THE OLD QUANTUM THEORY

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Preface

ALTHOUGH it is well known that for a proper discussion of atomic properties one needs wave mechanics and that the old quantum theory developed by Bohr, Sommerfeld, Kramers and many others between 1913 and 1926 is not a proper basis, there are many atomic phenomena which receive at least a qualitative explanation in the old quantum theory. An account of this theory seems therefore to be of some interest and in the present volume we sketch how it developed from Planck's first papers on black-body radiation through Einstein's and Rutherford's work to the rather complicated theory which was finally replaced by Schrödinger's wave mechanics and Heisenberg's matrix mechanics.

I should like to express my thanks to Professor R. E. Peierls for useful criticism, to Mrs. D. Gordon of the Yale Physics Department for her help in locating the relevant literature, and to my wife for help in preparing the manuscript. This book was written during a stay at Yale, and I should like to express my gratitude to Professor W. E. Lamb, Jr., and to other members of the Yale Physics Department for their hospitality. Finally, I express my thanks to the authors and publishers of the papers reprinted in Part 2 for their permission to do so.

D. TER HAAR

Introduction

THE nineteenth century saw the beginning of the enormous expansion of physics, which in the second half of the twentieth century is showing signs of exploding and of fragmenting physics into a collection of only loosely connected specialized disciplines. In the latter part of the nineteenth century it was felt that the laws of nature were well understood and that only patience and perseverance were needed to explain all physical phenomena. However, the first signs were beginning to show that there might still be effects which fell outside the framework of nineteenth-century physics. The atomistic nature of matter was known, but it was not yet realized in how far the classical, Newtonian laws were inadequate to explain phenomena at the atomic level. The present volume is concerned with the story of how the classical laws were modified by Planck, Einstein, Rutherford, Bohr and others to account for atomic phenomena. We shall be mainly concerned with the development of quantum theory from its start at the very end of the nineteenth century until the beginning of the twenties. A companion volume (Ludwig, 1967) will describe the change from the old quantum theory to the wave mechanics of Schrödinger and Heisenberg, while another volume (Hindmarsh, 1966) is devoted to a discussion of atomic spectra.

The old quantum theory although being, as we now know, an incomplete theory, by being based upon classical mechanics can be more easily visualized and, therefore, can give the student a rough idea of the processes which are important in atomic phenomena. For a more thorough understanding of such processes, one must have recourse to quantum mechanics textbooks (e.g. Landau and Lifshitz, 1965; Davydov, 1965), but for a first rough guide, the old quantum theory still has its undoubted merits.

In presenting the history of quantum mechanics from 1900 to the development of wave mechanics within the confines of a paperback, we must, of necessity, leave out much of interest. Roughly speaking, we shall discuss first of all Planck's discovery of his radiation law. Then we turn to Einstein's introduction of quanta. Next comes the Rutherford model of the atom and Bohr's postulates, so beautifully confirmed by the Franck–Hertz experiment. We conclude with a description of how Bohr's theory could explain the main features of the atomic spectra and with a brief summary of other important developments in the period covered by us.

There are many places where one can find an account of the historical development of the old quantum theory. Among semi-popular accounts, we may refer to Abro's book (1951), the account by Kramers and Holst (1923), and various articles in *Science* and other journals (Meissner, 1951; Einstein, 1951; Sommerfeld and Bopp, 1951; Mendelssohn, 1959; Bohr, 1962; Condon, 1962; Peierls, 1964). Accounts containing more scientific details can be found in various books. We mention only a few: the proceedings of the early Solvay Congresses (Solvay Congress 1911, 1913, 1921), those of the 1913 Wolfskehl meeting (Planck *et al.*, 1914), Sommerfeld's famous textbook (1923), Pauli's articles in the first edition of the old *Handbuch* and in Müller–Pouillet's book (Pauli, 1926, 1929), Rubinowicz's article (1933) in the old *Handbuch*, two articles by Rosenfeld (1936, 1963), Whittaker's comprehensive monograph (1954), and Tomonaga's textbook (1962). Various papers by M. J. Klein (1959, 1962, 1963 a, b, 1964, 1965) also contain useful discussions of specific points. We have made extensive use of most of these, and we refer to them for many details which we have omitted and for a discussion of those topics which lack of space prevented us from considering.

CHAPTER I

The Black Body Radiation Law

IT IS well known that a study of the black body radiation led Planck to the introduction of the quantum of action which then, through the work of Einstein, Bohr, Schrödinger and Heisenberg, was extended into modern quantum mechanics. The story of how Planck was led to the radiation law which bears his name has often been told (Rosenfeld, 1936; Einstein, 1951; Whittaker, 1954; Klein, 1962) and is also recounted by Planck himself, both in his Nobel Lecture (1920) and in personal reminiscences written, when he was eighty-five (Planck, 1943; see also Planck, 1949), to preserve for posterity the reasoning which led to the radiation law. However, it is instructive to compare these reminiscences with the many papers written by Planck between 1896 and 1900 (all Planck's papers were collected and reprinted on the occasion of the centenary of his birth (Planck, 1958) and are thus more or less readily available) as the development of Planck's ideas was not quite as uneventful as he remembered it to be.†

In the last half and especially the last decade of the nineteenth century, a great deal of effort was concentrated, both experimentally and theoretically, on finding out how the energy of the

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† This is also hinted at by von Laue in the preface to Planck's Collected Papers. Especially the importance of Kirchhoff's law that the radiation spectrum is independent of the nature of the black body, which Planck gives as the guiding principle of his investigations both in his Nobel Lecture and in the 1943 paper, is not referred to by him in any of his earlier papers on the subject, but only in the 1899 paper (Planck, 1899), which was later condensed by him together with four others in a paper in the *Annalen der Physik* (Planck, 1900a). Planck's own account of the developments has been repeated by Rosenfeld (1936), who bases his account clearly on Planck's Nobel Lecture.

