovered yet.) Thomson proposed a model wherein the positive charges were spread uniformly throughout a sphere the size of the atom, with electrons embedded in the uniform background. His model, which has been likened to "raisins in plum pudding," is shown schematically in Figure 4.1. The arrangement of charges had to be in stable equilibrium. In Thomson's view, when the atom was heated, the electrons could vibrate about their equilibrium positions, thus producing electromagnetic radiation. The emission frequencies of this radiation would fall in the range of visible light if the sphere of positive charges was of diameter $\sim 10^{-10}$ m, which was known to be the approximate size of an atom. Nevertheless, even though he tried for several

Thomson's model of the atom

years, Thomson was unable to calculate the light spectrum of hydrogen using his model.

In order to make further progress in deciphering atomic structure, a new approach was needed. This was supplied by Ernest Rutherford, who was already famous for his Nobel Prize–winning work (1908) on radioactivity. Because atoms are so small it was not possible to directly see or observe their internal structure. Scientists needed some other means and attempted to scatter other small objects from atoms in order to understand atomic structure. Rutherford, assisted by Hans Geiger, conceived a new technique for investigating the structure of matter by scattering energetic α particles* (emitted by radioactive sources) from atoms. Together with a young student, Ernest Marsden, Geiger showed in 1909 while working in Rutherford's lab that surprisingly many α particles were scattered from thin gold-leaf targets at backward angles greater than 90° (see Figure 4.2).

For several years Rutherford had pondered the structure of the atom. He was well aware of Thomson's model because he had worked for Thomson at the Cavendish Laboratory as a research student from 1895–1898, after receiving his undergraduate education in his native New Zealand. Although he greatly respected Thomson, Rutherford could see that Thomson's model agreed neither with spectroscopy nor with Geiger's latest experiment with alpha particles.

The experiments of Geiger and Marsden were instrumental in the development of Rutherford's model. The problem can be understood by a simple thought experiment with a .22-caliber rifle that is fired into a thin black box. If the box contains a homogeneous material such as wood or water (as in Thomson's "plum pudding" model), the bullet will pass through the box with little or no deviation in its path. However, if the box contains a few massive steel ball bearings, then occasionally a bullet will be deflected backward.

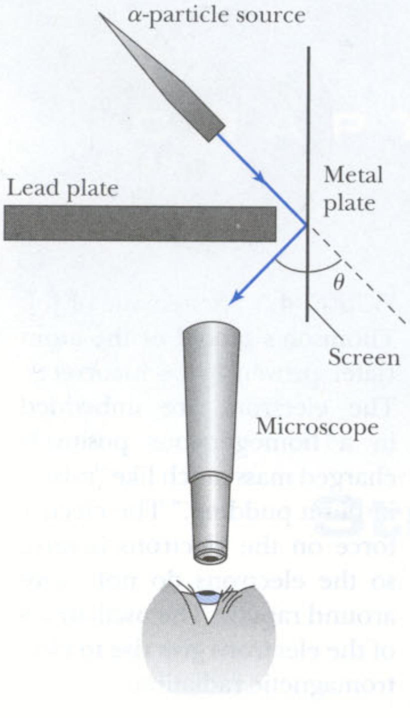

FIGURE 4.2 Schematic diagram of apparatus used by Geiger and Marsden to observe scattering of α particles past 90°. "A small fraction of the α particles falling upon a metal plate have their directions changed to such an extent that they emerge again at the side of incidence." *From Geiger and Marsden, Proceedings of Royal Society (London) 82, 495 (1909).*

Example 4.1

Geiger and Marsden (1909) observed backward-scattered ($\theta \geq 90°$) α particles when a beam of energetic α particles was directed at a gold foil as thin as 6×10^{-7} m. Assuming an α particle scatters from an electron in the foil, what is the maximum scattering angle?

Solution: The collision must obey the laws of conservation of momentum and energy. Assume the incident α particle has mass M_α and velocity v_α, while the mass of the electron is m_e. The maximum momentum transfer occurs when the α particle hits the electron (at rest) head-on, as shown in Figure 4.3.

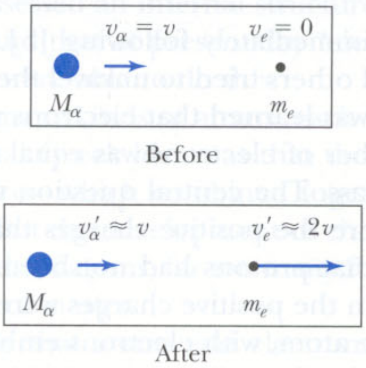

FIGURE 4.3 Schematic diagram (before and after) of an α particle of velocity $v = v_\alpha$ and mass M_α making a head-on collision with an electron initially at rest. Because the α particle is so much more massive than the electron, the α particle's velocity is hardly reduced.

Conservation of momentum (nonrelativistically) gives

$$M_\alpha \mathbf{v}_\alpha = M_\alpha \mathbf{v}'_\alpha + m_e \mathbf{v}'_e$$

Because the α particle is so much more massive than the electron ($M_\alpha / m_e \approx 4 \times 1837 = 7348$), the α particle's velocity is

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*Rutherford had already demonstrated that the α particle is an ionized helium atom.

hardly affected and $v'_\alpha \approx v_\alpha$. In an elastic collision with such unequal masses, $v'_e \approx 2v_\alpha$ in order to conserve both energy and linear momentum (see Problem 3). Thus the maximum momentum change of the α particle is simply

$$\Delta \mathbf{p}_\alpha = M_\alpha \mathbf{v}_\alpha - M_\alpha \mathbf{v}'_\alpha = m_e \mathbf{v}'_e$$

or

$$\Delta p_{\max} = 2m_e v_\alpha$$

Although this maximum momentum change is along the direction of motion, let's determine an upper limit for the angular deviation θ by letting $\Delta p_{\max}$ be perpendicular to the direction of motion as shown in Figure 4.4. (This value of θ is larger than can actually be observed because we know that the Δp_α we calculated was for a head-on collision, and the Δp_α for a glancing collision would be smaller.) Thus

$$\theta_{\max} = \frac{\Delta p_\alpha}{p_\alpha} = \frac{2m_e v_\alpha}{M_\alpha v_\alpha} = \frac{2m_e}{M_\alpha} = 2.7 \times 10^{-4} \text{ rad} = 0.016°$$

Thus it is impossible for an α particle to be deflected through a large angle by a single encounter with an electron.

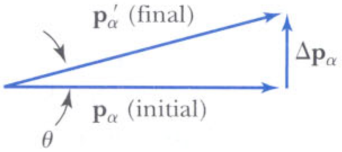

FIGURE 4.4 Vector diagram illustrating the change in momentum $\Delta \mathbf{p}_\alpha$ of the α particle after scattering from the electron.

Multiple scattering from electrons

What would happen if an α particle were scattered by *many* electrons in the target? Multiple scattering is possible, and a calculation for random multiple scattering from N targets results in an average scattering angle $\langle\theta\rangle_{\text{total}} \approx \sqrt{N}\,\theta$. The α particle is as likely to scatter on one side of its direction as the other side for each collision. We can estimate the number of atoms across the thin gold layer of 6×10^{-7} m used by Geiger and Marsden.

$$\frac{\text{number of molecules}}{\text{cm}^3} = \text{Avogadro's no.}\left(\frac{\text{molecules}}{\text{mole}}\right)$$

$$\times \frac{1}{\text{gram-molecular weight}}\left(\frac{\text{mole}}{\text{g}}\right) \times \text{Density}\left(\frac{\text{g}}{\text{cm}^3}\right)$$

$$= 6.02 \times 10^{23}\,\frac{\text{molecules}}{\text{mole}}\,\frac{1 \text{ mole}}{197 \text{ g}}\,\frac{19.3 \text{ g}}{\text{cm}^3} \qquad \text{(for gold)}$$

$$= 5.9 \times 10^{22}\,\frac{\text{molecules}}{\text{cm}^3} = 5.9 \times 10^{28}\,\frac{\text{atoms}}{\text{m}^3}$$

If there are 5.9×10^{28} atoms/m^3, then each atom occupies $(5.9 \times 10^{28})^{-1}$ m^3 of space. Assuming the atoms are equidistant, the distance d between centers is $d = (5.9 \times 10^{28})^{-1/3}$ m $= 2.6 \times 10^{-10}$ m. In the foil, then, there are

$$N = \frac{6 \times 10^{-7} \text{ m}}{2.6 \times 10^{-10} \text{ m}} = 2300 \text{ atoms}$$

along the α-particle's path. If we assume the α particle interacts with one electron from each atom, then

$$\langle\theta\rangle_{\text{total}} = \sqrt{2300}(0.016°) = 0.8°$$

where we have used the result for $\theta_{\max}$ from Example 4.1. Even if the alpha particle scattered from all 79 electrons in gold, $\langle\theta\rangle_{\text{total}} = 6.8°$.

Rutherford reported* in 1911 that the experimental results were not consistent with α-particle scattering from the atomic structure proposed by Thomson and that "it seems reasonable to suppose that the deflection through

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*E. Rutherford, *Philosophical Magazine* **21,** 669(1911).

Rutherford's atomic model

a large angle is due to a single atomic encounter." Rutherford proposed that an atom consisted mostly of empty space with a central charge, either positive or negative. Rutherford wrote in 1911 that "Considering the evidence as a whole, it seems simplest to suppose that the atom contains a central charge distributed through a very small volume, and that the large single deflections are due to the central charge as a whole, and not to its constituents." Rutherford worked out the scattering expected for the α particles as a function of angle, thickness of material, velocity, and charge. Geiger and Marsden immediately began an experimental investigation of Rutherford's ideas and reported* in 1913, "we have completely verified the theory given by Prof. Rutherford." In that same year, Rutherford coined the use of the word **nucleus** for the central charged core and definitely decided that the core (containing most of the mass) was *positively* charged, surrounded by the negative electrons.

The nucleus

The popular conception of an atom today, often depicted as in Figure 4.5, is due to Lord Rutherford. An extremely small positively charged core provides a Coulomb attraction for the negatively charged electrons flying at high speeds around the nucleus; this is the so-called "solar system," or "planetary" model. We now know that the nucleus is composed of positively charged protons and neutral neutrons, each having approximately the same mass, and the electrons do not execute prescribed orbital paths.

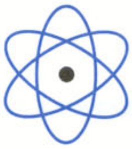

FIGURE 4.5 Solar or planetary model of the atom. Rutherford proposed that there is a massive, central core with a highly electric positive charge. According to Bohr, the electrons orbit around this nucleus. Although this is a useful pictorial, we now know this schematic is too simplistic.

4.2 Rutherford Scattering

Rutherford's "discovery of the nucleus" laid the foundation for many of today's atomic and nuclear scattering experiments. By means of scattering experiments similar in concept to those of Rutherford and his assistants, scientists have elucidated the electron structure of the atom, the internal structure of the nucleus, and even the internal structures of the nuclear constituents, protons and neutrons. Rutherford's calculations and procedures are well worth studying in some detail because of their applicability to many areas of physical and biological science.

Basic scattering experiments

In order to study matter at such a microscopic scale as atomic sizes, we perform scattering experiments. The material to be studied is bombarded with rapidly moving particles (like the 5- to 8-MeV α particles used by Geiger and Marsden) in a well-defined and collimated beam. Although the present discussion is limited to charged-particle beams, the general procedure applies to neutral particles such as neutrons; only the interaction between the beam particles and the target material is different.

Rutherford or Coulomb scattering

The scattering of charged particles by matter is called **Coulomb** or **Rutherford scattering** when it takes place at low energies, where only the Coulomb force is important. At higher beam energies other forces (for example, nuclear interactions) may become important. A typical scattering experiment is diagrammed in Figure 4.6. A charged particle of mass m, charge Z_1e and velocity v_0 is incident on the target material or scatterer of charge Z_2e. The distance b is called the classical *impact parameter;* it is the closest distance of approach between the beam particle and scatterer if the projectile had continued in a straight line. The angle θ between the incident beam direction and the direction of the deflected particle is called the *scattering angle.* Normally detectors are positioned at one or more scattering angles to count the particles scattered into the small cones of solid angle subtended by the detectors (see Figure 4.7). Depending on

Scattering angle

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*Hans Geiger and Ernest Marsden, *Philosophical Magazine* **25,** 604(1913).

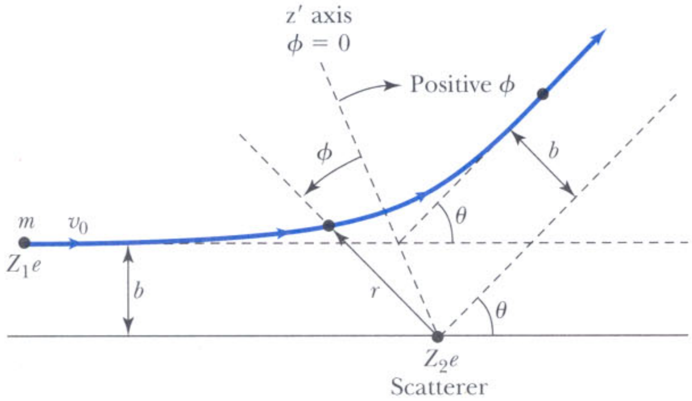

FIGURE 4.6 Representation of Coulomb or Rutherford scattering. The projectile of mass m and charge Z_1e scatters from a particle of charge Z_2e at rest. The parameters r and ϕ, which describe the projectile's orbit, are defined as shown. The angle $\phi = 0$ represents the position of closest approach. The impact parameter b and scattering angle θ are also displayed.

the functional form of the interaction between the particle and the scatterer, there will be a particular relationship between the impact parameter b and the scattering angle θ. In the case of Coulomb scattering between a positively charged α particle and a positively charged nucleus, the trajectories will resemble those in Figure 4.7. When the impact parameter is small, the distance of closest approach r_{min} is small and the Coulomb force is large. Therefore, the scattering angle can be large and the particle can be repelled backward. Conversely, for large impact parameters the particles never get close together, so the Coulomb force is small and the scattering angle is also small.

An important relationship for any interaction is that between b and θ. We wish to find this dependence for the Coulomb force. We will make the same assumptions as Rutherford:

Scattering assumptions

1. The scatterer is so massive that it does not significantly recoil; therefore the initial and final kinetic energies of the α particle are practically equal.
2. The target is so thin that only a single scattering occurs.
3. The bombarding particle and target scatterer are so small that they may be treated as point masses and charges.
4. Only the Coulomb force is effective.

