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## Historical Introduction

The principles of quantum mechanics are so contrary to ordinary intuition that they can best be motivated by taking a look at their prehistory. In this chapter we will consider the problems confronted by physicists in the first years of the twentieth century that ultimately led to modern quantum mechanics.

### 1.1 Photons

Quantum mechanics had its beginning in the study of black-body radiation. The universality of the frequency distribution of this radiation was established on thermodynamic grounds in 1859–1862 by Gustav Robert Kirchhoff (1824–1887), who also gave black-body radiation its name. Consider an enclosure whose walls are kept at a temperature  $T$ , and suppose that the energy per volume of radiation within this enclosure in a frequency interval between  $\nu$  and  $\nu + d\nu$  is some function  $\rho(\nu, T)$  times  $d\nu$ . Kirchhoff calculated the energy per time of the radiation in any frequency interval that strikes a small patch of area  $A$ . He reasoned that, from a point in the enclosure with polar coordinates  $r, \theta, \phi$  (with  $r$  the distance to the patch, and  $\theta$  measured from the normal to the patch), the patch will subtend a solid angle  $A \cos \theta / r^2$ , so the fraction of the energy at that point that is aimed at the patch will be  $A \cos \theta / 4\pi r^2$ . The total energy in a frequency interval between  $\nu$  and  $\nu + d\nu$  that strikes the patch in a time  $t$  is then the integral of  $A \cos \theta / 4\pi r^2 \times \rho(\nu, T) d\nu$  over a hemisphere with radius  $ct$ , where  $c$  is the speed of light:

$$2\pi \int_0^{ct} dr \int_0^{\pi/2} d\theta r^2 \sin \theta \times \frac{A \cos \theta \rho(\nu, T) d\nu}{4\pi r^2} = \frac{ctA \rho(\nu, T) d\nu}{4}.$$

If a fraction  $f(\nu, T)$  of this energy is absorbed by the walls of the enclosure, then the total energy per area and per time absorbed by the walls in a frequency interval between  $\nu$  and  $\nu + d\nu$  is

$$E(\nu, T) d\nu = \frac{c}{4} f(\nu, T) \rho(\nu, T) d\nu.$$

In order to be in equilibrium, this must also equal the energy per area and per time emitted by the walls in the same frequency interval. The walls cannot absorb more radiation than they receive, so the absorption fraction  $f(\nu, T)$  is at most equal to one. Any material for which  $f(\nu, T) = 1$  is called *black*. The function  $\rho(\nu, T)$  must be universal, for in order for it to be affected when some change is made in the enclosure, keeping it all at temperature  $T$ , energy at some frequencies would have to flow from the radiation to the walls or vice versa, which is impossible for materials at the same temperature.

Physicists in the last decades of the nineteenth century were greatly concerned to understand the distribution function  $\rho(\nu, T)$ . It had been measured, chiefly at a Berlin research institute, the *Physikalisch-Technische Reichsanstalt*, but how could one understand the measured values?

An answer was attempted using the statistical mechanics of the late nineteenth century, without quantum ideas, in a series of papers<sup>1</sup> in 1900 and 1905 by John William Strutt (1842–1919), more usually known as Lord Rayleigh, and by James Jeans (1877–1946). It was familiar that one can think of the radiation field in a box as a Fourier sum over normal modes. For instance, for a cubical box of width  $L$ , whatever boundary condition is satisfied on one face of the box must be satisfied on the opposite face, so the phase of the radiation field must change by an integer multiple of  $2\pi$  in a distance  $L$ . That is, the radiation field is the sum of terms proportional to  $\exp(i\mathbf{q} \cdot \mathbf{x})$ , with

$$\mathbf{q} = 2\pi\mathbf{n}/L, \quad (1.1.1)$$

where the vector  $\mathbf{n}$  has integer components. (For instance, to maintain translational invariance, it is convenient to impose periodic boundary conditions: each component of the electromagnetic field is assumed to be the same on opposite faces of the box.) Each normal mode is thus characterized by a triplet of integers  $n_1, n_2, n_3$  and a polarization state, which can be taken as either left- or right-circular polarization. The wavelength of a normal mode is  $\lambda = 2\pi/|\mathbf{q}|$ , so its frequency is given by

$$\nu = \frac{c}{\lambda} = \frac{|\mathbf{q}|c}{2\pi} = \frac{|\mathbf{n}|c}{L}. \quad (1.1.2)$$

