2 Matter and Field

Quantum mechanics is significantly different from classical mechanics in a number of ways. To establish this theory, old ideas had to be discarded and well-established principles had to be modified or even abandoned. For example, it was first necessary to be convinced of the physical reality of the atomic structure of matter; then to show that Newtonian mechanics is not directly applicable to the study of the atom; later to show that Maxwell's[1] electrodynamics alone does not describe all the elementary processes of interaction between an atom and other quantum particles, and so on.

The moral is obvious, but takes time to grasp: in order to understand QM, we need to free our physical intuition from much of the thinking generated by everyday prequantum experience, and reread nature as it presents itself to us with new evidence and phenomena, in as receptive but critical and objective an attitude as possible to our claimed new knowledge. One of the first steps, then, is to determine *which* prequantum ideas needed to be adapted, adjusted, or replaced, and *in what sense* they needed to be modified or replaced. This is the purpose and essence of this chapter. The following chapters open the door to the two pillars on which the quantum edifice as we know it today has been built, namely Heisenberg's rather abstract formulation and the more accessible Schrödinger theory. Once the student is familiar with the basic conceptual content of QM, he or she can then naturally move on to the more formal treatment of the subject in the following chapters.

2.1 Time of Rupture

By the beginning of the twentieth century, a number of fundamental problems had accumulated for which physics had no answers. This was partly due to the fact that a large amount of spectroscopic evidence of atomic and molecular origin had been collected during the nineteenth century, which needed to be explained. In addition, by the end of the century several unexpected radiations had been discovered, including X-rays and some manifestations of radioactivity. Experimental physics (and serendipity) opened the doors to the future. We are not talking about more or less complex

[1] James Clerk Maxwell (1831–1879) was a Scottish theoretical physicist and mathematician, considered one of the greatest scientists of all time. He formulated the classical electromagnetic theory, which unified electricity, magnetism, and light as an electromagnetic phenomenon, and established fields as an essential part of nature, on a par with matter. He also contributed to statistical physics (the classical distribution is called the Maxwell–Boltzmann distribution).

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problems that arose from the lack of a method, given the theory – as would be the case, for example, with the three-body gravitation problem, which is still alive and well – but about something more fundamental: problems that escaped the context of the physical theories that existed at the time, or for which at best (or at worst) incorrect solutions were obtained. In other words, it was understood that the physical laws known at the time were applicable to a certain (admittedly very broad) type of systems or phenomena, but that they left out much of physical reality, which became less and less explainable the more it was studied with the tools at hand.

This situation led to a questioning of the theories themselves. The intense crisis that ensued succeeded in shaking the conviction prevalent at the end of the century that physics was already a practically complete science, and forced recognition of the need for a fundamental change in part of the existing conception of the physical world.

The complexity of the problems encountered triggered a search that spanned several decades of intense and profoundly creative work, carried out by a large international (essentially central European) group of scientists – among them exceptionally brilliant figures – which led to the establishment of several new physical theories. For microsystems – atoms and molecules, and their structures as crystals, and so on – the new theory was quantum mechanics.

2.2 Planck: The First Quantum Leap

The first problem that revealed the need for a thorough revision of the classical theories on the interaction between matter and electromagnetic radiation was that of the blackbody. The blackbody is not a subject of great physical interest in itself, although it has many applications: blackbody-like materials are used for camouflage, as solar energy collectors or infrared thermal detectors, for example. Historically, however, the blackbody is of paramount importance because its solution revealed an emerging new situation in physics and paved the way for the formulation of the first quantum theory.

It is generally known that bodies absorb some of the incoming electromagnetic radiation; a perfect blackbody (a theoretical object) absorbs all of it. To make something that comes close to being a blackbody, it is enough to take a closed, hollow piece of metal at a fixed temperature T. If we open a very small hole in the cavity, practically all the radiation that enters through it will be trapped; this means that the cavity behaves (very approximately) like a perfect absorber, and the radiation that escapes through the hole can be regarded as blackbody radiation at that temperature (Fig. 2.1).

Several properties of blackbody radiation can be studied using classical thermodynamics. In particular, the energy density of the radiation follows the *Stefan–Boltzmann law*, derived by L. Stefan (1815–1863) and extended by L. Boltzmann,[2]

$$u(T) = aT^4, \tag{2.1}$$

[2] Ludwig Eduard Boltzmann (1844–1906) was an eminent Austrian physicist and philosopher. His most notable achievement was the development of statistical mechanics, in particular the statistical explanation of the second law of thermodynamics, and the introduction of the concept of entropy.

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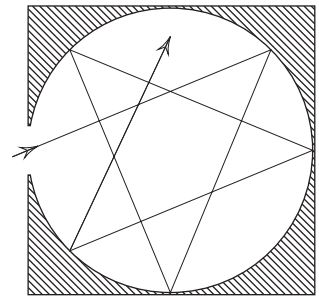


Figure 2.1 Diagram depicting a blackbody. Radiation entering through the small perforation is trapped inside the cavity after multiple reflections and has little chance of escaping. The cavity is therefore an almost perfect absorber.

where $a = 4\sigma/c$, and σ is a universal constant (independent of the material of the walls, their size or shape), called the Stefan-Boltzmann constant, with value $\sigma = 5.67 \times 10^{-5}$ erg cm^{-2} deg^{-4} sec^{-1}.

However, a serious problem arises when analyzing the spectral composition of u. The radiation field has components of all frequencies; if we filter only the frequencies between ω and $\omega + d\omega$, we obtain the *spectral energy density* $du = \rho(\omega, T)d\omega$, which when integrated over all frequencies gives the total energy density

$$u = \int_0^\infty \rho(\omega, T)d\omega. \tag{2.2}$$

Taking advantage of the fact that, according to Kirchhoff's law,[3] the spectral density of radiation from a blackbody is independent of the nature of the walls, Planck proposed to model the walls of the cavity as a collection of oscillators. This greatly simplifies the calculations, as will be shown in what follows.

Since each mechanical oscillator radiates when it vibrates, it is subject to a radiation force (called the *radiation reaction*); taking this force into account, the equation of motion of a charged oscillator with frequency ω is

$$\ddot{x} + \omega^2 x - \tau \dddot{x} = \frac{e}{m}\mathcal{E}_x, \tag{2.3}$$

where $\tau = 2e^2/3mc^3$ and $\mathcal{E}_x$ is the x-component of the radiation field in the cavity, which we take as a function of time only, independent of x. This so-called *long-wavelength approximation*[4] is justified by the fact that for the frequencies of interest (e.g., those of visible light), the wavelength of the radiation is $10^2 - 10^3$ times greater than the atomic radius, so that within the volume occupied by the atom the field $\mathcal{E}_x$ can be considered practically independent of position. Taking the Fourier transform of Eq. (2.3), we get

$$\tilde{x}(\omega') = \frac{e}{m}\,\frac{\tilde{\mathcal{E}}_x(\omega')}{\omega^2 - \omega'^2 + i\tau\omega'^3}, \tag{2.4}$$

where $\tilde{x}(\omega')$ is the Fourier transform of $x(t)$,

[3] Gustav Robert Kirchhoff (1824–1887) was a German (Prussian) physicist who among other things, derived important laws relating to linear electric circuits and blackbody radiation

[4] The long-wavelength approximation is equivalent to the electric dipole approximation, because in both cases the space-dependent coefficient of the electric field component e^{ikx} is replaced by 1.

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$$\tilde{x}(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} x(t)e^{-i\omega t}dt, \tag{2.5}$$

and similarly for $\tilde{\mathcal{E}}_x$. The energy of the oscillator averaged over a period is therefore

$$\overline{E(\omega,T)}^t = \overline{T+V}^t = \overline{2T}^t = m\overline{\dot{x}^2(t)}^t = \frac{e^2}{m}\int_{-\infty}^{+\infty}\frac{\omega'^2|\tilde{\mathcal{E}}_x(\omega')|^2}{(\omega^2-\omega'^2)^2+(\tau\omega'^3)^2}d\omega'. \tag{2.6}$$

It is easy to calculate an approximate value for this expression, noting that the integrand has a sharp maximum for frequencies close to ω because $\tau\omega \ll 1$; this allows one to replace ω' in the integral by ω, except, of course, where the difference $\xi = \omega - \omega'$ appears, and then extend the integration over ξ to the whole interval $(-\infty, \infty)$. This gives for the average energy of the oscillator in thermal equilibrium with the field in the cavity

$$\overline{E(\omega,T)}^t \simeq \frac{e^2}{4m}|\tilde{\mathcal{E}}_x(\omega)|^2\int_{-\infty}^{\infty}\frac{d\xi}{\xi^2+(e^2\omega^2/3mc^3)^2} = \frac{3\pi c^3}{4\omega^2}|\tilde{\mathcal{E}}_x(\omega)|^2. \tag{2.7}$$

On the other hand, the average energy density of the field is given by

$$\begin{aligned} u = \frac{1}{4\pi}\overline{\mathcal{E}^2}^t &= \frac{1}{4\pi}\overline{(\mathcal{E}_x^2+\mathcal{E}_y^2+\mathcal{E}_z^2)}^t = \frac{3}{4\pi}\overline{\mathcal{E}_x^2}^t \\ &= \frac{3}{4\pi}\int_0^{\infty}|\tilde{\mathcal{E}}_x(\omega)|^2 d\omega, \end{aligned} \tag{2.8}$$

whence its spectral energy density is given according to Eq. (2.2) by

$$\rho(\omega) = \frac{3}{4\pi}|\tilde{\mathcal{E}}_x(\omega)|^2. \tag{2.9}$$

Combining this expression with Eq. (2.7), we obtain Planck's formula (1899),

$$\rho(\omega,T) = \frac{\omega^2}{\pi^2c^3}\overline{E(\omega,T)}^t, \tag{2.10}$$

a remarkable result that we will use repeatedly. It tells us that the spectral energy density of blackbody radiation of frequency ω is proportional to the average energy of the mechanical oscillators with which it is in thermal equilibrium. The factor ω^2/π^2c^3 represents the *density of modes* of the field (or *density of states*, in its quantum version). Despite its simplicity, this factor – which had been calculated for an elastic medium around 1878 by Lord Rayleigh[5] – played an important role in the development of quantum theory, as it took some time to learn how to determine it for quantum systems.[6]

We now move on to calculate the average energy $\overline{E}$ of the oscillators using classical statistical mechanics. According to this theory, the average number of microsystems with energy E of a macrosystem in thermodynamic equilibrium at temperature T is given by the Boltzmann distribution

$$N(E) = N_0 e^{-\beta E}, \tag{2.11}$$

[5] John William Strutt (1842–1919), known as Lord Rayleigh, was a British mathematician and physicist who made extensive contributions to science, particularly optics and fluid dynamics. for which he was awarded the Nobel Prize in Physics in 1904.

