

Chapter 1

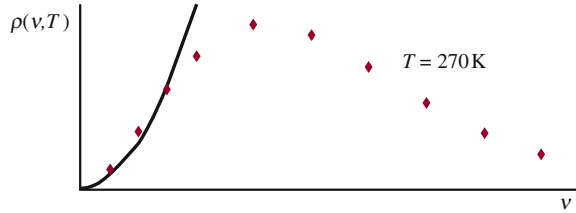
The Origin of Quantum Concepts

At the end of the nineteenth century, just when the classical theories had blossomed into beautiful and elegant formulations, new challenges troubled the scientific community. The spectroscopic methods applied to analyze the atomic and the blackbody radiations, accumulated evidences that could not be explained with the existing theories. The electromagnetic theory, that reached its summit with the Maxwell equations, at the time recognized the ether as the medium of wave propagation, even though the Michelson-Morley experiment denied it. With the discovery of electrons, in 1897, the interest in understanding the atomic structure grew up steadily to become soon a true challenge for experimental and theoretical physicists. These and other problems, underpinned a period of crisis and prolific creativity. Max Planck and Albert Einstein, are emblematic symbols of two new theories of the modern physics that grew out of the crisis: the quantum physics and the relativity theory. Both theories undermined the classical physics and introduced new concepts that not only changed physics but also pervaded and gave shape to the modern culture, dominated by the communications industry and the optoelectronic devices.

To understand the formalism of quantum physics this book deals with, it is instructive to review some major problems that spurred the crisis and the fundamental ideas and concepts that were used to explain them. In this and the following chapter, we will briefly discuss some of these problems. The order of the presentation will not necessarily be in chronological order.

One of the problems that revealed the need of fundamental changes in the classical theories, and the first whose explanation opened the wide world of the quantum physics, was the problem of the *blackbody radiation*. All bodies emit and absorb radiation, and the intensity and frequency distribution of this radiation depends on the body and its temperature. Before Max Planck put forward his theory, the low frequency description of the spectral density was quite satisfactory, but for high frequencies (see Fig. 1.1), it was completely wrong. Max Planck found the correct spectral density assuming oscillators in the walls of the blackbody cavities that could only absorb or emit multiples of discrete amounts of energy.

Fig. 1.1 The experimental behavior of the blackbody radiation density, as a function of the frequency ν . The continuous curve, for low frequencies, represents the classical theories description



Another problem that required a new approach, was the *photoelectric effect*, observed when light struck on a metal and is followed by electrons coming out of the metal surface. Prior to the explanation given by Albert Einstein to this problem, it was not clear why the emitted electrons energy depend on the light frequency ν instead of its intensity. Moreover, it was not clear why the electron emission ceased when the light frequency was lower than some critical value ν_c , which depended on the specific metal.

The discovery of the electron by Joseph J. Thompson, in 1897, opened up the atomic structure problem. This problem, and the explanation of the atomic emission lines, remained open for some years. It was clear that, if the electron (the negative electric charge) was part of a neutral atom, one had to admit the existence of positive charges. The problem was, how and where to put, in a stationary configuration, the positive and the negative charges together, and how can one then relate the electronic configuration with the emission lines.

An effect, that appeared some years later, whose explanation was fundamental to the understanding of the quantum phenomenology, was the *Compton effect*. In the Compton effect the light scattered by particles changes its color (i.e. changes its frequency), and the change is a function of the scattering angle, as shown in Fig. 1.4. The explanation of this effect corroborated the quantization concepts as well as some results of the special theory of relativity.

In the following sections we discuss these problems with more detail.

1.1 Blackbody Radiation

All bodies absorb and emit radiation with frequencies that cover the whole spectrum, with intensity distribution that depends on the body itself and its temperature. The problem of the intensity and the color of the radiated light was stated by Kirchhoff in 1859. This problem was also of interest to the electric companies interested in producing light bulbs with maximum efficiency. At the end of the nineteenth century, there were precise measurements of the emitted and absorbed radiation, but without a theoretical explanation. The isolation of the emitting body from other emission sources was an important requirement. One way to achieve this was, for example, to consider a closed box with the inner faces as the emitting surfaces. To observe the

radiation inside the box, one makes a small hole. The radiation that comes out from the hole is called the blackbody radiation. Some properties and important results about this radiation were known at the end of the nineteenth century. Among these properties, it was known that the radiation energy density could be obtained from the empirical formula

$$u = \sigma T^4, \quad \text{with } \sigma = 7.56 \times 10^{-16} \frac{J K^{-4}}{m^3}. \quad (1.1)$$

Since the energy density can be obtained when the spectral density, $\rho(\omega, T)$, per unit volume and unit frequency is known, it was clear that one had, first, to derive the frequency distribution of the radiation field.

By the end of the nineteenth century, it was usual to assume that the existing physical theories were perfectly competent to explain any experimental result, and could also be used to account for the observed results and to deduce (starting from the implicit first principles) the empirical formulas. It was then reasonable to expect that the radiation density (1.1) and the spectral density $\rho(\omega, T)$, whose behavior was as shown in Fig. 1.1, could be accounted for after an appropriate analysis. However, all theoretical attempts to obtain the spectral density $\rho(\omega, T)$ failed, even though the reasoning lines, as will be seen here, were correct. The failures had a different but subtle cause.

