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Part I

From classical to wave mechanics

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Experimental foundations of quantum theory

This chapter begins with a brief outline of some of the key motivations for considering a quantum theory: the early attempts to determine the spectral distribution of energy density of black bodies; stability of atoms and molecules; specific heats of solids; interference and diffraction of light beams; polarization of photons. The experimental foundations of wave mechanics are then presented in detail, but in a logical order quite different from its historical development: photo-emission of electrons by metallic surfaces, X- and γ-ray scattering from gases, liquids and solids, interference experiments, atomic spectra and the Bohr hypotheses, the experiment of Franck and Hertz, the Bragg experiment, diffraction of electrons by a crystal of nickel (Davisson and Germer), and measurements of position and velocity of an electron.

1.1 The need for a quantum theory

In the second half of the nineteenth century it seemed that the laws of classical mechanics, developed by the genius of Newton, Lagrange, Hamilton, Jacobi and Poincaré, the Maxwell theory of electromagnetic phenomena and the laws of classical statistical mechanics could account for all known physical phenomena. Still, it became gradually clear, after several decades of experimental and theoretical work, that one has to formulate a new kind of mechanics, which reduces to classical mechanics in a suitable limit, and makes it possible to obtain a consistent description of phenomena that cannot be understood within the classical framework. It is now appropriate to present a brief outline of this new class of phenomena, the systematic investigation of which is the object of the following sections and of chapters 4 and 14.

(i) In his attempt to derive the law for the spectral distribution of energy density of a body which is able to absorb all the radiant energy falling

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upon it, Planck was led to assume that the walls of such a body consist of harmonic oscillators, which exchange energy with the electromagnetic field inside the body only via integer multiples of a fundamental quantity ε_0. At this stage, to be consistent with another law that had been derived in a thermodynamical way and was hence of universal validity, the quantity ε_0 turned out to be proportional to the frequency of the radiation field, $\varepsilon_0 = h\nu$, and a new constant of nature, h, with dimension [energy] [time] and since then called the Planck constant, was introduced for the first time. These problems are part of the general theory of heat radiation (Planck 1991), and we have chosen to present them in some detail in chapter 14, which is devoted to the transition from classical to quantum statistical mechanics.

(ii) The crisis of classical physics, however, became even more evident when attempts were made to account for the stability of atoms and molecules. For example, if an atomic system, initially in an equilibrium state, is perturbed for a short time, it begins oscillating, and such oscillations are eventually transmitted to the electromagnetic field in its neighbourhood, so that the frequencies of the composite system can be observed by means of a spectrograph. In classical physics, independent of the precise form of the forces ruling the equilibrium stage, one would expect to be able to include the various frequencies in a scheme where some fundamental frequencies occur jointly with their harmonics. In contrast, the Ritz combination principle (see section 1.6) is found to hold, according to which all frequencies can be expressed as differences between some spectroscopic terms, the number of which is much smaller than the number of observed frequencies (Duck and Sudarshan 2000).

(iii) If one tries to overcome the above difficulties by postulating that the observed frequencies correspond to internal degrees of freedom of atomic systems, whereas the unknown laws of atomic forces forbid the occurrence of higher order harmonics (Dirac 1958), it becomes impossible to account for the experimental values of specific heats of solids at low temperatures (cf. section 14.8).

(iv) Interference and diffraction patterns of light can only be accounted for using a wave-like theory. This property is ‘dual’ to a particle-like picture, which is instead essential to understanding the emission of electrons by metallic surfaces that are hit by electromagnetic radiation (section 1.3) and the scattering of light by free electrons (section 1.4).

(v) It had already been a non-trivial achievement of Einstein to show that the energy of the electromagnetic field consists of elementary quantities $W = h\nu$, and it was as if these quanta of energy were localized in space

(Einstein 1905). In a subsequent paper, Einstein analysed a gas composed of several molecules that was able to emit or absorb radiation, and proved that, in such processes, linear momentum should be exchanged among the molecules, to avoid affecting the Maxwell distribution of velocities (Einstein 1917). This ensures, in turn, that statistical equilibrium is reached. Remarkably, the exchange of linear momentum cannot be obtained, unless one postulates that, if spontaneous emission occurs, this happens along a well-defined direction with corresponding vector $\vec{u}$, so that the linear momentum reads as

$$\vec{p} = \frac{W}{c}\vec{u} = \frac{h\nu}{c}\vec{u} = \frac{h}{\lambda}\vec{u}. \tag{1.1.1}$$

In contrast, if a molecule were able to emit radiation along all possible directions, as predicted by classical electromagnetic theory, the Maxwell distribution of velocities would be violated. There was, therefore, strong evidence that *spontaneous emission is directional.* Under certain circumstances, electromagnetic radiation behaves as if it were made of elementary quantities of energy $W = h\nu$, with speed c and linear momentum $\vec{p}$ as in Eq. (1.1.1). One then deals with the concept of energy quanta of the electromagnetic field, later called *photons* (Lewis 1926).