[6] Lord Rayleigh's calculation assumed a continuous exchange of energy, as does this text, which casts some doubt on its validity in the quantum case. Hence Einstein's concern to find an alternative, in principle unproblematic route to Planck's distribution; see Section 17.2.4.

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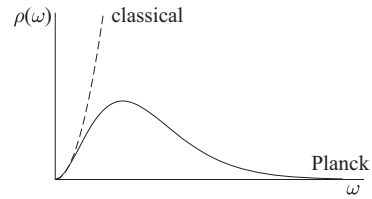


Figure 2.2 Spectral density of blackbody radiation as a function of frequency, at fixed temperature. The solid curve represents Planck's formula, which agrees with the experimental data, and the dashed curve represents the classical Rayleigh–Jeans formula.

where N_0 does not depend on energy nor temperature; β is the inverse temperature, $\beta = 1/kT$, with k the Boltzmann constant. The average energy obtained from this distribution is

$$\overline{E} = \frac{\int_0^\infty E e^{-\beta E} dE}{\int_0^\infty e^{-\beta E} dE} = -\frac{\partial}{\partial \beta} \ln \int_0^\infty e^{-\beta E} dE = \frac{\partial}{\partial \beta} \ln \beta = \frac{1}{\beta}, \tag{2.12}$$

which leads to equipartition between the oscillators,

$$\overline{E} = kT, \tag{2.13}$$

regardless of their nature and their frequency. In a system composed of a large number of independent similar oscillators (an ensemble), the result obtained by averaging over the ensemble of oscillators (as earlier) is expected to be equal to the time average of any one of them; this is the intuitive form of the *ergodic principle*. In substituting this expression in Eq. (2.10), we obtain the classical prediction

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} kT. \tag{2.14}$$

But this result, which is the so-called *Rayleigh–Jeans distribution*,[7] agrees with the experimental data only for small frequencies, as is shown in Fig. 2.2. Furthermore, according to this formula, $u = \int_0^\infty \rho d\omega$ is infinite at any temperature $T > 0$, an absurd result that contradicts the Stefan–Boltzmann law, Eq. (2.1). This is the *ultraviolet catastrophe*, as P. Ehrenfest[8] called it.

2.2.1 Energy quantization

The difficulty with the ultraviolet catastrophe survived a few years and found a solution only when Planck proposed in 1900 a new way of looking at the problem, which implied a profound change in the prevailing physical conceptions at the time. Briefly stated, we can summarize Planck's theory as follows. Equation (2.13) for the average energy was derived based on the assumption that each oscillator can have an arbitrary energy, within a continuum. Planck found it necessary to introduce a hypothesis in the form

[7] James Hopwood Jeans (1877–1946) was an English physicist, astronomer, and mathematician, who made important contributions in several areas of physics and astronomy.

[8] Paul Ehrenfest (1880–1933) was a renowned Austrian-Dutch theoretical physicist who made important contributions to statistical physics and its relation to QM. In Chapter 8 the student will learn about Ehrenfest's theorem.

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of a constraint, namely, that the material oscillators can only absorb multiples of a minimal amount of energy E_1 from the field,

$$E = nE_1, \quad n = 0, 1, 2, \ldots \tag{2.15}$$

where E_1, which Planck called *energy quantum*, depends on the frequency and perhaps other characteristics of the oscillator, but not on its temperature. This hypothesis violates a general principle of classical physical thought, that of energy as a continuum.

We now repeat the preceding calculation, but introduce Planck's postulate as a constraint, in the sense that the oscillators of a given frequency ω have an energy $E = nE_1$, with n an integer. Strictly speaking, according to Planck's argument, Eq. (2.16) refers to the (quantum) energy available for exchange with the field; the oscillators may have an additional (fixed) energy E_0 that does not participate in this exchange (see Section 2.6). The average energy is then obtained by introducing this constraint in Eq. (2.12),

$$\overline{E(\omega.\beta)} = \frac{\sum_{n=0}^{\infty} nE_1 e^{-\beta E_1 n}}{\sum_{n=0}^{\infty} e^{-\beta E_1 n}}. \tag{2.16}$$

To calculate the value of this expression, we introduce the auxiliary variable $x = e^{-\beta E_1}$. Deriving the formula $\sum_{n=0}^{\infty} x^n = (1-x)^{-1}$, we obtain

$$\frac{d}{dx}\sum_{n=0}^{\infty} x^n = \frac{1}{x}\sum_{n=0}^{\infty} nx^n = (1-x)^{-2}, \tag{2.17}$$

which allows us to write

$$\overline{E} = E_1 \frac{\sum_{n=0}^{\infty} nx^n}{\sum_{n=0}^{\infty} x^n} = E_1 \frac{x}{1-x} = \frac{E_1}{\frac{1}{x} - 1} = \frac{E_1}{e^{\beta E_1} - 1}. \tag{2.18}$$

whence from (2.6),

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{E_1}{e^{E_1/kT} - 1}. \tag{2.19}$$

The function $E_1(\omega)$ can be determined using Wien's[9] displacement law of thermodynamics as follows. By studying the adiabatic contraction of a perfectly reflecting body, Wien had shown that the spectral energy density must have the general form

$$\rho(\omega, T) = \omega^3 f(\omega/T), \tag{2.20}$$

where $f(\omega/T)$ is a universal function that could not be determined by classical theory. Comparing, we see that for Eq. (2.19) to obey this law, E_1 must be proportional to ω. Planck wrote this result in the form (we use modern notation)

$$E_1 = \hbar\omega, \tag{2.21}$$

where $\hbar$ is a constant to be determined with dimensions of action; it is the Planck constant divided by 2π. Equations (2.19) and (2.21) allow us to find the unknown function f; by combining them we get the famous *Planck distribution law*,

$$\rho(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{e^{\hbar\omega/kT} - 1}. \tag{2.22}$$

[9] Wilhelm Wien (1864–1928) was a German theoretical physicist, who was awarded the Nobel Prize in 1911 for his discoveries concerning the laws of thermal radiation.

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This result solves the problem,[10] because, on the one hand, it is free from the ultraviolet catastrophe and, on the other hand, it leads to the Stefan–Boltzmann law, Eq. (2.1),

$$u(T) = \int_0^\infty \rho(\omega, T) d\omega = \frac{\pi^2 k^4}{15 c^3 \hbar^3} T^4, \tag{2.23}$$

thus providing a theoretical expression for a in terms of fundamental constants, since it follows from a comparison with Eq. (2.1) that

$$a = \frac{\pi^2 k^4}{15 c^3 \hbar^3}. \tag{2.24}$$

Planck used this result, in reverse, to derive from it the numerical value of $\hbar$ given the empirical value of a, and obtained $\hbar = 1.05 \times 10^{-27}$ erg s. With this value of $\hbar$, Eq. (2.22) gives the solid curve shown in Fig. 2.2, which agrees with the experimental data. This theory also allowed Planck to obtain a number of collateral results, including a determination of the numerical value of the electric charge of the electron – by then a recent discovery by J. J. Thomson[11] – a result that convinced Rutherford[12] (and many other sceptics) of the validity of the atomic theory.

Suppose for a moment that in Eq. (2.22) we let the parameter $\hbar$ "tend to zero," keeping T and ω fixed (this is a purely formal procedure, since $\hbar$ is a constant of nature, not a parameter). As the exponent tends to zero, we can expand the exponential into a Taylor series, keeping only the first two terms of the expansion, to obtain

$$\rho(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3} \frac{1}{\left(1 + \frac{\hbar\omega}{kT} + \ldots\right) - 1} \simeq \frac{\hbar\omega^3}{\pi^2 c^3} \frac{kT}{\hbar\omega} = \frac{\omega^2}{\pi^2 c^3} kT, \tag{2.25}$$

which coincides with the classical Rayleigh–Jeans spectrum, Eq. (2.14). So we see that Planck's theory correctly reproduces the experimental results with $\hbar \neq 0$, and leads to the (incorrect or approximate) classical results with $\hbar = 0$. We conclude that the classical theory must be replaced by a new theory with $\hbar \neq 0$ (more precisely, with the numerical value given earlier).

Planck's constant $\hbar$ permeates all of modern physics, and its value has been determined by many different methods, so that it is now known with a high degree of accuracy. Since 2019, because of its central importance in QM, Planck's constant is taken to be exact by definition, along with other universal constants such as the elementary charge e, the speed of light in vacuum c, and the Boltzmann constant k.

[10] Based on plausibility arguments, Wien had published in 1896 the formula $\rho_W(\omega, T) = \left(\hbar\omega^3 / \pi^2 c^3\right) e^{-\hbar\omega/kT}$ for the spectral composition of the radiation, which, although approximate, gives excellent results for low temperatures (or high frequencies). The existence of this approximate formula was of great help to the later work of Planck and Einstein.

[11] Sir Joseph John Thomson FRS (1856–1940) was a distinguished British engineer and physicist, the discoverer of the electron, for which he won the Nobel Prize in 1906. He proposed the plum pudding model of the atom. He was an exceptional mentor to future scientists, half a dozen of whom went on to win the Nobel Prize in Physics or Chemistry.

The initials J. J. are important, firstly because there were several important quantum Thomsons, and secondly because he was popularly known as JJ.

[12] Ernest Rutherford (1871–1937) was an exceptional experimental New Zealand-born British physicist and chemist who discovered the atomic nucleus, for which he was awarded the Nobel Prize in Chemistry in 1908; he also identified and named the nuclear radiations α, β, γ, among many other contributions.

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We have introduced the symbol $\hbar$ (h-bar) to denote the quantity $h/2\pi$, where $h = 6.6249 \times 10^{-27}$ erg s is the constant originally introduced by Planck; the frequent appearance of the reduced Planck constant $\hbar$ in this text (and everywhere) is associated with the common use of the (angular) frequency ω instead of $\nu = \omega/2\pi$. We will refer interchangeably to both h and $\hbar$ as Planck's constant where there is no danger of confusion.