radiation emitted by a black body was distributed over the various wavelength—or frequencies. The names of Kirchhoff, Wien, Rayleigh and Jeans are closely connected with these developments, as well as that of Planck. A body at a definite temperature T will both emit and absorb radiation. If it absorbs all the radiation incident upon it, it is called a *black body*. From this it follows (Kirchhoff, 1859) that the radiation emitted by a black body will depend only on its temperature, but not on its nature: if we consider a number of bodies in equilibrium inside a cavity, the walls of which are kept at a constant temperature T, we should reach an equilibrium situation. At equilibrium, the ratio of the radiation of a given wavelength absorbed by one body to the radiation of the same wavelength emitted by the same body should be unity, as otherwise there would not be equilibrium. As the radiation absorbed will be determined by the radiation density in the cavity and hence by its temperature, we find that the radiation emitted by a black body will be a function of T only.

We now define $u(\nu, T)\,d\nu$ as the energy density of all radiation components with frequencies between ν and $\nu+d\nu$. It is remarkable how much one can find out about $u(\nu, T)$ from general considerations without considering a specific model. In fact we shall show presently how, from general thermodynamic considerations, one can derive that $u(\nu, T)$ must have the form

$$u(\nu, T) = \nu^3 f(\nu/T). \tag{1.1}$$

From this it follows, first of all, that if the spectral distribution shows a maximum at a frequency ν_m—as was found to be the case experimentally, long before it was proved theoretically—this frequency will shift with temperatures in such a way that

$$\nu_{\mathrm{m}}/T = \text{constant}, \tag{1.2}$$

or, if we introduce wavelengths instead of frequencies,

$$\lambda_{\mathrm{m}}\, T = \text{constant}, \tag{1.3}$$

which is *Wien's displacement law* (1893).

The proof is simple. From equation (1.1) it follows that if $u(\lambda, T)\,\mathrm{d}\lambda$ is the energy density for wavelengths between λ and $\lambda+\mathrm{d}\lambda$, it is given by the expression

$$u(\lambda, T) = \frac{c^4}{\lambda^5} f\left(\frac{c}{\lambda T}\right), \tag{1.4}$$

where c is the velocity of light ($c = \nu\lambda$). The condition $\mathrm{d}u/\mathrm{d}\lambda = 0$ from which we find the wavelength λ_m at which the maximum occurs is then the solution of the equation

$$-\frac{c^5}{\lambda T}\left[\frac{c}{\lambda T} f'\left(\frac{c}{\lambda T}\right) + 5f\left(\frac{c}{\lambda T}\right)\right] = 0, \tag{1.5}$$

from which equation (1.3) follows.

Secondly, we find from equation (1.1) the Stefan–Boltzmann law (Stefan, 1879; Boltzmann, 1884) which states that the total radiation energy density, $u(T)$, is proportional to the fourth power of the absolute temperature. Indeed,

$$\begin{aligned} u(T) &= \int_0^\infty u(\nu, T)\,d\nu = \int_0^\infty \nu^3 f(\nu/T)\,d\nu \\ &= T^4 \int_0^\infty y^3 f(y)\,dy, \quad y = \nu/T. \end{aligned} \tag{1.6}$$

To prove equation (1.1), we shall proceed slightly differently from Wien's procedure (1893; see, for instance, Planck, 1921, or Born, 1935) by using the concept of parameter or adiabatic invariance,† following a discussion given elsewhere (ter Haar and Wergeland, 1966, § V. 3. 3). The proof consists of three parts: first we show that in a reversible adiabatic transformation the ratio ν/T is invariant; secondly, we note that the total energy of the radiation field can be written as the sum of the contributions from different frequencies and that each contribution can be written as a function of ν/T multiplied by T or by ν; finally, we find the number of eigenfrequencies in a volume V lying between ν and $\nu+d\nu$ and thus we can obtain the total energy density in that region, for which we find equation (1.1).

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† For a discussion of adiabatic invariance see, for instance, the review article by Ehrenfest (1923).

We shall consider the radiation field in a volume V in the shape of a cube of edgelength L with reflecting walls. The equilibrium radiation field will then consist of standing waves, and the condition that the electric field vanish at the walls which means that one must "fit" the electromagnetic waves into the cube leads to the following relation for the frequency:

$$\left(\frac{\nu L}{c}\right)^2 = l^2+m^2+n^2, \tag{1.7}$$

where l, m, and n are integers.

We now first of all note that if we consider an adiabatic change in V, the quantities l, m and n being integers and thus being unable to change infinitesimally will remain invariant. Under an adiabatic transformation νL will thus be invariant, or introducing the volume V instead of L:

$$\nu^3 V = \text{invariant under adiabatic transformation.} \tag{1.8}$$

One can prove that this result is independent of the shape of the volume.

It will be more convenient to have a relation between ν and T rather than between ν and V. To find that relation, we must consider the entropy of the radiation field. From electromagnetic theory (for instance, Planck, 1921, § 59) it follows that the radiation pressure P is one-third of the total radiation energy density $u(T)$:

$$P = \tfrac{1}{3}u(T). \tag{1.9}$$

Combining equation (1.9) with the thermodynamic equation of state (ter Haar and Wergeland, 1966, § II. 7. 1)

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P, \tag{1.10}$$

and the relation $U = uV$, gives us

$$u = \tfrac{1}{3}T\frac{du}{dT} - \tfrac{1}{3}u, \tag{1.11}$$

or

$$u = aT^4, \tag{1.12}$$

in accordance with equation (1.6).