Assumption 1 means that $K \equiv \text{K.E.}_{\text{initial}} \approx \text{K.E.}_{\text{final}}$ for the α particle. For central forces like the Coulomb force, the angular momentum, mv_0b, where v_0 is the initial velocity of the particle, is also conserved (see Problem 48). This means that the trajectory of the scattered particle lies in a plane.

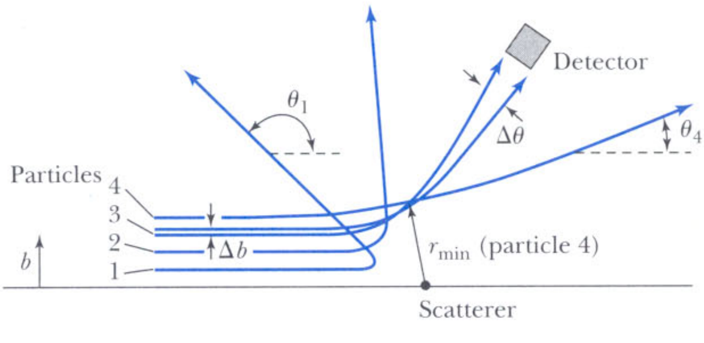

FIGURE 4.7 The relationship between the impact parameter b and scattering angle θ. Particles with small impact parameters approach the nucleus most closely (r_{min}) and scatter to the largest angles. Particles within the range of impact parameters Δb will be scattered within $\Delta\theta$.

LORD RUTHERFORD OF NELSON

We choose to highlight the life of Ernest Rutherford not only because of his extraordinary talents as a physicist, but also because of the many contributions he made to others throughout the world. He nurtured many young physicists in the laboratories he headed, including several who later made outstanding scientific contributions themselves. They include O. Hahn and F. Soddy at McGill University in Canada; H. Geiger, E. Marsden, N. Bohr, and H. G. J. Moseley at Manchester University in England; and J. Chadwick, P. M. S. Blackett, J. D. Cockcroft, E. T. S. Walton, M. Oliphant, M. Goldhaber, and others at Cambridge University in England. The account here is from *Rutherford** and from *The World of the Atom*†.

Ernest Rutherford was born of Scottish parents on August 30, 1871 near the town of Nelson, New Zealand. Rutherford, one of eleven children, made excellent marks in school and received a scholarship to Nelson College where his interest in science blossomed. At eighteen he obtained another scholarship to attend Canterbury College of the University of New Zealand in Christchurch, where in 1894 he received both a bachelor's and a master's degree. It was there that he began significant research on the magnetization of iron and constructed a Hertz oscillator capable of generating high-frequency electric currents. His magnetic detector was able to receive electromagnetic waves over a distance of 60 feet through walls, quite a feat at the time.

In 1895 Rutherford won a competition to bring able men to British Universities from abroad. He was digging potatoes when his mother told him of his selection and he is reported to have said with a laugh as he threw the spade away, "That's the last potato I'll dig." Rutherford was the first research student to arrive to work for the famous Professor J. J. Thomson of the Cavendish Laboratory under a new program just initiated by Cambridge University. Rutherford's primary research continued to be on the transmission and detection of "wireless waves," for which he obtained a considerable reputation. Thomson was quite impressed by Rutherford and encouraged him to publish his results and make presentations at scientific meetings. He presented his work on the magnetic detector before the Royal Society in June, 1896, when he was only 24. Besides his own work on electromagnetic radiation, Rutherford began investigations with Thomson on the effects of x-ray radiation from uranium in various gases. This research continued into 1898 when Rutherford applied for and received a chaired appointment as Professor of Physics at McGill University in Montreal, Canada.

Barely 27 years of age, he arrived in Montreal in September, 1898, to take up his new duties in the Macdonald Physics Laboratories. This lab was endowed by a generous benefactor, Sir William Macdonald, who besides endowing the laboratory and Rutherford's chair, could also be called upon to provide specialized equipment when needed. Rutherford's studies on radioactivity continued, and he had frequent correspondence and occasional visits with scientists from abroad including, of course, Thomson, but also Poynting, FitzGerald, and Crookes. Early in 1900 he published a paper in the *Philosophical Magazine* in which he named *alpha*, *beta*, and *gamma* as the three types of radiation from thorium and uranium. In 1900 Rutherford returned briefly to New Zealand where he married Mary Newton of Christchurch and visited with his parents. Rutherford received several offers of appointment from American universities, but he longed to return to England, which he considered to be the leading center of physics. In 1901 he wrote Thomson inquiring of any possibilities.

Rutherford attracted the aid of a young research chemist, Frederick Soddy of Oxford, who had arrived at McGill in 1900 only after a position he had sought at Toronto had been filled. Soddy obtained a demonstratorship in the chemistry lab, but his radioactivity research with Rutherford progressed so well that he joined Rutherford's lab fulltime in 1901. Rutherford and Soddy discovered, in 1902, that the elements, heretofore considered immute, actually decayed to other elements. They found radiation coming from a substance they called thorium X, which was a result of thorium decay. They found that thorium X not only decayed exponentially, but that a new supply of it was also produced exponentially from thorium. During the next few years Rutherford investigated α particles and the radioactive decay chains of radium, thorium, and uranium.

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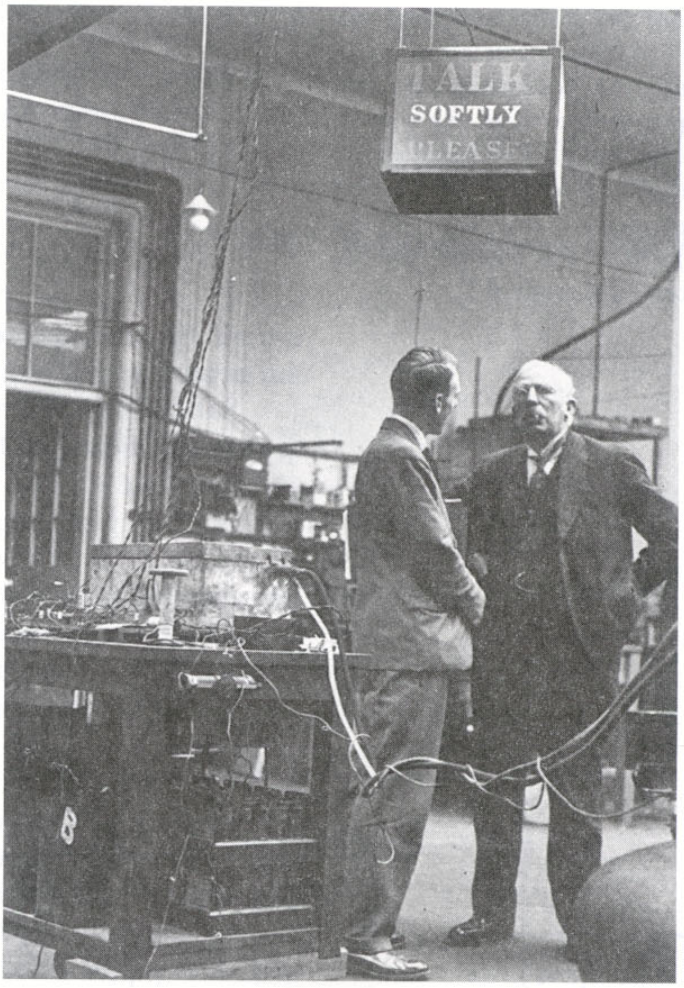
*A. S. Eve, *Rutherford*. New York: Macmillan, 1939.

†H. A. Boorse, and L. Motz eds. *The World of the Atom*. New York: Basic Books, 1966.

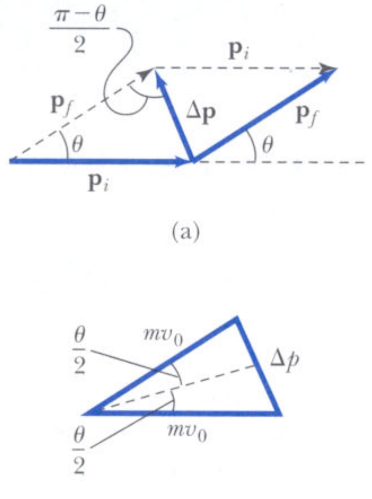
In 1907 Rutherford returned to England as Professor of Physics at the University of Manchester where he did his greatest work. He left McGill University with deep regret, but with high hopes for the future. His first success was the proof that α particles were indeed helium ions. In 1908 Rutherford received word that he had won the Nobel Prize for the work he and Soddy had done, but Rutherford was startled and amused to learn it was in chemistry, not physics. He remarked at a banquet in the Stockholm Royal Palace that the quickest transformation (note the pun) he had observed was his own from a physicist to a chemist.

It was during the next few years that Rutherford carried out his research into the nature of the atom that culminated with his discovery of the nucleus. Rutherford was already an international figure in great demand as a lecturer while at McGill, but now his stature increased even more. Research students flocked to Manchester to work with Rutherford, and laboratory space was in great demand. In 1912 Rutherford wrote to a colleague, "Bohr, a Dane, has pulled out of Cambridge and turned up here to get some experience in radioactive work." That momentous trip resulted in the "Rutherford-Bohr atom." The work at Manchester is too voluminous to describe, but the research of Hans Geiger, Ernest Marsden, and Henry Moseley was to have dramatic consequences. Curiously enough, it was the experiment of Geiger and Marsden, not his own, that led Rutherford to the nuclear model of the atom. Rutherford coined the word *proton* to describe the fast hydrogen nuclei produced when he bombarded hydrogen and nitrogen with fast α particles. In this case, Rutherford performed most of the research himself in 1919, being aided by an assistant only in observing scintillations.

World War I broke up the family of research students working at Manchester, and in 1919 Rutherford accepted the Cavendish Professorship at Cambridge, the post just vacated by J. J. Thomson, who remained as Master of Trinity College. Thomson continued to do physics research in the lab and eventually outlived Rutherford. Being the successor at Cambridge to Maxwell, Rayleigh, and Thomson was no small feat, and Rutherford's initial research at Cambridge with James Chadwick as his collaborator produced many interesting results as well as the predictions, in 1920, of the existence of a mass 2 isotope of hydrogen and of a neutral particle with about the proton's mass. These were discovered 12 years later by Urey and Chadwick, respectively. Earlier in 1914 Rutherford had been knighted, and in 1931 he was made a Baron, choosing the town of Nelson near his boyhood home to become "Lord Rutherford of Nelson." Rutherford was greatly admired by all who came in contact with him. He was the greatest experimental physicist of his day, yet he was said to have "never made an enemy and never lost a friend." He was still doing important research until the time of his sudden death in 1937 of hernia complications at the age of 66.



Ernest Rutherford is shown here with J. A. Ratcliffe in the Cavendish Laboratory in 1936. The sign above Rutherford (on the right) reads "TALK SOFTLY PLEASE," because the detectors being used were very sensitive to vibrations and noise. Rutherford, whose deep booming voice disturbed the detectors more than anyone else, didn't seem to think the warning applied to him and was in a loud conversation when this photo was taken. *AIP Emilio Segrè Visual Archives.*



(a)

(b)

FIGURE 4.8 (a) The scattering angle θ and momentum change $\Delta\mathbf{p}$ are determined from the initial and final values of the α particle's momentum. (b) Because $\mathbf{p}_f$, $\mathbf{p}_i$, and $\Delta\mathbf{p}$ almost form an exact isosceles triangle, we determine the magnitude of $\Delta\mathbf{p}$ by bisecting the angle θ and finding the length of the triangle leg opposite the angle $\theta/2$.

We define the instantaneous position of the particle by the angle ϕ and the distance r from the force center, where $\phi = 0$ (which defines the z' axis) when the distance r is a minimum, as is shown in Figure 4.6. The change in momentum must be equal to the impulse.

$$\Delta\mathbf{p} = \int \mathbf{F}_{\Delta p}\, dt \tag{4.1}$$

where $\mathbf{F}_{\Delta p}$ is the force along the direction of $\Delta\mathbf{p}$. The massive scatterer absorbs this (small) momentum change without gaining any appreciable kinetic energy (no recoil). Using the diagram of Figure 4.8,

$$\Delta\mathbf{p} = \mathbf{p}_{\mathrm{f}} - \mathbf{p}_{\mathrm{i}} \tag{4.2}$$

where the subscripts i and f indicate the initial and final values of the projectile's momentum, respectively. Because $p_f \approx p_i = mv_0$, the triangle between $\mathbf{p}_f$, $\mathbf{p}_i$, and $\Delta\mathbf{p}$ is isosceles. We redraw the triangle in Figure 4.8b, indicating the bisector of angle θ. The magnitude Δp of $\Delta\mathbf{p}$ is now

$$\Delta p = 2mv_0 \sin\frac{\theta}{2} \tag{4.3}$$

The direction of $\Delta\mathbf{p}$ is the z' axis (where $\phi = 0$), so we need the component of $\mathbf{F}$ along z' in Equation (4.1). The Coulomb force $\mathbf{F}$ is along the instantaneous direction of the position vector $\mathbf{r}$ (unit vector $\mathbf{e}_r$)

$$\mathbf{F} = \frac{1}{4\pi\epsilon_0}\frac{Z_1Z_2e^2}{r^2\mathbf{e}_r} = F\mathbf{e}_r \tag{4.4}$$

and

$$F_{\Delta p} = F\cos\phi \tag{4.5}$$

where $F_{\Delta p}$ is the component of the force $\mathbf{F}$ along the direction of $\Delta\mathbf{p}$ that we need.