As mentioned before, if the spectral density $\rho(\omega, T)$ would be known, the product

$$du = \rho(\omega, T)d\omega = \rho_v(\nu, T)d\nu,$$

integrated over the whole domain of frequencies, should give the energy density sought. In other words, given the spectral density $\rho(\omega, T)$, the energy density would be

$$u = \int_0^\infty \rho(\omega, T)d\omega = \int_0^\infty \rho_v(\nu, T)d\nu = \sigma T^4. \quad (1.2)$$

Therefore, the aim was to determine $\rho(\omega, T)$. The theoretical attempts led to a number of basic results and properties. Some of them useful and valid, others not. Let us now mention three of them: the Wien displacement law, as a general condition on the function $\rho(\omega, T)$, and two results that make evident the nature of the problem and the solution offered by Max Planck.

- (i) *Wien's displacement law*, refers to the displacement of the maximum of $\rho_v(\nu, T)$ with the temperature, i.e. the change of color of the emitted radiation as the body is heated up or cooled down. This phenomenon implies a necessary condition on the spectral density $\rho_v(\nu, T)$. To obtain the empirical law (1.1), the spectral density should be a function like

$$\rho_v(\nu, T) = \nu^3 f(\nu/T), \quad (1.3)$$

with $f(\nu/T)$ a function to be determined. It is easy to verify that a spectral density like this will certainly produce a result that goes as T^4 .

- (ii) An important result, that was shown experimentally, was the independence of the blackbody radiation from the specific material of the emitting walls. Taking into account this result, it was clear that one could model the radiating walls as if they were made up of independent harmonic oscillators. If each oscillator has a characteristic oscillation frequency ν , and the characteristic frequencies have a distribution function $\rho_\nu(\nu)$, one will obtain, using the classical physics laws, the average oscillator energy (per degree of freedom¹).

$$\bar{E} = \frac{\pi^2 c^3}{\omega^2} \rho(\omega) = \frac{c^3}{8\pi \nu^2} \rho_\nu(\nu). \quad (1.4)$$

- (iii) On the other hand, from the classical statistical physics it was known that the average energy per degree of freedom in thermal equilibrium at temperature T , is given by

$$\bar{E} = \frac{1}{2} k_B T, \quad (1.5)$$

with k_B the Boltzmann constant.²

Combining these results, and taking into account that waves polarize in two perpendicular planes, the classical physics analysis led to the spectral density

$$\rho_\nu(\nu, T) = \frac{8\pi \nu^2}{c^3} k_B T, \quad (1.6)$$

known as the Rayleigh-Jeans formula. This expression fulfills the Wien law when

$$f(\nu/T) = \frac{8\pi k_B}{c^3} \frac{1}{\nu/T}, \quad (1.7)$$

and predicts a spectral distribution that grows quadratically with the frequency ν . As can be seen in Fig. 1.1, the Rayleigh-Jeans formula plotted as a continuous curve, describes well the experimental curve only in the low frequency region.³ Although the Rayleigh-Jeans distribution is compatible with the Wien displacement law, it diverges in the high frequency region. Thus, the integral (1.2) also diverges. This behavior was known as the “ultraviolet catastrophe”.⁴

¹ For derivations of the average energy and some other important expressions, see *Lectures on Physics* by Richard P. Feynman, Robert Leighton and Matthew Sands (Addison-Wesley, 1964) and *Introducción a la mecánica cuántica* by L. de la Peña (Fondo de Cultura Económica and UNAM, México, 1991).

² $k_B = 1.38065810^{-23} \text{ J/K}^{-1}$.

³ J. W. S. Rayleigh, *Philosophical Magazine*, series 5, 49 (301): 539 (1900); J. H. Jeans, *Phil. Trans. R. Soc. A*, **196** 274: 397 (1901).

⁴ Apparently this term was coined by Paul Ehrenfest, some years later.

In the twilight of the nineteenth century, on December 14th of 1900, Max Planck presented to the German Society of Physics and published in the *Annalen der Physik*,⁵ the first unconventional solution to this problem. To explain the blackbody spectrum, Planck introduced the formal assumption that the electromagnetic energy could be absorbed and emitted only in a quantized form. He found that he could account for the observed spectra, and could prevent the divergence of the energy density, if the oscillators in the walls of the radiating and absorbing cavity, oscillating with a frequency ν , lose or gain energy in multiples of a characteristic energy E_ν , called a quantum of energy.