Combining equations (1.9) and (1.12) with the thermodynamic Maxwell relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V, \tag{1.13}$$

we find

$$S = \tfrac{4}{3}aT^3V. \tag{1.14}$$

Comparing equations (1.14) and (1.8), we see that under an adiabatic (or isentropic) transformation the ratio ν/T must be invariant, which concludes the first part of our proof.

As the resolution of a spectrum into its components—by means of gratings, say—is a reversible process, the entropy s per unit volume can be written as the sum of contributions $s_\nu(T)$ corresponding to different frequencies. Each of these terms, being a function of ν and being the entropy density corresponding to the specific frequency ν, can depend on ν and T only through the adiabatic invariant ν/T, or

$$s = \sum_\nu s(\nu/T). \tag{1.15}$$

Writing

$$u(T) = \sum_\nu u_\nu(T), \tag{1.16}$$

and using equation (1.12) and (1.14), from which follows that

$$s = \frac{4u}{3T}, \tag{1.17}$$

and hence

$$u_\nu(T) = Tf_1(\nu/T) = \nu f_2(\nu/T), \tag{1.18}$$

and thus

$$u(T) = \sum_\nu \nu f_2(\nu/T),$$

$$= \int \nu Z(\nu)\,d\nu f_2(\nu/T), \tag{1.19}$$

corresponding to the following equation for the function $u(\nu, T)$ defined at the beginning of this section:†

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† Whereas $u_\nu(T)$ is the energy density corresponding to one of a set of discrete frequencies which has the dimensions of energy per unit volume, $u(\nu, T)$ is the energy density per unit frequency range with dimensions energy per unit volume per unit frequency.

$$u(\nu, T) = \nu Z(\nu) f_2(\nu/T). \tag{1.20}$$

In equations (1.19) and (1.20), $Z(\nu)\,d\nu$ is the number of frequencies between ν and $\nu + d\nu$ which is present in the radiation. From equation (1.7), we see that the number is proportional to the number of points with integral coordinates within the spherical shell between the spheres with radii $\nu L/c$ and $(\nu + d\nu)L/c$, and we find thus

$$Z(\nu) = C\nu^2, \tag{1.21}$$

where C is a constant $(= 8\pi/c^3)$, independent of ν. Combining equations (1.20) and (1.21), we find equation (1.1), which concludes our proof.

We have now exhausted the information which can be obtained from the thermodynamics alone. The form of the function of $f(\nu/T)$ in equation (1.1) cannot be obtained this way. We shall, however, follow Planck's reasoning (1900a) and pursue the thermodynamical argument a little further. We can use Kirchhoff's law, which states that the radiation field is the same independent of what body is in equilibrium with it. Therefore we assume that the black body consists of a system of Hertzian vibrators, that is, radiating harmonic oscillators, as such a system enables us to calculate the radiation field explicitly. The radiation emitted per unit time by an oscillating dipole is given by the expression (for instance, Born, 1935)

$$E_{\text{em}} = \frac{8\pi^2 e^2 \nu^2}{3mc^3}\,\bar{\varepsilon}, \tag{1.22}$$

where e, m and $\bar{\varepsilon}$ are the oscillating charge, its mass, and the average value of the energy of the harmonic oscillator. Similarly, the energy absorbed per unit time by the vibrator is given by

$$E_{\text{abs}} = \frac{\pi e^2}{3m}\,u(\nu, T). \tag{1.23}$$

In equilibrium $E_{\text{em}} = E_{\text{abs}}$, or

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3}\,\bar{\varepsilon}. \tag{1.24}$$

The natural thing to do would now be to take for $\bar{\varepsilon}$ the average energy of an harmonic oscillator at a temperature T. If Planck had done this, he would have used the classical value kT (k = Boltzmann's constant; see, for instance, ter Haar, 1966, §2.4) for the average energy of a one-dimensional harmonic oscillator and would have obtained the so-called Rayleigh–Jeans law (Rayleigh, 1900; Jeans, 1905), which was, indeed, obtained by this method, Jeans' contribution being essentially the correction of a numerical factor in Rayleigh's expression:

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3} kT, \tag{1.25}$$

which is—as should be the case—an example of equation (1.1).

Fortunately, it is likely that Planck was not aware of Rayleigh's paper because he would almost certainly have agreed with Rayleigh's reasoning even though it was well known that expression (1.25) did not agree with experimental data.† In fact, until 1900 the experimental data were better represented by Wien's law (1896):

$$u(\nu, T) = b\nu^3 e^{-a\nu/T}. \tag{1.26}$$

As Planck himself remarked on several occasions (1943, 1949), very few physicists were interested in entropy, a subject which he had studied for most of his active career. Most people were trying to find the energy density of the radiation field as function of ν and T, but Planck suspected that the key to the problem was to be found in the relation between the entropy density s_ν and the oscillator energy $\bar{\varepsilon}$.

To find this relation, Planck (1900b) proceeded as follows. Consider a set of n identical, independent oscillators, which behave in exactly the same way. Their total energy ε_n is then equal to $n\varepsilon$, the excess of this energy over the equilibrium value $n\,\Delta\varepsilon = \Delta\varepsilon_n$, the rate of change $d\varepsilon_n/dt = n\,d\varepsilon/dt$, and their entropy $S_n = nS$. The change in the energy of this set of oscillators will

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† Klein (1962, 1963a) suggests that Planck knew of Rayleigh's paper, but did not attach any significance to it.

be related to an increase in entropy. Planck showed that for a single oscillator the rate of change of the entropy satisfies the equation.

$$\frac{dS}{dt} = -\frac{d\varepsilon}{dt}\Delta\varepsilon f(\varepsilon), \qquad f(\varepsilon) = -\frac{3}{5}\frac{d^2S}{d\varepsilon^2}. \tag{1.27}$$