Substituting the magnitudes from Equations (4.3) and (4.5) into the components of Equation (4.1) along the z' axis ($\phi = 0$) gives

$$\Delta p = 2mv_0\sin\frac{\theta}{2} = \int F\cos\phi\, dt$$

$$= \frac{Z_1Z_2e^2}{4\pi\epsilon_0}\int\frac{\cos\phi}{r^2}\, dt$$

The instantaneous angular momentum must be conserved, so

$$mr^2\frac{d\phi}{dt} = mv_0b$$

and

$$r^2 = \frac{v_0b}{\dfrac{d\phi}{dt}}$$

Therefore,

$$2mv_0\sin\frac{\theta}{2} = \frac{Z_1Z_2e^2}{4\pi\epsilon_0}\int\frac{\cos\phi}{v_0b}\frac{d\phi}{dt}\, dt$$

$$= \frac{Z_1Z_2e^2}{4\pi\epsilon_0v_0b}\int_{\phi_i}^{\phi_f}\cos\phi\, d\phi$$

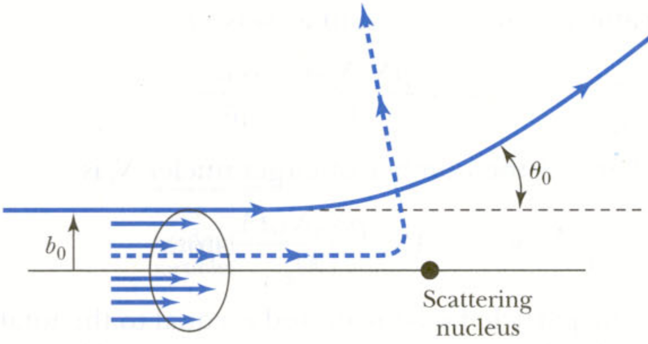


FIGURE 4.9 All particles with impact parameters less than b_0 will scatter at angles *greater* than θ_0.

We let the initial angle ϕ_i be on the negative side and the final angle ϕ_f be on the positive side of the z' axis ($\phi = 0$, see Figure 4.6). Then $\phi_i = -\phi_f$, $-\phi_i + \phi_f + \theta = \pi$, so $\phi_i = -(\pi - \theta)/2$ and $\phi_f = +(\pi - \theta)/2$.

$$\frac{8\pi\epsilon_0 m v_0{}^2 b}{Z_1 Z_2 e^2} \sin\frac{\theta}{2} = \int_{-\left(\frac{\pi-\theta}{2}\right)}^{+\left(\frac{\pi-\theta}{2}\right)} \cos\phi \, d\phi = 2\cos\frac{\theta}{2}$$

We now solve this equation for the impact parameter b.

$$b = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 m v_0{}^2} \cot\frac{\theta}{2}$$

or with $K = \frac{1}{2} m v_0{}^2$

$$b = \frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \cot\frac{\theta}{2} \tag{4.6}$$

Relation between b and θ

where $K = m v_0{}^2/2$ is the kinetic energy of the bombarding particle. This is the fundamental relationship between the impact parameter b and scattering angle θ that we have been seeking for the Coulomb force.

In an experiment we are not able to select individual impact parameters b. When we put a detector at a particular angle θ, we cover a finite $\Delta\theta$ which corresponds to a range of impact parameters Δb. The bombarding particles are incident at varied impact parameters all around the scatterer as shown in Figure 4.9. All the particles with impact parameters less than b_0 will be scattered at angles greater than θ_0. Any particle with impact parameter inside the area of the circle of area $\pi b_0{}^2$ (radius b_0) will be similarly scattered. For the case of Coulomb scattering, we denote the cross section by the symbol σ, where

$$\sigma = \pi b^2 \tag{4.7}$$

is the cross section for scattering through an angle θ or more. The cross section σ is related to the *probability* for a particle being scattered by a nucleus. If we have a target foil of thickness t with n atoms/volume, the number of target nuclei per unit area is nt. Because we assumed a thin target of area A and all nuclei are exposed as shown in Figure 4.10, the number of target nuclei is simply ntA. The value of n is the density ρ (g/cm^3) times Avogadro's number N_A (molecules/mole) times the number of atoms/molecule N_M divided by the gram-molecular weight M_g (g/mole).

$$n = \frac{\rho\left(\frac{\text{g}}{\text{cm}^3}\right) N_A \left(\frac{\text{molecules}}{\text{mole}}\right) N_M \left(\frac{\text{atoms}}{\text{molecule}}\right)}{M_g\left(\frac{\text{g}}{\text{mole}}\right)} = \frac{\rho N_A N_M}{M_g} \, \frac{\text{atoms}}{\text{cm}^3} \tag{4.8}$$

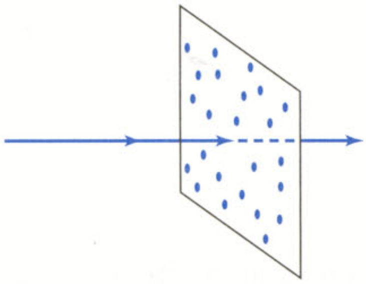


FIGURE 4.10 The target is assumed to be so thin that all nuclei are exposed to the bombarding particles. No nucleus is hidden behind another.

The number of scattering nuclei per unit area is nt.

$$nt = \frac{\rho N_{\mathrm{A}} N_M t}{M_g}\ \frac{\text{atoms}}{\text{cm}^2} \tag{4.9}$$

If we have a foil of area A the number of target nuclei N_s is

$$N_s = ntA = \frac{\rho N_{\mathrm{A}} N_M t A}{M_g}\ \text{atoms} \tag{4.10}$$

The probability of the particle being scattered is equal to the total target area exposed for all the nuclei divided by the total target area A. If σ is the cross section for each nucleus, then $ntA\sigma$ is the total area exposed by the target nuclei, and the fraction of incident particles scattered by an angle of θ or greater is

$$\begin{aligned} f &= \frac{\text{Target area exposed by scatterers}}{\text{Total target area}} = \frac{ntA\sigma}{A} \\ &= nt\sigma = nt\pi b^2 \end{aligned} \tag{4.11}$$

$$f = \pi nt \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot^2 \frac{\theta}{2} \tag{4.12}$$

Example 4.2

Find the fraction of 7.7-MeV α particles that is deflected at an angle of 90° or more from a gold foil of 10^{-6} m thickness.

Solution: To use Equation (4.12) we first need to calculate n, the number of atoms/cm^3. The density of gold is 19.3 g/cm^3 and the atomic weight is 197 u. We use Equation (4.8) to determine n.

$$n = \frac{\left(19.3\ \frac{\text{g}}{\text{cm}^3}\right)\left(6.02 \times 10^{23}\ \frac{\text{molecules}}{\text{mole}}\right)\left(1\ \frac{\text{atom}}{\text{molecule}}\right)}{197\ \text{g/mole}}$$

$$= 5.90 \times 10^{22}\ \frac{\text{atoms}}{\text{cm}^3} = 5.90 \times 10^{28}\ \frac{\text{atoms}}{\text{m}^3}$$

We insert this value of n into Equation (4.12) and find

$$f = \pi \left(5.90 \times 10^{28}\ \frac{\text{atoms}}{\text{m}^3}\right)(10^{-6}\ \text{m}) \times \left[\frac{(79)(2)(1.6 \times 10^{-19}\ \text{C})^2 (9 \times 10^9\ \text{N} \cdot \text{m}^2/\text{C}^2)}{(8)(7.7\ \text{MeV})(1.6 \times 10^{-13}\ \text{J/MeV})} \right]^2 (\cot 45°)^2$$

$$= 4 \times 10^{-5}$$

One α particle in 25,000 would be deflected by 90° or greater.

In an actual experiment, however, a detector is positioned only over a range of angle θ, θ to $\theta + \Delta\theta$, as shown in Figure 4.11. Thus we need to find the number of particles scattered between θ and $\theta + d\theta$ that corresponds to incident particles with impact parameters between b and $b + db$ as displayed in Figure 4.12. The fraction of the incident particles scattered between θ and $\theta + d\theta$ is $df/d\theta$. The derivative of Equation (4.12) is

$$df = -\pi nt \left(\frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \right)^2 \cot \frac{\theta}{2} \csc^2 \frac{\theta}{2}\ d\theta$$

If the total number of incident particles is N_i, the number of particles scattered into the ring about $d\theta$ is $N_i|df|$. The area dA into which the particles scatter

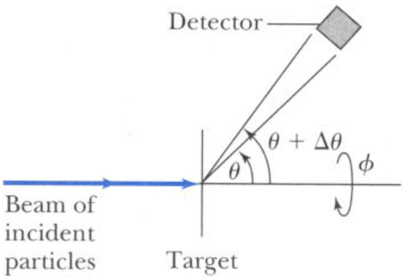


FIGURE 4.11 In most experiments, the detectors cover only a small angular range, from θ to $\theta + \Delta\theta$, and measurements are made for different θ. The detector also usually covers a small angular range in ϕ (angle around beam direction). Because there is usually symmetry about the beam axis, the ϕ angle is not normally varied.

is $(r\,d\theta)(2\pi r \sin\theta) = 2\pi r^2 \sin\theta\, d\theta$. Therefore, the number of particles scattered per unit area, $N(\theta)$, into the ring at scattering angle θ is

$$N(\theta) = \frac{N_i|\,df\,|}{dA} = \frac{N_i \pi n t \left(\dfrac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K}\right)^2}{2\pi r^2 \sin\theta\, d\theta} \cot\frac{\theta}{2}\csc^2\frac{\theta}{2}\, d\theta$$

$$N(\theta) = \frac{N_i n t}{16}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{{Z_1}^2 {Z_2}^2}{r^2 K^2 \sin^4(\theta/2)} \qquad (4.13)$$

Rutherford scattering equation

This is the famous **Rutherford scattering equation.** The important points are

1. The scattering is proportional to the square of the atomic number of both the incident particle (Z_1) and the target scatterer (Z_2).
2. The number of scattered particles is inversely proportional to the square of the kinetic energy K of the incident particle.
3. The scattering is inversely proportional to the fourth power of $\sin\frac{\theta}{2}$, where θ is the scattering angle.
4. The scattering is proportional to the target thickness for thin targets.

These very specific predictions by Rutherford in 1911 were confirmed experimentally by Geiger and Marsden in 1913. The angular dependence is particularly characteristic and can be verified in a well-equipped undergraduate physics laboratory, as we see from some actual data shown in Figure 4.13.

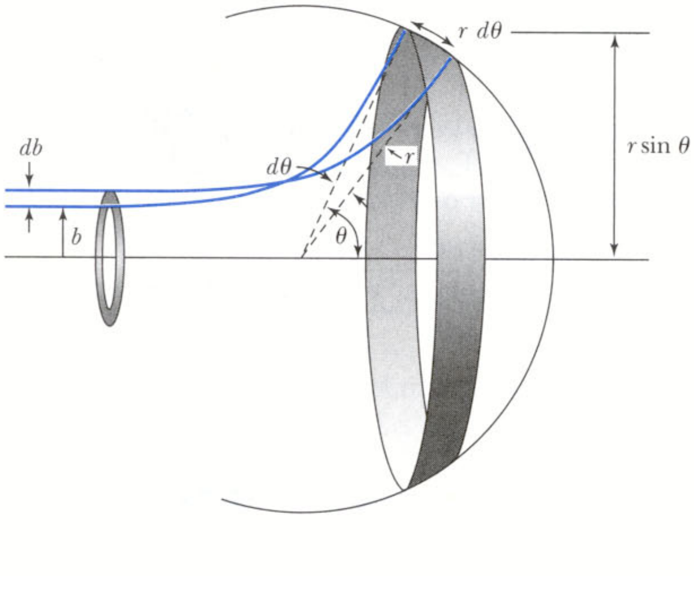


FIGURE 4.12 Particles over the range of impact parameters from b to $b + db$ will scatter into the angular range θ to $\theta + d\theta$ (with db positive, $d\theta$ will be negative).

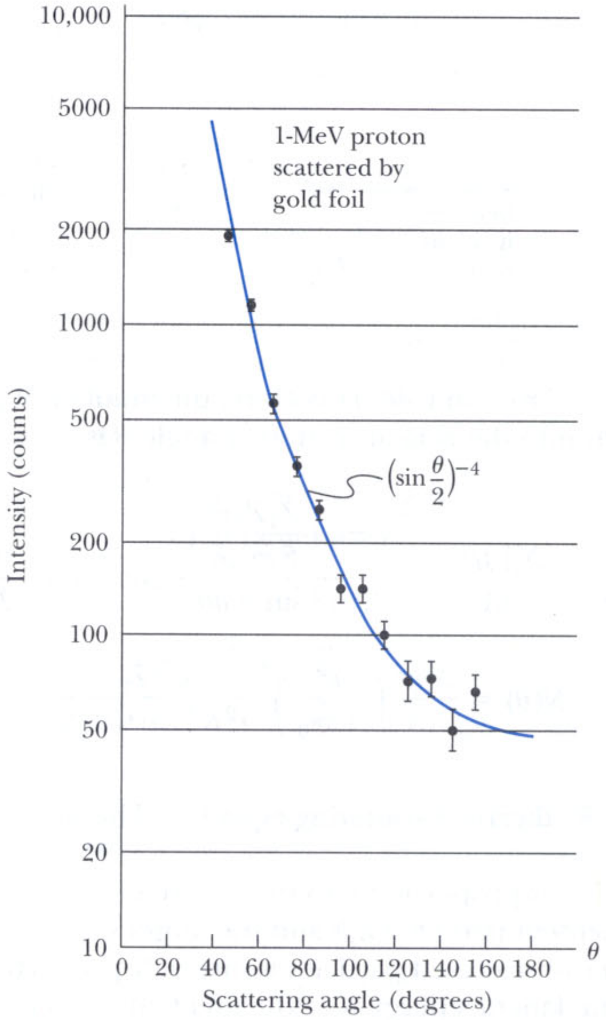


FIGURE 4.13 Results of undergraduate laboratory experiment of scattering 1-MeV protons from a gold target. The solid line shows the $(\sin\theta/2)^{-4}$ angular dependence of the data, verifying Rutherford's calculation.

Example 4.3

Calculate the fraction per mm^2 area of 7.7-MeV α particles scattered at 45° from a gold foil of thickness 2.1×10^{-8} m at a distance of 1 cm from the target.

