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978-1-107-07604-4 — Advanced Concepts in Quantum Mechanics
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1 Introduction: the need for a quantum theory

1.1 Introducing quantum mechanics

Interference phenomena of material particles (say, electrons, neutrons, etc.) provide us with the most convincing evidence for the need to elaborate on a new mechanics that goes beyond and encompasses classical mechanics. At the same time, 'corpuscular' behaviour of radiation, i.e. light, as exhibited in phenomena like photoelectric and Compton effects (see Sections 2.2 and 2.3, respectively), shows that the description of radiation also has to undergo significant changes.

If we examine the relation between corpuscular-like and wave-like behaviour, we find that it is fully described by the following phenomenological equations:

$$E = h\nu = \hbar\omega, \ \vec{p} = \hbar\vec{k}, \tag{1.1.1}$$

which can be re-expressed in an invariant way with the help of 1-form notation (see Chapter 15) through the **Einstein–de Broglie** relation:

$$p_j \, dx^j - E \, dt = \hbar(k_j \, dx^j - \omega \, dt). \tag{1.1.2}$$

This relation between the 1-form $p_j \, dx^j - E \, dt$ on the phase space over space–time and the 1-form $\hbar\left(k_j \, dx^j - \omega \, dt\right)$ on the optical phase space establishes a relation between momentum and energy of the 'corpuscular' behaviour and the frequency of the 'wave' behaviour. The proportionality coefficient is the Planck constant. Such a relation likely summarizes one of the main new concepts encoded in quantum mechanics.

The way we use this relation is to predict under which experimental conditions light of a given wavelength and frequency will be detected as a corpuscle with a corresponding momentum and energy and vice-versa, i.e. when an electron will be detected as a wave in the appropriate experimental conditions. (To help dealing with orders of magnitude, we recall that the frequency associated with an electron of kinetic energy equal to 1 eV is $2.42 \cdot 10^{14}$ Hz, while the corresponding wavelength and wave number are $1.23 \cdot 10^{-9}$ m and $5.12 \cdot 10^{9}$ m^{-1}, respectively. Two standard length units are angstrom = Å$= 10^{-10}$ m and fermi = Fm $= 10^{-15}$ m.)

If we examine more closely an interference experiment, like the double-slit one, we find some peculiar aspects for which we do not have a simple interpretation in the classical setting.

If the experiment is performed in such a way that we make sure that, at each time, only one electron is present between the source and the screen, we find that the electron 'interferes with itself' and at the same time impinges on the screen at 'given points'.

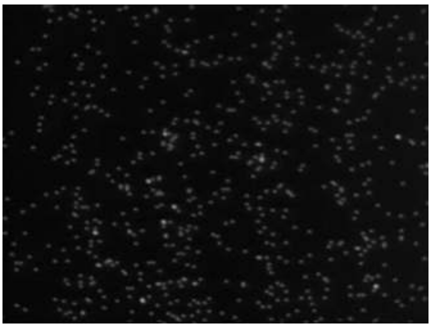

Fig. 1.1 The electrons impinge on the screen at given points. Reproduced with permission from A. Tonomura, J. Endo, T. Matsuda, T. Kawasaki, and H. Ezawa, Demonstration of single-electron build-up of an interference pattern, Am. J. Phys. 57, 117–20 (1989) copyright (1989), American Association of Physics Teachers.

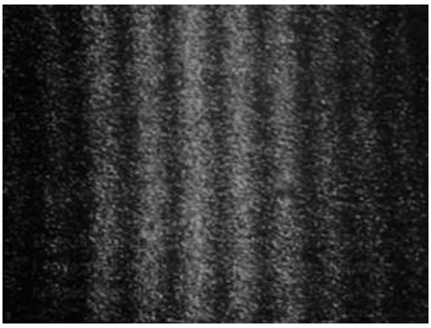

Fig. 1.2 Typical interference pattern resulting from the passage of a few thousand electrons. Reproduced with permission from A. Tonomura, J. Endo, T. Matsuda, T. Kawasaki, and H. Ezawa, Demonstration of single-electron build-up of an interference pattern, Am. J. Phys. 57, 117–20 (1989) copyright (1989), American Association of Physics Teachers.