Each normal mode occupies a cell of unit volume in the space of the vectors  $\mathbf{n}$ , so the number of normal modes  $N(\nu) d\nu$  in the range of frequencies between  $\nu$  and  $\nu + d\nu$  is twice the volume of the corresponding shell in this space:

$$N(\nu) d\nu = 2 \times 4\pi |\mathbf{n}|^2 d|\mathbf{n}| = 8\pi (L/c)^3 \nu^2 d\nu, \quad (1.1.3)$$

the extra factor of 2 taking account of the two possible polarizations for each wave number. In classical statistical mechanics, in any system that can be regarded as a collection of harmonic oscillators, the mean energy of each

<sup>1</sup> Lord Rayleigh, *Phil. Mag.* **49**, 539 (1900); *Nature* **72**, 54 (1905); J. Jeans, *Phil. Mag.* **10**, 91 (1905).

oscillator  $\bar{E}(T)$  is simply proportional to the temperature, a relation written as  $\bar{E}(T) = k_B T$ , where  $k_B$  is a fundamental constant, known as Boltzmann's constant. (The derivation is given below.) If this applied to radiation, the energy density in the radiation between frequencies  $\nu$  and  $\nu + d\nu$  would then be given by what has come to be called the Rayleigh–Jeans formula

$$\rho(\nu, T) d\nu = \frac{\bar{E}(T) N(\nu) d\nu}{L^3} = \frac{8\pi k_B T \nu^2 d\nu}{c^3}. \quad (1.1.4)$$

The prediction that  $\rho(\nu, T)$  is proportional to  $T\nu^2$  was actually in agreement with observation for small values of  $\nu/T$ , but failed badly for larger values. Indeed, if it held for all frequencies at a given temperature, then the total energy density  $\int \rho(\nu, T) d\nu$  would be infinite. This became known as the *ultraviolet catastrophe*.

To be a bit more specific about who did what when, Rayleigh in 1900 showed in effect that  $\rho(\nu, T)$  is proportional for low frequency to  $T\nu^2$ , but he did not attempt to calculate the constant of proportionality in Eq. (1.1.3) or in  $\bar{E}(T)$ , and hence could not give the constant factor in Eq. (1.1.4). To avoid the ultraviolet catastrophe, he also included an *ad hoc* factor that decayed exponentially for large values of  $\nu/T$ , without attempting to calculate the values of  $\nu/T$  at which the decay becomes appreciable. Rayleigh went further in 1905, and calculated the constant factor in Eq. (1.1.3), but obtained a result 8 times too large. The correct result was given a little later by Jeans (in a postscript to his 1905 article), who also correctly gave  $\bar{E}(T) = k_B T$ , and hence obtained (1.1.4) as a low-frequency limit.

The correct complete result had already been published by Max Planck (1858–1947) in 1900.<sup>2</sup> Planck noted that the data on black-body radiation could be fit with the formula

$$\rho(\nu, T) d\nu = \frac{8\pi h}{c^3} \frac{\nu^3 d\nu}{\exp(h\nu/k_B T) - 1}, \quad (1.1.5)$$

where  $h$  was a new constant, known ever after as *Planck's constant*. Comparison with observation gave  $k_B \approx 1.4 \times 10^{-16}$  erg/K and<sup>3</sup>  $h \approx 6.6 \times 10^{-27}$  erg sec. This formula was at first just guesswork, but a little later Planck gave a derivation of the formula,<sup>4</sup> based on the assumption that the radiation was the same as if it were in equilibrium with a large number of charged oscillators with different frequencies, the energy of any oscillator of frequency  $\nu$  being an integer multiple of  $h\nu$ . Planck's derivation is lengthy and not worth repeating here, since its basis is very different from what soon replaced it.

<sup>2</sup> M. Planck, *Verh. deutsch. phys. Ges.* **2**, 202 (1900).

<sup>3</sup> The modern value is  $6.62606891(9) \times 10^{-27}$  erg sec; see E. R. Williams, R. L. Steiner, D. B. Newell, and P. T. Olson, *Phys. Rev. Lett.* **81**, 2404 (1998).