Exercise E2.1. On the scale of $\hbar$

Estimate the number of energy quanta $E_1 = \hbar\omega$ contained in a macroscopic but small oscillator with mass $m = 1$ g oscillating with an amplitude a of 1 mm and frequency $\nu = 100$ Hz. Compare with the result obtained for an electron with mass $m \sim 10^{-27}$ g oscillating with the same amplitude and frequency,

Solution. The energy of the macroscopic oscillator is

$$E = \tfrac{1}{2}m\omega^2 a^2 = \tfrac{1}{2} \times 1.0 \times (2\pi \times 10^2)^2 \times 10^{-2} \text{ erg} \simeq 2000 \text{ erg}. \tag{2.26}$$

In terms of Planck's energy unit $E_1 = \hbar\omega$, this corresponds to

$$n = \frac{E}{\hbar\omega} = \frac{2 \times 10^3}{1.05 \times 10^{-27} \times 2\pi \times 10^2} \simeq 3 \times 10^{27}. \tag{2.27}$$

Assuming that we can measure changes in the energy of one part in a million, we would not be able to record changes in n smaller than

$$|\Delta n| = 3 \times 10^{21}. \tag{2.28}$$

It is clear that under these conditions it is impossible to observe variations in the system when n changes by a few units; any such change will appear to us to be continuous.

For the electron the energy is 2×10^{-25} erg, hence $n \simeq 3$, and minimal (discrete) changes in the energy will substantially modify its behavior. It is precisely the smallness of $\hbar$ that hides the quantum phenomenon outside the atomic scale. This explains why it was precisely when experimental physics reached the atomic level that the quantum phenomena became observable and contradictions with classical notions arose.

Planck's formula for the spectral energy density, Eq. (2.22), implies that the mean thermal energy of an oscillator is given by

$$\overline{E} = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}, \tag{2.29}$$

as can be verified by combining Eqs. (2.18) and (2.21). An important consequence is that oscillators of the same frequency all share the same spectrum, regardless of their nature; this is in particular the case with the material oscillators and those of the blackbody radiation field. However, the explicit statement of this conclusion still required some years of maturation, as we will see later.

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2.3 Einstein: Quantization as a Universal Phenomenon

Planck arrived at his blackbody formula after renouncing any attempt to explain the observed results in terms of a continuous spectrum, insisting that it should be applied only to the absorption of radiation by the walls of the thermal cavity. For his part, around 1905 Einstein began a novel analysis of Planck's results and concluded that the electromagnetic field itself had a discrete, corpuscular character. This was a drastic revision of the dominant wave (continuous) conception of light since the work of Young[13] and Fresnel[14] in the early nineteenth century. Much later, in 1926, the US physicist-chemist G. N. Lewis (1875–1946) proposed to call the quantum of the radiation field a *photon*, a name that is common today and that we will use from now on when appropriate (Einstein never used it).

Einstein reached his conclusion by studying the statistical behavior of a very faint monochromatic radiation field, showing that under these conditions things happen as if it were something similar to a dilute gas in which individual molecules, which are independent of each other, are responsible for the fluctuations. Convinced that $\hbar\omega$ represents the energy of each photon, he reinterpreted Planck's results by saying that the cause of the discrete behavior of the energy exchanged by Planck's oscillators is to be sought not in the oscillators themselves, but in the radiation field, thus making Planck's result the natural consequence of the discrete properties of this field, that is, a manifestation of its organization into photons.

As his work progressed, Einstein was able to show that the Planck distribution is consistent only with the hypothesis that when an atom emits energy $\hbar\omega$, a momentum of value $\hbar\omega/c$ (a pencil of radiation) is transferred to it in the opposite direction to that of propagation. This means that the emitted photon has a well-defined direction; on the contrary, if the emitted radiation had the structure of a spherical wave, as was usually assumed, the recoil momentum would be zero. To quote Einstein:

> Outgoing radiation in the form of spherical waves does not exist. During the elementary process of radiative loss, the molecule undergoes a regression of magnitude $h\nu/c$ in a direction that is determined by "chance", according to the current state of the theory …. These properties of elementary processes … make the formulation of a quantum theory of radiation inevitable.

Later it was shown that these quanta of the radiation field also have a defined angular momentum (polarization state), of magnitude $\hbar$ and always parallel or antiparallel to the direction of propagation (this corresponds to the spin of the photon).

It is easy to be convinced that a photon with energy $h\nu$ has a momentum of value $h\nu/c$, if we apply the well-known relativistic formula relating momentum and energy *of a particle*, $E = c\sqrt{m^2c^2 + p^2}$, to the case of the photon whose mass is zero, so

$$E = h\nu = cp. \tag{2.30}$$

[13] Thomas Young (1773–1829) was a British polymath who made notable contributions to human vision, mechanics of solids, energy, physiology, and even Egyptology. He established the wave theory of light and was described as "the last man who knows everything."

[14] Augustin-Jean Fresnel (1788–1827) was a French civil engineer and physicist whose research in optics led to the generalized acceptance of the wave theory of light.

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Since the momentum is concentrated in the direction of propagation, we can rewrite this result in vector form,

$$\boldsymbol{p} = \frac{h\nu}{c}\hat{\mathbf{k}} = \frac{h}{\lambda}\hat{\mathbf{k}} = \hbar\boldsymbol{k}, \tag{2.31}$$

where $\lambda = c/\nu$ is the length of the electromagnetic wave, which propagates in the $\hat{\mathbf{k}}$ direction; $\boldsymbol{k} = (2\pi/\lambda)\hat{\mathbf{k}}$ is the wave vector and its magnitude is the *wave number*. Formula (2.31) agrees with electromagnetic theory, which states that the momentum carried by a plane wave of energy E is $\boldsymbol{p} = \hat{\mathbf{k}}E/c$, but it was derived starting from the notion of photon, not from that of wave, which is an extended object, not a point entity.

2.3.1 The photoelectric effect

Einstein immediately applied his photonic conception of light to the study of various problems. Firstly, in his early work of 1905 he revised the problem of the *photoelectric effect* and showed that the new theory allowed him to address serious unresolved theoretical difficulties. Let us briefly review the situation.

In 1887, during the laboratory work that led him to demonstrate the existence of electromagnetic waves, H. Hertz[15] observed a new phenomenon that today we can describe as the emission of electrons when light falls on an alkali metal. The experimental study of this phenomenon soon led to results that were paradoxical to the classical theories. For example, the maximum energy of the electrons emitted does not depend on the intensity of the incident light, but on its frequency (its color); on the other hand, the number of photoelectrons emitted depends on the intensity of the light beam. It was also found that for each material there is a characteristic frequency of the incident radiation, below which there is no photoelectric effect.

All these peculiarities, inexplicable in classical physics, become natural in the photon theory, according to which a given atom will either absorb a photon of energy $\hbar\omega$ or nothing at all. In the first case the atomic electron receiving this energy will escape, overcoming the attraction of the material, which becomes charged (ionized). During its escape the electron will do some work W against the material it leaves (W is the so-called *work function* of the metal), so it will be emitted with a maximum energy given by

$$\tfrac{1}{2}mv^2 = \hbar\omega - W, \tag{2.32}$$

which is indeed independent of the intensity of the light, but dependent on its frequency. If $\omega < W/\hbar$, no electron will be emitted. Furthermore, the number of emitted electrons can be expected to be proportional to the number of available photons, i.e., to grow with the intensity of the incident light.

Subsequent very fine experiments by Millikan[16] in 1914–1916 confirmed the validity of the theory and showed that the constant used in these formulae was exactly Planck's constant.

[15] Heinrich Rudolf Hertz (1857–1894) was an outstanding German experimental physicist who validated Maxwell's theory by building the first radio communication system in his laboratory (and unwittingly became the first radio amateur in history, although without a partner). The international unit of frequency, a lunar crater and an asteroid are named after him.

[16] Robert Andrews Millikan (1868–1953) was a US experimental physicist who was awarded the Nobel Prize in Physics in 1923 for his measurement of the electric charge of the electron and his verification of the quantum theory of the photoelectric effect.

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2.3.2 The specific heat of solids

Inspired by Planck's work, Einstein also tackled the problem of the heat capacity of solids, again taking a radical stance. In 1906 he published another of his famous papers, in which he argued that we should expect other oscillators, such as those used in the theory of heat, to behave in a similar way to the blackbody. According to the classical law of energy equipartition, the specific heat (at constant volume) of a solid is a constant (this is the so-called *Dulong–Petit law*),

$$c_V = \left(\partial \overline{E}/\partial T\right)_V \sim \partial\left(kT\right)/\partial T = \text{const.} \tag{2.33}$$

However, already in 1900 there were indications – thanks to the work of W. Nernst[17] and others – that the specific heat of solids actually tends to zero as the absolute temperature approaches zero. The contradiction is resolved by adopting the viewpoint proposed by Einstein, that is, by treating each atom of the solid as an oscillator with a common frequency $\nu = \omega/2\pi$. The N atoms composing a mole of the solid contain the average energy

$$\overline{E} = \frac{3Nh\nu}{e^{h\nu/kT} - 1}, \tag{2.34}$$

as follows from Eq. (2.29) applied to the $3N$ degrees of freedom of the solid. Therefore, the specific heat at constant volume is

$$c_V = \left(\frac{\partial \overline{E}}{\partial T}\right)_V = 3R\left(\frac{h\nu}{kT}\right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}, \tag{2.35}$$

where $R = kN$ is the gas constant. This formula reproduces the classical result for large temperatures (with respect to the so-called *Debye temperature*, which is characteristic of the material and is of the order of 200 K for most solids), and shows that c_V does indeed go to zero with T,

$$c_V = 3R\left(\frac{h\nu}{kT}\right)^2 e^{-h\nu/kT} \quad (T \to 0). \tag{2.36}$$

Einstein's comparison of the experimental data for the heat capacity of diamond with his formula (2.35), shown in Fig. 2.3, confirms the decrease in the heat capacity at low temperatures. A more detailed description was later developed by P. Debye,[18] Born, T. von Kármán (1881–1963), and others, using elaborations of the Einstein model just discussed – which is now regarded as the beginning of solid-state quantum theory.

2.3.3 The Compton effect

In 1921–1923, photon theory received a new boost with the Compton effect, a phenomenon that A. H. Compton[19] discovered experimentally with the newly invented X-ray spectrometer and also explained theoretically.

[17] Walther Hermann Nernst Görbitz (1864–1941) was a German physicist and chemist who was awarded the Nobel Prize in Chemistry in 1920 for his studies of chemical affinity in accordance with the third law of thermodynamics. As early as 1916, he proposed that the mechanism for compensating for the energy lost by atomic electrons could be found in the ZPF (see Section 2.9).

[18] Peter Debye (1884–1966) was a distinguished Dutch physico-chemist who was awarded the Nobel Prize in Chemistry in 1936.

[19] Arthur Holly Compton 1892–1962 was a prominent US experimentalist who received the Nobel Prize in 1927 for his discovery, verification, and explanation of the Compton effect.