After a few hundred electrons have passed, we find a picture of random spots distributed on the screen (Figure 1.1). However, with several thousands electrons, a very clear typical interference pattern is obtained (Figure 1.2).

The same situation occurs again if we experiment with photons (light quanta), with an experimental setup that makes sure that only one photon is present at a time.

This experiment suggests that the new theory must include a wave character (to take into account the interference aspects) and, in addition, statistical–probabilistic, character along with an intrinsically discrete aspect, i.e. a corpuscular nature. All this is quite counterintuitive for particles, but it is even more unexpected for light. Within the classical setting we have to accept that it is not so simple to provide a single model capable of capturing these various aspects at the same time.

From the historical point of view, things developed differently because inconsistencies already arose in the derivation of the law for the spectral distribution of energy density of a black body. Planck conceived of the idea of emission and absorption of radiation by quanta in order to explain the finite energy density of black-body radiation (Section 2.1). The theory of classical electrodynamics gave an infinite density for this radiation. Indeed, the energy density per unit frequency was $8\pi \nu^2 KT/c^3$, as calculated on the basis of this theory, and the integral over the frequency ν is clearly divergent. Based in part on intuition, partly on experimental information and partly to agree with Wien's displacement law, Planck replaced the previous formula by

$$\frac{8\pi h\nu^3/c^3}{\left(e^{h\nu/KT}-1\right)}.$$

To give an 'explanation' of it, he postulated that both emission and absorption of radiation occur instantaneously and in finite quanta.

Moreover, it was not possible to account for the stability of atoms and molecules along with the detected atomic spectra. To account for the experimental facts, Bohr postulated the quantum condition for electronic orbits. This hypothesis was highly successful in describing the spectrum of atomic hydrogen clearly and also in a qualitative way the periodic system, and hence some basic properties of all atoms. In spite of these partial successes, the absence of mathematically sound rules on the basis of which the electronic orbits, and therefore the energy levels, could be determined was greatly disturbing. It was also quite unclear how the electron jumps from one precisely defined orbit to another. The next chapter is devoted to a detailed description of some crucial experiments mentioned above, presented in their historical sequence, with the aim of providing the physical background from which the new theory of quanta emerged.

Eventually, the efforts of theoreticians gave rise to two alternative, but equivalent, formulations of quantum mechanics. They are usually called the Schrödinger picture and the Heisenberg picture. As will be seen in the coming chapters, the first one uses as a primary object the carrier space of states, while the latter uses as carrier space the space of observables. The former picture is built in analogy with wave propagation, the latter in analogy with Hamiltonian mechanics on phase space, i.e. the corpuscular behaviour.

The Schrödinger equation has the form

$$i\hbar \frac{d}{dt}\psi = \widehat{H}\psi. \tag{1.1.3}$$

The complex-valued function ψ is called the *wave function*, it is defined on the configuration space of the system we are considering, and it is interpreted as a probabilistic amplitude. This interpretation requires that ($d\mu$ being the integration measure)

$$\int_D \psi^* \psi \, d\mu = 1, \tag{1.1.4}$$

i.e. because of the probabilistic interpretation, $\psi^*\psi$ must be a probability density and therefore ψ is required to be square-integrable. Thus, wave functions must be elements of a Hilbert space of square-integrable functions. The operator $\widehat{H}$, acting on wave functions, is the infinitesimal generator of a 1-parameter group (see Chapter 15) of unitary transformations describing the evolution of the system under consideration. The unitarity requirement results from imposing that the evolution of an isolated system should be compatible with the probabilistic interpretation.