Assuming now (i) that the same expression holds for the set of n oscillators and (ii) that the rate of change of the entropy of n oscillators is equal to n times the rate of change of the entropy of a single oscillator, we find

$$\frac{d\varepsilon_n}{dt}\Delta\varepsilon_n f(\varepsilon_n) = n\frac{d\varepsilon}{dt}\Delta\varepsilon f(\varepsilon), \tag{1.28}$$

or

$$f(n\varepsilon) = \frac{1}{n}f(\varepsilon). \tag{1.29}$$

The solution of this functional equation is $f(\varepsilon) = \text{constant}/\varepsilon$, and thus we have

$$\frac{d^2S}{d\varepsilon^2} = -\frac{\alpha}{\varepsilon}, \tag{1.30}$$

or

$$\frac{dS}{d\varepsilon} = -\alpha \ln \gamma\varepsilon. \tag{1.31}$$

Combining this with the thermodynamic relation

$$\frac{dS}{d\bar{\varepsilon}} = \frac{1}{T}, \tag{1.32}$$

we find

$$\bar{\varepsilon} = \frac{1}{\gamma}e^{-1/\alpha T}. \tag{1.33}$$

From the equation (1.24) and the knowledge that $u(\nu, T)$ must satisfy equation (1.1), we now obtain Wien's law (1.26).

In fact, Planck had derived Wien's law in his earlier paper (1900a), but had clarified his proof in the later paper (Planck, 1900b) as evidence began to accumulate against Wien's law.

However, the experimental evidence that at longer wavelengths Wien's law did not agree with experiments became too overwhelming, and Planck became obliged to modify his argument. He realized that it might be possible—although, as he himself put it, "not easily understandable and, in any case, difficult to prove" —that the left-hand side of equation (1.28) could not be found by the argument given, but that it might depend on $\bar{\varepsilon}$ in a more complicated manner. Instead of using equation (1.30), Planck tried other expressions for $d^2S/d\bar{\varepsilon}^2$ and found that the relatively small change to

$$\frac{d^2S}{d\bar{\varepsilon}^2} = -\frac{\alpha'}{\bar{\varepsilon}(\beta+\bar{\varepsilon})}, \tag{1.34}$$

together with equations (1.32) and (1.24) leads to

$$u(\nu, T) = \frac{b\nu^3}{e^{a\nu/T}-1}, \tag{1.35}$$

the expression which bears Planck's name and which was and is in excellent agreement with experimental data. In equation (1.35) a and b are related to α' and β by the equations

$$a\nu = \frac{\beta}{\alpha'}, \qquad b\nu = \frac{8\pi}{c^3}\,\beta. \tag{1.36}$$

Once Planck had seen that his radiation law fitted the experimental data, he tried to invest the formulae—which had been derived completely by an *ad hoc* argument—with a physical meaning. He had "until then not bothered about the connexion between entropy and probability" but "after a few weeks of the most strenuous work of his life" he presented on 14 December 1900 (Planck, 1900d; reprinted in this volume on p. 82), less than two months after he had presented the Planck radiation law (Planck, 1900c; reprinted in this volume on p. 79), a derivation of equation (1.35) based upon Boltzmann's relation between entropy and probability,

$$S = k \ln W, \tag{1.37}$$

where k is a constant and W the probability that a certain state is realized. We may note here that k in Boltzmann's papers appeared in the ratio of the gas constant R and Avogadro's number N_{Av} and that it was Planck who was the first to introduce k so that its name *Boltzmann's constant* is a slight, though understandable, misnomer. It was also Planck who determined its numerical value for the first time and Meissner (1951) suggests Planck–Boltzmann constant for k, while Lorentz often refers to it simply as Planck's constant. Planck himself calls $\frac{3}{2}k$ (the average kinetic energy at absolute temperature 1°K) the Boltzmann–Drude constant.

To find W, Planck proceeded as follows. Let ε_N again be the energy of the N oscillators of a given frequency and let $\bar{\varepsilon}$ be their average energy; we have

$$\varepsilon_N = N\bar{\varepsilon} \tag{1.38}$$

while for the entropy we have

$$S_N = NS, \tag{1.39}$$

if we assume that the oscillators are independent. To find W it is *necessary* (as noted by Planck) to consider ε_N as a quantity which can only be divided into an integral finite number P of equal parts Δ and not as a quantity which can be divided continuously into infinitesimal parts; we thus have

$$\varepsilon_N = P\Delta, \tag{1.40}$$

where P is a (large) integer, and the number of ways W, in which we can divide the P equal parts over the N oscillators is given by the equation

$$W = \frac{(N+P-1)!}{(N-1)!\,P!}. \tag{1.41}$$

This follows as W is the number of ways in which $N-1$ strokes and P dots can be arranged (see Fig. I.1).

(...|..|.||...|..|.....|..)

FIG. I.1. The $(N-1)$ strokes divide the N resonators and the dots represent the P quantities Δ.

As N and P are large numbers, we can neglect the 1's in the enumerator and the denominator of (1.41) and use for the factorial the Stirling formula

$$x! \approx \frac{x^x}{e^x}, \tag{1.42}$$

so that we get from equations (1.37), (1.41) and (1.42)

$$S_N = k\{(N+P)\ln(N+P) - N\ln N - P\ln P\}, \tag{1.43}$$

or, from equations (1.40), (1.38) and (1.39),

$$S = k\left\{\left(1+\frac{\bar{\varepsilon}}{\Delta}\right)\ln\left(1+\frac{\bar{\varepsilon}}{\Delta}\right) - \frac{\bar{\varepsilon}}{\Delta}\ln\frac{\bar{\varepsilon}}{\Delta}\right\}. \tag{1.44}$$