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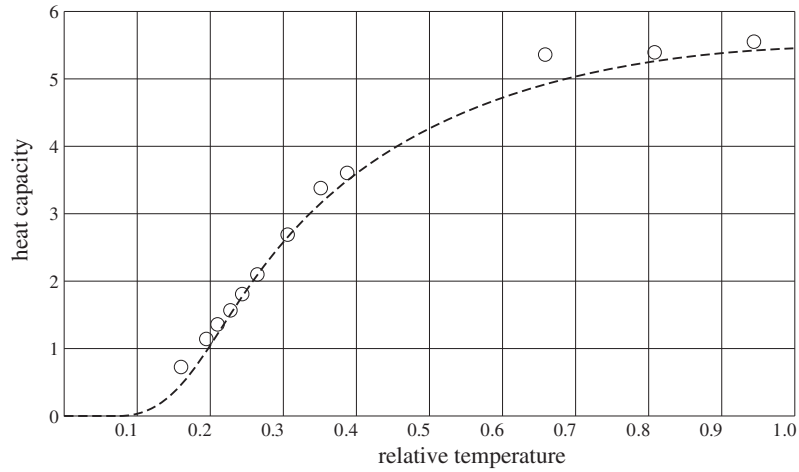


Figure 2.3 Variation of the heat capacity of diamond with temperature. Comparison of the predictions of Einstein's theory with experimental data (small circles) of the time. Figure adapted from Einstein (1907).

According to classical theory, the frequency of an electromagnetic beam does not change when it is scattered by an electron. However, using high-energy X-rays emitted by molybdenum and incident on graphite, Compton observed that part of the scattered beam had a frequency ω lower than the frequency ω_0 of the incident beam and that the difference $\omega_0 - \omega$ varied as a function of the scattering angle θ. The photon theory offers the following explanation.

Each scattering event is considered as an elastic collision between an electron at rest and a corpuscle (the photon) with speed c and initial energy $\hbar\omega_0$. Let us assume that the electron is free or loosely bound to an atom. Under these conditions, the conservation equations are, according to Eqs. (2.30) and (2.31),

$$\hbar\omega_0 + E_0 = \hbar\omega + E, \tag{2.37}$$

$$\hbar\boldsymbol{k}_0 + \boldsymbol{p}_0 = \hbar\boldsymbol{k} + \boldsymbol{p}. \tag{2.38}$$

For an electron initially at rest, $E_0 = m_0c^2$ and $\boldsymbol{p}_0 = 0$; the moving electron has momentum $\boldsymbol{p} = m\boldsymbol{v}$ and energy $E = mc^2$, with $m = m_0/\sqrt{1 - v^2/c^2} \equiv m_0\gamma$. With these substitutions, the preceding system is rewritten as

$$\hbar\omega_0 - \hbar\omega = mc^2 - m_0c^2, \tag{2.39}$$

$$\hbar\boldsymbol{k}_0 - \hbar\boldsymbol{k} = m\boldsymbol{v}. \tag{2.40}$$

It is left as an exercise to show that the electron at rest cannot absorb all the energy of the incident photon, so in all cases only part of it is absorbed. We now square the system of equations:

$$\omega_0^2 + \omega^2 - 2\omega_0\omega = (m - m_0)^2c^4/\hbar^2, \tag{2.41}$$

$$k_0^2 + k^2 - 2k_0k\cos\theta = m^2v^2/\hbar^2, \tag{2.42}$$

eliminate k from the second, using the formula $\omega = kc$, and subtract the result from the first, which, after some simplifications, gives

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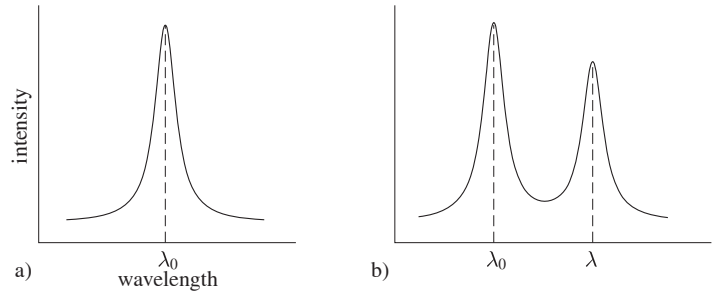


Figure 2.4 The Compton effect. Spectral distribution (a) of the incident X-rays and (b) of the scattered X-rays, with the first maximum at the original wavelength corresponding to Thomson scattering by tightly bound electrons and the second at a larger wavelength corresponding to Compton scattering by weakly bound electrons.

$$\omega_0\omega(1-\cos\theta)=\frac{c^4}{2\hbar^2}\left[\frac{m^2v^2}{c^2}-(m-m_0)^2\right]=\frac{m_0c^2}{\hbar}(\omega_0-\omega). \tag{2.43}$$

Substituting $\omega = 2\pi c/\lambda$ and dividing the result by $\omega_0\omega$, we obtain the following expression for the change in wavelength of the scattered photon as a function of the scattering angle,

$$\Delta\lambda=\lambda-\lambda_0=\frac{2\pi\hbar}{m_0c}(1-\cos\theta)=2\lambda_C\sin^2\frac{\theta}{2}. \tag{2.44}$$

The quantity

$$\lambda_C=\frac{2\pi\hbar}{m_0c}=\frac{h}{m_0c} \tag{2.45}$$

is an important parameter characteristic of the particle, known as the *Compton wavelength*. For the electron, its value is 2.4×10^{-10} cm.

From Eq. (2.44) we see that the difference between the initial and final wavelengths increases with the scattering angle. Now suppose that the incident radiation has a spectral distribution as shown in Fig. 2.4a. Since the scattering material has a large number of tightly bound atomic electrons oscillating about their equilibrium position, there will be a scattered component that does not change its wavelength; this primary radiation is correctly described by classical physics (it is the *Thomson scattering*) and corresponds to the first maximum in Fig. 2.4b. However, weakly bound (almost free) electrons will produce *Compton scattering* and cause the appearance of a secondary maximum centered at $\lambda > \lambda_0$, as shown in the same figure.

As the Compton wavelength of elementary particles is relatively small, Compton scattering is observed only at relatively small wavelengths, that is, with X- and γ-rays. For example, for visible light with $\lambda \sim 10^{-5}$ cm

$$\frac{\Delta\lambda}{\lambda}\sim\frac{\lambda_C}{\lambda}\sim10^{-5}, \tag{2.46}$$

while for X-rays with $\lambda \sim 10^{-9}$ cm,

$$\frac{\Delta\lambda}{\lambda}\sim\frac{\lambda_C}{\lambda}\sim10^{-1}. \tag{2.47}$$

Compton's work of 1926 is now regarded as the definitive confirmation of the photon theory of light. Of particular importance was the fact that it confirmed the validity of

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the laws of conservation of momentum and energy for individual events of radiation–matter interaction (there had been doubts about their general validity in microphysics). It also confirmed that the emitted photons travel in a well-defined direction, like a radiation pencil, as established by Einstein, contrary to the previous popular belief that the emission has spherical symmetry. The reader should note the significance of these statements: the radiation pencil refers to a specific, isolated, one-particle event, whereas spherical symmetry results from a large number of similar events randomly distributed in all directions.

2.4 Early Attempts to Model the Atom

Already by 1912, many physicists were taking the quantum hypothesis seriously. The work of atomic spectroscopists and that of J. J. Thomson, Rutherford, and others on the electron and the atomic structure had provided sufficient experimental evidence to complement the field quantization results of Planck and Einstein. The conditions were ripe for the emergence of the first quantum theory of the structure of matter, namely Bohr's model of the hydrogen atom (1913), which gave rise to what is known as *primitive quantum mechanics*, which already considered quantized (stationary) atomic orbits.

The problem that initially concerned Bohr was merely that of constructing a model of the atom; with the development of his own work, Bohr turned his attention to a second problem closely related to the first: the structure of atomic absorption and emission spectra. Let us briefly review the situation of these two problems around 1912.

The first idea that came to mind is that the atom must be a static system, since according to electrodynamics an accelerated electric charge e radiates, emitting an average energy W_L per second given by Larmor's formula,

$$W_L = \frac{2e^2}{3c^3}\overline{\ddot{\boldsymbol{r}}^2} \tag{2.48}$$

(the bar indicates orbital (time) average). On this basis, J. J. Thomson had proposed in 1903 to visualize the atom as a uniform distribution of positive charge filling the entire atomic volume (with a radius of the order of 10^{-8} cm), with the (point) electrons in equilibrium inside, the so-called *plum pudding model*. However, later experiments on the scattering of α-particles (i.e., helium nuclei with two protons and two neutrons) by thin metal foils, conducted in Thomson's laboratory in Cambridge and by Rutherford and his colleagues H. Geiger (1862–1945) and E. Marsden (1889–1970) in Manchester, showed a relatively large number of particles scattered at large angles ($\sim$150°).

These observations led Rutherford to propose an alternative model of the atom, with the positive charge of the protons concentrated in a very small central region (the nucleus), which carry virtually all the atomic mass, and sufficient orbital electrons to ensure the electrical neutrality of the atom. Positive particles that come very close to the nucleus are violently repelled and deflected by the strong central and quasi-point-like field (in fact a head-on collision would result in total reflection of the α-particle), which explains the frequent occurrence of large scattering angles. Using this model, Rutherford was able to correctly predict the fraction of scattered particles within the

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solid angle $d\Omega$, that is, to calculate the angular distribution of the scattered particles.[20] These results meant the end of Thomson's model and of other earlier alternatives, but introduced a new difficulty: the problem of the stability of the atom, since the orbiting electrons of a planetary model should radiate until they collapse on the nucleus.

Bohr – who had joined Rutherford's group in 1911 for a few months after a longer stay with Thomson – felt that the way out of this difficulty should be sought in Planck and Einstein's quantum theory, which, he hoped, might well be compatible with the idea of a nonradiating accelerated electron. A second difficulty with Rutherford's model, the fact that it did not assign a size to the atom, suggested to Bohr the idea that there should be an additional principle in the form of a *constraint* that would fix the atomic scale. A dimensional analysis shows that $\hbar$, e, and m can be used to construct an elementary length of appropriate value for the atom ($\hbar^2/me^2 \approx 10^{-9}$ cm), which is not possible with e and m alone, a fact that confirmed Bohr's suspicion that $\hbar$ plays a central role.