<sup>4</sup> M. Planck, *Verh. deutsch. phys. Ges.* **2**, 237 (1900).

Planck's formula agrees with the Rayleigh–Jeans formula (1.1.4) for  $\nu/T \ll k_B/h$ , but it gives an energy density that falls off exponentially for  $\nu/T \gg k_B/h$ , yielding a finite total energy density

$$\int_0^\infty \rho(\nu, T) d\nu = a_B T^4, \quad a_B \equiv \frac{8\pi^5 k_B^4}{15h^3 c^3}. \quad (1.1.6)$$

(Using modern values of constants, this gives  $a_B = 7.56577(5) \times 10^{-15}$  erg  $\text{cm}^{-3} \text{K}^{-4}$ .) According to the Kirchhoff relation between  $\rho(\nu, T)$  and the rate of emission from a black body, the total rate of energy emission per area from a black body is  $\sigma T^4$ , where  $\sigma$  is the Stefan–Boltzmann constant:

$$\sigma = \frac{ca_B}{4} = \frac{2\pi^5 k_B^4}{15h^3 c^2} = 5.670373(21) \times 10^{-5} \text{ erg cm}^{-2} \text{ sec}^{-1} \text{K}^{-4}.$$

Perhaps the most important immediate consequence of Planck's work was to provide long-sought values for atomic constants. The theory of ideal gases gives the well-known law  $pV = nRT$ , where  $p$  is the pressure of a volume  $V$  of  $n$  moles of gas at temperature  $T$ , with the constant  $R$  given by  $R = k_B N_A$ , where  $N_A$  is Avogadro's number, the number of molecules in one mole of gas. Measurements of gas properties had long given values for  $R$ , so with  $k_B$  known it was possible for Planck to infer a value for  $N_A$ , the reciprocal of the mass of a hypothetical atom with unit atomic weight (close to the mass of a hydrogen atom). This was in good agreement with estimates of  $N_A$  from properties of non-ideal gases that depend on number density and not just mass density, such as viscosity. Knowing the mass of individual atoms, and assuming that atoms in solids are closely packed so that the mass to volume ratio of an atom is similar to the measured density of macroscopic solid samples of that element, one could estimate the sizes of atoms. Similarly, measurements of the amount of various elements produced by electrolysis had given a value for the faraday,  $F = eN_A$ , where  $e$  is the electric charge transferred in producing one atom of unit valence, so with  $N_A$  known,  $e$  could be calculated. It could be assumed that  $e$  is the charge of the electron, which had been discovered in 1897 by Joseph John Thomson (1856–1940), so this amounted to a measurement of the charge of the electron, a measurement much more precise than any direct measurement that could be carried out at the time. Thomson had measured the ratio of  $e$  to the mass of the electron, by observing the bending of cathode rays in electric and magnetic fields, so this also gave a value for the electron mass.

It is ironic that all this could have been done by Rayleigh in 1900, without introducing quantum ideas, if he had obtained the correct Rayleigh–Jeans formula (1.1.4) then. He would only have had to compare this formula with experimental data at small values of  $\nu/T$ , where the formula works, and use the result to find  $k_B$  – for this,  $h$  is not needed.

Planck's quantization assumption applied to the matter that emits and absorbs radiation, not to radiation itself. As George Gamow later remarked, Planck

thought that radiation was like butter; butter itself comes in any quantity, but it can be bought and sold only in multiples of one quarter pound. It was Albert Einstein (1879–1955) who in 1905 proposed that the energy of radiation of frequency  $\nu$  was itself an integer multiple of  $h\nu$ .<sup>5</sup> He used this to predict that in the photoelectric effect no electrons are emitted when light shines on a metal surface unless the frequency of the light exceeds a minimum value  $\nu_{\min}$ , where  $h\nu_{\min}$  is the energy required to remove a single electron from the metal (the “work function”). The electrons then have energy  $h(\nu - \nu_{\min})$ . Experiments<sup>6</sup> by Robert Millikan (1868–1953) in 1914–1916 verified this formula, and gave a value for  $h$  in agreement with that derived from black-body radiation.