From equation (1.44) we find

$$\frac{d^2S}{d\bar{\varepsilon}^2} = \frac{-k}{\bar{\varepsilon}(\Delta+\bar{\varepsilon})}, \tag{1.45}$$

which is in fact the same as equation (1.34) with

$$k = \alpha', \qquad \Delta = \beta. \tag{1.46}$$

From equation (1.18) it follows that T/v is a function of ε/v and thus from equation (1.32) that S is a function of ε/v. Comparing this with equation (1.44) it follows that Δ must be proportional to v:

$$\Delta = hv, \tag{1.47}$$

and we can then use equations (1.35), (1.36), (1.46) and (1.47) to find for the radiation energy density:

$$u(v, T) = \frac{8\pi hv^3}{c^3}\frac{1}{e^{hv/kT}-1}. \tag{1.48}$$

As Planck himself emphasizes, to obtain agreement between (1.48) and the experimental data, it is necessary to keep h finite, although classical arguments require the limit $h \to 0$, which leads to equation (1.25). As Planck wrote in 1943: "Now the theoretically most difficult problem arose to give a physical meaning to this peculiar constant (h), as its introduction meant a break with classical theory which was much more fundamental than I had suspected at the beginning. . . . During many years, I time and again attempted to fit the quantum of action in the framework of classical physics." It was not until Einstein's introduction of light quanta that the physical meaning of h and of the basis of Planck's theory became clearer (see next chapter).

From the experimental data on $u(\nu, T)$ Planck was able to determine the numerical values of h and k for which he found (Planck, 1901)

$$h = 6{\cdot}55 \times 10^{-27}\,\text{erg sec}, \qquad k = 1{\cdot}346 \times 10^{-16}\,\text{erg/°K}, \tag{1.49}$$

which are remarkably close to the present values (Cohen and DuMond, 1963):

$$h = 6{\cdot}626 \times 10^{-27}\,\text{erg sec}, \qquad k = 1{\cdot}3805 \times 10^{-16}\,\text{erg/°K}. \tag{1.50}$$

CHAPTER II

Light Quanta

PLANCK'S papers seem to have been hardly noticed by his contemporaries and certainly the implications of his procedure were not realized. In 1905 Einstein published in one volume of the *Annalen der Physik* three epoch-making papers (Einstein, 1905a, b, c; the first of these is reprinted in this volume on p. 91). One was his paper on Brownian motion, one his paper on the special theory of relativity, and the first of the three papers—for which Einstein received his Nobel Prize, which was not awarded for his work on the relativity theory—was his introduction of light quanta. Although Einstein quotes Planck's radiation law, it is only because it was known to represent better than any other formula the experimental data. Einstein felt then, as he states in a later paper (Einstein, 1906), that his and Planck's considerations were to some extent complementary, but in this later paper he shows that, in fact, Planck was using the concept of light quanta which he developed in his 1905 paper.

Although one often reads the statement that Einstein was concerned in his 1905 paper with an explanation of the photo-electric effect, a study of the paper reveals that this is not the case; in fact, the measurements of this effect at that time were not really sufficiently accurate to point without any doubt to a violation of classical behaviour. In his paper, Einstein sketches how he came to the idea that a ray of light when propagating through space is not continuously spread over space, but consists of a finite number of light quanta—or energy quanta, as Einstein calls them. From his account it becomes clear that he was worried not so much by the evidence concerning the photo-electric effect as well as by the impossibility of fitting black-body radiation into classical Maxwell theory, and that he appealed to fluorescence, photo-electricity, and photo-ionization data as evidence in favour of his thesis.

It is interesting to follow Einstein's reasoning and to compare it with some of the steps in Planck's derivation of the radiation law. First of all, Einstein points out that classical theory should lead to Rayleigh's law (1.25) for the radiation density—in contradiction to experimental data—and that this radiation density would lead to an infinite energy density in space, if it were valid for all values of ν—what is nowadays called the ultraviolet catastrophe. He noted that Planck's radiation law, which he quotes in the form (1.35) rather than (1.48), leads in the limit as T/ν is large to the classical formula (1.25), and he concludes that, therefore, for long wavelengths and high temperatures† the classical argument should be valid. However, for small values of T/ν the classical theory is clearly insufficient.

For low temperatures and short wavelengths, Planck's law goes over into Wien's law (1.26). In the region where Wien's law is valid we get by integrating equation (1.31) and using equations (1.26), (1.24) and (1.33), for the entropy density σ the equation

$$\sigma = -\frac{u(\nu, T)}{a\nu}\left[\ln\frac{u(\nu, T)}{b\nu^3} - 1\right]. \tag{2.1}$$

If E is the total energy in a volume V in the frequency interval ν, $\nu+d\nu$ and S its entropy, so that we have

$$E = Vu(\nu, T)\,d\nu, \qquad S = \sigma V\,d\nu, \tag{2.2}$$

we find from equations (2.1) and (2.2)

$$S = -\frac{E}{a\nu}\left[\ln\frac{E}{Vb\nu^3\,d\nu} - 1\right], \tag{2.3}$$

and if we compare the entropy S with the entropy S_0 of the same amount of radiative energy E in the same frequency range, but

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† Einstein uses the term "radiation density" often when he means "temperature", without clearly stating their interrelation.

within a volume V_0, we find

$$S - S_0 = \frac{E}{a\nu} \ln \frac{V}{V_0}. \tag{2.4}$$

Comparing this with the formula for the entropy change of a perfect gas of n particles (e.g. ter Haar and Wergeland, 1966, §2.5),

$$S - S_0 = nk \ln \frac{V}{V_0}, \tag{2.5}$$

Einstein concluded that in the region where Wien's law is valid, one can say that thermodynamically speaking monochromatic radiation consists of independent energy quanta of magnitude $ka\nu$, or using the fact that $a = h/k$ of magnitude $h\nu$.