Solution: We use Equation (4.13) to determine the fraction per unit area $N(\theta)/N_i$. We calculated $n = 5.90 \times 10^{28}$ atoms/m^3 in Example 4.2.

$$\frac{N(\theta)}{N_i} = \frac{\left(5.90\times10^{28}\,\frac{\text{atoms}}{\text{m}^3}\right)(2.1\times10^{-7}\text{ m})\left((1.6\times10^{-19}\text{ C})^2\left(9\times10^9\,\frac{\text{N}\cdot\text{m}^2}{\text{C}^2}\right)\right)^2}{16}$$

$$\times\frac{(2)^2(79)^2}{(10^{-2}\text{ m})^2\left(7.7\text{ MeV}\times\frac{10^6\text{ eV}}{\text{MeV}}\times\frac{1.6\times10^{-19}\text{ J}}{\text{eV}}\right)^2}\,\frac{1}{\sin^4(45^\circ/2)}$$

$$\frac{N(\theta)}{N_i} = 3.2\times10^{-1}\text{ m}^{-2} = 3.2\times10^{-7}\text{ mm}^{-2}$$

This is the theoretical basis for the experiment performed by Geiger and Marsden in 1913 to check the validity of Rutherford's calculation. Our calculated result agrees with their experimental result of 3.7×10^{-7} mm^{-2} when the experimental uncertainty is taken into account.

For a given kinetic energy K and impact parameter b there is a distance of closest approach between a bombarding particle and target scatterer of like charge. The minimum separation occurs for a head-on collision. The particle turns around and scatters backward at 180°. At the instant the particle turns around, the entire kinetic energy has been converted into Coulomb potential energy.

$$K = \frac{(Z_1 e)(Z_2 e)}{4\pi\epsilon_0 r} \tag{4.14}$$

We solve this equation to determine r_{min}.

$$r_{\text{min}} = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 K} \tag{4.15}$$

Distance of closest approach

For α particles of 7.7-MeV kinetic energy scattering on aluminum ($Z_2 = 13$) or gold ($Z_2 = 79$), the values of r_{min} are 5×10^{-15} m (Al) and 3×10^{-14} m (Au). We now know that nuclear radii vary from 1 to 10×10^{-15} m. Thus when α particles scatter from aluminum, an α particle may approach the nucleus quite closely and may even be affected by the nuclear force as we shall see in Chapter 12. In this case we might expect some deviation from the Rutherford scattering equation.

4.3 The Classical Atomic Model

After Rutherford presented his calculations of charged-particle scattering in 1911, it was generally conceded that the atom consisted of a small, massive, positively charged "nucleus" surrounded by moving electrons. Thomson's "plum-pudding" model was definitively excluded by the data. Actually, Thomson had previously considered a planetary model resembling the solar system (where the planets move in elliptical orbits about the sun) but had rejected it because, although both gravitational and Coulomb forces vary inversely with the square of the distance, the planets *attract* one another while orbiting around the sun, whereas the electrons would *repel* one another. Thomson considered this to be a fatal flaw from his knowledge of planetary theory.

Let us examine the simplest atom, hydrogen. We will assume circular electron orbits for simplicity rather than the more general elliptical ones. The force of attraction on the electron due to the nucleus (charge $= +e$) is

$$\mathbf{F}_e = \frac{-1}{4\pi\epsilon_0} \frac{e^2}{r^2} \mathbf{e}_r \tag{4.16}$$

where the negative sign indicates the force is attractive and $\mathbf{e}_r$ is a unit vector in the direction from the nucleus to the electron. This electrostatic force provides the centripetal force needed for the electron to move in a circular orbit at constant speed. Its radial acceleration is

$$a_r = \frac{v^2}{r} \tag{4.17}$$

where v is the tangential velocity of the electron. Newton's second law now gives

$$\frac{1}{4\pi\epsilon_0} \frac{e^2}{r^2} = \frac{mv^2}{r} \tag{4.18}$$

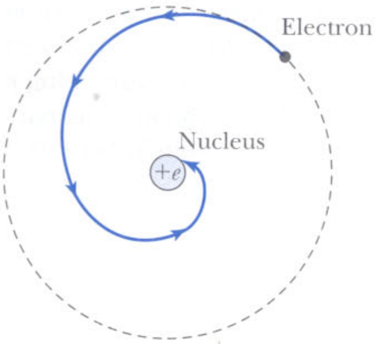


FIGURE 4.14 The electromagnetic radiation of an orbiting electron in the planetary model of the atom will cause the electron to spiral inward until it crashes into the nucleus.

and

$$v = \frac{e}{\sqrt{4\pi\epsilon_0 mr}} \tag{4.19}$$

(where we are using m without a subscript to be the electron's mass. When it is not clear which particle m refers to, we write the electron mass as m_e.) The size of an atom was thought to be about 10^{-10} m, so by letting $r = 0.5 \times 10^{-10}$ m, we can use Equation (4.19) to estimate the electron's velocity.

$$v \approx \frac{(1.6 \times 10^{-19}\text{ C})(9 \times 10^{9}\text{ N}\cdot\text{m}^2/\text{C}^2)^{1/2}}{(9.11 \times 10^{-31}\text{ kg})^{1/2}(0.5 \times 10^{-10}\text{ m})^{1/2}}$$

$$\approx 2.2 \times 10^{6}\text{ m/s} < 0.01c$$

This justifies a nonrelativistic treatment.

The kinetic energy of the system is due to the electron, $K = mv^2/2$. The nucleus is so massive compared to the electron ($m_{\text{proton}} = 1836\ m$) that the nucleus may be considered to be at rest. The potential energy V is simply $-e^2/4\pi\epsilon_0 r$, so the total mechanical energy is

$$E = K + V = \frac{1}{2}mv^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{4.20}$$

If we substitute for v from Equation (4.19), we have

$$E = \frac{e^2}{8\pi\epsilon_0 r} - \frac{e^2}{4\pi\epsilon_0 r} = \frac{-e^2}{8\pi\epsilon_0 r} \tag{4.21}$$

The total energy is negative, indicating a bound, attractive system.

Thus far, the classical atomic model seems plausible. The problem arises when we consider that the electron is accelerating due to its circular motion about the nucleus. We know from classical electromagnetic theory that an accelerated electric charge continuously radiates energy in the form of electromagnetic radiation. If the electron is radiating energy, then the total energy E of the system, Equation (4.21), must decrease continuously. In order for this to happen, the radius r must decrease. The electron will continuously radiate energy as the electron orbit becomes smaller and smaller until the electron crashes into the nucleus! This process, displayed in Figure 4.14, would occur in about 10^{-9} s (see Problem 18).

Planetary model is doomed.

Thus the classical theories of Newton and Maxwell, which had served Rutherford so well in his analysis of α-particle scattering and had thereby enabled him to discover the nucleus, also led to the failure of the planetary model of the atom. Physics had reached a decisive turning point like that encountered almost two decades earlier with Planck's revolutionary hypothesis of the quantum behavior of radiation. In the early 1910s, however, the answer would not be long in coming, as we shall see in the next section.

4.4 Bohr Model of the Hydrogen Atom

Shortly after receiving his Ph.D. from the University of Copenhagen in 1911, the 26-year-old Danish physicist Niels Bohr traveled to Cambridge University to work with J. J. Thomson. Upon meeting Ernest Rutherford early in 1912, Bohr decided to spend a few months at the University of Manchester to gain more experience in experimental physics. Upon arriving in Manchester in March, 1912, he became so involved in the mysteries of the new Rutherford model of the atom and the many experiments going on that he decided to continue his study on the structure of the atom that he had begun earlier in Cambridge under Thomson. Upon leaving Manchester for a position at the University of Copenhagen in the summer of 1912, Bohr still had many questions about atomic structure. Like several others, he believed that a fundamental length about the size of an atom (10^{-10} m) was needed for an atomic model. This fundamental length might somehow be connected to Planck's new constant h. The pieces finally came together during the fall and winter of 1912 when Bohr learned of new precise measurements of the hydrogen spectrum and of the empirical formulas describing them. He set out to find a fundamental basis from which to derive the Balmer formula Equation (3.12), the Rydberg equation (3.13), and Ritz's combination principles (see Problem 19).

Bohr was well acquainted with Planck's work on the quantum nature of radiation. Like Einstein, Bohr believed that quantum principles should govern more phenomena than just the blackbody spectrum. He was impressed by Einstein's application of the quantum theory to the photoelectric effect and to the specific heat of solids (see Chapter 9).

In 1913, following several discussions with Rutherford during 1912 and 1913, Bohr published the paper* "On the Constitution of Atoms and Molecules." He subsequently published several other papers refining and restating his "assumptions" and their predicted results. We will generally follow Bohr's papers in our discussion.

Bohr assumed that electrons moved around a massive, positively charged nucleus. We will assume for simplicity (as did Bohr at first) that the electron orbits are circular rather than elliptical and that the nuclear mass is so much greater than the electron's mass that it may be taken to be infinite. The electron has charge $-e$ and mass m and revolves around a nucleus of charge $+e$ in a circle of radius a. The size of the nucleus is small compared to the radius a.

Bohr's model may best be summarized by the following "*general assumptions*" of his 1915 paper:

Bohr's general assumptions

A. Certain "stationary states" exist in atoms, which differ from the classical stable states in that the orbiting electrons do not continuously radiate electromagnetic energy. The stationary states are states of definite total energy.

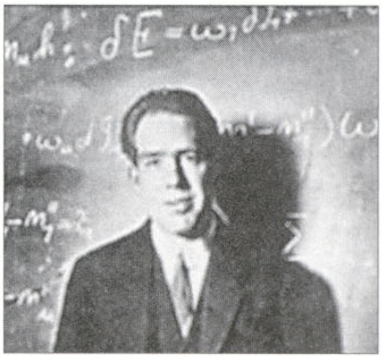
B. The emission or absorption of electromagnetic radiation can occur only in conjunction with a transition between two stationary states. The frequency ν of the emitted or absorbed radiation is proportional to the difference in energy of the two stationary states (1 and 2)

$$E = E_1 - E_2 = h\nu$$

where h is Planck's constant.

C. The dynamical equilibrium of the system in the stationary states is governed by classical laws of physics, but these laws do not apply to transitions between stationary states.

D. The mean value K of the kinetic energy of the electron–nucleus system is given by $K = nh\nu_{\text{orb}}/2$, where ν_{orb} is the frequency of rotation. For a circular orbit, Bohr pointed out that this assumption is equivalent to the angular momentum of the system in a stationary state being an integral multiple of $h/2\pi$. (This combination of constants occurs so often that we give it a separate symbol, $\hbar \equiv h/2\pi$, pronounced "h bar".)



Niels Bohr (1885–1962) was more than just a discoverer of modern physics theories. Born in Denmark, he was the son of a university professor and began high school at about the time Planck announced his results. After his education in Denmark, Bohr traveled to England in 1911 where he worked first with J. J. Thomson and later with Ernest Rutherford. Except for a year in 1913–1914 when he returned to Denmark, Bohr remained in England working mostly with Rutherford until 1916. Bohr nurtured many young theoretical physicists in his Institute of Theoretical Physics (now called the Niels Bohr Institute) formed in Copenhagen in 1921, the year before Bohr won the Nobel Prize. Many of the world's greatest physicists spent time in Copenhagen under the tutelage of Bohr, an outstanding teacher and developer of physicists. *American Institute of Physics.*

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*Niels Bohr, *Philosophical Magazine* **26,** 1(1913) and **30,** 394(1915).

These four assumptions were all that Bohr needed to derive the Rydberg equation. Bohr believed that Assumptions A and C were self-evident because atoms were stable: atoms exist and do not continuously radiate energy (therefore Assumption A). It also seemed that the classical laws of physics could not explain the observed behavior of the atom (therefore Assumption C).

Bohr later stated (1915) that Assumption B "appears to be necessary in order to account for experimental facts." However, Assumption D was the hardest for Bohr's critics to accept. It is central to the derivation of the binding energy of the hydrogen atom in terms of fundamental constants; hence Bohr restated and defended it in several ways in his papers. We have emphasized here the quantization of angular momentum aspect of Assumption D. This leads to a particularly simple derivation of the Rydberg equation.

Bohr's four assumptions were chosen to keep as much as possible of classical physics by introducing just those new ideas that were needed to describe the atom. Bohr's recognition that something new was needed and his attempt to tie this to Planck's quantum hypothesis represented an advance in understanding perhaps even greater than Einstein's theory of the photoelectric effect.

Let us now proceed to derive the Rydberg equation using Bohr's assumptions. The total energy (potential plus kinetic) of a hydrogen atom was derived previously, in Equation (4.21). For circular motion, the magnitude of the angular momentum L of the electron is

$$L = |\mathbf{r} \times \mathbf{p}| = mvr$$

Assumption D states this should equal $n\hbar$:

$$L = mvr = n\hbar \tag{4.22a}$$

Principal quantum number

where n is an integer called the **principal quantum number.** We solve the previous equation for the velocity and obtain

$$v = \frac{n\hbar}{mr} \tag{4.22b}$$

Equation (4.19) yields an independent relation between v and r. If we determine v^2 from Equations (4.19) and (4.22b) and set them equal, we find

$$v^2 = \frac{e^2}{4\pi\epsilon_0 mr} = \frac{n^2\hbar^2}{m^2r^2} \tag{4.23}$$

From Equation (4.23) we see that only certain values of r are allowed.

$$r_n = \frac{4\pi\epsilon_0 n^2\hbar^2}{me^2} \equiv n^2 a_0 \tag{4.24}$$

Bohr radius

where the **Bohr radius** a_0 is given by

$$\begin{aligned} a_0 &= \frac{4\pi\epsilon_0\hbar^2}{me^2} \\ &= \frac{(1.055 \times 10^{-34}\,\mathrm{J \cdot s})^2}{\left(8.99 \times 10^9 \dfrac{\mathrm{N \cdot m^2}}{\mathrm{C^2}}\right)(9.11 \times 10^{-31}\,\mathrm{kg})\,(1.6 \times 10^{-19}\,\mathrm{C})^2} \\ &= 0.53 \times 10^{-10}\,\mathrm{m} \end{aligned}$$

Notice that the smallest diameter of the hydrogen atom is $2r_1 = 2a_0 \approx 10^{-10}$ m, the known size of the hydrogen atom! Bohr had found the fundamental length

a_0 that he sought in terms of the fundamental constants ϵ_0, h, e, and m. This fundamental length is determined for the value $n = 1$. Note from Equation (4.24) that the atomic radius is now quantized. The quantization of various physical values arises because of the principal quantum number n. The value $n = 1$ gives the radius of the hydrogen atom in its lowest energy state (called the "ground" state). The values of $n > 1$ determine other possible radii where the hydrogen atom is in an "excited" state.