The concrete way of incorporating quantum theory into Rutherford's planetary model was suggested to Bohr by means of an analysis of the characteristics of atomic spectra. Atomic spectroscopy had reached a high level of development and the visible absorption and emission spectra (spectra consisting of series of characteristic lines) of many elements were known in sufficient detail. In 1885 J. Balmer (1825–1898) – a Swiss mathematician, numerologist, and elementary-school teacher – showed that the four visible lines of the emission spectrum of hydrogen have a wavelength λ given by the expression

$$\lambda = a\,\frac{n^2}{n^2-4}\,, \tag{2.49}$$

where $a = 3645.6 \times 10^{-7}$ cm and $n = 3, 4, 5, 6$. Balmer later proved that the same formula correctly gave the other eight lines of the series, now called Balmer's series. He was also able to accurately predict – on the basis of purely numerological studies – the characteristic properties of the various series that could be obtained by replacing the number 4 by the square of a higher integer.

A few years later J. Rydberg (1854–1919) proved that all known series of the hydrogen spectrum, including Balmer's, can be obtained from a simple formula if the wave number $k = 2\pi/\lambda = \omega/c$ is used instead of the wavelength $\lambda = c/\nu$.[21] The formula he proposed, taking into account minor subsequent modifications, is

$$k = 2\pi R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \tag{2.50}$$

where R is a universal, empirical constant, called the *Rydberg constant*, of value 109,737.3 cm^{-1}. The numbers n_1 and n_2 are positive integers, of which n_1 defines the series, while $n_2 > n_1$ defines the line of the series; the Balmer series corresponds to

[20] In Section 18.2 we will have the opportunity to study this problem with quantum methods. As we shall see, the formula derived by Rutherford using classical methods coincides exactly with the corresponding quantum version, a fortuitous fact that certainly facilitated the development of quantum theory.

[21] The Rydberg relation $k = 2\pi/\lambda$ can be rewritten in the form $\lambda = h/p$, with $p = hk$; this is just the de Broglie relation in Equation (2.73). It will reappear in the next chapter associated with the Schödinger equation.

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$n_1 = 2$. Equation (2.50) incorporates the *combination principle* proposed in 1908 by W. Ritz (1878–1909), which states that the frequency of each spectral line ($\omega = kc$) of any element can be expressed as the difference of two spectral terms, each containing an integer. The empirical law (2.50) finds no theoretical justification in any classical model, according to which the emitted frequency should have a continuous spectrum instead of the observed discrete one.

2.5 Bohr's Quantum Atom Model

It was precisely Eq. (2.50) that inspired Bohr's creativity by interpreting it as an expression of energy conservation. Bohr assumed that the electrons move in stationary orbits but can occasionally "jump" from one orbit n to another n', emitting a photon. Considering that a spectral line is produced by photons of (angular) frequency $\omega = ck$, and using Einstein's quantum relation $E = \hbar\omega$, he obtained

$$\hbar\omega = 2\pi\hbar cR\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = E_1 - E_2, \tag{2.51}$$

whence

$$E_n = \frac{2\pi\hbar cR}{n^2}. \tag{2.52}$$

On the other hand, using the quantum rule for angular momentum L, obtained in 1912 on the basis of spectroscopic studies by J. W. Nicholson (1881–1955), and assuming circular orbits with $L_n = n\hbar$, Bohr obtained

$$r_n = \frac{n^2\hbar^2}{e^2 m}, \qquad E_n = -\frac{e^2}{2r_n} = -\frac{e^4 m}{2\hbar^2 n^2}, \tag{2.53}$$

which led him to the formula for the Rydberg constant R (with $e' = e_0 = -e$),

$$R = \frac{me^4}{2c\hbar^3}. \tag{2.54}$$

This result is in excellent agreement with the empirical value.

The quantum model of the atom proposed by Bohr in 1913 can thus be summarized in two postulates:

I. The atom has stationary orbits – that is, the electrons orbiting the nucleus do not radiate – corresponding to discrete values of energy $E_n = E_1/n^2$. Changes in the energy of the system can occur only at transitions between orbits.

II. The radiation absorbed or emitted by the atom during a transition between two stationary states of energy E' and E'' is monochromatic and its frequency ω is given by the formula (for $E' > E''$)

$$\hbar\omega = E' - E''. \tag{2.55}$$

Bohr chose a form of Postulate I that was consistent with Rydberg's formula for the H atom, and the result was surprising: the ionization energy, the radius of the atom, the frequencies of the emission lines, etc., were immediately correct.

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Armed with his theory, Bohr was able to draw a number of additional conclusions. For example, he deduced the existence of a series of lines in the infrared, corresponding to $n_1 = 3\,(n_2 = 4, 5, 6, \dots)$, predicted by Ritz and observed in 1908 by F. Paschen (1865–1947), and another one in the ultraviolet, corresponding to $n_1 = 1\,(n_2 = 2, 3, 4, \dots)$, observed the following year by T. Lyman (1874–1954). The series for $n_1 = 4$ and 5 were observed in 1922 and 1924, respectively. Furthermore, Bohr's theory found convincing experimental support with his own interpretation of a highly irregular series, discovered by E. Pickering (1846–1919) in the light of a star in 1896, as being due to He (see Section 12.6), and not to H, as was verified in the same year (1913).

Direct experimental confirmation of the existence of stationary and discrete atomic levels, as postulated by Bohr's theory, was provided by the famous work of J. Franck[22] and G. L. Hertz (1887–1975). By bombarding atoms (e.g., mercury vapor) with electrons, they found that as soon as the collision energy exceeded certain well-defined values, new emission lines appeared. The quantum interpretation of this phenomenon is straightforward: if the collisions between the electrons and the atoms in the vapor are energetic enough, they can induce transitions between levels, exciting the atoms; when an atom is de-excited, it emits the excess energy in the form of light. Using this method, it became possible to directly determine the atomic levels of many elements and verify the validity of Bohr's hypothesis.

Bohr's model enjoyed other great successes. One of the most important was Sommerfeld's[23] text *Atomic Structure and Spectral Lines* (1919), which was based on Bohr's theory and became the bible in its field until the advent of contemporary quantum theory. However, it also had major limitations, since it was based on a semiclassical theory developed specifically for the H atom, which does not allow for extension even to He. It also did not allow the intensity of the spectral lines to be determined. In short, it was clear that a new mechanics of atomic systems still had to be constructed, which would, of course, have to incorporate essentially the quantum aspect, while at the same time generalizing and explaining Bohr's postulates.

Another important shortcoming of Bohr's model is the following. The assumption of a stationary electron orbiting the nucleus contradicts electrodynamics, which shows that accelerated electric charges radiate and thus lose energy. Bohr *solved* the problem in a convenient way: he simply *postulated* that atomic electrons moving in closed orbits do not radiate, relying on the other apparent violations of electromagnetism known at the time. This is a historical problem that has haunted us for decades, the solution to which we will have the opportunity to discuss in Chapter 10 and elsewhere in this book.

[22] James Franck (1882–1964) was a German physicist, who shared the 1925 Nobel Prize in Physics with Gustav Hertz for the first electrical measurement that clearly showed the quantum nature of atoms.

[23] Arnold Johannes Wilhelm Sommerfeld (1868–1951) was a German physicist known for his pioneering work in quantum and atomic physics. He also served as a mentor to several scientists who excelled in their respective fields, including Pauli, Debye, Heisenberg, and Bethe. By his much sought-after high-quality physics textbooks, he alone could be considered a forerunner of Landau–Lifschitz.

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2.6 The Early Quantization Rules

The Bohr model contains only a single quantum number n, which labels the energies of the stationary states. It soon was realized that more quantum numbers needed to be introduced to give a more complete picture of atomic structure and spectra. The establishment of general quantization rules therefore became a central problem. Over time several rules were proposed, generally approximate but very useful, one of which will be briefly discussed here.

Consider a system of N particles whose dynamical behavior is described in classical mechanics by the $3N$ generalized coordinates $q_1, q_2, \ldots, q_{3N}$ and their $3N$ conjugate canonical momenta $p_1, p_2, \ldots, p_{3N}$. The laws of motion are Hamilton's equations,

$$\dot{q}_i = \frac{\partial H}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}, \tag{2.56}$$

where the Hamiltonian H of the system is the total energy expressed as a function of the variables q_i and p_i and time, when appropriate. For separable (i.e., integrable) systems with periodic motions, it is convenient to introduce the action variables J_i defined as

$$J_i = \oint p_i dq_i, \tag{2.57}$$

where the integration is carried out over a complete period (of oscillation or rotation, as the case may be); the generalized coordinate conjugate to J_i is the angle variable θ_i that satisfies the canonical equation

$$\nu_i \equiv \dot{\theta}_i = \frac{\partial H}{\partial J_i}, \tag{2.58}$$

where ν_i is the frequency associated with the periodicity of q_i. The variables J_i are also known as adiabatic invariants, because they are invariant to very slow (adiabatic) changes in the system parameters (lengths, electric charges, etc.).

The Bohr quantization postulate, in the form given to it by W. Wilson (1887–1948) in 1915 and Sommerfeld in 1916, known as the *Wilson–Sommerfeld rule*, consists in proposing that the numerical value of each of the adiabatic invariants is an integer multiple of Planck's constant:

$$J_i = hn_i = 2\pi\hbar n_i, \tag{2.59}$$

where the quantum number n_i can take any of the values $n_i = 1, 2, 3, \ldots$. The quantization postulate proposed by Bohr corresponds to the special case of the angular momentum of the orbital electron.

The Wilson–Sommerfeld quantization rule reproduces Bohr's formula (2.51), as shown in the following Exercise E2.2 for the case of circular orbits. Sommerfeld himself (1916) studied the more complicated case of elliptical orbits and, to his amazement, arrived at the same formula, showing that the energy depends only on the orbital quantum number n. This is a well-known example of *degeneracy of states*, the reason for which will be explained in detail in Section 12.5.

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Exercise E2.2. Applying the Wilson–Sommerfeld quantization rule
Use the Wilson–Sommerfeld quantization rule to obtain the emission spectrum of the hydrogen-like atom.