These are the basic ingredients appearing in the Schrödinger evolution equation. The presence of the new fundamental constant $\hbar$ within the new class of phenomena implies some fundamental aspects completely different from the previous classical ones. For instance, it is clear that any measurement process requires an exchange of energy (or information) between the object being measured and the measuring apparatus. The existence of $\hbar$ requires that these exchanges cannot be made arbitrarily small and therefore idealized to be negligible. Thus, the presence of $\hbar$ in the quantum theory means that in the measurement process we cannot conceive of a sharp separation between the 'object' and the 'apparatus' so that we may 'forget the apparatus' altogether.

In particular, it follows that even if the apparatus is described classically it should be considered as a quantum system with a quantum interaction with the object to be measured. Moreover, in the measurement process, there is an inherent ambiguity in the 'cut' between what we identify as the object and what we identify as apparatus.

The problem of measurement in quantum theory is a very profound one and goes beyond the scope of our manuscript. It is worth mentioning that, within the von Neumann formulation of quantum mechanics, the measurement problem gives rise to the so-called 'wave-function collapse'. The state vector of the system we are considering, when we measure some real dynamical variable A, i.e. a linear operator acting on the Hilbert space $\mathcal{H}$, is projected onto one of the eigenspaces of A, with some probability that can be computed. Since our aim is only to highlight the various structures occurring in the different formulations of quantum mechanics, we shall adhere to the von Neumann projection prescription.

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2 Experimental foundations of quantum theory

The experimental foundations of quantum theory are presented in some detail in this chapter: on the one hand, the investigation of black-body radiation, which helps in developing an interdisciplinary view of physics, besides having historical interest; on the other hand, the energy and linear momentum of photons, atomic spectra, discrete energy levels, wave-like properties of electrons, interference phenomena and uncertainty relations.

2.1 Black-body radiation

Black-body radiation is not just a topic of historical interest. From a pedagogical point of view, it helps in developing an interdisciplinary view of physics, since it involves, among the other, branches of physics such as electrodynamics and thermodynamics, as well as a new constant of nature, the Planck constant, which is peculiar to quantum theory and quantum statistics. Moreover, looking at modern developments, the radiation that pervades the whole universe (Gamow 1946, Penzias and Wilson 1965, Smoot *et al.* 1992, Spergel *et al.* 2003) is a black-body radiation, and the expected emission of particles from black holes (space–time regions where gravity is so strong that no light ray can escape to infinity, and all nearby matter gets eaten up) is also (approximately) a black-body radiation (Hawking 1974, 1975).

In this section, relying in part on Born (1969), we are aiming to derive the law of heat radiation, following Planck's method. We think of a box for which the walls are heated to a definite temperature T. The walls of the box send out energy to each other in the form of heat radiation, so that within the box there exists a radiation field. This electromagnetic field may be characterized by specifying the average energy density u, which in the case of equilibrium is the same for every internal point; if we split the radiation into its spectral components, we denote by $u_\nu \, d\nu$ the energy density of all radiation components for which the frequency falls in the interval between ν and $\nu + d\nu$. (The spectral density is not the only specification; we need to know the state of the entire radiation field including the photon multiplicity.) Thus, the function u_ν extends over all frequencies from 0 to ∞, and represents a continuous spectrum. Note that, unlike individual atoms in rarefied gases, which emit line spectra, molecules, which consist of a limited number of atoms, emit narrow 'bands', which are often resolvable. A solid represents an infinite number of vibrating systems of all frequencies, and hence emits an effectively continuous spectrum. But inside a black cavity all bodies emit a continuous spectrum characteristic of the temperature.

The first important property in our investigation is a theorem by Kirchhoff (1860), which states that the ratio of the emissive and absorptive powers of a body depends only on the *temperature* of the body, and not on its nature (recall that the *emissive power* is, by definition, the radiant energy emitted by the body per unit time, whereas the *absorptive power* is the fraction of the radiant energy falling upon it that the body absorbs). A *black body* is meant to be a body with absorptive power equal to unity, i.e. a body that absorbs all of the radiant energy that falls upon it. The radiation emitted by such a body, called *black-body radiation*, is therefore a function of the temperature alone, and it is important to know the spectral distribution of the intensity of this radiation. Any object inside the black cavity emits the same amount of radiant energy. We are now aiming to determine the law of this intensity, but before doing so it is instructive to describe in detail some arguments in the original paper by Kirchhoff (cf. Stewart 1858).