The energies of the stationary states can now be determined from Equations (4.21) and (4.24).

$$E_n = -\frac{e^2}{8\pi\epsilon_0 r_n} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \equiv -\frac{E_0}{n^2} \tag{4.25}$$

The lowest-energy state ($n = 1$) is $E_1 = -E_0$ where

$$E_0 = \frac{e^2}{8\pi\epsilon_0 a_0} = \frac{e^2}{(8\pi\epsilon_0)}\frac{me^2}{4\pi\epsilon_0\hbar^2} = \frac{me^4}{2\hbar^2(4\pi\epsilon_0)^2} = 13.6 \text{ eV} \tag{4.26}$$

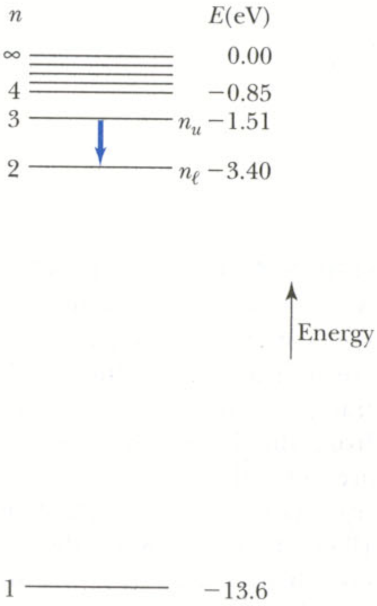

FIGURE 4.15 The energy-level diagram of the hydrogen atom. The principal quantum numbers n are shown on the left, with the energy of each level indicated on the right. The ground-state energy is −13.6 eV; negative total energy indicates a bound, attractive system. When an atom is in an excited state (for example, $n_u = 3$) and decays to a lower stationary state (for example, $n_\ell = 2$), the hydrogen atom must emit the energy difference in the form of electromagnetic radiation, that is, a photon emerges.

This is the experimentally measured ionization energy of the hydrogen atom. Bohr's assumptions C and D imply that the atom can exist only in "stationary states" with definite, quantized energies E_n, displayed in the **energy-level diagram** of Figure 4.15. Emission of a quantum of light occurs when the atom is in an excited state (quantum number $n = n_u$) and decays to a lower energy state ($n = n_\ell$). A transition between two energy levels is schematically illustrated in Figure 4.15. According to Assumption B we have

$$h\nu = E_u - E_\ell \tag{4.27}$$

where ν is the frequency of the emitted light quantum (photon). Because $\lambda\nu = c$, we have

$$\begin{aligned}\frac{1}{\lambda} &= \frac{\nu}{c} = \frac{E_u - E_\ell}{hc} \\ &= \frac{-E_0}{hc}\left(\frac{1}{{n_u}^2} - \frac{1}{{n_\ell}^2}\right) = \frac{E_0}{hc}\left(\frac{1}{{n_\ell}^2} - \frac{1}{{n_u}^2}\right)\end{aligned} \tag{4.28}$$

where

$$\frac{E_0}{hc} = \frac{me^4}{4\pi c\hbar^3(4\pi\epsilon_0)^2} \equiv R_\infty \tag{4.29}$$

This constant R_∞ is called the **Rydberg constant** (for an infinite nuclear mass). Equation (4.28) becomes

$$\frac{1}{\lambda} = R_\infty\left(\frac{1}{{n_\ell}^2} - \frac{1}{{n_u}^2}\right) \tag{4.30}$$

which is similar to the Rydberg equation (3.13). The value of $R_\infty = 1.097373 \times 10^7 \text{ m}^{-1}$ calculated from Equation (4.29) agrees well with the experimental values given in Chapter 3, and we will obtain an even more accurate result in the next section.

Bohr's model predicts the frequencies (and wavelengths) of all possible transitions in atomic hydrogen. Several of the series are shown in Figure 4.16. The Lyman series represents transitions to the lowest state with $n_\ell = 1$; the Balmer series results from downward transitions to the stationary state $n_\ell = 2$, and the Paschen series from transitions to $n_\ell = 3$. As mentioned in Section 3.3, not all of these series were known experimentally in 1913, but it was clear that Bohr had successfully accounted for the known spectral lines of hydrogen.

Bohr predicts new hydrogen wavelengths.

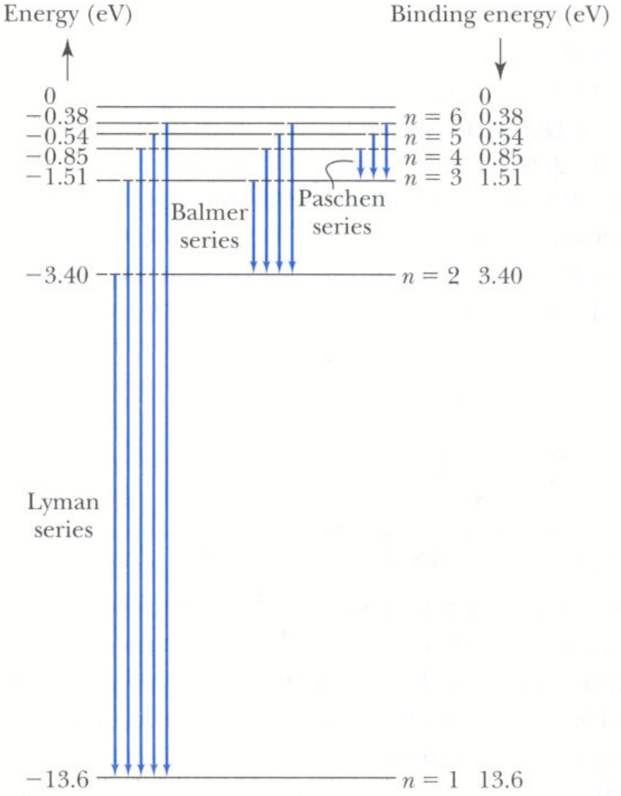

FIGURE 4.16 Transitions between many of the stationary states in the hydrogen atom are indicated. Transitions (ultraviolet) to the $n = 1$ state from the higher lying states are called the *Lyman series.* The transitions to the $n = 2$ state (Balmer series) were discovered first because they are in the visible wavelength range. The Paschen series (transitions to $n = 3$) are in the infrared. The energies of each state as well as the binding energies are denoted.

Absorption and emission spectra

The frequencies of the photons in the emission spectrum of an element are directly proportional to the differences in energy of the stationary states. When we pass white light (composed of all visible photon frequencies) through atomic hydrogen gas, we find that certain frequencies are absent. This pattern of dark lines is called an **absorption spectrum.** The missing frequencies are *precisely* the ones observed in the corresponding **emission spectrum.** In absorption, certain photons of light are absorbed, giving up energy to the atom and enabling the electron to move from a lower (ℓ) to a higher (u) stationary state. Equations (4.27) and (4.30) describe the frequencies and wavelengths of the absorbed photons. The atom will remain in the excited state for only a very short time (on the order of 10^{-10} s) before emitting a photon and returning to a lower stationary state. Thus, at ordinary temperatures practically all hydrogen atoms exist in the lowest possible energy state, $n = 1$, and only the absorption spectra of the Lyman series are normally observed. However, these lines are not in the visible region.

We can determine the electron's velocity in the Bohr model from Equations (4.22b) and (4.23).

$$v_n = \frac{n\hbar}{mr_n} = \frac{n\hbar}{mn^2a_0} = \frac{1}{n}\frac{\hbar}{ma_0} \tag{4.31}$$

or

$$v_n = \frac{1}{n}\frac{e^2}{4\pi\epsilon_0\hbar}$$

The value of $v_1 = \hbar/ma_0 = 2.2 \times 10^6$ m/s, which is less than 1% of the speed of light. We define the dimensionless quantity ratio of v_1 to c by

Fine structure constant

$$\alpha \equiv \frac{v_1}{c} = \frac{\hbar}{ma_0c} = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137} \tag{4.32}$$

This ratio is called the **fine structure constant.** It appears often in atomic structure calculations.

Example 4.4

Atomic hydrogen in its lowest energy state absorbs a photon, raising the electron to an $n = 3$ state. If we assume the lifetime of the excited state is 10^{-10} s, and if we make the rudimentary assumption that the electron orbits around the proton, how many revolutions does the electron make in the excited state before returning to a lower energy state?

Solution: The velocity of the electron will be

$$v = \frac{\text{Circumference}}{\text{Period}} = \frac{2\pi r}{T}$$

Therefore

$$T = \frac{2\pi r_3}{v_3} = \frac{(2\pi)(9a_0)(3)(4\pi\epsilon_0\hbar)}{e^2}$$

$$T = \frac{(54\pi)(0.53\times10^{-10}\ \text{m})(1.055\times10^{-34}\ \text{J}\cdot\text{s})}{(1.6\times10^{-19}\ \text{C})^2\left(9\times10^9\ \dfrac{\text{N}\cdot\text{m}^2}{\text{C}^2}\right)}$$

$$= 4.1\times10^{-15}\ \text{s}$$

$$\text{Number of revolutions} = \frac{10^{-10}\ \text{s}}{4.1\times10^{-15}\ \text{s}} = 2.4\times10^4$$

The electron revolves many times in the excited state before decaying to a lower energy state.

A note of caution

We must insert a word of caution at this point. Bohr's model represented a significant step forward in understanding the structure of the atom. Although it had many successes, we know now that, in principle, it is wrong. We will discuss some of its successes and failures in the next section and will discuss the correct quantum theory in Chapter 6. For example, contrary to the previous example, the electron does not exactly revolve around the nucleus in orbits. The correct explanation uses a wave picture and a probability description of the electron's position. Nevertheless, the simple picture given by Bohr is useful in our first attempt in understanding the structure of the atom.

The Correspondence Principle. Early in the 1900s physicists had trouble relating well-known and well-understood classical physics results with the new quantum ones. Sometimes completely different results were valid in their own domains. For example, there were two radiation laws: One used classical electrodynamics to determine the properties of radiation from an accelerated charge, but there was another one due to Bohr and his model. Physicists were proposing various kinds of correspondence principles to relate the new modern results with the old classical ones that had worked so well in their own domain. In his 1913 paper Bohr proposed perhaps the best *correspondence principle* to guide physicists in developing new theories. This principle was refined several times over the next few years.

Correspondence principle

Bohr's correspondence principle: In the limits where classical and quantum theories should agree, the quantum theory must reduce to the classical result.

Let us examine the predictions of the two radiation laws. The frequency of the radiation produced by the atomic electrons in the Bohr model of the hydrogen atom should agree with that predicted by classical electrodynamics in a region where the finite size of Planck's constant is unimportant—for large quantum numbers n where quantization effects are minimized. To see how this works we recall that classically the frequency of the radiation emitted is equal to the orbital frequency ν_{orb} of the electron around the nucleus:

$$\nu_{\text{classical}} = \nu_{\text{orb}} = \frac{\omega}{2\pi} = \frac{1}{2\pi}\frac{v}{r} \tag{4.33a}$$

If we substitute for v from Equation (4.19), we find

$$\nu_{\text{classical}} = \frac{1}{2\pi}\left(\frac{e^2}{4\pi\epsilon_0 m r^3}\right)^{1/2} \tag{4.33b}$$

We make the connection to the Bohr model by inserting the orbital radius r from Equation (4.24) into Equation (4.33b). We know then the classical frequency in terms of fundamental constants and the principal quantum number n.

$$\nu_{\text{classical}} = \frac{me^4}{4\epsilon_0{}^2 h^3}\frac{1}{n^3} \tag{4.34}$$

In the Bohr model, the nearest we can come to continuous radiation is a cascade of transitions from a level with principal quantum number $n + 1$ to the next lowest and so on:

$$n + 1 \longrightarrow n \longrightarrow n - 1 \longrightarrow \cdots$$

The frequency of the transition from $n + 1 \longrightarrow n$ is

$$\begin{aligned}\nu_{\text{Bohr}} &= \frac{E_0}{h}\left(\frac{1}{n^2} - \frac{1}{(n+1)^2}\right)\\ &= \frac{E_0}{h}\left(\frac{n^2 + 2n + 1 - n^2}{n^2(n+1)^2}\right) = \frac{E_0}{h}\left(\frac{2n+1}{n^2(n+1)^2}\right)\end{aligned}$$

which for large n becomes

$$\nu_{\text{Bohr}} \approx \frac{2nE_0}{hn^4} = \frac{2E_0}{hn^3}$$

If we substitute E_0 from Equation (4.26), the result is

Equivalence of Bohr and classical frequencies

$$\nu_{\text{Bohr}} = \frac{me^4}{4\epsilon_0{}^2 h^3}\frac{1}{n^3} = \nu_{\text{classical}} \tag{4.35}$$

so the frequencies of the radiated energy agree between classical theory and the Bohr model for large values of the quantum number n. Bohr's correspondence principle is thus verified for large orbits, where classical and quantum physics should agree.

By 1915, as Bohr's model gained widespread acceptance, the critics of the quantum concept were finding it harder to gain an audience. Bohr had demonstrated the necessity of Planck's quantum constant in understanding atomic structure, and Einstein's conception of the photoelectric effect was generally accepted as well. The *assumption* of quantized angular momentum $L_n = n\hbar$ led to the quantization of other quantities r, v, and E. We collect the following three equations here for easy reference.

Orbital radius $$r_n = \frac{4\pi\epsilon_0\hbar^2}{me^2}n^2 \tag{4.24}$$

Velocity $$v_n = \frac{n\hbar}{mr_n} \tag{4.22b}$$

Energy $$E_n = \frac{-e^2}{8\pi\epsilon_0 a_0}\frac{1}{n^2} \tag{4.25}$$

4.5 Successes and Failures of the Bohr Model

Wavelength measurements for the atomic spectrum of hydrogen are very precise and exhibit a small disagreement with the Bohr model results just presented. These disagreements can be corrected by looking more carefully at our original assumptions, one of which was to assume an infinite nuclear mass. The electron and hydrogen nucleus actually revolve about their mutual center of mass as shown in Figure 4.17. A straightforward analysis derived from classical mechanics shows that the only change required in the results of Section 4.4 is to replace the electron mass m_e by its reduced mass μ_e where

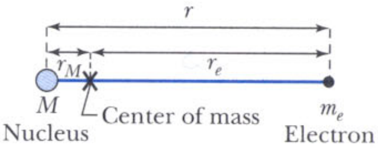

FIGURE 4.17 Because the nucleus does not actually have an infinite mass, the electron and nucleus rotate about a common center of mass that is located very near the nucleus.