Solution. We consider a hydrogen-like atom with Z protons in its nucleus and a single orbital electron. We denote by m the reduced mass of the system and by e_0 the charge of the proton; in the polar coordinate system in the plane of the orbit, the Hamiltonian reads

$$H = \frac{p_r^2}{2m} + \frac{p_\phi^2}{2mr^2} - \frac{Ze_0^2}{r}. \tag{2.60}$$

Hamilton's equations can be written as two equations of motion for the radial and angular momenta, respectively,

$$\dot{p}_r = -\frac{\partial H}{\partial r} = \frac{p_\phi^2}{mr^3} - \frac{Ze_0^2}{r^2}, \quad \dot{p}_\phi = -\frac{\partial H}{\partial \phi} = 0, \tag{2.61}$$

and two relations between velocities and generalized momenta,

$$p_r = m\dot{r} = m\frac{\partial H}{\partial p_r}, \quad p_\phi = mr^2\dot{\phi} = mr^2\frac{\partial H}{\partial p_\phi}. \tag{2.62}$$

Integrating the second Eq. (2.61) gives the law of conservation of angular momentum, $p_\phi = mr^2\dot{\phi} = \text{const}$. We will limit ourselves to the case of circular orbits for the sake of simplicity. In this case $\dot{r} = 0$, so $p_r = 0$ and from the first Eq. (2.61) it follows that

$$p_\phi^2 = Ze_0^2 mr. \tag{2.63}$$

The Hamiltonian is thus reduced to

$$H = -\frac{Ze_0^2}{2r}. \tag{2.64}$$

All the preceding results are classical; to make contact with the quantization methods, we restate them in terms of the adiabatic invariants. Since there is only one periodic degree of freedom in the present problem, there is only one adiabatic invariant, which is

$$J_\phi = \oint p_\phi d\phi = 2\pi p_\phi. \tag{2.65}$$

We now express the radius of the orbit, the angular frequency and the energy (the numerical value of the Hamiltonian) in terms of J_ϕ,

$$r = J_\phi^2/4\pi^2 Zme_0^2; \tag{2.66}$$

$$\dot{\phi} = 8\pi^3 Z^2 me_0^4/J_\phi^3; \tag{2.67}$$

$$H = -2\pi^2 Z^2 me_0^4/J_\phi^2 \tag{2.68}$$

To quantize these classical results, we apply the Wilson–Sommerfeld rule,

$$J_\phi = 2\pi\hbar n, \quad n = 1, 2, 3, \ldots \tag{2.69}$$

With this we obtain for the energy levels of the atom

$$E_n = -\frac{Z^2 e_0^4 m}{2\hbar^2}\frac{1}{n^2} \tag{2.70}$$

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and for the corresponding atomic radius

$$r_n = \frac{\hbar^2}{Ze_0^2 m} n^2. \tag{2.71}$$

Finally, the emission spectrum of the atom is obtained by applying Bohr's Postulate II,

$$\omega_{nn'} = \frac{E_n - E_{n'}}{\hbar} = \frac{Z^2 e_0^4 m}{2\hbar^3} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right). \tag{2.72}$$

The model correctly predicts the quantization of the hydrogen-like atom and the value of the Rydberg constant, justifying the quantization procedure. This was the first successful quantum model of an atom, and its success helped to establish the notion of both the atomic disposition of matter and its quantum nature.

2.7 De Broglie: Waves Associated with Corpuscular Motion

In 1923–1924, de Broglie published a series of articles related to his doctoral work, in which he proposed to give serious consideration to a new quantum feature he had discovered, namely a wave phenomenon accompanying the motion of quantum particles. Reconciling the wave and particle descriptions of the behavior of light had been his aim from the beginning of his studies, but he went much further by introducing the concept of matter waves.

Leaving aside the details, de Broglie's idea was as follows. As explained in Section 2.3, the combination of the relativistic formula relating the energy of a photon to its momentum, $E = cp$, with Einstein's formula, $E = \hbar\omega$, results in Eq. (2.30), $\hbar\omega = cp$. Furthermore, for a wave traveling at the speed c the equation $c = \lambda\omega/2\pi$ holds, so that λ and p are related by $\lambda = 2\pi c/\omega = h/p$ (see Eq. (2.31)). De Broglie skillfully combined arguments drawn from optics and special relativity to identify the particle's velocity v with the group velocity of a modulated wave packet that supposedly accompanies the particle. He concluded that the wavelength of this phase wave is in general given by $\lambda = h/p$, that is, that this relationship holds for *all* quantum corpuscles, whatever their mass,

$$\lambda = \frac{h}{p}. \tag{2.73}$$

This is the essence of de Broglie's major and original contribution to our knowledge of the quantum world. For de Broglie, all quantum particles behave in a similar way to the photon, regardless of whether they have zero mass or not, which means that there is always a *wave* phenomenon of wavelength λ associated with the particle's linear momentum p. The physical nature of this phase wave was not specified by de Broglie and has been the subject of much controversy ever since, embodied in the seemingly paradoxical wave–particle dual behavior of quantum objects. We will have several opportunities to return to this important issue, and in particular in Chapter 10 we will discuss a way out of the controversy.

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Einstein reached a similar conclusion to de Broglie almost simultaneously, although he did so by a different route. This was based on an idea proposed to him by N. Bose.[24] Einstein began in 1925 to construct quantum statistics,[25] which he applied to the case of ideal gases, using his old method of energy fluctuations. Applied for simplicity to a gas of photons (considered as noninteracting molecules with zero chemical potential, of which there can be any number in any one state), the argument is basically as follows. The average energy of the gas at temperature $T = 1/k\beta$ is given by Eqs. (2.16) and (2.18),

$$\overline{E} = \frac{\sum_{n=0}^{\infty} nE_1 e^{-\beta E_1 n}}{\sum_{n=0}^{\infty} e^{-\beta E_1 n}} = \frac{E_1}{e^{\beta E_1} - 1}. \tag{2.74}$$

Further, it is a simple exercise to show that the mean square energy is given by (see also Exercise 15.44)

$$\overline{E^2} = \frac{\sum_{n=0}^{\infty} n^2 E_1^2 e^{-\beta E_1 n}}{\sum_{n=0}^{\infty} e^{-\beta E_1 n}} = \overline{E}(2\overline{E} + E_1). \tag{2.75}$$

Therefore, the dispersion (variance or mean square deviation) of the energy is given by

$$(\Delta E)^2 = \overline{E^2} - \overline{E}^2 = \overline{E}^2 + E_1\overline{E}. \tag{2.76}$$

The first term on the right is dominant at high temperatures, and can therefore be interpreted as classical or wave-like; the second term is proportional to the average number of energy packets $\bar{n}E_1$ and can therefore be considered as corpuscular in nature. The presence of the corpuscular term is natural because we are dealing with energy packets, but the wave term suggested to Einstein that the molecules of a quantum gas also manifest wave properties and that it should therefore be possible to observe, for example, interference phenomena in molecular beams. As predicted by Einstein, experiments conducted at the end of the twentieth century using *Bose–Einstein condensates* (bosons cooled to near absolute zero, which tend to concentrate in the ground state, giving rise to a highly correlated and coherent state) revealed the predicted interference between two small but macroscopic volumes of atoms, suitably prepared. Einstein further noted that he was aware of similar results, which linked a wave phenomenon to the motion of quantum corpuscles, that had been proposed "by a young French physicist."[26]

Armed with his ideas, de Broglie reinterpreted the Wilson–Sommerfeld quantization rule $J = \oint pdq = nh$ as the condition for the electronic orbit to fit precisely an integer number of wavelengths. He explained that this was the only stable solution by arguing that any other orbit that might initially exist would tend to disappear due to the destructive interferences produced by the superposition of waves with different phases. In other words, de Broglie identified the quantization postulate with the condition of stability of the orbit, thereby adding a new content to Bohr's ideas.

[24] Satyendra Nath Bose (1894–1974) was an Indian polymath, best known for his work in the early 1920s in developing the foundations of Bose–Einstein statistics for bosons and the theory of the Bose–Einstein condensate. Considering the frequent reference to bosons in the normal quantum literature, Bose's name is probably the most directly or indirectly cited in the physics literature, and although he was often proposed for the Nobel Prize, he did not receive it.

[25] The quantum statistics describing the behavior of fermions is called Fermi–Dirac statistics. Both quantum statistics have the same limiting classical statistics at high temperatures (see Chapter 15).

[26] Paul Langevin, who was to chair de Broglie's examination committee, had sent Einstein a copy of de Broglie's doctoral thesis, requesting his opinion.

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2.8 Electron Beam Diffraction

For de Broglie himself, the waves associated with corpuscular motion had a physical character; thus, in reply to J. Perrin[27] during his doctoral examination he stated that it should be possible to demonstrate the existence of such physical waves by an electron-diffraction experiment. Shortly afterwards, a series of electron diffraction experiments showed that there are indeed situations in which electrons behave in an analogous way to X-rays, with precisely the wavelength h/mv predicted by de Broglie's theory.

In 1927 C. J. Davisson,[28] together with L. Germer (1896–1971), observed – thanks to a lucky event correctly interpreted by Born's group – that a piece of nickel crystal produced electron scattering similar to that which would be obtained with X-rays. To reveal the wave properties of the electrons, their de Broglie wavelength must be of the order of the lattice constant of the crystal, i.e., $\lambda \sim 10^{-8}\mathrm{cm} = 1\,\text{Å}$, which is of the order of the wavelength of soft X-rays. Since, according to Eq. (2.77), the de Broglie wavelength is given by

$$\lambda = \frac{h}{mv} = \frac{h}{\sqrt{2meV}}, \tag{2.77}$$

where V is the accelerating voltage, this must be of the order of a few tens of volts, a sufficiently high value to guarantee an essentially monoenergetic beam, but low enough for the electrons to be scattered only by the surface layer of the crystal.[29]

An electron-diffraction device is shown schematically in Fig. 2.5. Assume that the electron beam is incident perpendicular to the crystal surface, so that it can be represented by a plane wave. The atoms on the crystal surface will scatter the electrons, and

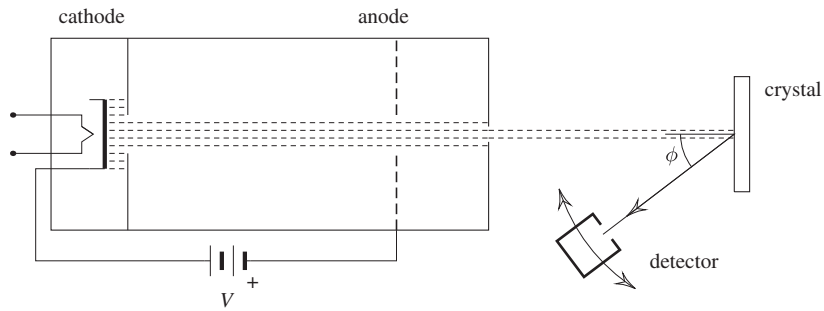


Figure 2.5 Diffraction of an electron beam by the surface of a crystal. A monoenergetic beam is emitted from the electron gun; the detector is placed at different angles ϕ to receive the scattered electrons.

[27] Jean Baptiste Perrin (1870–1942) was a French physicist who was awarded the Nobel Prize in Physics in 1926 for his experimental work on Brownian motion, which served to verify Einstein's theory of the phenomenon, confirming the atomic nature of matter (see Chapter 10).