2.1.1 Kirchhoff laws

The brightness $\mathcal{B}$ is the energy flux per unit frequency, per unit surface, for a given solid angle per unit time. Thus, if $\mathrm{d}E$ is the energy incident on a surface $\mathrm{d}S$ with solid angle $\mathrm{d}\Omega$ in a time $\mathrm{d}t$ with frequency $\mathrm{d}\nu$, we have (θ being the incidence angle)

$$\mathrm{d}E = \mathcal{B}\ \mathrm{d}\nu\ \mathrm{d}S\ \mathrm{d}\Omega\ \cos\theta\ \mathrm{d}t. \tag{2.1.1}$$

The brightness $\mathcal{B}$ is independent of position, direction and the nature of the material. This is proved as follows.

(i) $\mathcal{B}$ cannot depend on position, since otherwise two bodies absorbing energy at the same frequency and placed at different points P_1 and P_2 would absorb different amounts of energy, although they were initially at the same temperature T equal to the temperature of the cavity. We would then obtain the spontaneous creation of a difference of temperature, which would make it possible to realize a perpetual motion of the second kind, hence violating the second principle of thermodynamics, which is of course impossible.

(ii) $\mathcal{B}$ cannot depend on direction either. Let us insert into the cavity a mirror S of negligible thickness, and imagine we can move it along a direction parallel to its plane. In such a way no work is performed, and hence the equilibrium of radiation remains unaffected. Then let A and B be two bodies placed at different directions with respect to S and absorbing in the same frequency interval. If the amount of radiation incident upon B along the BS direction is smaller than that along the AS direction, bodies A and B attain spontaneously different temperatures, although they were initially in equilibrium at the same temperature! Thermodynamics forbids this phenomenon as well.

(iii) Once equilibrium is reached, $\mathcal{B}$ is also independent of the material the cavity is made of. Let the cavities C_1 and C_2 be made of different materials, and suppose they are at the same temperature and linked by a tube such that only radiation of frequency ν can pass through it. If $\mathcal{B}$ were different for C_1 and C_2 a non-vanishing energy flux through the tube would therefore be obtained. Thus, the two cavities would change their temperature spontaneously, against the second law of thermodynamics. Similar considerations prove $\mathcal{B}$ to be independent of the shape of the cavity as well.

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By virtue of (i)–(iii) Eq. (2.1.1) reads, more precisely, as

$$dE = \mathcal{B}(\nu, T)d\nu \; dS \; d\Omega \; \cos\theta \; dt. \tag{2.1.2}$$

Moreover, the energy absorbed by the surface element dS of the wall once equilibrium is reached is (x denoting all variables other than ν, T)

$$dE_{\text{abs}} = a_{\text{m}}(\nu, T, x)dE, \tag{2.1.3}$$

while the emitted energy is

$$dE_{\text{em}} = e_{\text{m}}(\nu, T, x)d\nu \; dS \; d\Omega \; \cos\theta \; dt. \tag{2.1.4}$$

Under equilibrium conditions, the amounts of energy dE_{em} and dE_{abs} are equal, and hence

$$\frac{e_{\text{m}}(\nu, T, x)}{a_{\text{m}}(\nu, T, x)} = \mathcal{B} = \mathcal{B}(\nu, T). \tag{2.1.5}$$

Thus, the ratio of emissive and absorptive powers is equal to the brightness and hence can only depend on frequency and temperature, although both e_{m} and a_{m} can separately depend on the nature of materials.

As far as the production of black-body radiation is concerned, it has been proved by Kirchhoff that an enclosure (typically, an oven) at uniform temperature, in the wall of which there is a small opening, behaves as a black body. Indeed, all the radiation which falls on the opening from the outside passes through it into the enclosure, and is, after repeated reflection at the walls, completely absorbed by them. The radiation in the interior, and hence also the radiation which emerges again from the opening, should therefore possess exactly the spectral distribution of intensity, which is characteristic of the radiation of a black body.