(vi) It is instructive, following Dirac (1958), to anticipate the description of polarized photons in the quantum theory we are going to develop. It is well known from experiments that the polarization of light is deeply intertwined with its corpuscular properties, and one comes to the conclusion that photons are, themselves, polarized. For example, a light beam with linear polarization should be viewed as consisting of photons each of which is linearly polarized in the same direction. Similarly, a light beam with circular polarization consists of photons that are all circularly polarized. One is thus led to say that each photon is in a given *polarization state.* The problem arises of how to apply this new concept to the spectral resolution of light into its polarized components, and to the recombination of such components. For this purpose, let us consider a light beam that passes through a tourmaline crystal, assuming that only linearly polarized light, perpendicular to the optical axis of the crystal, is found to emerge. According to classical electrodynamics, if the beam is polarized perpendicularly to the optical axis $\mathcal{O}$, it will pass through the crystal while remaining unaffected; if its polarization is parallel to $\mathcal{O}$, the light beam is instead unable to pass through the crystal; lastly, if the polarization direction of the beam forms an angle α with $\mathcal{O}$, only a fraction $\sin^2 \alpha$ passes through the crystal.

Let us assume, for simplicity, that the incoming beam consists of one photon only, and that one can detect what comes out on the other side of the crystal. We will learn that, according to quantum mechanics, in a number of experiments the whole photon is detected on the other side of the crystal, with energy equal to that of the incoming photon, whereas, in other circumstances, no photon is eventually detected. When a photon is detected, its polarization turns out to be perpendicular to the optical axis, but under no circumstances whatsoever shall we find, on the other side of the crystal, only a fraction of the incoming photon. However, *on repeating the experiment a sufficiently large number of times*, a photon will eventually be detected for a number of times equal to a fraction $\sin^2 \alpha$ of the total number of experiments. In other words, the photon is found to have a *probability* $\sin^2 \alpha$ of passing through the tourmaline, and a probability $\cos^2 \alpha$ of being, instead, absorbed by the tourmaline. A deep property, which will be the object of several sections from now on, is then found to emerge: when a series of experiments are performed, one can only predict a set of possible results with the corresponding probabilities.

As we will see in the rest of the chapter, the interpretation provided by quantum mechanics requires that a photon with oblique polarization can be viewed as being in part in a polarization state parallel to $\mathcal{O}$, and in part in a polarization state perpendicular to $\mathcal{O}$. In other words, a state of oblique polarization results from a 'superposition' of polarizations that are perpendicular and parallel to $\mathcal{O}$. It is hence possible to decompose any polarization state into two mutually orthogonal polarization states, i.e. to express it as a superposition of such states.

Moreover, when we perform an observation, we can tell whether the photon is polarized in a direction parallel or perpendicular to $\mathcal{O}$, because the measurement process makes the photon be in one of these two polarization states. Such a theoretical description requires a sudden change from a linear superposition of polarization states (prior to measurement) to a state where the polarization of the photon is *either* parallel *or* perpendicular to $\mathcal{O}$ (after the measurement).

Our brief outline has described many new problems that the general reader is not expected to know already. Now that his intellectual curiosity has been stimulated, we can begin a thorough investigation of all such topics. The journey is not an easy one, but the effort to understand what leads to a quantum theory will hopefully engender a better understanding of the physical world.

1.2 Our path towards quantum theory

Unlike the historical development outlined in the previous section, our path towards quantum theory, with emphasis on wave mechanics, will rely on the following properties.

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(i) The photoelectric effect, Compton effect and interference phenomena provide clear experimental evidence for the existence of photons. 'Corpuscular' and 'wave' behaviour require that we use both 'attributes', therefore we need a relation between wave concepts and corpuscular concepts. This is provided for photons by the Einstein identification (see appendix 1.A)

$$\left(\vec{k} \cdot \mathrm{d}\vec{x} - \omega \, \mathrm{d}t\right) = \frac{1}{\hbar}\left(\vec{p} \cdot \mathrm{d}\vec{x} - p_0 \, \mathrm{d}x_0\right). \tag{1.2.1a}$$

More precisely, light has a corpuscular nature that becomes evident thanks to the photoelectric and Compton effects, but also a wave-like nature as is shown by interference experiments. Although photons are massless, one can associate to them a linear momentum $\vec{p} = \hbar\vec{k}$, and their energy equals $\hbar\omega = h\nu$.

(ii) The form of the emission and absorption spectra, and the Bohr hypotheses (section 1.6). Experimental evidence of the existence of energy levels (section 1.7).