Having thus shown the plausibility of the concept of light quanta from considerations of black-body radiation under conditions where Wien's law holds, Einstein points out that, on this basis, one would expect that in fluorescence the emitted light should have a lower frequency than the incident light (Stokes' rule), that in the photo-electric effect the energy E of the electrons freed from a metal by an incident light ray should be independent of the intensity of the light, but depend on the frequency ν of the light in a *linear* way, as follows:†

$$E = h\nu - \phi, \tag{2.6}$$

where ϕ is the energy needed to free an electron from the metal (the work function), and finally that for photo-ionization also the frequency of the light must exceed a limiting value.

In his 1906 paper, Einstein states that he had now realized that light quanta occur in an essential way in Planck's derivation of the black-body radiation law. He then states the essential assumptions implied in Planck's arguments: (i) the energy of a resonator must be an integral number of $h\nu$; (ii) the energy of a resonator changes discontinuously in absorption or emission by an amount which is an integral number of $h\nu$; and (iii), in using equation (1.22) one applies Maxwell's theory; although it is not applicable to the

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† It is interesting to note that equation (2.6) is a special case—for the case of continuously changing energies—of the Bohr relation (4.8).

resonators, one may put the average energy of a resonator equal to the energy evaluated from the Maxwell theory. There still remains one point which must be cleared up. Going through Einstein's reasoning backwards, one ends up *not* with Planck's radiation law but with the Wien law. We must yet find another link in the chain, which leads from the quantum hypothesis to the black-body radiation law. Planck's derivation of expression (1.41) for W meant that each state in which there are n_1 quanta $h\nu_1$, n_2 quanta $h\nu_2, \ldots$ has the same statistical weight. If we had applied classical arguments, the weights would not have been equal, but inversely proportional to $n_1!n_2!\ldots$ (compare the discussion in ter Haar, 1966, chap. IV). This point was made by Einstein in his paper on the theory of specific heats (Einstein, 1907). Nowadays we would say that it expresses the fact that light quanta or *photons* are bosons. In this connexion, it is of interest to return to equations (1.34) or (1.45) (see Einstein, 1909).

Let us now invert equation (1.37) to obtain an expression for the probability P for finding a state with entropy S:

$$P = C\,e^{S/k}, \tag{2.7}$$

where C is a normalizing constant.

If we now consider a situation where S and thus P are functions of the energy E and where E can fluctuate around its equilibrium value E_0, for instance, because E is the energy of a small part of a larger system, the total energy of which is fixed, we can use equation (2.7) to calculate the dispersion in E. The equilibrium value E_0 is clearly determined from the condition that P be an extremum, so that we find on expanding $S(E)$ around E_0 that we have

$$S(E) = S(E_0) + \frac{1}{2}\left(\frac{\partial^2 S}{\partial E^2}\right)_0 (E-E_0)^2 + \ldots, \tag{2.8}$$

since $(\partial S/\partial E)_0$ vanishes. Note that as $S(E_0)$ is a maximum, $(\partial^2 S/\partial E^2)_0$ is negative.

From equations (2.7) and (2.8), we now find for the fluctuations $\overline{\Delta E^2}$ in energy

$$\overline{\Delta E^2} = \overline{(E-E_0)^2} = \frac{\int (E-E_0)^2 P(E)\,dE}{\int P(E)\,dE}$$
$$= -k\left[\frac{\partial^2 S}{\partial E^2}\right]^{-1}, \tag{2.9}$$

which shows the physical meaning of the left-hand side of equation (1.34).

We now wish to apply this formula to the radiation field. Using equations (1.45) and (1.47), we get

$$\overline{\Delta \bar{\varepsilon}^2} = \bar{\varepsilon}^2 + h\nu\bar{\varepsilon}. \tag{2.10}$$

If we write $\bar{\varepsilon} = nh\nu$ in accordance with Einstein's light quanta hypothesis, this equation becomes

$$\overline{\Delta n^2} = \overline{(n-n_0)^2} = n_0^2 + n_0. \tag{2.11}$$

This is, indeed, the formula for the fluctuations in the number of bosons (see, for example, ter Haar, 1966, chap. VI). We note that, if we neglect the first term on the right-hand side of equation (2.11), we would have found for $\overline{\Delta n^2}$ exactly the expression we would have expected for the random fluctuations in the number of independent particles within a certain volume: it expresses the corpuscular nature of light. The fact that there is a second term expresses that the quanta are not independent: their interdependence is a statistical one, which we express by saying that photons are bosons.

Another way of looking at the first term on the right-hand side of equation (2.10) is to say that it expresses the wave nature of light. To see this, we remind ourselves that in classical electromagnetic theory fluctuations arise from the interference of light rays with approximately the same wave vectors. Without going into a detailed calculation of this term, based upon classical electromagnetic theory, we can use dimensional analysis to find its form—apart from a possible dimensionless multiplying factor of order of magnitude unity (Einstein, 1909).

We first of all notice that as the components of different frequencies are independent, the total dispersion in the energy E corresponding to radiation with frequencies between ν and $\nu+d\nu$ in a volume V, will be given by the equation

$$\overline{\Delta E^2} = \int_{\nu}^{\nu+d\nu} \overline{\Delta\varepsilon^2}\, Z(\nu) V\, d\nu = \overline{\Delta\varepsilon^2}\, Z(\nu) V\, d\nu, \tag{2.12}$$

with $Z(\nu)$ given by equation (1.21). Secondly, we expect that $\overline{\Delta E^2}$ will depend only on the wavelength λ $(=c/\nu)$, $d\lambda$ $(=c\,d\nu/\nu^2)$, the radiation energy density $u(\lambda, T)$ $[=u(\nu, T)(d\nu/d\lambda)]$, and V. Moreover, because of the independence of the various components of the radiation field, we would expect $\overline{\Delta E^2}$ to be proportional to V and $d\lambda$. From dimensional arguments, it then follows that we have

$$\overline{\Delta E^2} = C[u(\lambda, T)]^2 \lambda^4 V\, d\lambda, \tag{2.13}$$

where C is a numerical factor which the exact calculation shows to be equal to $1/8\pi$. Using equations (2.12) and (1.24), we see that equation (2.13) indeed gives the first term on the right-hand side of equation (2.10).†