Reduced mass correction

$$\mu_e = \frac{m_e M}{m_e + M} = \frac{m_e}{1 + \dfrac{m_e}{M}} \tag{4.36}$$

and M is the mass of the nucleus. The correction for the hydrogen atom is $\mu_e = 0.999456\ m_e$, only 5 parts in 10,000, but this difference can easily be measured experimentally. The Rydberg constant for infinite nuclear mass, R_∞, defined in Equation (4.29), should be replaced by R, where

$$R = \frac{\mu_e}{m_e} R_\infty = \frac{1}{1 + \dfrac{m_e}{M}} R_\infty = \frac{\mu_e e^4}{4\pi c \hbar^3 (4\pi\epsilon_0)^2} \tag{4.37}$$

The Rydberg constant for hydrogen is $R_H = 1.096776 \times 10^7\ \text{m}^{-1}$.

Example 4.5

Calculate the wavelength for the $n_u = 3 \rightarrow n_\ell = 2$ transition (called the H_α *line*) for the atoms of hydrogen, deuterium, and tritium.

Solution: The following masses are obtained by subtracting the electron mass from the atomic masses given in Appendix 8.

Proton = 1.007276 u
Deuteron = 2.013553 u
Triton (tritium nucleus) = 3.015500 u

The electron mass is $m_e = 0.0005485799$ u. The Rydberg constants are

$$R_H = \frac{1}{1 + \dfrac{0.0005486}{1.00728}} R_\infty = 0.99946\ R_\infty \qquad \text{Hydrogen}$$

$$R_D = \frac{1}{1 + \dfrac{0.0005486}{2.01355}} R_\infty = 0.99973\ R_\infty \qquad \text{Deuterium}$$

$$R_T = \frac{1}{1 + \dfrac{0.0005486}{3.01550}} R_\infty = 0.99982\ R_\infty \qquad \text{Tritium}$$

The calculated wavelength for the H_α line is

$$\frac{1}{\lambda} = R\left(\frac{1}{2^2} - \frac{1}{3^2}\right) = 0.13889\ R$$

$$\lambda(H_\alpha, \text{hydrogen}) = 656.47\ \text{nm}$$

$$\lambda(H_\alpha, \text{deuterium}) = 656.29\ \text{nm}$$

$$\lambda(H_\alpha, \text{tritium}) = 656.23\ \text{nm}$$

Deuterium was discovered when two closely spaced spectral lines of hydrogen near 656.4 nm were observed in 1932. These proved to be the H_α lines of atomic hydrogen and deuterium.

The Bohr model may be applied to any single-electron atom (hydrogen-like) even if the nuclear charge is greater than 1 proton charge ($+e$), for example He^+ and Li^{++}. The only change needed is in the calculation of the Coulomb force, where e^2 is replaced by Ze^2 to account for the nuclear charge of $+Ze$. Bohr applied his model to the case of singly ionized helium, He^+. The Rydberg equation (4.30) now becomes

$$\frac{1}{\lambda} = Z^2 R\left(\frac{1}{{n_\ell}^2} - \frac{1}{{n_u}^2}\right) \tag{4.38}$$

where the Rydberg constant is given by Equation (4.37). We emphasize that Equation (4.38) is only valid for single-electron atoms (H, He^+, Li^{++}, etc.) and does not apply to any other atoms (for example He, Li, Li^+). Charged atoms like He^+ and Li^{++} are called *ions*.

In his original paper of 1913, Bohr predicted the spectral lines of He^+ although they had not yet been identified in the lab. He showed that certain lines (generally ascribed to hydrogen) that had been observed by Pickering in stellar spectra, and by Fowler in vacuum tubes containing both hydrogen and helium, could be identified with singly ionized helium. Bohr showed that the wavelengths predicted for He^+ with $n_\ell = 4$ are almost identical to those of H for $n_\ell = 2$, except that He^+ has *additional lines* between those of H (see Problem 33). The correct explanation of this fact by Bohr gave credibility to his model.

Example 4.6

Calculate the shortest wavelength that can be emitted by the Li^{++} ion.

Solution: This occurs when the electron changes from the highest state (unbound, $n_u = \infty$) to the lowest state ($n_\ell = 1$).

$$\frac{1}{\lambda} = (3)^2 R\left(\frac{1}{1^2} - \frac{1}{\infty}\right) = 9R$$

$$\lambda = \frac{1}{9R} = 10.1 \text{ nm}$$

When we let $n_u = \infty$, we have what is known as the *series limit,* which is the shortest wavelength possibly emitted for each of the named series.

As the level of precision increased in optical spectrographs, it was observed that each of the lines, originally believed to be single, actually could be resolved into two or more lines. Sommerfeld adapted the special theory of relativity (assuming some of the electron orbits were elliptical) to Bohr's hypotheses and was able to account for some of the "splitting" of spectral lines. Subsequently it has been found that other factors (especially the electron's *spin,* or *intrinsic angular momentum*) also affect the fine structure of spectral lines.

It was soon observed that external magnetic fields (the Zeeman effect) and external electric fields (the Stark effect) applied to the radiating atoms affected the spectral lines, splitting and broadening them. Although classical electromagnetic theory could quantitatively explain the (normal) Zeeman effect (see Chapter 7), it was unable to account for the Stark effect; for this the quantum model of Bohr and Sommerfeld was necessary.

Although the Bohr model was a great step forward in the application of the new quantum theory to understanding the tiny atom, it soon became apparent that the model had its limitations:

Limitations of Bohr model

1. It could be successfully applied only to single-electron atoms (H, He^+, Li^{++}, etc.).
2. It was not able to account for the intensities or the fine structure of the spectral lines.
3. Bohr's model could not explain the binding of atoms into molecules.

We discuss in Chapter 7 the full quantum mechanical theory of the hydrogen atom which accounts for all of these phenomena. The Bohr model was an ad hoc theory to explain the hydrogen spectral lines. Although it was useful in the beginnings of quantum physics, we now know that the Bohr model does not correctly describe atoms. Despite its flaws, however, Bohr's model should not be denigrated. It was the first step from a purely classical description of the atom to the correct quantum explanation. As usually happens in such tremendous changes of understanding, Bohr's model simply did not go far enough—he retained too many classical concepts. Einstein, many years later, noted* that Bohr's achievement "appeared to me like a miracle and appears as a miracle even today."

4.6 Characteristic X-Ray Spectra and Atomic Number

By 1913 when Bohr's model was published, little progress had been made in understanding the structure of many-electron atoms. It was believed that the general characteristics of the Bohr-Rutherford atom would prevail. We discussed the production of x rays from the bombardment of various materials by electrons in Section 3.7. It was known that an x-ray tube with an anode made from a given element of the periodic table produced a continuous spectrum of bremsstrahlung x rays upon which are superimposed several peaks whose frequencies are characteristic to that element (see Figure 3.17).

We can now understand these **characteristic x-ray** wavelengths by adopting Bohr's *electron shell* hypothesis. Bohr's model suggests that an electron shell based on the radius r_n can be associated with each of the principal quantum numbers n. Electrons with lower values of n are more tightly bound to the nucleus than those with higher values. The radii of the electron orbits increase as n^2 [Equation (4.24)]. An energy is associated with each value of n. We may assume that when we add electrons to a fully ionized many-electron atom, the inner shells (low values of n) are filled before the outer shells, because the former have lower energies. We have not yet discussed how many electrons each shell contains or even why electrons tend to form shells, rather than a featureless glob, for example. Historically, the shells were given letter names: the $n = 1$ shell was called the K shell, $n = 2$ was the L shell, and so on. The shell structure of an atom is indicated in Figure 4.18. In heavy atoms with many electrons, we may suppose that several shells contain electrons. What happens when a high-energy electron in an x-ray tube collides with one of the K-shell electrons (we shall call these *K electrons*) in a target atom? If enough energy can be transferred to the

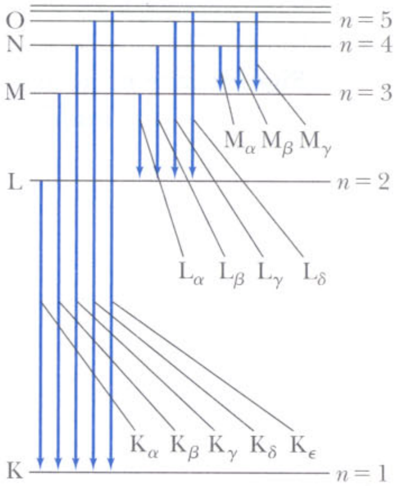

FIGURE 4.18 Historically, the stationary states were also given letter identifications: K shell ($n = 1$), L shell ($n = 2$), M shell ($n = 3$), etc. The x rays emitted when an atom changes energy states are given different names depending on the initial and final states. The Greek letter subscripts indicate the value of Δn and the roman letters the value of n for the final state.

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*P. A. Schillp, ed. *Albert Einstein, Philosopher-Scientist,* La Salle, IL: The Open Court, 1949.

K electron to dislodge it from the atom, the atom will be left with a vacancy in its K shell. The atom is most stable in its lowest energy state or *ground state,* so it is likely that an electron from one of the higher shells will change its state and fill the inner-shell vacancy at lower energy, emitting radiation as the electron changes its state. When this occurs in a heavy atom we call the electromagnetic radiation emitted an *x ray,* and it has the energy

Ground state

$$E\ (\text{x ray}) = E_u - E_\ell \tag{4.39}$$

The process is precisely analogous to what happens in an excited hydrogen atom. The photon produced when the electron falls from the L shell into the K shell is called a K_α x ray; when it falls from the M shell into the K shell, the photon is called a K_β x ray. This scheme of x-ray identification is diagrammed in Figure 4.18. The relative positions of the energy levels of the various shells differ for each element, so the characteristic x-ray energies of the elements are simply the energy differences between the shells. The two strong peaks in the molybdenum spectrum of Figure 3.17 are the K_α and K_β x rays.

This simple description of the electron shells, which will be modified later by the full quantum mechanical treatment, was not understood by early 1913. The experimental field of x-ray detection was beginning to flourish (see Section 3.3), and the precise identification of the wavelengths of characteristic x rays was possible. In 1913 H. G. J. Moseley, working in Rutherford's Manchester laboratory, was engaged in cataloguing the characteristic x-ray spectra of a series of elements. He concentrated on the K- and L-shell x rays produced in an x-ray tube. In 1913 physicists in Rutherford's Manchester lab had already fully accepted the concept of the atomic number, although there was no firm experimental evidence for doing so. Most of the European physicists still believed that **atomic weight** A was the important factor, and the periodic table of elements was so structured. The **atomic number** is the number of protons in the nucleus and is denoted by Z. The makeup of the nucleus was unknown at the time, so Z was related to the positive charge of the nucleus.

Significance of atomic number

Moseley compared the frequencies of the characteristic x rays with the then-supposed atomic number of the elements and found empirically an amazing linear result when he plotted the atomic number Z versus the square root of the measured frequency as shown in Figure 4.19:

$$\nu_{K_\alpha} = \frac{3cR}{4}(Z-1)^2 \tag{4.40}$$

This result holds for the K_α x rays, and a similar result was found for the L shell. The data shown in Figure 4.19 are known as a *Moseley plot.* Moseley began his work in 1913 in Manchester and, after moving to Oxford late in 1913, completed the investigation in early 1914. Although it is clear that Bohr and Moseley discussed physics and even corresponded after Bohr left for Copenhagen, Moseley does not mention Bohr's model in his 1914 paper. Thus, it is not known whether Bohr's ideas had any influence on Moseley's work.

Using Bohr's model we can easily understand Moseley's empirical result, Equation (4.40). If a vacancy occurs in the K shell, there is still one electron remaining in the K shell. (We will learn in Chapter 8 that at most, two electrons can occupy the K shell.) An electron in the L shell will feel an effective charge of $(Z-1)e$ due to $+Ze$ from the nucleus and $-e$ from the remaining K-shell electron, because the L-shell orbit is well outside the K-shell orbit. An application of Gauss's law with a Gaussian sphere slightly larger than the K shell is useful in understanding this effect. The other electrons outside the K shell hardly affect the

L-shell electron. The x ray produced when a transition occurs from the $n = 2$ to the $n = 1$ shell has the wavelength, from Equation (4.38), of

$$\frac{1}{\lambda_{K_\alpha}} = R(Z-1)^2\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4}R(Z-1)^2 \tag{4.41}$$

or

$$\nu_{K_\alpha} = \frac{c}{\lambda_{K_\alpha}} = \frac{3cR}{4}(Z-1)^2 \tag{4.42}$$

Henry G. J. Moseley (1887–1915), shown here working in 1910 in the Balliol-Trinity laboratory of Oxford University, was a brilliant young experimental physicist with varied interests. Unfortunately, he was killed in action at the young age of 27 during the English expedition to the Dardanelles. Moseley volunteered and insisted on combat duty in World War I, despite the attempts of Rutherford and others to keep him out of action. *University of Oxford, Museum of the History of Science/Courtesy AIP Niels Bohr Library.*