(iii) The wave-like behaviour of massive particles postulated by de Broglie (1923) and found in the experiment of Davisson and Germer (1927, diffraction of electrons by a crystal of nickel). For such particles one can perform the de Broglie identification

$$\left(\vec{p} \cdot \mathrm{d}\vec{x} - p_0 \, \mathrm{d}x_0\right) = \hbar\left(\vec{k} \cdot \mathrm{d}\vec{x} - \omega \, \mathrm{d}t\right). \tag{1.2.1b}$$

It is then possible to estimate when the corpuscular or wave-like aspects of particles are relevant in some physical processes.

1.3 Photoelectric effect

In the analysis of black-body radiation one met, for the first time, the hypothesis of quanta: whenever matter emits or absorbs radiation, it does so in a sequence of elementary acts, in each of which an amount of energy ε is emitted or absorbed proportional to the frequency ν of the radiation: $\varepsilon = h\nu$, where h is the universal constant known as Planck's constant. We are now going to see how the ideas developed along similar lines make it possible to obtain a satisfactory understanding of the photoelectric effect.

The photoelectric effect was discovered by Hertz and Hallwachs in 1887. The effect consists of the emission of electrons from the surface of a solid when electromagnetic radiation is incident upon it (Hughes and DuBridge 1932, DuBridge 1933, Holton 2000). The three empirical laws of such an effect are as follows (see figures 1.1 and 1.2; the Millikan experiment

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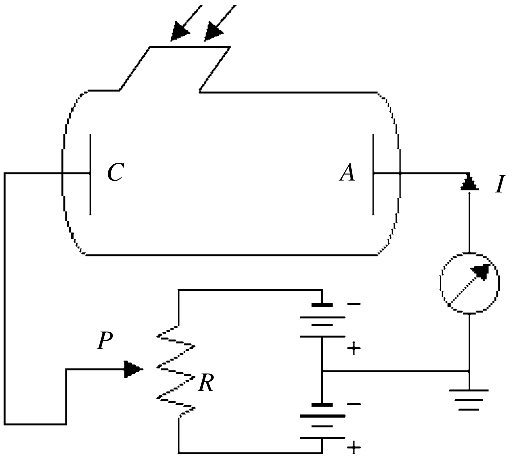

Fig. 1.1. The circuit used in the Millikan experiment. The energy with which the electron leaves the surface is measured by the product of its charge with the potential difference against which it is just able to drive itself before being brought to rest. Millikan was careful enough to use only light for which the illuminated electrode was photoelectrically sensitive, but for which the surrounding walls were not photosensitive.

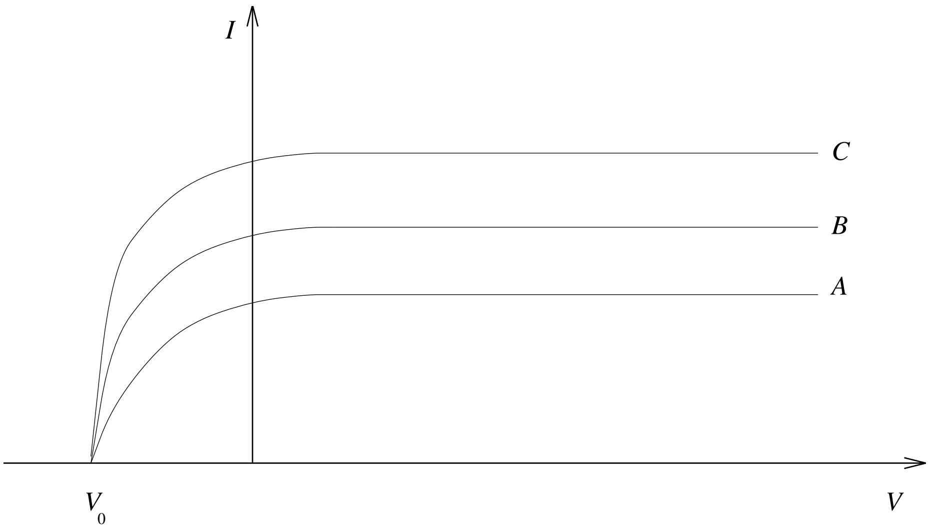

Fig. 1.2. Variation of the photoelectric current with voltage, for given values of the intensity.

quoted therein should not be confused with the measuremt of the electron charge, also due to Millikan).

(i) The electrons are emitted only if the frequency of the incoming radiation is greater than a certain value ν_0, which is a peculiar property of the metal used in the experiment, and is called *the photoelectric threshold*.

(ii) The velocities of the electrons emitted by the surface range from 0 to a maximum value of $v_{\rm max}$. The kinetic energy corresponding to $v_{\rm max}$ depends linearly on the frequency ν: $T_{\rm max} = k(\nu - \nu_0), k > 0$. $T_{\rm max}$ does not depend on the intensity of the incoming radiation.