If the energy that is absorbed or emitted by an oscillator with frequency ν , is

$$E = nE_\nu \quad n = 1, 2, 3, \dots, \quad (1.8)$$

a multiple of a characteristic energy E_ν , the probability of finding the oscillator in a state of energy E , which in the continuous energy description is given by the Boltzmann distribution function

$$p(E, T) = \frac{e^{-E/k_B T}}{\int e^{-E/k_B T} dE}, \quad (1.9)$$

will change to

$$p(E_\nu, T) = \frac{e^{-nE_\nu/k_B T}}{\sum_n e^{-nE_\nu/k_B T}}. \quad (1.10)$$

With energy discretization the integrals have to be replaced by sums. This seemingly inconsequential change, was at the end a fundamental one. With a discretized distribution function the average energy becomes

$$\bar{E} = \frac{\sum_n nE_\nu e^{-nE_\nu/k_B T}}{\sum_n e^{-nE_\nu/k_B T}}. \quad (1.11)$$

It is not difficult to see that the sums in the numerator and denominator can easily be evaluated. Indeed if we remember that

$$\frac{1}{1-x} = 1 + x + x^2 + \dots = \sum_{n=0}^{\infty} x^n, \quad (1.12)$$

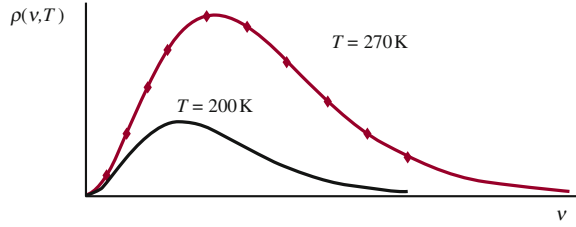
for absolute value of x less than 1, and also that

$$\frac{d}{dx} \sum_{n=0}^{\infty} x^n = \frac{1}{x} \sum_{n=0}^{\infty} nx^n = \frac{1}{(1-x)^2}, \quad (1.13)$$

we can show that the energy average is given by

⁵ M. Planck, *Ann. Phys.*, **4**, 553 (1901).

Fig. 1.2 The experimental spectral distribution and the Planck distribution for different temperatures. The description is perfect from low to high frequencies



$$\bar{E} = \frac{E_\nu}{e^{E_\nu/k_B T} - 1}. \quad (1.14)$$

Using $e^x \simeq 1 + x$ for small x , this expression reduces to $k_B T$ in the high temperatures limit. Combining with the average energy of equation (1.4), we have

$$\rho_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{E_\nu}{e^{E_\nu/k_B T} - 1}. \quad (1.15)$$

For this distribution to satisfy the Wien displacement law, the characteristic energy E_ν , the minimum energy, absorbed or emitted, must be proportional to the frequency ν . Writing the characteristic energy as

$$E_\nu = h\nu, \quad (1.16)$$

with h the famous *Planck constant*,⁶ Max Planck found the spectral density

$$\rho_\nu(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/k_B T} - 1}, \quad (1.17)$$

that is known as *the Planck spectral density*. This density describes the experimental results all the way from the low to the high frequencies (see Fig. 1.2). It is easy to verify that at high temperatures, for which $k_B T \gg h\nu$, the Planck spectral density reduces to the spectral density of Rayleigh and Jeans.

An important test for the Planck spectral density is the calculation of the energy density of the radiation field. Using Planck's spectral density, we have

$$u = \frac{8\pi h}{c^3} \int_0^\infty \frac{\nu^3 d\nu}{e^{h\nu/k_B T} - 1} = \frac{8\pi k_B^4}{c^3 h^3} T^4 \int_0^\infty \frac{x^3 dx}{e^x - 1}, \quad (1.18)$$

where $x = h\nu/k_B T$. As the integral on the right-hand side of (1.18) is a finite number (in fact equal to $\pi^4/15$), this energy has not only the correct temperature dependence, it can be used, based on the empirical energy density of (1.1), to obtain the Planck constant

⁶ This is one of the fundamental constants in physics and of the laws of nature.

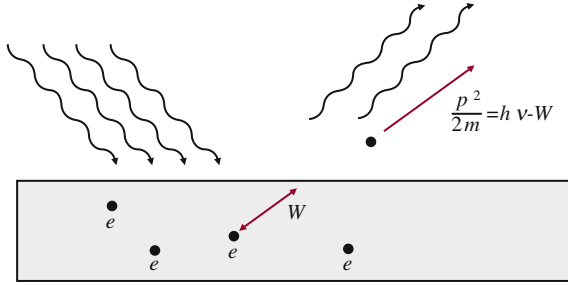


Fig. 1.3 The photoelectric effect. When an electromagnetic radiation, with energy $h\nu$, strikes a metal surface, the electrons absorb the whole energy and pay part for releasing the electrons from the metal (known as the work function W) to become free particles. The remaining energy $h\nu - W$, if some is left, transforms into the electron's kinetic energy $p^2/2m$

$$h = 6.6260755 \times 10^{-34} \text{Js} = 4.1356692 \times 10^{-15} \text{eVs}.$$