The connection between Einstein’s hypothesis and the Planck black-body formula is best explained in a derivation of the black-body formula by Hendrik Lorentz (1853–1928) in 1910.<sup>7</sup> Lorentz made use of the fundamental result of statistical mechanics due to J. Willard Gibbs (1839–1903),<sup>8</sup> that in a system containing a large number of identical systems in thermal equilibrium at a given temperature  $T$  (like light quanta in a black-body cavity), the probability that one of these systems has an energy  $E$  is proportional to  $\exp(-E/k_{\text{B}}T)$ , with an energy-independent constant of proportionality. If the energies of light quanta were continuously distributed, this would give a mean energy

$$\bar{E} = \frac{\int_0^{\infty} \exp(-E/k_{\text{B}}T) E dE}{\int_0^{\infty} \exp(-E/k_{\text{B}}T) dE} = k_{\text{B}}T,$$

the assumption used in deriving the Rayleigh–Jeans formula (1.1.4). But if the energies are instead integer multiples of  $h\nu$ , then the mean energy is

$$\bar{E} = \frac{\sum_{n=0}^{\infty} \exp(-nh\nu/k_{\text{B}}T) nh\nu}{\sum_{n=0}^{\infty} \exp(-nh\nu/k_{\text{B}}T)} = \frac{h\nu}{\exp(h\nu/k_{\text{B}}T) - 1}. \quad (1.1.7)$$

The energy density in radiation between frequencies  $\nu$  and  $\nu + d\nu$  is again given by  $\rho d\nu = \bar{E} N d\nu/L^3$ , which now with Eqs. (1.1.3) and (1.1.7) yields the Planck formula (1.1.5).

Even after Millikan’s experiments had verified Einstein’s prediction for the energies of photoelectrons, there remained considerable skepticism about the reality of light quanta. This was largely dispelled by experiments on the scattering of X-rays by Arthur Compton (1892–1962) in 1922–23.<sup>9</sup> The energy of X-rays is sufficiently high that it is possible to ignore the much smaller binding energy of the electron in a light atom, treating the electron as a free particle. Special relativity says that if a quantum of light has energy  $E = h\nu$ , then it

<sup>5</sup> A. Einstein, *Ann. Physik* **17**, 132 (1905).

<sup>6</sup> R. A. Millikan, *Phys. Rev.* **7**, 355 (1916).

<sup>7</sup> H. A. Lorentz, *Phys. Z.* **11**, 1234 (1910).

<sup>8</sup> J. W. Gibbs, *Elementary Principles in Statistical Mechanics* (Charles Scribner’s Sons, New York, 1902).

<sup>9</sup> A. H. Compton, *Phys. Rev.* **21**, 207 (1923).

has momentum  $p = hv/c$ , in order to have  $m_{\nu}^2 c^4 = E^2 - p^2 c^2 = 0$ . If, for instance, a light quantum striking an electron at rest is scattered backwards, then the scattered quantum has frequency  $\nu'$  and the electron scattered forward has momentum  $h\nu/c + h\nu'/c$ , where  $\nu'$  is given by the energy conservation condition:

$$h\nu + m_e c^2 = h\nu' + \sqrt{m_e^2 c^4 + (h\nu/c + h\nu'/c)^2 c^2}$$

(where  $m_e$  is the electron mass), so

$$\nu' = \frac{\nu m_e c^2}{2h\nu + m_e c^2}.$$

This is conventionally written as a formula relating the wavelengths  $\lambda = c/\nu$  and  $\lambda' = c/\nu'$ :

$$\lambda' = \lambda + 2h/m_e c. \quad (1.1.8)$$

The length  $h/m_e c = 2.425 \times 10^{-10}$  cm is known as the Compton wavelength of the electron. (For scattering at an angle  $\theta$  to the forward direction, the factor 2 in Eq. (1.1.8) is replaced with  $1 - \cos \theta$ .) Verification of such relations convinced physicists of the existence of these quanta. A little later the chemist G. N. Lewis<sup>10</sup> gave the quantum of light the name by which it has been known ever since, the *photon*.