2.1.2 Electromagnetic field in a hollow cavity

According to classical electrodynamics, a hollow cavity filled with electromagnetic radiation (possibly in thermodynamical equilibrium with the cavity surfaces) contains energy stored in the electromagnetic field as described by the expression[1]

$$\mathcal{E} = \frac{1}{8\pi} \int \left(|\vec{E}|^2 + |\vec{B}|^2 \right) dV, \tag{2.1.6}$$

where the fields $\vec{E}$ and $\vec{B}$ satisfy the Maxwell equations

$$\vec{\nabla} \wedge \vec{E} = -\frac{1}{c}\frac{\partial}{\partial t}\vec{B}, \qquad \vec{\nabla} \cdot \vec{B} = 0, \tag{2.1.7}$$

$$\vec{\nabla} \wedge \vec{B} = \frac{1}{c}\frac{\partial}{\partial t}\vec{E} + \frac{4\pi}{c}\vec{J}, \qquad \vec{\nabla} \cdot \vec{E} = 4\pi\rho, \tag{2.1.8}$$

with ρ and $\vec{J}$ denoting the charge and current density, respectively. The most general solution of Eqs. (2.1.7) expresses the fields $\vec{E}$ and $\vec{B}$ in terms of scalar and vector potentials as

$$\vec{B} = \vec{\nabla} \wedge \vec{A}, \qquad \vec{E} = -\vec{\nabla}\phi - \frac{1}{c}\frac{\partial}{\partial t}\vec{A}. \tag{2.1.9}$$

[1] Hereafter we will use Gaussian units, see for example Jackson (1975), for a detailed discussion.

Once the electromagnetic fields are given, Eqs. (2.1.9) do not fix ϕ and $\vec{A}$. In fact, if according to Eq. (2.1.9) ϕ and $\vec{A}$ yield $\vec{E}$ and $\vec{B}$, from the pair ϕ' and $\vec{A}'$ defined by

$$\vec{A}' \equiv \vec{A} - \vec{\nabla}\chi, \qquad \phi' \equiv \phi + \frac{1}{c}\frac{\partial}{\partial t}\chi, \tag{2.1.10}$$

the same electromagnetic fields for every arbitrary χ function are obtained. Such a level of freedom in choosing the scalar and vector potentials associated with given electromagnetic fields, which makes the former physically unobservable, is commonly denoted as *gauge symmetry*. In the case of Maxwell equations in vacuum, a the gauge symmetry can be completely exploited by imposing simultaneously the conditions

$$\vec{\nabla} \cdot \vec{A} = \partial^i A_i = 0, \qquad \phi = 0, \tag{2.1.11}$$

which is a particular case of *transverse gauge*. By substituting Eqs. (2.1.9) in (2.1.8) for the vacuum case and using the conditions (2.1.11) we get the wave equation for the transverse degrees of freedom of $\vec{A}$, i.e. (hereafter $\triangle \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ if expressed in Cartesian coordinates)

$$\left(\triangle - \frac{1}{c^2}\frac{\partial^2}{\partial t^2}\right)\vec{A}_t \equiv \Box \vec{A}_t = 0, \tag{2.1.12}$$

$$\vec{\nabla} \cdot \vec{A}_t = 0. \tag{2.1.13}$$

As already proved in the previous subsection, the energy density of a hollow cavity filled of electromagnetic radiation in thermal equilibrium with the cavity surface *cannot depend on the nature and shape* of the cavity. For this reason, we can choose the particular case of a cubic cavity with periodic boundary conditions, which allows a simpler treatment of the electromagnetic problem.