It is common to express $h\nu$ as $\hbar\omega$ with $\hbar = h/2\pi = 1.054572 \times 10^{-34} \text{Js}$ and $\omega = 2\pi\nu$. Note that the units of h are energy \times time. It is not difficult to show that the very small magnitude of h hides the quantum phenomena. Indeed, if the frequencies of oscillations were, say of the order of 10 Hz, the absorbed or emitted energies would be, as mentioned earlier, multiples of $h\nu \approx 10^{-32} \text{J}$; a very small amount of energy. We can then ask if changes of this magnitude can be observed or not in the macroscopic physical systems. To answer this question let us suppose that we have a classical oscillator, which is a particle of mass $m = 1 \text{g}$ attached to a spring of constant $k = 10 \text{N/m}$. If the particle's oscillations amplitude is, say $x_o = 1 \text{cm}$, its energy and oscillations frequency would be, respectively, of the order of $E \simeq 5 \times 10^{-4} \text{J}$ and $\nu \simeq 10 \text{Hz}$. Furthermore, if the precision measuring the energy is, say $\Delta E \simeq 10^{-6} E$, the number of *quanta* of energy contained in ΔE would be $n = \Delta E/h\nu$, of the order of 10^{22} ; a very large number! Hence, the contribution of one quantum of energy is rather negligible. We will see later that the number of quanta will be considerably less, of the order of one, when the energies and particles are of atomic dimensions (Figs. 1.3, 1.4).

1.2 The Photoelectric Effect

In 1887, Heinrich Hertz noticed that when a metal surface was illuminated with UV light, electrons were ejected from the surface - provided the light's frequency was above a certain, metal-dependent, threshold ν_c . The main properties related with these phenomena are:

- (i) *the speed of the ejected electrons depends only on the frequency of the incident light;*

- (ii) *the number of emitted electrons depends on the intensity of the incident radiation;*
- (iii) *for each metal there is a frequency ν_c , called the critical frequency, below which no photoelectric phenomenon is observed.*

In 1902 Philipp Lenard noticed that “the usual conception that the light energy is continuously distributed over the space through which it spreads, encounters serious difficulties when trying to explain the photoelectric phenomenon”.⁷ In 1905 applying Planck’s idea of quantization of the absorbed and emitted radiation energy, Albert Einstein was able to explain the photoelectric effect by assuming a “corpuscular” nature for the quanta of light, i.e. a dual nature where a wave and a particle property coexist, and are part of the fundamental characteristics of the same object.

If the quantum of radiation, the light corpuscle, has an energy $h\nu$, and this energy is transmitted to an electron in the corpuscle-electron interaction, part of the energy is used to expel the electron from the metal⁸ and the remaining is transformed into its kinetic energy. This means that:

$$\frac{1}{2}m_e v^2 = h\nu - W. \quad (1.19)$$

When the frequency ν of the incident radiation is such that $h\nu$ coincides with W , the kinetic energy is zero, but when $h\nu < W$ the electron will not be able to get out of the metal. Thus $h\nu = W$ is a particular condition that defines the critical frequency $\nu_c = W/h$. Each metal has its own critical frequency. When $\nu \geq \nu_c$, each photon, absorbed in the electron-photon interaction, makes possible the release of one free electron, the number of free electrons depends then on the number of the photons, i.e. on the radiation intensity. In this way, all three characteristics of the photoelectric effect got a rather simple explanation.

Furthermore, according to the special theory of relativity, a massless particle, like the radiation field corpuscle,⁹ has the linear momentum

$$p = \frac{E_\nu}{c} = \frac{h\nu}{c}. \quad (1.20)$$

Since the wave velocity c is equal to the product $\nu\lambda$, where λ is the wave length, we can write this relation as

$$p = \frac{h}{\lambda} = \hbar k, \quad (1.21)$$

where $k = 2\pi/\lambda = w/c$ is the wavenumber. Since both, p and k , are vector quantities we must write in general as

⁷ In A. Einstein, *Ann. Phys.* **17**,132 (1905).

⁸ This is known as the work function W , and it is related to the electron’s binding energy.

⁹ In the especial theory of relativity we have the relation $E^2 = p^2 c^2 + (m_o c^2)^2$ between energy E , momentum p and the rest energy $m_o c^2$. It is clear that for $m_o = 0$, we are left with $E = pc$. If m is the mass of the particle when it is moving and $E = mc^2$, the rest mass m_o and the moving particle mass m are related by $m^2(1 - v^2/c^2) = m_o^2$.

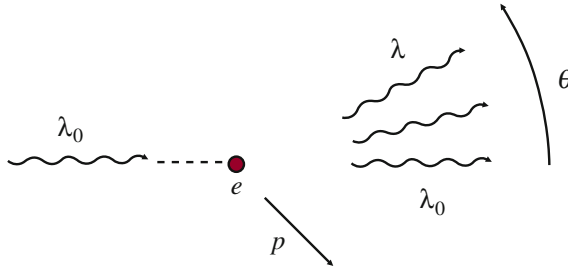


Fig. 1.4 The Compton effect. The change of the scattered radiation wave length $\Delta\lambda = \lambda - \lambda_0$ (or change of frequency $\Delta\omega = \omega - \omega_0$), depends on the scattering angle θ . This effect can be explained when the radiation-electron interaction is modeled as a collision of particles

$$\mathbf{p} = \hbar\mathbf{k}. \quad (1.22)$$

This is a very important and recurrent relation in quantum theory, and will be useful to explain the Compton effect, that we will discuss now, and to derive the Schrödinger equation later.