[28] Clinton Joseph Davisson (1881–1958) was a US-born physicist who shared the 1937 Nobel Prize in Physics with G. P. Thomson for their discovery of electron diffraction.

[29] The Davisson-Germer experiment led to the analytical technique called low-energy electron diffraction, which is used to study crystal surfaces and the processes that take place on them. The electrons used have energies between 10 eV and 200 eV, corresponding to wavelengths of about 1 to 4 Å.

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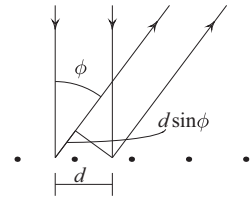


Figure 2.6 A collimated monoenergetic electron beam incident perpendicular to the crystal surface is scattered at different angles ϕ given by Eq. (2.78) with $n = 0, 1, 2, \ldots$ The most pronounced diffraction maximum is obtained for $n = 1$.

the accompanying wave at any point will be nonzero only in the directions in which there is constructive interference between the various components scattered to that point. As illustrated in Fig. 2.6, the condition for maximum constructive interference is that the optical path difference must be an integer multiple of the wavelength (von Laue, 1912),

$$d \sin \phi = n\lambda, \quad n = 0, 1, 2, \ldots, \tag{2.78}$$

where ϕ is the scattering angle. The wavelength obtained from the results of Davisson and Germer turned out to be in perfect agreement with that predicted by de Broglie's formula.

It is known that X-rays can be diffracted not only by single crystals, but also by polycrystals. G. P. Thomson[30] showed in 1927 that the same is true for electrons, by passing an electron beam with an energy of a few thousand eV through a very thin polycrystalline film whose crystals are randomly oriented. The analysis of the three-dimensional problem is quite complicated. However, it can be simplified by using the method proposed by W. L. Bragg,[31] which consists of considering the reflection of the beam from successive planes of atoms at equal distances d from each other. Maximum constructive interference occurs when the difference in optical paths between adjacent beams is an integer multiple of the wavelength, as shown in Fig. 2.7a. Therefore,

$$2d \sin \theta = n\lambda, \quad n = 0, 1, \ldots \tag{2.79}$$

where θ is the angle measured from the plane, determined by the orientation of the crystal, which varies randomly.

It is clear that among the multitude of crystals that make up the sample, there will be some oriented precisely in directions that satisfy Bragg's Law, producing luminous points on the screen (such as P in Fig. 2.7b). Since the orientation of the crystals is random, there will also be some whose orientation differs from that of the previous ones only by a rotation around the beam direction (i.e., the device has axial symmetry). These crystals form a diffraction ring, whose radius R can be calculated from the formula

$$\frac{R}{L} = \tan 2\theta, \tag{2.80}$$

[30] George Paget Thomson (1892–1975) was an English physicist, the son of J. J. Thomson. He shared the 1937 Nobel Prize in Physics with Davisson for his experiments on electron diffraction.
[31] William Lawrence Bragg (1890–1971) was a British physicist, who shared the 1915 Nobel Prize in Physics with his father William Henry Bragg for their analysis of crystal structure by means of X-rays.

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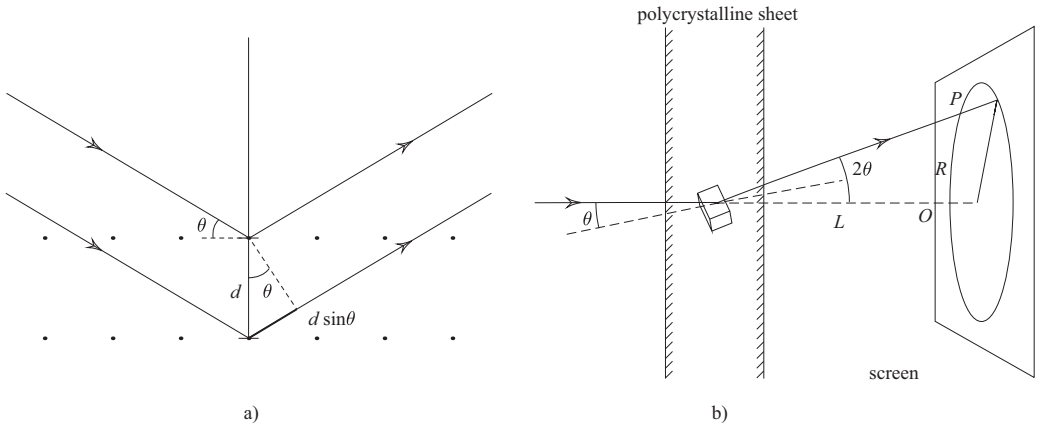


Figure 2.7 (a) Diagram of the reflection of a collimated monoenergetic electron beam by a three-dimensional lattice, leading to the Bragg equation (2.79). (b) Schematic of Thomson's electron diffraction experiment using a thin polycrystalline sheet. The orientation of the small crystals varies randomly, resulting in a circular diffraction pattern consisting of a series of concentric rings.

where L is the distance between the sample and the screen, as in Figure 2.7b. This equation was confirmed experimentally by Thomson using de Broglie's formula for the wavelength λ.

Davisson himself stated at a conference held in 1928:

> In the course of the last few years we have concluded that there are circumstances under which it is convenient, if not necessary, to regard electrons as waves rather than as particles, and we are making more and more use of terms such as diffraction, reflection, refraction and dispersion to describe their behavior.

Subsequently, it was shown experimentally that wave behavior is indeed shared by molecular beams of H or He (Estermann, Frisch and Stern, 1930–31), neutrons (Fermi and Marshall, 1947), and so on. Today it is accepted as a property associated with the motion of all corpuscles, as proposed by de Broglie, and is even used in the manufacture of various technological devices. For example, in electron or proton microscopes using electromagnetic lenses, the corpuscles are treated as a wave beam with a de Broglie wavelength much smaller than that of visible light and a resolution of the order of 10^3 times higher than that of conventional optical microscopes. An analogous principle is used in the construction of several other devices in modern electron optics.

The de Broglie wave is only important for particles on the atomic or subatomic scale, as its wavelength becomes negligible for macroscopic bodies. To get an idea of the scale involved, let us consider the case of the electron, which has a mass of about 9.1×10^{-28} g. If the electron moves at a speed of about one hundredth of the speed of light, the de Broglie wavelength is of the order of 10^{-8} cm, which is about the first Bohr orbit radius of H. In fact, we should expect that the wave properties of the corpuscles will manifest themselves only when the de Broglie wavelengths are comparable to the characteristic dimensions of the system. This helps us to understand why quantum phenomena remained hidden as long as physics was not directly concerned with the study of matter at the atomic or molecular scale.

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In the usual interpretation of QM, the corpuscular and wave properties of quantum objects have often been regarded as mutually exclusive. It is now difficult to maintain this position, since experiments (with photons) have been carried out which show that, by small changes in the experimental setup, both aspects of their behavior can be manifested simultaneously. The first of these experiments was carried out by Grangier, Roger, and Aspect (1985); a more recent one is described by Mizobuchi and Ohtaké (1992). Strictly speaking, in diffraction experiments one ultimately observes both the (statistical) interference patterns and the corpuscular structure of the individual spots.

2.9 Back to Planck: Completing the Spectral Law with the Zero-Point Field

In 1911, while searching for a well-founded quantum theory for the blackbody problem,[32] Planck discovered the need to add an extra contribution to his spectral energy distribution law, in the form of a zero-point term carrier of an energy

$$E_0 = \frac{1}{2}\hbar\omega \tag{2.81}$$

per mode of frequency ω. He found that the thermal field inside the blackbody was always accompanied by this nonthermal (i.e., *zero-point*) field, which meant that the reference level of the field energy had to be shifted by $\hbar\omega/2$. Therefore, the average energy per normal mode given by Eq. (2.29) should be completed with Eq. (2.81),

$$\overline{E} = \frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1}, \tag{2.82}$$

Planck's complete blackbody radiation formula reads

$$\rho(\omega, T) = \frac{\hbar\omega^3}{\pi^2 c^3}\left(\frac{1}{2} + \frac{1}{e^{\hbar\omega/kT} - 1}\right) \tag{2.83}$$

instead of (2.22). The first term,

$$\rho_0(\omega) = \frac{\hbar\omega^3}{2\pi^2 c^3}, \tag{2.84}$$

is the spectral energy density of the added ZPF, which is the product of the energy of the mode and the density of modes (see Section 10.2),

$$\rho_0(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \cdot \frac{1}{2}\hbar\omega. \tag{2.85}$$

Although Planck's theory was not to become generally accepted, the associated hypothesis of zero-point energy remained alive. In particular, it was vigorously defended by Nernst (1916), who argued that if radiation and matter are in statistical equilibrium with each other, then their respective mean energies must be described

[32] The most significant challenge for Planck arose from his prolonged rejection of the necessity for field quantization. It was Einstein who first proposed a correct and convincing derivation of the Planck distribution.

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by the same law (i.e., a *single* law), namely by Planck's complete radiation law, which includes the zero-point term. Nernst regarded the ZPF as a fluctuating electromagnetic field of unknown origin, present everywhere and at all times. He postulated that interaction with this field was the mechanism responsible for atomic stability and the source of the quantum behavior of matter.

Nernst's proposal seems to have been well known in Germany, yet it did not enter the mainstream of physics at the time. With the advent of quantum formalism in 1925 the concept of ZPE – albeit of the mechanical oscillators – became necessary, as it is identified with their ground-state energy. It is commonly seen, both in textbooks and research papers, as a direct consequence of Heisenberg's uncertainty principle. But we can look at it the other way round: the Heisenberg uncertainty principle as a *consequence* of the ZPE, not as a principle in itself (see what follows).

The ZPE is not exclusive to the blackbody radiation; as we will see later (see in particular Chapters 9 and 17), QM has taught us that the minimum energy (the *ground-state energy*) of *any* harmonic oscillator of frequency ω is indeed $\hbar\omega/2$. More generally, current quantum field theory endows space with several "virtual" zero-point fields, including the electromagnetic (quantum) vacuum fluctuations. However, for Planck – and for Nernst – the ZPE was associated with the ground state of a *real* Maxwellian electromagnetic radiation field. Planck's (original) blackbody formula contains the thermal part of the radiation, that which is exchanged in the form of well-defined energy packets (photons) during atomic and molecular transitions. The nonthermal part does not participate in the (photonic) energy exchange, it constitutes the invisible (or dark) part of the radiation field. But its presence certainly has physical consequences, as is to be expected and as is shown throughout this text.

Exercise E2.3. Energy density of the zero-point field

Calculate the energy density of the ZPF contained in a large cavity surrounded by conducting walls, assuming a cutoff frequency ω_C.