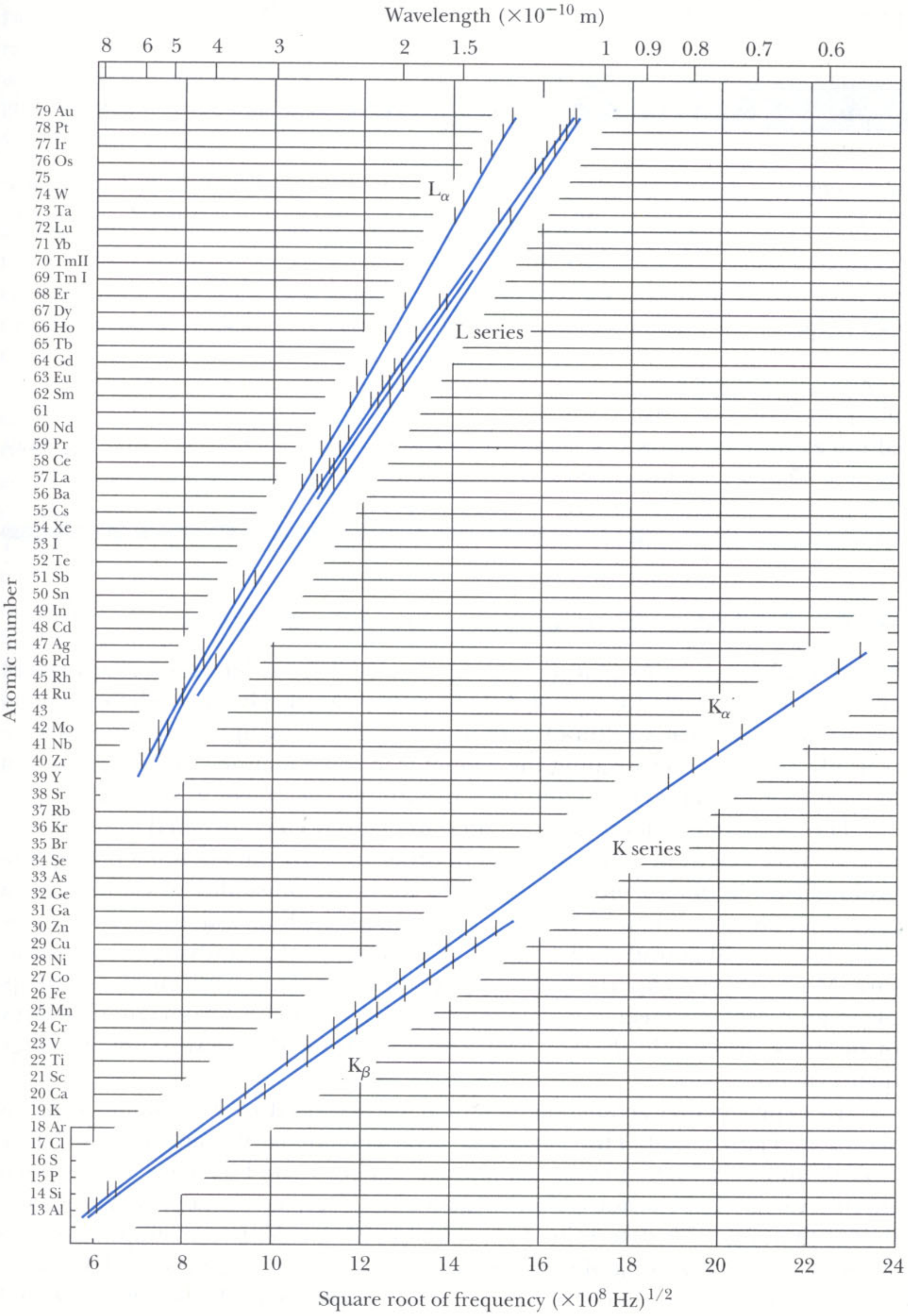


FIGURE 4.19 The original data of Moseley indicating the relationship between the atomic number Z and the characteristic x-ray frequencies. Notice the missing entries for elements $Z = 43$, 61, and 75, which had not yet been identified. There are also a few errors in the atomic number designations for the elements. © *From H. G. J. Moseley, Philosophical Magazine (6), **27**, 703 (1914).*

which is precisely the equation Moseley found describing the K_α-shell x rays. Moseley correctly concluded that the atomic number Z was the determining factor in the ordering of the periodic table, and this reordering was more consistent with chemical properties than one based on atomic weight. It put potassium ($Z = 19$, $A = 39.10$) after argon ($Z = 18$, $A = 39.95$) by atomic number rather than the reverse by atomic weight. Moseley concluded that the atomic number of an element should be identified with the number of positive units of electricity in the nucleus (that is, the number of protons). He tabulated all the atomic numbers between Al ($Z = 13$) and Au ($Z = 79$) and pointed out there were still three elements ($Z = 43$, 61, and 75) yet to be discovered! The element promethium ($Z = 61$) was not finally discovered until about 1940.

Missing atomic numbers

Example 4.7

Moseley found experimentally that the equation describing the frequency of the L_α spectral line was

$$\nu_{L_\alpha} = \frac{5}{36} cR(Z - 7.4)^2$$

How can the Bohr model explain this result?

Solution: The L_α x ray results from a transition from the M shell ($n_u = 3$) to the L shell ($n_\ell = 2$). There may be several electrons in the L shell and two electrons in the K shell that shield the nuclear charge $+Ze$ from the M-shell electron making the transition to the L shell. Let's assume the effective charge that the electron sees is $+Z_{\text{eff}}e$. Then using Equation (4.38) we have

$$\nu_{L_\alpha} = \frac{c}{\lambda_{L_\alpha}} = cR\, Z^2{}_{\text{eff}}\left(\frac{1}{2^2} - \frac{1}{3^2}\right)$$

$$\nu_{L_\alpha} = \frac{5cR\, Z_{\text{eff}}^2}{36}$$

According to Moseley's data the effective charge Z_{eff} must be $Z - 7.4$.

4.7 Atomic Excitation by Electrons

All the evidence for the quantum theory discussed so far has involved quanta of electromagnetic radiation (photons). In particular, the Bohr model explained experimental optical spectra of certain atoms. Spectroscopic experiments were typically performed by exciting the elements in some manner (for example, in a high-voltage discharge tube) and then examining the emission spectra.

The German physicists James Franck and Gustav Hertz decided to study electron bombardment of gaseous vapors in order to study the phenomenon of ionization. They explicitly set out in 1914 to study the possibility of transferring a part of an electron's kinetic energy to an atom. If such measurements were possible, they would provide a distinctive new technique for studying atomic structure. Moreover, the experiment would demonstrate that quantization would apply to an electron's mechanical energy as well as to the electromagnetic energy of photons, and would thereby provide evidence for the universality of energy quantization.

An experimental arrangement similar to that used by Franck and Hertz is shown in Figure 4.20. This particular arrangement is one actually used in a typical undergraduate physics laboratory experiment. Electrons are emitted thermionically from a hot cathode (filament), then accelerated by an electric field with its intensity determined by a variable (0 to 45 V) power supply, and pass through a grid consisting of wire mesh. After passing through the grid, the electrons feel the effects of a decelerating voltage (typically 1.5 V) between grid and

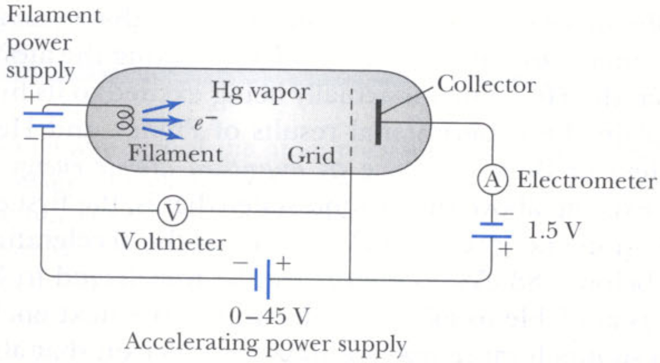
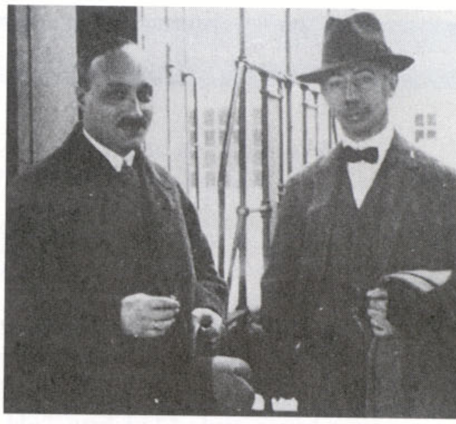


FIGURE 4.20 Schematic diagram of apparatus used in an undergraduate physics laboratory for the Franck-Hertz experiment. The hot filament produces electrons, which are accelerated through the mercury vapor toward the grid. A decelerating voltage between grid and collector prevents the electrons from registering in the electrometer unless the electron has a certain minimum energy.

anode (collector). If the electrons have greater than 1.5 eV after passing through the grid they will have enough energy to reach the collector and be registered as current in an extremely sensitive ammeter (called an *electrometer*). A voltmeter measures the accelerating voltage V. The experiment consists of measuring the current I in the electrometer as a function of V.

The accelerating electrons pass through a region containing mercury (Hg) vapor (a monoatomic gas). Is there any way that energy can be transferred between an electron and a Hg atom? Franck and Hertz found that as long as the accelerating voltage V was below about 5 V (that is, the maximum kinetic energy of the electrons was below 5 eV), the electrons apparently did not lose energy. The electron current registered in the electrometer continued to increase as V increased. However, as the accelerating voltage increased above 5 V, there was a sudden drop in the current (see Figure 4.21, which was constructed using data taken by students performing this experiment). As the accelerating voltage continues to increase above 5 V, the current increases again, but suddenly drops again above 10 V. Franck and Hertz first interpreted this behavior of the current



James Franck (1882–1964), shown here on the left with Gustav Hertz in Tübingen, Germany in 1926, came to America in 1935 to avoid Nazi persecution and became an important American scientist who trained many experimental physicists. Gustav Hertz (1887–1975), the nephew of Heinrich Hertz who discovered electromagnetic waves, worked in German universities and industrial labs before going to the Soviet Union in 1945. They received the Nobel Prize for physics in 1925. *AIP Emilio Segrè Visual Archives.*

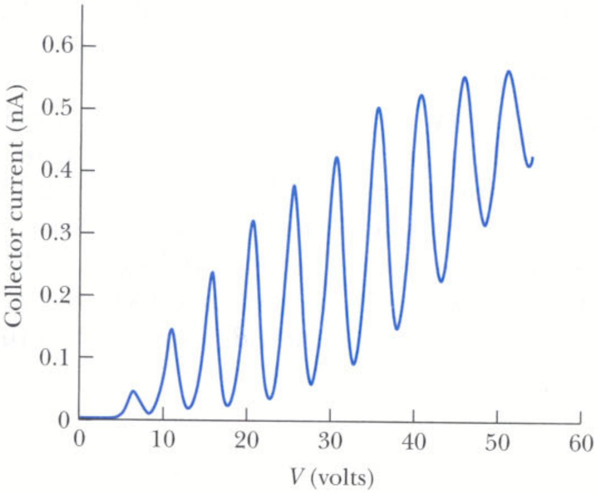


FIGURE 4.21 Data from an undergraduate student's Franck-Hertz experiment using apparatus similar to that shown in Figure 4.20. The energy difference between peaks is about 5 V, but the first peak is not at 5 V because of the work function differences of the metals used for the filament and grid.

with voltage as the onset of ionization of the Hg atom; that is, an atomic electron is given enough energy to remove it from the Hg, leaving the atom ionized. They later realized that the Hg atom was actually being excited to its first excited state.

We can explain the experimental results of Franck and Hertz quite easily within the context of Bohr's picture of *quantized atomic energy levels*. The first quantized state existing above the ground state (that is, the first excited state) in Hg is at an excitation energy of 4.88 eV. As long as the accelerating electron's kinetic energy is below 4.88 eV, no energy can be transferred to Hg because not enough energy is available to excite an electron to the next energy level in Hg. The Hg atom is so much more massive than the electron that almost no kinetic energy is transferred to the recoil of the Hg atom; the collision is *elastic*. The electron can only bounce off the Hg atom and continue along a new path with about the same kinetic energy. If the electron gains at least 4.88 eV of kinetic energy from the accelerating potential, it can transfer 4.88 eV to an electron in Hg, promoting it to the first excited state. This is an *inelastic* collision. An electron that has lost energy in an inelastic collision then has too little energy (after it passes the grid) to reach the collector. Above 4.88 V, the current dramatically drops because the inelastically scattered electrons no longer reach the collector.

When the accelerating voltage is increased to 7 or 8 V, even electrons that have already made an inelastic collision have enough remaining energy to reach the collector. Once again the current increases with V. However, when the accelerating voltage approaches 10 V, the electrons have enough energy to excite two Hg atoms in successive inelastic collisions, losing 4.88 eV in each (2×4.88 eV $= 9.76$ eV). The current drops sharply again. As we see in Figure 4.21, even with simple apparatus it is possible to observe several successive excitations as the accelerating voltage is increased. Notice that the energy differences between peaks are typically 4.9 eV. The first peak does not occur at 4.9 eV because of the difference in the work functions between the dissimilar metals used as cathode and anode. There are other highly excited states in Hg that could also be excited in an inelastic collision, but the probability of exciting them is much smaller than that for the first excited state, and so they are more difficult to observe.

The Franck-Hertz experiment convincingly proved the quantization of atomic electron energy levels. The bombarding electron's kinetic energy can change only by certain discrete amounts determined by the atomic energy levels of the mercury atom.

The observation of atomic excitation by collisions with electrons is a vivid example of the quantum theory. Franck and Hertz even carefully observed radiation emitted from the Hg vapor region. They observed no radiation emitted when the electron's kinetic energy was below about 5 V, but as soon as the current dropped, indicating excitation of Hg, an emission line of wavelength 254 nm (ultraviolet) was observed. Franck and Hertz set $E = 4.88 \text{ eV} = h\nu = (hc)/\lambda$ and showed that the value of h determined from $\lambda = 254$ nm was in good agreement with values of Planck's constant determined by other means.

Summary

Rutherford proposed a model of the atom consisting of a very massive, very compact (relative to the size of the atom), positively charged nucleus surrounded by electrons. His assistants, Geiger and Marsden, performed scattering experiments with energetic alpha particles and showed that the number of backward-scattered α particles could be accounted for only if the model were correct. The relation between the impact parameter b and scattering angle θ for Coulomb scattering is

$$b = \frac{Z_1 Z_2 e^2}{8\pi\epsilon_0 K} \cot\frac{\theta}{2} \tag{4.6}$$

Rutherford's equation for the number of particles scattered at angle θ is

$$N(\theta) = \frac{N_i n t}{16}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2 \frac{{Z_1}^2 {Z_2}^2}{r^2 K^2 \sin^4(\theta/2)} \tag{4.13}$$

where the dependence on charges Z_1 and Z_2, the kinetic energy K, the target thickness t, and the scattering angle θ were verified experimentally. The classical planetary atomic model predicts the rapid demise of the atom because of electromagnetic radiation.

Niels Bohr was able to derive the empirical Rydberg formula for the wavelengths of the optical spectrum of hydrogen using more fundamental principles. His "general assumptions" led to the quantization of various physical parameters of the hydrogen atom, including the radius, $r_n = n^2 a_0$, where $a_0 = 0.53 \times 10^{-10}$ m, and the energy, $E_n = -E_0/n^2$, where $E_0 = 13.6$ eV. The Rydberg equation

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

gives the wavelengths, where n_ℓ and n_u are the quantum numbers for the lower and upper stationary states, respectively. The Bohr model could explain the optical spectra of hydrogenlike atoms such as He^+ and Li^{++}, but could not account for the characteristics of many-electron atoms. This indicated that the model was incomplete and only approximate. Bohr's correspondence principle relates quantum theories to classical ones in the limit of large quantum numbers.