Photons possess momentum as well as energy. If the number of photons with frequency ν per unit volume is n_ν, the energy density is $n_\nu h\nu$ and the energy flux density $cn_\nu h\nu$. One of the consequences of the theory of relativity and the equivalence of mass and energy is, as was shown by Planck (1908), that the momentum density of the radiation field is equal to the energy flux divided by c^2. This leads to a momentum density equal to $n_\nu h\nu/c$, showing that the momentum of a photon is equal to its energy divided by c (compare also Einstein, 1917, and the discussion in Chapter VI).

This result was obtained by Einstein (1909) by a consideration of the Brownian motion of a reflecting mirror in a gas in which there is also black-body radiation. The collisions of the gas

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† A simpler derivation of equation (2.10) or of the complete equation for $\overline{\Delta E^2}$ is given by a straightforward thermostatistics argument (e.g. ter Haar, 1966, § 8.2).

molecules will make the mirror move. Its motion will be subject to frictional forces, partly due to the gas, but partly due to the fact that the radiation pressure on a moving mirror is different on its two sides. If there were no fluctuations in the radiation pressure, the net result would be that the energy of the gas would be transformed into radiative energy: there would not be an equilibrium situation. Equilibrium exists because there are fluctuations in the radiation pressure such that the force on the mirror is just sufficient to restrict the kinetic energy of the mirror to $\frac{1}{2}kT$ as required by the general theory of Brownian motion. One can use electromagnetic theory to calculate the radiation pressure fluctuations and the result is (Einstein and Hopf, 1910) that the fluctuations in the momentum density are exactly $1/c$ times the fluctuations in the energy density as following from equation (2.10), from which follows that the momentum of a photon is equal to $h\nu/c$.

In Chapter VI we shall discuss Einstein's contribution to the theory of the emission and absorption of light by atoms, but we shall conclude the present chapter with a discussion of Einstein's theory of specific heats (1907). Soon after his 1905 and 1906 papers on the light quanta hypothesis, Einstein came to the conclusion that if the theory were to have a firm foundation, the average energy $\bar{\varepsilon}$ of a harmonic oscillator should be given by the equation (compare equation 1.48)

$$\bar{\varepsilon} = \frac{h\nu}{e^{h\nu/kT} - 1}, \tag{2.14}$$

independent of whether we are dealing with one of the Planck resonators or with an oscillator occurring in some other physical system. If this is the case, we must expect consequences of this expression in the thermal behaviour of solids. A crystal of N atoms will have $3N$ degrees of freedom. If we assume that all atoms are freely vibrating with frequency ν, the total energy E of the crystal at temperature T will be given by $3N\bar{\varepsilon}$, or

$$E = \frac{3Nh\nu}{e^{h\nu/kT} - 1}, \tag{2.15}$$

and its specific heat by

$$C_V = \frac{dE}{dT} = 3Nk\left(\frac{h\nu}{kT}\right)^2 [e^{h\nu/kT}-1]^{-2}\, e^{h\nu/kT}. \qquad (2.16)$$

We first of all note that in the limit as $h\nu \ll kT$, $C_V = 3Nk$, which is the classical Dulong–Petit expression. However, at low temperatures when $h\nu > kT$, the specific heat dips well below its classical value, behaving asymptomically as $3Nk(h\nu/kT)^2 e^{-h\nu/kT}$. Einstein compared expression (2.16) with experimental data on diamond and found reasonable agreement, although from the figure given in his paper (Einstein, 1907, p. 186) it looks as if the theoretical value of C_V becomes too small for $h\nu/kT \lesssim 0{\cdot}2$. Einstein emphasizes that his theory is correct only if the absorption spectrum of the solid shows a single line, and from the agreement between the theoretical and experimental data for diamond he concludes that diamond should show an absorption maximum at a wavelength of $11\,\mu$. The value of ν follows by adjusting the theoretical curve, which depends on $h\nu/kT$ only, until it fits the experimental curve.

Once one accepts the basic assumption of Einstein's calculation of the specific heat of solids, one can easily extend it to cover the case, where the eigenvibrations of the solid do not have all the same frequency, but show a spectrum. Let $g(\nu)\,d\nu$ be the number of eigenfrequencies in the range ν, $\nu + d\nu$. As the total number of degrees of freedom in the solid is still $3N$, we must have

$$\int_0^\infty g(\nu)\,d\nu = 3N. \qquad (2.17)$$

One can make detailed calculations of $g(\nu)$, making suitable assumptions about the crystal structure and the forces acting between the atoms or ions in the crystal. The first such calculations were made by Born and von Kármán (1912, 1913; for a general review of such questions, see Blackman, 1955, or Haug, 1967), but we shall restrict our discussion to the Debye model of a solid (Debye, 1912). Debye considered the solid to be an elastic continuum in which the longitudinal and transverse velocities of sound were assumed to be equal. In that case, the eigenvibrations are elastic waves and by the same argument which led to equation (1.21), we find that

$$g(\nu) = \frac{12\pi V \nu^2}{s^3}, \tag{2.18}$$

where s is the velocity of the elastic waves (sound waves) in the solid, which we have assumed to be the same for transverse and longitudinal waves. The factor 12 rather than 8 occurs here because sound waves have three polarization degrees of freedom, as against the two polarization degrees of light waves.