1.3 The Compton Effect

In 1923, A. H. Compton noticed that the wavelength of X-rays scattered by electrons in graphite increases as a function of the scattering angle θ . It turns out that these phenomena can be understood by making use of the dual particle-wave nature for the quantum particles involved in this process, together with the basic relations of the special theory of relativity, that was already well established in those years. Indeed, when the electron-photon interaction is analyzed as a collision of two particles, the conservation laws of energy and momentum lead to

$$\hbar\omega_0 + E_0 = \hbar\omega + E, \quad (1.23)$$

and

$$\hbar\mathbf{k}_0 + \mathbf{p}_0 = \hbar\mathbf{k} + \mathbf{p}. \quad (1.24)$$

Here $E_0 = m_0c^2$, $E = mc^2 = m_0c^2/\sqrt{1 - v^2/c^2}$, $\mathbf{p}_0 = 0$ and $\mathbf{p} = m\mathbf{v}$ are the electron energies and momenta, before and after the collision, respectively. Taking the squares of these equations, written as

$$m^2c^4 = m_0^2c^4 + 2m_0c^2\hbar(\omega_0 - \omega) + \hbar^2(\omega_0 - \omega)^2 \quad (1.25)$$

and

$$\hbar^2(k^2 + k_0^2 - 2kk_0 \cos \theta) = m^2v^2, \quad (1.26)$$

and using the relations $k = \omega/c$, $k_0 = \omega_0/c$ and $m^2c^4 = m_0^2c^4 + m^2v^2c^2$, we can easily obtain the following equation

$$\omega\omega_0(1 - \cos\theta) = \frac{m_0c^2}{\hbar}(\omega_0 - \omega), \quad (1.27)$$

that can be written also as

$$\lambda - \lambda_0 = \frac{h}{m_0c}(1 - \cos\theta) = 2\lambda_c \sin^2 \frac{\theta}{2}. \quad (1.28)$$

In the last equation the Compton wavelength $\lambda_c = h/m_0c$ was introduced. A definition that ascribes an undulatory property, the wavelength, to particles with mass. A quantity that tends to zero as the mass increases. For electrons $\lambda_c \approx 2.4 \times 10^{-3}\text{nm}$. It is evident from (1.28) that $\lambda \geq \lambda_0$. It shows also that the difference $\Delta\lambda = \lambda - \lambda_0$ reaches its maximum value when the dispersion is backwards (“backscattering”), i.e. when $\theta = \pi$. The relative change of the wavelength $\Delta\lambda/\lambda_0$, is of the order of λ_c/λ_0 . This ratio allows one to establish whether the Compton effect will be observed or not. If the incident radiation is a visible light, λ_0 from 400 to 750 nm, the relative change will be of the order of 10^{-5} . In contrast, if the incident radiation has a wavelength shorter than those of the visible light, the relative change will be greater, and the Compton effect might be seen. For instance, for X-ray with $\lambda_0 \approx 10^{-2}\text{nm}$ the relative change is of the order of 10^{-1} , which means 10% of the incident wavelength. This effect can easily be observed and was observed indeed!

1.4 Rutherford’s Atom and Bohr’s Postulates

Searching for the atomic structure, Rutherford studied the dispersion of α particles by thin films of gold. To explain the high amount of α particles at high dispersion angles, Rutherford suggested that atoms have a charge $+Ne$ at the center, surrounded by N electrons which, following the “saturnian” atom hypothesis proposed by Hantaro Nagaoka, rotate in saturnian rings of radii R . With this model of atoms, Rutherford deduced the angular distribution of the scattered particles. The results agreed substantially with those obtained by Geiger in 1910. Although these experiments and the theory did not reveal the sign of the charge, Rutherford assumed always that the positive charge was at the center.

According to the classical theory, an electron that rotates in a circular orbit around a positive charge Ze is subject to a “centrifugal” force and to an attractive Coulomb force. When the magnitudes of these forces are equal, it is possible to express the electron energy as

$$E = -\frac{1}{2}m\omega^2 \left(\frac{Ze^2}{2E} \right)^2, \quad (1.29)$$

and the angular frequency by

$$\omega = \frac{2}{e^2 Z} \sqrt{\frac{2|E|^3}{m}}. \quad (1.30)$$

Here m and e are the mass and charge of the electron, while E is its energy. If the absolute electron energy E takes any real value, the frequency ω will take also any real value. But the experimental results showed that the emitted frequencies were discrete.¹⁰ In 1885, J. J. Balmer found that the wavelengths of the four visible lines of the Hydrogen spectrum can be obtained from

$$\frac{1}{\lambda} = \kappa \left(\frac{1}{4} - \frac{1}{n^2} \right), \quad \text{with } n = 3, 4, 5, 6, \quad (1.31)$$

and $\kappa = 17465\text{cm}^{-1}$. Shortly after J. R. Rydberg showed that all known series can be obtained from

$$k = \frac{2\pi}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad \text{with } n_1 < n_2, \quad (1.32)$$

and $R = 109735.83\text{cm}^{-1}$. This constant is known as Rydberg's constant. Some time later, Niels Bohr, using Rutherford's model and the fundamental ideas introduced by Planck and Einstein, on the quantization of energy, proposed the following postulates on the stationary states of atoms and on the emitted and absorbed radiation frequencies:

- I. *an atomic system can only exist in a number of discrete states;*
- II. *the absorbed or emitted radiation during a transition between two stationary states has a frequency ν given by $h\nu = E_i - E_f$.*

With these postulates he showed that it is possible to explain the separation and regularity of the spectral lines, and the Rydberg formula for the Hydrogen spectrum. Indeed, if one assumes that the energy is quantized as¹¹

$$E_n = nh\nu/2, \quad (1.33)$$

one can easily obtain the energy

$$E_n = -\frac{2\pi^2 me^4}{h^2 n^2}, \quad \text{with } n = 1, 2, 3, \dots \quad (1.34)$$

¹⁰ At that time it was common to assume that the emitted radiation frequency was related with the electron's oscillation frequency.

¹¹ N. Bohr, *Philosophical Magazine*, ser. 6 vol. 26, 1 (1913). Notice the factor 1/2.

Given this energy it is possible to evaluate the difference $E_{n_2} - E_{n_1}$ (associated with the transition $E_{n_1} \rightarrow E_{n_2}$) and to obtain Rydberg's formula.

$$E_{n_2} - E_{n_1} = \frac{2\pi^2 m e^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \quad \text{with } n = 1, 2, 3, \dots \quad (1.35)$$

In the early years of the twentieth century, the electromagnetic theory was considered one of the most firmly established theories. It was known that accelerated charges radiate energy (Bremsstrahlung). In Rutherford's model the orbiting electrons are accelerated charges, therefore they must lose energy and eventually collapse into the nucleus. Nonetheless, that did not seem to occur. Given the coincidence with the Rydberg formula, and the difficulty to explain these basic contradictions, Bohr's postulates were accepted, for some years, as factual statements that reflect the behavior of nature at the microscopic level:

$$h\nu = E_{n_2} - E_{n_1} = \frac{2\pi^2 m e^4}{h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right). \quad (1.36)$$

Bohr's model accounts for the observed results but does not explain why an accelerated electron remains in a stable orbit, neither the emission mechanism, nor the laws that determine the transition probabilities. Nevertheless, these postulates and the correspondence principle with the classical description in the limit of large quantum numbers n (also proposed by Bohr), were held for many years, and constituted what later was called the old quantum theory. Meanwhile, there were many attempts to explain them on a firmer basis, as well as to give them experimental support or to question their general validity. In these attempts two fundamental schools became pre-eminent in the future development of the quantum theory: the school of Arnold Sommerfeld in Munich and the work of Max Born and collaborators in Göttingen. It is beyond the purpose of this book to analyze in detail the work of Sommerfeld, Born, Van Vleck, Heisenberg, Jordan, Pauli, Dirac etc.. We just recall and recognize that the cumulative work of all of them reached, in the joint work of Born, Heisenberg and Jordan, a zenithal point with the matrix version of the quantum theory, the matrix mechanics. A few months later, following a different line of thought, closer to the particle diffraction experiments and to the wave-particle duality proposed by Louis de Broglie, Erwin Schrödinger introduced the wave version of the quantum theory, the quantum wave mechanics. In the following chapter we discuss with more detail this alternative approach to quantum theory. To conclude this chapter we will summarize the ideas of Einstein published¹² in 1917, with the title "About the quantum theory of radiation" where, among other results, Einstein deduced the Planck distribution and the second postulate of Niels Bohr.

¹² A. Einstein, *Mitteilungen der Physikalischen Gesellschaft Zürich* **18**, 47 (1916) and *Phys. Zs.* **18**, 121 (1917).

1.5 On Einstein's Radiation Theory

As an extension of the ideas that were used to explain the photoelectric effect, where the quantization concept was not restricted to the emission and absorption mechanism but taken also as a characteristic property of the radiation field, Einstein derived the Planck distribution and the Bohr postulate, assuming that the emitting and absorbing molecules in the walls, in thermal equilibrium with the blackbody radiation, are themselves allowed to exist only in a discrete set of states.

1.5.1 Planck's Distribution and the Second Postulate of Bohr

Einstein assumed that if a molecule exists only in a discrete set of states with energies E_1, E_2, \dots the relative frequency of finding the molecule in the state n , in analogy with the Boltzmann-Gibbs distribution, should be given by

$$f_n = c_n e^{-E_n/k_B T}, \quad (1.37)$$

where c_n is a normalization constant. A molecule in the state of energy E_n , in thermal equilibrium with an electromagnetic field characterized by a spectral density ρ , absorbs or emits energy and changes to the state of energy E_m , with $E_m < E_n$ in the absorption process and $E_m > E_n$ in the emission process. The probabilities for these processes to occur during a time interval dt are

$$dW_n^m = B_n^m \rho dt \quad \text{and} \quad dW_m^n = B_m^n \rho dt. \quad (1.38)$$