Let us consider a cube with edge length L; the generic field $\vec{A}_t(\vec{r}, t)$ simultaneously periodic along the three coordinate directions can be expanded as

$$\vec{A}_t(\vec{r}, t) = \sum_{l,n,m \in \mathbb{Z}} \left\{ \vec{a}_{lnm}(t) \cos\left[\frac{2\pi}{L}(l\,x + m\,y + n\,z)\right] \right.$$
$$\left. + \vec{b}_{lnm}(t) \sin\left[\frac{2\pi}{L}(l\,x + m\,y + n\,z)\right]\right\}. \tag{2.1.14}$$

By defining the propagation vector $\vec{k} \equiv (2\pi/L)(l, m, n)$, the condition $\vec{\nabla} \cdot \vec{A}_t = 0$ implies $\vec{k} \cdot \vec{a}_{lnm}(t) = \vec{k} \cdot \vec{b}_{lnm}(t) = 0$ (transverse condition).

Hence Eq. (2.1.14) can be rewritten

$$\vec{A}_t(\vec{r}, t) = \sum_{\vec{k},\mu}\left[\vec{a}_{\vec{k},\mu}(t) \cos\left(\vec{k} \cdot \vec{r}\right) + \vec{b}_{\vec{k},\mu}(t) \sin\left(\vec{k} \cdot \vec{r}\right)\right], \tag{2.1.15}$$

where the index μ labels the two independent solutions of the transverse condition, and Eq. (2.1.12) gives

$$\left(\frac{d^2}{dt^2} + |\vec{k}|^2 c^2\right)\vec{a}_{\vec{k},\mu}(t) = 0,$$
$$\left(\frac{d^2}{dt^2} + |\vec{k}|^2 c^2\right)\vec{b}_{\vec{k},\mu}(t) = 0, \tag{2.1.16}$$

which show that $\vec{a}_{\vec{k},\mu}$ and $\vec{b}_{\vec{k},\mu}$ behave as harmonic oscillators with angular frequency $\omega = |\vec{k}|\, c$, where $|\vec{k}| \equiv (2\,\pi/L)\sqrt{l^2+m^2+n^2}$.

By deriving from Eq. (2.1.15) the corresponding electromagnetic fields and substituting them in Eq. (2.1.6) we get

$$\mathcal{E} = \frac{L^3}{8\pi c^2}\sum_{\vec{k},\mu}\frac{1}{2}\left\{\left[\left|\frac{\mathrm{d}}{\mathrm{d}t}\left(\vec{a}_{\vec{k},\mu}+\vec{a}_{-\vec{k},\mu}\right)\right|^2+|\vec{k}|^2\,c^2\left|\left(\vec{a}_{\vec{k},\mu}+\vec{a}_{-\vec{k},\mu}\right)\right|^2\right]\right.$$
$$\left.+\left[\left|\frac{\mathrm{d}}{\mathrm{d}t}\left(\vec{b}_{\vec{k},\mu}-\vec{b}_{-\vec{k},\mu}\right)\right|^2+|\vec{k}|^2\,c^2\left|\left(\vec{b}_{\vec{k},\mu}-\vec{b}_{-\vec{k},\mu}\right)\right|^2\right]\right\}. \tag{2.1.17}$$

From Eq. (2.1.17) deduce that the electromagnetic energy in a hollow cavity receives contributions from the sum of countable and separate harmonic oscillator-type degrees of freedom with mass equal to $L^3/(8\pi c^2)$ and angular frequency ω. For each particular mode, i.e. for each $\vec{k}$, the two independent polarizations are labelled by μ. Note that the presence in Eq. (2.1.17) of terms proportional to $\vec{a}_{\vec{k},\mu}+\vec{a}_{-\vec{k},\mu}$ and $\vec{b}_{\vec{k},\mu}-\vec{b}_{-\vec{k},\mu}$, even though they have particular properties of symmetry with respect to $\vec{k}\to-\vec{k}$, ensures one independent degree of freedom for each value of $\vec{k}$ and μ.

By virtue of the isotropy expected for the radiation energy density in the hollow cavity describing the black body, the expression in square brackets on the right-hand side of Eq. (2.1.17) (total energy of the single harmonic oscillator) can depend on ω only, hence in the sum of Eq. (2.1.17) the directional degrees of freedom can be integrated out.