Solution. Consider a rectangular cavity with dimensions $L_1 \times L_2 \times L_3 = V$. For the tangential component of the electric field on the conducting surfaces to vanish, the field modes contained in the cavity must be

$$u_x = A_1 \cos k_1 x \sin k_2 y \sin k_3 z,$$
$$u_y = A_2 \sin k_1 x \cos k_2 y \sin k_3 z,$$

and

$$u_z = A_3 \sin k_1 x \sin k_2 y \cos k_3 z, \tag{2.86}$$

where $k_i = n_i \pi / L_i$ and n_i $(i = 1, 2, 3)$ are nonnegative integers with at least two of them nonzero. The frequency of the mode is $\omega_k = c(k_1^2 + k_2^2 + k_3^2)^{1/2}$. The condition $\nabla \cdot \boldsymbol{E} = 0$ implies $\sum A_i k_i = 0$, which confirms that there are two independent polarizations for each wavenumber $\boldsymbol{k}$, except when one of the integers n_i is zero.

When the cavity is large, the allowed values of $\boldsymbol{k}$ can be considered to form a continuum and the density of modes in the positive $\boldsymbol{k}$-space is $2V/\pi^3$. The total energy density of the ZPF modes of frequency $\omega < \omega_C$ is therefore given by the integral over the full $\boldsymbol{k}$-sphere divided by 8,

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$$\frac{2}{V}\sum_{\boldsymbol{k}}\frac{1}{2}\hbar\omega_k \rightarrow \frac{2}{8\pi^3c^3}\int_0^{\omega_C}\frac{1}{2}\hbar\omega\, 4\pi\omega^2 d\omega = \frac{\hbar\omega_C^4}{8\pi^2c^3}. \tag{2.87}$$

It is clear that the energy density is dominated by the high-frequency modes. Taking a minimum wavelength of $\lambda_C = 0.4 \times 10^{-6}\,\mathrm{m}$, so as to include the visible light, we get an energy density of $23\,\mathrm{J/m^3}$, which is 10^9 times that of a 100 W light bulb at a distance of one meter (Ballentine 2010, ch. 19). In Chapter 10 we return to the issue of the (in principle) infinite energy content of the ZPF, and discuss the Casimir effect as a result of the change in energy content due to the presence of material bodies.

2.9.1 Stochastic electrodynamics

Stochastic electrodynamics is the theory developed by taking the ZPF at face value, as a real fluctuating Maxwellian field that pervades the whole space the whole time. Some back-of-the-envelope calculations show that the properties of the stochastic motions impressed on the electrons by the ZPF are fully consistent with quantum fluctuations. In particular, Heisenberg's inequality is readily obtained by taking into account that the energy of an oscillator is limited from below by the ZPE, and by using the virial theorem to calculate the dispersions of p and x (for details see Chapter 8), to get

$$\frac{\langle(\Delta p)^2\rangle}{2m} = \frac{m\omega^2\langle(\Delta x)^2\rangle}{2} \geq \frac{\hbar\omega}{4}, \tag{2.88}$$

whence $\Delta p\Delta x \geq \hbar/2$, with $\Delta x = \langle(\Delta x)^2\rangle^{1/2}$ and similarly for p. This is a simple version of Heisenberg's inequality, albeit without any mystery. In Chapter 10 and elsewhere in the book, it will be shown that the constant interaction of the particle with the ZPF has indeed far-reaching consequences, in that it provides a physical basis for quantum formalism, both in the Schrödinger and in the Heisenberg descriptions. Moreover, as will be shown in Chapter 17, inclusion of the ZPF *ab initio* – as an irremovable integral component of the matter-field system – allows us to go beyond QM and make contact with the more complete theory of (nonrelativistic) *quantum electrodynamics* (QED), without the need to introduce additional elements or ad hoc assumptions.

2.10 Corollary: The Electrodynamic Essence of Quantum Mechanics

It should be clear by now that atomic matter does not live in isolation, but is in constant contact with electromagnetic radiation, among other possible vacuum fields – although the net effects of those other fields appear to be negligible compared to the electromagnetic one for the purposes of usual QM. As we have seen throughout this chapter, the development of QM has been marked from the beginning by numerous demonstrations of this contact and its decisive influence on both matter and field. In fact, what is generally called "quantum mechanics" is not just a mechanical theory; it is the *quantum theory of matter in its interaction with the radiation field*, even if the latter is

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not usually made explicit. Although this book focuses primarily on the quantum behavior of *matter*, in due course we will approach the study of the matter-field system from an integrated perspective in order to provide a more comprehensive understanding of quantum phenomena.

Problems

P2.1 Obtain the limit expressions of the Planck distribution for small and large frequencies, at a fixed temperature. What is the form of the function $f(\omega/T)$ that appears in Wien's law (2.20) for high frequencies, and why is it not possible to determine it classically? Discuss your results.

P2.2 Show that Planck's law predicts that the spectral density of blackbody radiation has a maximum for each temperature, which occurs at the wavelength

$$\lambda_n = \frac{2\pi c\hbar}{4.965}\frac{1}{k_B T}. \tag{2.89}$$

Calculate ν_m and explain why $\nu_n \neq c/\lambda_n$. This formula – known as *Wien's displacement law* – shows that as the temperature of the blackbody rises, the maximum intensity of the radiation shifts toward shorter wavelengths.

P2.3 Construct a graph of the average energy of the Planck oscillators versus frequency and use it to show that Planck's postulate, $E_n = n\hbar\omega$, introduces a cutoff in frequency space. Find this cutoff frequency. This result shows that the postulate prevents arbitrarily high frequency modes from being excited at a given temperature, in agreement with experimental observations.

P2.4 Calculate the energy of a quantum of visible light of wavelength 6000Å. Calculate the number of quanta of this wavelength that are emitted per second by a 10-watt light source.

P2.5 Taking the Sun as a blackbody at 5700 K, find the fraction of its mass that it emits as electromagnetic radiation per year.

P2.6 Ultraviolet light of wavelength 3500Å is incident on a potassium surface. The maximum energy of the emitted photoelectrons is observed to be 1.6 eV. Calculate the work function of potassium, neglecting thermal corrections.

P2.7 A 100 MeV photon collides with an electron at rest and is scattered at 45° from the direction of incidence. Calculate the energy of each particle after the collision and determine the final direction of the electron.

P2.8 Assuming that the relevant classical laws apply, calculate the power emitted by an electron moving in a circular Bohr orbit characterized by the quantum number n.

P2.9 Deuterium is an isotope of hydrogen whose nucleus consists of a tightly bound proton and neutron, with atomic weight 2 (the masses of the proton and neutron are nearly equal). Determine: (a) the Rydberg constant for deuterium in terms of that for hydrogen; (b) the ratio of the wavelengths of the deuterium spectrum to those of the corresponding hydrogen transitions.

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P2.10 Use the Wilson–Sommerfeld quantization rule to determine the emission spectrum of a particle moving in the potential

$$V(r) = V_0 \left(\frac{r}{a}\right)^k, \tag{2.90}$$

with $k \gg 1$, assuming that it is possible to restrict oneself to the study of circular orbits.[33] Draw a representative graph of this potential, and compare your results with those of 2.22.

P2.11 Calculate the de Broglie wavelength of a point particle moving at speed $c/100$, in the following cases:

(a) an electron ($m_e = 9.1 \times 10^{-28}$ g),
(b) a proton (m_p =1 836.1 m_e),
(c) a pebble ($m = 10$ g),
(d) the Earth ($M_T = 6 \times 10^{27}$ g).

Compare your results with the wavelength of yellow light and with the radius of the first Bohr orbit ($a = 0.529 \times 10^{-8}$ cm).

P2.12 Find the expression for the orbital speed of the electron of a hydrogen atom that is in its lowest energy state using the Bohr model. Since this state is stationary, it can be described by an ensemble of H atoms in their ground state. Use this observation to determine the wavelength associated with the corresponding orbital velocity, and compare it with the circumference of the orbit. Discuss the result.

P2.13 In traditional optics, an optical instrument cannot resolve details of an object smaller than the wavelength used for observation. For example, a virus 200 Å in diameter cannot be studied with an instrument that uses visible light in the region of thousands of angstroms. An electron microscope, however, makes it possible. Determine the acceleration potential required to obtain electrons with a de Broglie wavelength $10^2 - 10^3$ times smaller than the dimensions of the virus.

P2.14 Determine the wavelength of a beam of neutrons which undergoes first-order diffraction by a crystal. The beam is incident at an angle of 40^0 with respect to the set of planes of the crystal lattice, whose spacing is 2.85 Å. What is the kinetic energy of the incident neutrons?

P2.15 A technique for monochromatizing[34] a beam of slow neutrons consists of directing the entire beam toward a crystal of known structure and positioning the collector to receive the monochromatic beam of diffracted neutrons. Suppose that a crystal is used whose distance between successive layers is 1.2 Å. Considering only Bragg diffraction of order 1, at what angle with respect to

[33] Bertrand's theorem (1873) of classical mechanics establishes that the only central forces that can give rise to bounded orbits, *all* of them closed for classical problems, are those proportional to r (Hooke's law) or to r^{-2} (law of gravitation). Therefore, for arbitrary k in the corresponding classical problem, the orbits are generically open and it is artificial to apply the quantization rules. However, all of these central problems do have *circular* orbits; see José and Saletan (1998).

[34] By analogy with optics, the term monochromatic is used to refer to a beam whose particles all have the same de Broglie wavelength (if all the particles have the same mass, the beam is both monoenergetic and monochromatic).

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the initial direction of the beam should the collector be oriented to select the neutrons with $\lambda = 0.8$ Å?

P2.16 Compare the zero-point energy of a radiation field mode of wavelength 6000Å, with the average thermal energy of the same field mode at room temperature.

P2.17 An electron in an antenna is subject to oscillations at a frequency $\nu = 10^{15}$ Hz. Calculate the mean amplitude Δx of the oscillations at zero temperature and at room temperature.

Bibliographical Notes

Planck's seminal work on blackbody radiation: Planck (1901).

On Hamiltonian mechanics, see, e.g., Landau and Lifshitz (1976) section 49, José and Saletan (1998) section 6.4, or Goldstein et al. (2011).

Weinberger (2006) revisits de Broglie's crucial contribution to the birth of QM.

Stone (2015) reveals the significance of Einstein's major contributions to quantum theory.

Planck introduced the ZPF in his second radiation theory by means of the concept of zero-point energy (Planck 1911, 1912, 1913). Most of Planck's articles on radiation and quantum theory are conveniently collected in Planck (1958).

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