Here, the coefficient B_n^m represents the transition probability per unit of time, from the state with energy E_n to the state with energy E_m . These are transitions induced by the molecule-field interaction. Since the state n occurs with the frequency f_n given in (1.37), the number of transitions per unit time, from n to m , can be written as

$$c_n e^{-E_n/k_B T} B_n^m \rho dt. \quad (1.39)$$

For the excited molecules, Einstein envisaged also the possibility of making transitions to lower states by spontaneous emission, independent of the field. Therefore the probability that a molecule emits during a time dt is

$$dW = (A_m^n + B_m^n \rho) dt, \quad (1.40)$$

with A_m^n the probability of spontaneous emission per unit of time. To preserve the equilibrium of these processes, one needs the balance condition

$$e^{-E_n/k_B T} B_n^m \rho = e^{-E_m/k_B T} (A_m^n + B_m^n \rho). \quad (1.41)$$

It is easy to verify that this condition, with $B_n^m = B_m^n$, leads to the spectral density

$$\rho = \frac{A_m^n}{B_m^n} \frac{1}{e^{(E_m - E_n)/k_B T} - 1}. \quad (1.42)$$

From Wien's displacement law, it follows that

$$\frac{A_m^n}{B_m^n} = \alpha \nu_{nm}^3 \quad \text{and} \quad E_m - E_n = h \nu_{nm}, \quad (1.43)$$

with α and h constants to be determined, for example, by comparing with the Rydberg and the Rayleigh-Jeans formulas at high temperatures. It is worth noticing that Einstein deduced, at the same time, Planck's distribution and the second postulate of Niels Bohr. We shall now briefly refer to Einstein's specific heat model.

1.5.2 Einstein's Specific Heat Model

In an exercise of congruence, Einstein suggested in 1907 that the quantization hypothesis should explain also other physical problems where the classical description was in contradiction with the experimental observations. One of these was the specific heat of solids that, according to classical theory, must be constant, but experimentally tends to zero as the temperature goes to zero. If atoms in a solid are represented by oscillators, the average energy of one atom, per degree of freedom, will be given by

$$\bar{E} = \frac{h\nu}{e^{h\nu/k_B T} - 1}, \quad (1.44)$$

with $\nu = \omega/2\pi$ the average frequency of oscillations. If all atoms, in the Einstein model vibrate with the average frequency ν , the internal energy of a solid containing N atoms, with 3 degrees of freedom each, is given by

$$U = \frac{3N\hbar\omega}{e^{\hbar\omega/k_B T} - 1}. \quad (1.45)$$

When the temperatures are high, the internal energy of the solid takes the form

$$U = 3Nk_B T, \quad (1.46)$$

and the specific heat will be

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 3Nk_B. \quad (1.47)$$

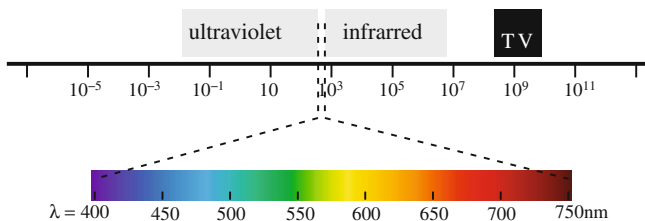


Fig. 1.5 The visible electromagnetic spectrum

This expression coincides with the classical results. If temperatures are low, we have

$$C_V = 3Nk_B \left(\frac{\hbar\omega}{kT} \right)^2 e^{-\hbar\omega/kT}, \quad (1.48)$$

an expression that tends to zero exponentially when $T \rightarrow 0$. This function agrees qualitatively well with the experimental results at low temperatures, a result that was well known at the beginning of the 20th century. A more quantitative approach and in actual agreement with C_V that really behaves as T^3 was derived by Debye.¹³

1.6 Solved Problems

Exercise 1 A quantum of electromagnetic radiation has an energy of 1.77 eV. What is the associated wavelength? To what color does this radiation correspond? (Fig. 1.5)

Solution We will use Planck's relation $E = h\nu = hc/\lambda$. The constant hc in this and other problems is

$$\begin{aligned} hc &= 6.63 \cdot 10^{-34} \text{ Js } 3.0 \cdot 10^8 \frac{\text{m}}{\text{s}} \\ &= 19.89 \cdot 10^{-26} \text{ Jm } \frac{1 \text{ eV}}{1.6 \cdot 10^{-19} \text{ J}} \frac{1 \text{ nm}}{10^{-9} \text{ m}} \\ &= 1243 \text{ eV nm}. \end{aligned} \quad (1.49)$$

With this result we get

$$\lambda = \frac{hc}{E} = \frac{1243}{1.77} \text{ nm} = 702.25 \text{ nm}. \quad (1.50)$$

¹³ By adopting the idea of Einstein and limiting the frequency ω to a maximum frequency ω_D .

This wavelength corresponds to red light, which includes wavelengths between 640 and 750 nm, approximately.

Exercise 2 A mass of 2kg attached to a spring, whose constant is $k = 200$ N/m, is moving harmonically with an amplitude of 10 cm on a smooth surface without friction. If we assume that its energy can be written as a multiple of the quantum of energy $\hbar\omega$ i.e. as $E = n\hbar\omega$, determine the number of quanta n . If the energy is determined with an error ΔE of one part in a million, i.e. $\Delta = \pm E/1000000$, how many quanta of energy are contained in ΔE ?