If we fix $\vec{k}$, the infinitesimal number of oscillators around this value is

$$\delta n = \mathrm{d}l\,\mathrm{d}m\,\mathrm{d}n = L^3/(2\pi)^3\,\mathrm{d}k_x\,\mathrm{d}k_y\,\mathrm{d}k_z = L^3/(2\pi)^3\,|\vec{k}|^2\,\mathrm{d}|\vec{k}|\,\mathrm{d}\Omega. \tag{2.1.18}$$

Once the angular integration is performed the total number of oscillators between the frequencies ν and $\nu+\mathrm{d}\nu$ is obtained, i.e.

$$\delta N = \frac{8\pi V}{c^3}\,\nu^2\,\mathrm{d}\nu, \tag{2.1.19}$$

where we have used the relation $\nu = |\vec{k}|\,c/(2\pi)$, added an extra factor 2 to Eq. (2.1.19) to take into account the different polarizations, and denoted with V the volume of the cavity $V = L^3$. By using Eqs. (2.1.17) and (2.1.19) we get for the cubic cavity

$$\frac{1}{V}\frac{\mathrm{d}\mathcal{E}}{\mathrm{d}\nu} = \frac{8\pi V}{c^3}\,\nu^2\,e_{\mathrm{ho}}(\nu), \tag{2.1.20}$$

where $e_{\mathrm{ho}}(\nu)$ denotes the energy contribution of the harmonic-oscillator-like degrees of freedom with frequency ν appearing on the right-hand side of Eq. (2.1.17).

The expression of $\mathcal{E}$ can then be obtained by determining the explicit expression of $e_{\mathrm{ho}}(\nu)$. In the following we will take a different approach, but we will revert to Eq. (2.1.20) to physically interpret our results.

2.1.3 Stefan and displacement laws

Remaining within the framework of thermodynamics and the electromagnetic theory of light, two laws can be deduced concerning the way in which black-body radiation depends on the temperature. First, the Stefan law states that the total emitted radiation is proportional to the fourth power of the temperature of the radiator. Thus, the hotter the body, the more it radiates. Second, Wien found the *displacement law* (1896), which states that the spectral distribution of the energy density is given by an equation of the form

$$u_\nu(\nu, T) = \nu^3 F(\nu/T), \tag{2.1.21}$$

where F is a function of the ratio of the frequency to the temperature, but cannot be determined more precisely with the help of thermodynamical methods. This formula can be proved by using the approach of previous subsection, i.e. describing the black body as a hollow cavity of volume V in the shape of a cube of edge length L. As shown before, the equilibrium radiation field will consist of standing waves and this leads to the following relation for the frequency:

$$\left(\frac{\nu L}{c}\right)^2 = l^2 + m^2 + n^2, \tag{2.1.22}$$

where l, m and n are integers. If an adiabatic change of volume is performed, the quantities l, m and n, being integers and hence unable to change infinitesimally, will remain invariant. Under an adiabatic transformation the product νL is therefore invariant, or, introducing the volume V instead of L,

$$\nu^3 V = \text{invariant}, \tag{2.1.23}$$

under adiabatic transformation. The result can be proved to be independent of the shape of the volume.

However, it is more convenient to have a relation between ν and T, and for this purpose the entropy of the radiation field must be considered. Classical electrodynamics tells us that the radiation pressure P is one-third of the total radiation energy density $u(T)$:

$$P = \frac{1}{3} u(T). \tag{2.1.24}$$

On combining Eq. (2.1.24) with the thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = T \left(\frac{\partial P}{\partial T}\right)_V - P, \tag{2.1.25}$$

and the relation $U = uV$, the differential equation,

$$u = \frac{1}{3} T \frac{\mathrm{d}u}{\mathrm{d}T} - \frac{1}{3} u, \tag{2.1.26}$$

which is solved by using the Stefan law is obtained,

$$u(T) = aT^4. \tag{2.1.27}$$

Equations (2.1.24) and (2.1.27), when combined with the thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \tag{2.1.28}$$

yield

$$S = \frac{4}{3} a T^3 V. \tag{2.1.29}$$