By examining the characteristic x-ray spectra of the chemical elements, Moseley proved the fundamental significance of the atomic number. We can derive the empirical Moseley relation

$$\nu_{K_\alpha} = \frac{3cR}{4}(Z-1)^2 \tag{4.40}$$

from the structure of the atom proposed by Rutherford, together with Bohr's model of hydrogenlike energy levels.

Another way of studying atomic structure is by using electron scattering rather than photon or optical methods. Franck and Hertz were able to confirm the quantized structure of the atom and determine a value of Planck's constant h in good agreement with other methods.

Questions

1. Thomson himself was perhaps the biggest critic of the model referred to as "plum pudding." He tried for years to make it work. What experimental data could he not predict? Why couldn't he make the planetary model of Rutherford-Bohr work?
2. Does it seem fortuitous that most of the successful physicists who helped unravel the secrets of atomic structure (Thomson, Rutherford, Bohr, Geiger, and Moseley) worked either together or in close proximity in England? Why do you suppose we don't hear of names from other European countries or from the United States?
3. Could the scattering of α particles past 90° be due to scattering from electrons collected together (say 100 e^-) in one place over a volume of diameter 10^{-15} m? Explain.
4. In an intense electron bombardment of the hydrogen atom, significant electromagnetic radiation is produced in all directions upon decay. Which emission line would you expect to be most intense? Why?
5. Why are peaks due to higher-lying excited states in the Franck-Hertz experiment not more observable?
6. As the voltage increases above 5 V in the Franck-Hertz experiment, why doesn't the current suddenly jump back up to the value it had below 5 V?
7. Using Hg in the Franck-Hertz experiment, approximately what range of voltages would you expect for the first peak? Explain.
8. When are photons likely to be emitted in the Franck-Hertz experiment?
9. Is an electron most strongly bound in an H, He^+, or Li^{++} atom? Explain.

10. Why do we refer to atoms as being in the "ground" state or "at rest"? What does an "excited" state mean?
11. What lines would be missing for hydrogen in an absorption spectrum? What wavelengths are missing for hydrogen in an emission spectrum?
12. Why can the Bohr model not be applied to the He atom? What difficulties do you think Bohr had in modifying his model for He?
13. Describe how the hydrogen atom might absorb a photon of energy less than 13.6 eV. Describe a process by which a 9.8-eV photon might be absorbed. What about a 15.2-eV photon?

Problems

4.1 The Atomic Models of Thomson and Rutherford

1. In Thomson's "plum pudding" model, devise an atomic composition for carbon that consists of a pudding of charge $+6e$ along with six electrons. Try to configure a system where the charged particles move only about points in stable equilibrium.
2. How large an error in the velocity do we make by treating the velocity of a 7.7-MeV α particle nonrelativistically?
3. In Example 4.1, show that the electron's velocity must be $v_e' \approx 2v_\alpha$ in order to conserve energy and linear momentum.
4. Thomson worked out many of the calculations for multiple scattering. If we find an average scattering angle of 1° for α scattering, what would be the probability that from multiple scattering the α particle could scatter by as much as 80°? The probability for large-angle scattering is $\exp[-(\theta/\langle\theta\rangle)^2]$. Geiger and Marsden found that about 1 in 8000 α particles were deflected past 90°. Can multiple scattering explain the experimental results of Geiger and Marsden?

4.2 Rutherford Scattering

5. Calculate the impact parameter for scattering a 7.7-MeV α particle from gold at an angle of (a) 1° and (b) 90°.
6. A beam of 8-MeV α particles scatters from a thin gold foil. What is the ratio of the number of α particles scattered to angles greater than 1° to the number scattered to angles greater than 2°?
7. For aluminum ($Z = 13$) and gold ($Z = 79$) targets, what is the ratio of α-particle scattering at any angle for equal numbers of scattering nuclei per unit area?
8. What fraction of 5-MeV α particles will be scattered through angles greater than 6° from a gold foil ($Z = 79$, density $= 19.3\ \mathrm{g/cm^3}$) of thickness 10^{-8} m?
9. In an experiment done by scattering 5.5 MeV α particles on a thin gold foil, students find that 10,000 α particles are scattered at an angle greater than 50°. (a) How many of these α particles will be scattered greater than 90°? (b) How many will be scattered between 70° and 80°?
10. Students want to construct a scattering experiment using a very powerful source of 5.5-MeV α particles to scatter from a gold foil. They want to be able to count 1 particle/s at 50°, but their detector is limited to a maximum count rate of 2000 particles/s. Their detector subtends a small angle. Will their experiment work without modifying the detector if the other angle they want to measure is 6°?
11. The nuclear radii of aluminum and gold are approximately $r = 3.6$ fm and 7.0 fm, respectively. The radii of protons and alpha particles are 1.3 fm and 2.6 fm, respectively. (a) What energy α particles would be needed in head-on collisions for the nuclear surfaces to just touch? (This is about where the nuclear force becomes effective.) (b) What energy protons would be needed? In both (a) and (b) perform the calculation for both aluminum and gold.
12. Consider the scattering of an alpha particle from the positively charged part of the Thomson "plum pudding" model. Let the kinetic energy of the α particle be K (nonrelativistic) and let the atomic radius be R. (a) Assuming that the maximum transverse Coulomb force acts on the α particle for a time $\Delta t = 2R/v$ (where v is the initial speed of the α particle), show that the largest scattering angle we can expect from a single atom is

$$\theta = \frac{2Z_2e^2}{4\pi\epsilon_0 KR}$$

(b) Evaluate θ for an 8-MeV α particle scattering from a gold atom of radius ~0.1 nm.

13. Using the results of the previous problem, (a) find the average scattering angle of a 10-MeV α particle from a gold atom ($R \approx 10^{-10}$ m) for the positively charged part of the Thomson model. (b) How does this compare with the scattering from the electrons?
14. The radius of a hydrogen nucleus is believed to be about $r = 1.2 \times 10^{-15}$ m. (a) If an electron moves around the nucleus at that radius, what would be its speed according to the planetary model? (b) What would the total mechanical energy be? (c) Are these reasonable?

15. Assume that the nucleus is composed of electrons and that the protons are outside. (a) If the size of an atom were about 10^{-10} m, what would be the speed of a proton? (b) What would be the total mechanical energy? (c) What is wrong with this model?

4.3 The Classical Atomic Model

16. Calculate the speed and radial acceleration for an electron in the hydrogen atom. Do the same for the Li^{++} ion.

17. What is the total mechanical energy for a ground-state electron in H, He^+, and Li^{++} atoms? For which atom is the electron most strongly bound? Why?

18. Calculate the time, according to classical laws, it would take the electron of the hydrogen atom to radiate its energy and crash into the nucleus. (*Hint:* The radiated power P is given by $(1/4\pi\epsilon_0)(2Q^2/3c^3)(d^2\mathbf{r}/dt^2)^2$ where Q is the charge, c the speed of light, and $\mathbf{r}$ the position vector of the electron from the center of the atom).

4.4 Bohr Model of the Hydrogen Atom

19. The Ritz combination rules expressed relationships between observed frequencies of the emission optical spectra. Explain one of the more important ones:

$$\nu(K_\alpha) + \nu(L_\alpha) = \nu(K_\beta)$$

where K_α and K_β refer to the Lyman series and L_α to the Balmer series of hydrogen (Figure 4.18).

20. Calculate the angular momentum in $kg \cdot m^2/s$ for the lowest electron orbit in the hydrogen atom.

21. Use the known values of ϵ_0, h, m, and e and calculate the following to five significant figures: hc (in eV·nm), $e^2/4\pi\epsilon_0$ (in eV·nm), mc^2 (in keV), a_0 (in nm), and E_0 (in eV).

22. What is the speed (ratio of v/c) of the electron in the first three Bohr orbits of the H atom?

23. A hydrogen atom in an excited state absorbs a photon of wavelength 434 nm. What were the initial and final states of the hydrogen atom?

24. A hydrogen atom in an excited state emits a photon of wavelength 95 nm. What are the initial and final states of the hydrogen atom?

25. What is the calculated binding energy of the electron in the ground state of (a) deuterium? (b) He^+, and (c) Be^{+++}?

26. Describe the visible absorption spectra for (a) hydrogen atom and (b) ionized helium atom, He^+.

27. A hydrogen atom exists in an excited state for typically 10^{-8} s. How many revolutions would an electron make in an $n = 3$ state before decaying?

28. Electromagnetic radiation of wavelength 100 nm is incident upon the ground-state hydrogen atom at rest. What is the highest state to which hydrogen can be excited?

29. A muonic atom consists of a muon ($m = 106\ MeV/c^2$) in place of an electron. For the muon in a hydrogen atom, what is (a) the smallest radius and (b) the binding energy of the muon in the ground state? (c) Calculate the series limit of the wavelength for the first three series.

30. Positronium is an atom composed of an electron and a positron ($m = m_e$, $Q = +e$). Calculate the distance between the particles and the energy of the lowest energy state of positronium. (*Hint:* what is the reduced mass of the two particles? See Problem 49.)

31. (a) Find the Bohr radius of the positronium atom described in the previous problem. (b) Find the wavelength for the transition from $n_u = 2$ to $n_\ell = 1$ for positronium.

32. What is the difference in the various Bohr radii r_n for the hydrogen atom: (a) between r_1 and r_2, (b) between r_5 and r_2, (b) between r_5 and r_6, and (c) between r_{10} and r_{11}?

4.5 Successes and Failures of the Bohr Model

33. Compare the Balmer series of hydrogen with the series where $n_\ell = 4$ for the ionized helium atom He^+. What is the difference between the L_α and L_β line of hydrogen and the $n_u = 6$ and 8 of He^+? Is there a member of the Balmer series very similar to all values where $n_\ell = 4$ in He^+?

34. Calculate the Rydberg constant for helium, potassium, and uranium. Compare each of them with R_∞ and determine the percentage difference.

35. In 1896 Pickering found lines from the star ζ-Puppis that had not been observed on Earth. Bohr showed in 1913 that the lines were due to He^+. Show that an equation giving these wavelengths is

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

What value should the Rydberg constant R have in this case?

4.6 Characteristic X-Ray Spectra and Atomic Number

36. What wavelengths for the L_α lines did Moseley predict for the missing $Z = 43$, 61, and 75 elements (see Example 4.7)?

37. If the resolution of a spectrograph is $\Delta\lambda = 10^{-12}$ m, would it be able to separate the K_α lines for platinum and gold? Explain.

38. Determine the correct equation to describe the K_β frequencies measured by Moseley. Compare that with Moseley's equation for K_α frequencies. Does the result agree with the data in Figure 4.19? Explain.

39. Calculate the K_α and K_β wavelengths for He and Li.

40. (a) Calculate the ratio of K_α wavelengths for uranium and carbon. (b) Calculate the ratio of L_α wavelengths for tungsten and calcium.

4.7 Atomic Excitation by Electrons

41. If an electron of 40 eV had a head-on collision with a Hg atom at rest, what would be the kinetic energy of the recoiling Hg atom? Assume an elastic collision.

42. In the Franck-Hertz experiment, explain why the small potential difference between the grid and collector plate is useful. Redraw the data of Figure 4.21 the way you believe the data would be without this small retarding potential.

43. Calculate the value of Planck's constant determined by Franck and Hertz when they observed the 254-nm ultraviolet radiation using Hg vapor.

44. Consider an element having excited states at 3.6 eV and 4.6 eV used as a gas in the Franck-Hertz experiment. Assume the work functions of the materials involved cancel out. List all the possible peaks that *might* be observed with electron scattering up to an accelerating voltage of 18 V.

General Problems

45. The redshift measurements of spectra from magnesium and iron are important in understanding galaxies very far away. What are the K_α and L_α wavelengths for magnesium and iron?

46. In the early 1960s the strange optical emission lines from starlike objects that also were producing tremendous radio signals confused scientists. Finally, in 1963 Maarten Schmidt of the Mount Palomar observatory discovered that the optical spectra were just those of hydrogen, but redshifted because of the tremendous velocity of the object with respect to Earth. The object was moving away from Earth at a speed of 50,000 km/s! Compare the wavelengths of the normal and redshifted spectral lines for the K_α and K_β lines of the hydrogen atom.

47. A beam of 8-MeV α particles scatters from a gold foil of thickness 0.4 μm. (a) What fraction of the α particles is scattered between 1° and 2°? (b) What is the ratio of α particles scattered through angles greater than 1° to the number scattered through angles greater than 10°; greater than 90°?

48. In Rutherford scattering we noted that angular momentum is conserved. The angular momentum of the incident α particle relative to the target nucleus is mv_0b where m is the mass, v_0 is the initial velocity of the α particle, and b is the impact parameter. Start with $\mathbf{L} = \mathbf{r} \times \mathbf{p}$ and show that angular momentum is conserved, and the magnitude is given by mv_0b along the entire path of the α particle's path while it is scattered by the Coulomb force from a gold nucleus.

49. The proton (mass M) and electron (mass m) in a hydrogen atom actually rotate about their common center of mass as shown in Figure 4.17. The distance $r = r_e + r_M$ is still defined to be the electron-nucleus distance. Show that Equation (4.24) is only modified by substituting for m by

$$\mu = \frac{m}{1 + m/M}$$

50. In Bohr's Assumption D, he assumed the mean value K of the kinetic energy of the electron-nucleus system to be $nh\nu_{\text{orb}}/2$ where ν_{orb} is the orbital frequency of the electron around the nucleus. Calculate ν_{orb} in the ground state in the following ways: (a) Use $\nu_{\text{classical}}$ in Equation (4.34). (b) Use Equation (4.33a), but first determine v and r, (c) Show that the mean value K is equal to the absolute value of the electron-nucleus system total energy and that this is 13.6 eV. (d) Use this value of K to determine ν_{orb} from the relation for K stated above.

51. Show that the quantization of angular momentum $L = n\hbar$ follows from Bohr's Assumption D that the mean value K of the kinetic energy of the electron-nucleus system is given by $K = nh\nu_{\text{orb}}/2$. Assume a circular orbit.