Solution We will calculate first the energy of the system. This is a classical system and its energy at the maximum elongation point (when the kinetic energy is zero) is

$$E = \frac{1}{2}kA^2 = \frac{1}{2}200 \frac{\text{N}}{\text{m}}(0.1)^2 [\text{m}^2] = 1 \text{ J}. \quad (1.51)$$

The error will be then

$$\Delta E = \pm \frac{1}{1000000} E = \pm 0.000001 E. \quad (1.52)$$

To use the energy $n\hbar\nu$ and get the number n , we need the frequency

$$\begin{aligned} \nu &= \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\frac{200}{2}} \\ &= \frac{10}{2\pi} \text{ Hz} = 1.5915 \text{ Hz}. \end{aligned} \quad (1.53)$$

Therefore

$$n = \frac{E}{\hbar\nu} = \frac{1 \text{ J}}{6.63 \cdot 10^{-34} \text{ J s } 1.5915 [\text{Hz}]} = 9.4769 \cdot 10^{32}. \quad (1.54)$$

This is a very big number. The number of quanta of energy to which the error ΔE corresponds is

$$\Delta n = \frac{\Delta E}{\hbar\nu} = \pm \frac{0.000001 \text{ J}}{6.63 \cdot 10^{-34} \text{ J s } 1.5915 \text{ Hz}} = \pm 9.4769 \cdot 10^{26}. \quad (1.55)$$

Exercise 3 Let us assume that X-rays are produced in a collision of electrons with a target. If electrons deliver all their energy in this process, what minimum-acceleration voltage is required to produce X-rays with a wavelength of 0.05nm?

Solution When an electron is accelerated by a potential difference ΔV , it acquires a potential energy $e\Delta V$. If this energy is transformed into the energy $h\nu$ of a photon of wavelength $\lambda = c/\nu$, we have

$$e\Delta V = hc/\lambda. \quad (1.56)$$

Hence

$$\begin{aligned}\Delta V &= \frac{\hbar c}{e\lambda} = \frac{1243 \text{ eV nm}}{1.6 \cdot 10^{-19} \text{ C} \cdot 0.05 \text{ nm}} \frac{1.6 \cdot 10^{-19} \text{ J}}{1 \text{ eV}} \\ &= 24860 \frac{\text{J}}{\text{C}}.\end{aligned}\quad (1.57)$$

Thus the required accelerating potential is $\Delta V = 24860 \text{ V}$.

1.7 Problems

1. Find the average energy in equation (1.14).
2. Show and discuss Wien's displacement law.
3. Show that Planck's spectral density can also be written as

$$\rho(\omega, T) = \frac{\omega^2}{\pi^2 c^3} \frac{\hbar \omega}{e^{\hbar \omega / k_B T} - 1}. \quad (1.58)$$

4. Consider the equation (1.14) and show that to fulfil the Wien displacement law, the minimum absorbed or emitted energy E_ν must be proportional to the frequency ν .
5. Show that at high temperatures, the Planck distribution reduces to that of Rayleigh and Jeans.
6. Plot Planck's spectral density as a function of the frequency ν for three different temperatures: $T = 50 \text{ K}$, 200 K and 300 K . Determine the frequency where the spectral density reaches its maximum value. Determine in which direction the maximum of the spectral density moves as the temperature increases.
7. Prove that Planck's constant can be expressed as

$$\hbar = \frac{k_B}{c} \left(\frac{\pi^2 k_B}{15a} \right)^{1/3}, \quad (1.59)$$

and obtain its numerical value in Js and eVs.

8. If the escape energy of electrons from a metal surface is 1.0 eV when the metal is irradiated with green light, what is the work function for that metal?
9. If a potassium photocathode is irradiated with photons of wavelength $\lambda = 253.7 \text{ nm}$ (corresponding to the resonant line of mercury), the maximum energy of the emitted electrons is 3.14 eV . If a visible radiation with $\lambda = 589 \text{ nm}$ (resonance line of sodium) is used, the maximum energy of emitted electrons is 0.36 eV .
 - a. Calculate the Planck constant.
 - b. Calculate the work function for the extraction of electrons in potassium.

- c. What is the maximum radiation wavelength to produce the photoelectric effect in potassium?
10. a) An antenna radiates with a frequency of 1 MHz and an output power of 1 kW. How many photons are emitted per second? b) A first-magnitude star emits a light flux of $\sim 1.6 \cdot 10^{-10} \text{ W/m}^2$, measured at the earth surface, with an average wavelength of 556 nm. How many photons per second pass through the pupil of an eye?
11. Derive equations (1.27) and (1.28).
12. A 10MeV photon hits an electron at rest. Determine the maximum loss of photon energy. Would this loss change if the collision is with a proton at rest?
13. Determine the relative change in wavelength when the incident radiation in a Compton experiment is of X-rays (with wavelength $\lambda_0 \sim 10^{-9} \text{ cm}$) on graphite.
14. Determine the wavelengths of the Balmer series for Hydrogen.
15. What is the energy difference $E_m - E_n$ if the emitted light is: a) yellow b) red and c) blue?

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