(iii) For a given value of the frequency ν of the incoming radiation, the *number* of electrons emitted per cm^2 per second is proportional to the intensity.

These properties cannot be understood if one assumes that classical electromagnetic theory rules the phenomenon. In particular, if one assumes that the energy is uniformly distributed over the metallic surface, it is unclear how the emission of electrons can occur when the intensity of the radiation is extremely low (which would require a long time before the electron would receive enough energy to escape from the metal). The experiments of Lawrence and Beans showed that the time lag between the incidence of radiation on a surface and the appearance of (photo)electrons is less than 10^{-9} s.

However, the peculiar emission of electrons is naturally accounted for, if Planck's hypothesis is accepted. More precisely, one has to assume that the energy of radiation is quantized not only when emission or absorption occur, but can also travel in space in the form of elementary quanta of radiation with energy $h\nu$. Correspondingly, the photoelectric effect should be thought of as a collision process between the incoming quanta of radiation and the electrons belonging to the atoms of the metallic surface. According to this quantum scheme, the atom upon which the photon falls receives, all at once, the energy $h\nu$. As a result of this process, an electron can be emitted only if the energy $h\nu$ is greater than the work function W_0:

$$h\nu > W_0. \tag{1.3.1}$$

The first experimental law, (i), is therefore understood, provided one identifies the photoelectric threshold with $\frac{W_0}{h}$:

$$\nu_0 = \frac{W_0}{h}. \tag{1.3.2}$$

If the inequality (1.3.1) is satisfied, the electron can leave the metallic plate with an energy which, at the very best, is $W = h\nu - W_0$, which implies

$$W_{\max} = h(\nu - \nu_0). \tag{1.3.3}$$

This agrees completely with the second law, (ii). Lastly, upon varying the intensity of the incoming radiation, the number of quanta falling upon the surface in a given time interval changes, but from the above formulae it is clear that the energy of the quanta, and hence of the electrons emitted, is not affected by the intensity.

In the experimental apparatus (see figure 1.1), ultraviolet or X-rays fall upon a clean metal cathode, and an electrode collects the electrons that are emitted with kinetic energy $T = h\nu - W_0$. If V_0 is the potential for which the current vanishes, one has (see figure 1.3)

$$V_0 = \frac{h\nu}{e} - \frac{W_0}{e}. \tag{1.3.4}$$

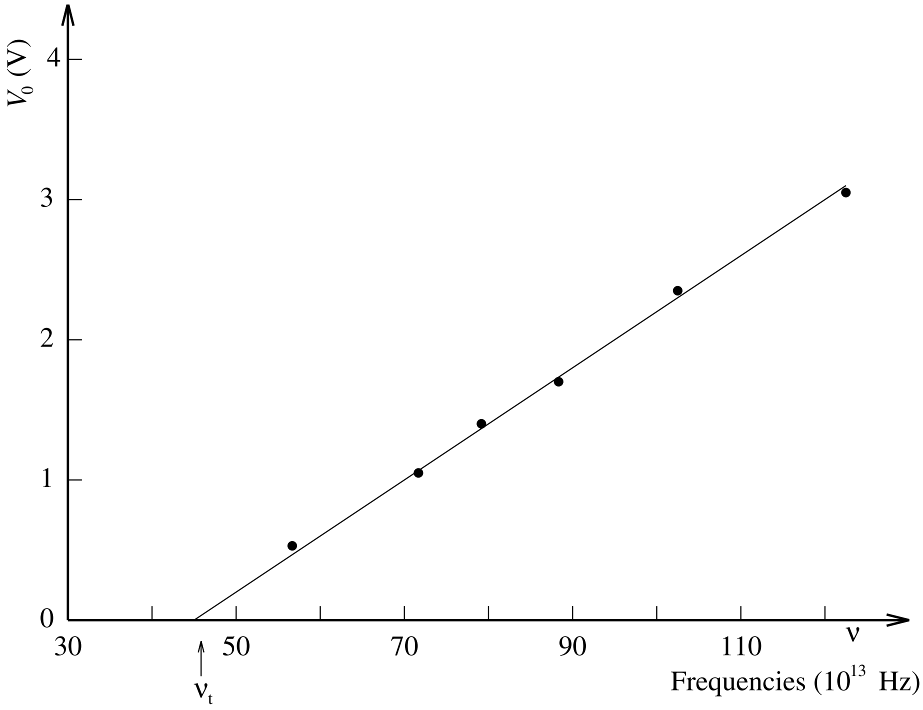

Fig. 1.3. Results of the Millikan experiment for the retarding potential V_0 expressed as a function of frequency (Millikan 1916, © the American Physical Society). A linear relation is found between V_0 and ν, and the slope of the corresponding line is numerically equal to $\frac{h}{e}$. The intercept of such a line on the ν axis is the lowest frequency at which the metal in question can be photoelectrically active.