## 1.2 Atomic Spectra

Another problem confronted physicists throughout the nineteenth and early twentieth centuries. In 1802 William Hyde Wollaston (1766–1828) discovered dark lines in the spectrum of the Sun, but these lines were not studied in detail until around 1814, when they were re-discovered by Joseph von Fraunhofer (1787–1826). Later it was realized that hot atomic gases emit and absorb light only at certain definite frequencies, the pattern of frequencies, or spectrum, depending on the element in question. The dark lines discovered by Wollaston and Fraunhofer are caused by the absorption of light as it rises through the cooler outer layers of the Sun's photosphere. The study of bright and dark spectral lines became a useful tool for chemical analysis, for astronomy, and for the discovery of new elements, such as helium, discovered in the spectrum of the Sun. But, like writing in a forgotten language, these atomic spectra provided no intelligible message.

No progress could be made in understanding atomic spectra without knowing something about the structure of atoms. After Thomson's discovery of the electron in 1897, it was widely believed that atoms were like puddings, with

<sup>10</sup> G. N. Lewis, *Nature*, **118**, 874 (1926).

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negatively charged electrons stuck in like raisins in a smooth background of positive charge. This picture was radically changed by experiments carried out in the laboratory of Ernest Rutherford (1871–1937) at the University of Manchester in 1909–1911. In these experiments a post-doc, Hans Geiger (1882–1945), and an undergraduate, Ernest Marsden (1889–1970), let a collimated beam of alpha particles ( ${}^4\text{He}$  nuclei) from a radium source strike a thin gold foil. The alpha particles passing through the foil were detected by flashes of light when they struck a sheet of zinc sulfide. As expected, the beam was found to be slightly spread out by scattering of alpha particles by the gold atoms. Then for some reason Rutherford had the idea of asking Geiger and Marsden to check whether any alpha particles were scattered at large angles. This would not be expected if the alpha particle hit a much lighter particle like the electron. If a particle of mass  $M$  with velocity  $v$  hits a particle of mass  $m$  that is at rest, and continues along the same line with velocity  $v'$ , giving the target particle a velocity  $u$ , the equations of momentum and energy conservation give

$$Mv = mu + Mv', \quad \frac{1}{2}Mv^2 = \frac{1}{2}Mv'^2 + \frac{1}{2}mu^2. \quad (1.2.1)$$

(In the notation used here, a positive velocity is in the same direction as the original velocity of the alpha particle, while a negative velocity is in the opposite direction.) Eliminating  $u$ , we obtain a quadratic equation for  $v'/v$ :

$$0 = (1 + M/m)(v'/v)^2 - 2(M/m)(v'/v) - 1 + M/m.$$

This has two solutions. One solution is  $v' = v$ . This solution is one for which nothing happens – the incident particle just continues with the velocity it had at the beginning. The interesting solution is the other one:

$$v' = -v \left( \frac{m - M}{m + M} \right). \quad (1.2.2)$$

But this has a negative value (that is, a recoil backwards) only if  $m > M$ . (Somewhat weaker limits on  $m$  can be inferred from scattering at any large angle.)

Nevertheless, alpha particles were observed to be scattered at large angles. As Rutherford later explained, “It was quite the most incredible event that has ever happened to me in my life. It was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper, and it came back and hit you.”<sup>11</sup>

So the alpha particle must have been hitting something in the gold atom much heavier than an electron, whose mass is only about 1/7300 the mass of an alpha particle. Furthermore, the target particle must be quite small to stop the alpha particle by the Coulomb repulsion of positive charges. If the charge of the target

<sup>11</sup> Quoted by E. N. da Costa Andrade, *Rutherford and the Nature of the Atom* (Doubleday, Garden City, NY, 1964).

particle is  $+Ze$ , then in order to stop the alpha particle with charge  $+2e$  at a distance  $r$  from the target particle, the kinetic energy  $Mv^2/2$  must be converted into a potential energy  $(2e)(Ze)/r$ , so  $r = 4Ze^2/Mv^2$ . The velocity of the alpha particles emitted from radium is  $2.09 \times 10^9$  cm/sec, so the distance at which they would be stopped by a heavy target particle was  $3Z \times 10^{-14}$  cm, which for any reasonable  $Z$  (even  $Z \approx 100$ ) is much smaller than the size of the gold atom, a few times  $10^{-8}$  cm.

Rutherford concluded<sup>12</sup> then that the positive charge of the atom is concentrated in a small heavy nucleus, around which the much lighter negatively charged electrons circulate in orbits, like planets around the Sun. But this only heightened the mystery surrounding atomic spectra. A charged particle like the electron circulating in orbit would be expected to radiate light, with the same frequency as the orbital motion. The frequencies of these orbital motions could be anything. Worse, as the electron lost energy to radiation it would spiral down into the atomic nucleus. How could atoms remain stable?

In 1913 an answer was offered by a young visitor to Rutherford's Manchester laboratory, Niels Bohr (1885–1962). Bohr proposed in the first place that the energies of atoms are quantized, in the sense that the atom exists in only a discrete set of states, with energies (in increasing order)  $E_1, E_2, \dots$ . The frequency of a photon emitted in a transition  $m \rightarrow n$  or absorbed in a transition  $n \rightarrow m$  is given by Einstein's formula  $E = h\nu$  and energy conservation by

$$\nu = (E_m - E_n)/h. \quad (1.2.3)$$

A bright or dark spectral line is formed by atoms emitting or absorbing photons in a transition from a higher to a lower energy state, or vice versa. This explained a rule, known as the Ritz combination principle, that had been noticed experimentally by Walther Ritz (1878–1909) in 1908<sup>13</sup> (but without explaining it), that the spectrum of any atom could be described more compactly by a set of so-called "terms," the frequencies of the spectrum being all given by differences of the terms. These terms, according to Bohr, were just the energies  $E_n$ , divided by  $h$ .

Bohr also offered a method for calculating the energies  $E_n$ , at least for electrons in a Coulomb field, as in hydrogen, singly ionized helium, etc. Bohr noted that Planck's constant  $h$  has the same dimensions as angular momentum, and he guessed that the angular momentum  $m_e v r$  of an electron of velocity  $v$  in a circular atomic orbit of radius  $r$  is an integer multiple of some constant  $\hbar$ ,<sup>14</sup> presumably of the same order of magnitude as  $h$ :

$$m_e v r = n\hbar, \quad n = 1, 2, \dots \quad (1.2.4)$$

<sup>12</sup> E. Rutherford, *Phil. Mag.* **21**, 669 (1911).

<sup>13</sup> W. Ritz, *Phys. Z.* **9**, 521 (1908).

<sup>14</sup> N. Bohr, *Phil. Mag.* **26**, 1, 476, 857 (1913); *Nature* **92**, 231 (1913).

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(Bohr did not use the symbol  $\hbar$ . Readers who know how  $\hbar$  is related to  $h$  should temporarily forget that information; for the present  $\hbar$  is just another constant.) Bohr combined this with the equation for the equilibrium of the orbit,

$$\frac{m_e v^2}{r} = \frac{Z e^2}{r^2}, \quad (1.2.5)$$

and the formula for the electron's energy,

$$E = \frac{m_e v^2}{2} - \frac{Z e^2}{r}. \quad (1.2.6)$$

This gives

$$v = \frac{Z e^2}{n \hbar}, \quad r = \frac{n^2 \hbar^2}{Z m_e e^2}, \quad E = -\frac{Z^2 e^4 m_e}{2 n^2 \hbar^2}. \quad (1.2.7)$$

Using the Einstein relation between energy and frequency, the frequency of a photon emitted in a transition from an orbit with quantum number  $n$  to one with quantum number  $n' < n$  is

$$\nu = \frac{\Delta E}{h} = \frac{Z^2 e^4 m_e}{2 h \hbar^2} \left( \frac{1}{n'^2} - \frac{1}{n^2} \right). \quad (1.2.8)$$

To find  $\hbar$ , Bohr relied on a *correspondence principle*, that the results of classical physics should apply for large orbits – that is, for large  $n$ . If  $n \gg 1$  and  $n' = n - 1$ , Eq. (1.2.8) gives  $\nu = Z^2 e^4 m_e / h \hbar^2 n^3$ . This may be compared with the frequency of the electron in its orbit,  $\nu / 2\pi r = Z^2 e^4 m_e / 2\pi n^3 \hbar^3$ . According to classical electrodynamics these two frequencies should be equal, so Bohr could conclude that  $\hbar = h / 2\pi$ . Using the value of  $h$  obtained by matching observations of black-body radiation with Planck's formula, Bohr was able to derive numerical values for the velocity, radial coordinate, and energy of the electron:

$$v = \frac{Z e^2}{n \hbar} \simeq \frac{Z c}{137 n}, \quad (1.2.9)$$

$$r = \frac{n^2 \hbar^2}{Z m_e e^2} \simeq n^2 \times 0.529 Z^{-1} \times 10^{-8} \text{ cm}, \quad (1.2.10)$$

$$E = -\frac{Z^2 e^4 m_e}{2 n^2 \hbar^2} \simeq -\frac{13.6 Z^2 \text{ eV}}{n^2}. \quad (1.2.11)$$

The striking agreement of Eq. (1.2.11) with the atomic energy levels of hydrogen inferred from the frequencies of spectral lines was a strong indication that Bohr was on the right track. The case for Bohr's theory became even stronger when he pointed out (in the *Nature* article cited in footnote 14) that Eq. (1.2.11) also accounts for the spectrum of singly ionized helium (observed both astronomically and in laboratory experiments), with a small but detectable correction.

Bohr realized that the mass appearing in these formulas should be not precisely the electron mass, but rather the reduced mass  $\mu \equiv m_e/(1 + m_e/m_N)$ , where  $m_N$  is the nuclear mass. (This is discussed in Section 2.4.) Hence the constant of proportionality between  $E$  and  $1/n^2$  is larger for helium than for hydrogen by a factor that is not simply equal to  $Z_{\text{He}}^2 = 4$ , but rather by a factor  $4(1 + m_e/m_H)/(1 + m_e/m_{\text{He}}) = 4.00163$ , in agreement with experiment.

In this derivation Bohr had relied on the old idea of classical radiation theory, that the frequencies of spectral lines should agree with the frequency of the electron's orbital motion, but he had assumed this only for the largest orbits, with large  $n$ . The light frequencies he calculated for transitions between lower states, such as  $n = 2 \rightarrow n = 1$ , did not at all agree with the orbital frequency of the initial or final state. So Bohr's work represented another large step away from classical physics.

Bohr's formulas could be used not only for single-electron atoms, like hydrogen or singly ionized helium, but also roughly for the innermost orbits in heavier atoms, where the charge of the nucleus is not screened by electrons, and we can take  $Ze$  as the actual charge of the nucleus. For  $Z \geq 10$ , the energy of a photon emitted in a transition from  $n = 2$  to  $n = 1$  orbits is greater than 1 keV, and hence is in the X-ray spectrum. By measuring these X-ray energies, H. G. J. Moseley (1887–1915) was able to find  $Z$  for a range of atoms from calcium to zinc. He discovered that, within experimental uncertainty,  $Z$  is an integer, suggesting that the positive charge of atomic nuclei is carried by particles of charge  $+e$ , much heavier than the electron, to which Rutherford gave the name *protons*. Also, with just a few exceptions,  $Z$  increased by one unit in going from any element to the element with the next largest atomic weight  $A$  (roughly, the mass of the atom in units of the hydrogen atom mass). But  $Z$  turned out to be not equal to  $A$ . For instance, zinc has  $A = 65.38$ , and it turned out to have  $Z = 30.00$ . For some years it was thought that the atomic weight  $A$  was approximately equal to the number of protons, with the extra charge canceled by  $A - Z$  electrons. The discovery by James Chadwick (1891–1974) in 1935 of the neutron,<sup>15</sup> which was found to have a mass close to that of the hydrogen atom, showed that instead nuclei contain  $Z$  protons and approximately  $A - Z$  neutrons. (The atomic weight is not precisely equal to the number of protons plus the number of neutrons, both because the neutron mass is not precisely the same as the proton mass, and also because, according to Einstein's formula  $E = mc^2$ , the energy of interaction of the particles inside a nucleus contributes to the nuclear mass.)

Incidentally, Eqs. (1.2.9)–(1.2.11) also hold roughly for electrons in the outermost orbits in heavy atoms, where most of the charge of the nucleus is screened by inner electrons, and  $Z$  can therefore be taken to be of order unity. This is why the sizes of heavy atoms are not very much larger than those of light atoms,

<sup>15</sup> J. Chadwick, *Nature* **129**, 312 (1932).