Equation (2.18) holds only as long as ν is less than a maximum frequency ν_{m} which is determined from equation (2.17):

$$\int_0^{\nu_{\mathrm{m}}} g(\nu)\, d\nu = 3N, \tag{2.19}$$

or

$$\nu_{\mathrm{m}} = s\left(\frac{3N}{4\pi V}\right)^{\frac{1}{3}}. \tag{2.20}$$

The energy and specific heat of the solid will now be given by the equation

$$E = \int_0^{\nu_{\mathrm{m}}} \frac{h\nu g(\nu)\, d\nu}{e^{h\nu/kT}-1} = 9Nh\nu_{\mathrm{m}}\left(\frac{T}{\Theta}\right)^4 \int_0^{x_{\mathrm{m}}} \frac{x^3\, dx}{e^x-1}, \tag{2.21}$$

$$\begin{aligned} C_V &= k\int_0^{\nu_{\mathrm{m}}} \left(\frac{h\nu}{kT}\right)^2 e^{h\nu/kT}\,[e^{h\nu/kT}-1]^{-2}\, g(\nu)\, d\nu \\ &= 9Nk\left(\frac{T}{\Theta}\right)^3 \int_0^{x} \frac{x^4\, dx}{(e^x-1)(1-e^{-x})}, \end{aligned} \tag{2.22}$$

where

$$x = \frac{h\nu}{kT}, \qquad x_{\mathrm{m}} = \frac{\Theta}{T}, \qquad \Theta = \frac{h\nu_{\mathrm{m}}}{k}. \tag{2.23}$$

We note that C_V is a function of T/Θ as is $E/h\nu_{\mathrm{m}}$. We also note that, whatever the form of $g(\nu)$, at sufficiently high temperatures, $E \to 3NkT$ and $C_V \to 3Nk$, leading again to the Dulong–Petit law.

On the other hand, the Debye model leads at low temperatures ($T \ll \Theta$) to a T^3-law for C_V, a behaviour which is in good agreement with experimental data. The quantity Θ which has the dimensions of a temperature and which measures the deviations from classical behaviour, is called the *Debye temperature.* For typical solids, it is of the order of a few hundred °K, for instance, 315°K for copper and 170°K for gold.

The quantum theory as applied to the theory of specific heats of solids and, with some reservations on the part of several physicists, as applied to the theory of temperature radiation, was well established and accepted at the beginning of the second decade of the twentieth century, as can be seen from the proceedings of the 1911 and 1913 Solvay Congresses, to which most of the leading physicists of the time were invited. The next step forward was to be found in the development of a theory of atomic structure and we shall turn to this in the following chapters.

CHAPTER III

Rutherford's Atom

AT THE start of the twentieth century many atomic phenomena were known, such as radioactivity, and the existence of electrons had been demonstrated by J. J. Thomson and used by Lorentz to explain the Zeeman effect. As many different methods for determining the size of an atom all led to consistent results, it was also slowly generally accepted that matter consisted of atoms, but the structure of the atoms themselves had not been the subject of much speculation.

In his Silliman Lectures Thomson (1904a; see also Thomson, 1904b, and for an earlier, similar model, Kelvin, 1902) proposed a model of atoms which for about a decade became the generally accepted one. Although Rutherford's nuclear model—which is nowadays accepted to give a more reliable representation—was published early in 1911, there is no mention of it at the 1911 Solvay Congress, where Rutherford was present, and even at the 1913 Solvay Congress, which was held after Bohr had published his first paper on the quantum model, the main contribution was a long paper by Thomson on his own model, while only in the discussion was Rutherford's atom mentioned briefly, and Bohr's work was not mentioned at all.†

Thomson's model was invented to explain radioactivity. He assumed that the atom consists of a sphere of uniformly distributed positive charge in which are embedded negatively charged electrons (which he calls corpuscles). The total charge of the atom was

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† It is interesting to note that at the 1913 Solvay Congress, Lorentz remarked that it was doubtful whether a classical model such as Thomson's could lead to the true radiation law.

zero. Thomson first investigated possible electron configurations assuming the electrons to be at rest. If the number of electrons is small, they can be distributed symmetrically on a spherical surface inside the atom, but this configuration is no longer stable when the number of electrons becomes large. He suggested possible stable configurations following experiments by Mayer (1878, 1879) on magnetized needles. Mayer found that if he put these needles in corks and made them float with the same pole up and if he then approached them with the opposite pole of a large bar magnet, the needles would arrange themselves in a regular pattern, which, for three, four or five needles, was a triangle, square or pentagon, but for larger numbers of needles consisted of concentric regular polygons. Similarly, Thomson suggested that the electrons would arrange themselves in a spherical shells.

Thomson was able to account qualitatively for many atomic phenomena. For instance, on his model it is natural to expect a break in the atomic properties when a new shell of electrons is started and this is represented in the periodic behaviour of the atomic properties when we go through the periodic table of elements. Moreover, if the atomic spectra are assumed to be due to the eigen-vibrations of the electrons around their equilibrium positions, it is natural to expect elements in the same column of the periodic table to have similar spectra, as is found to be the case. Thomson's explanation of different valencies is completely analogous to the explanation given in the Bohr model: the near completion of a shell in an atom entails that the atom prefers to attach to it extra electrons, while the first electrons in a new shell are more easily removed. We do not want to discuss here other applications of Thomson's atom, but his own account of the various aspects of it which he gave in his Silliman Lectures well repays reading, and his concept of the "corpuscular temperature", which determines the kinetic energy of the electrons inside his atom and which, as he stresses, does not come to equilibrium with the temperature of the system of which the atoms form part, clearly resembles the concept of the nuclear temperature used in the statistical theory of nuclear reactions.

The real test for Thomson's atom came with the experiments on the scattering of α-particles. Experiments on β-ray scattering by Crowther (1910) seemed to be in agreement with the Thomson model, if one assumed that multiple scattering of the β-ray by the electrons inside the atom could take place. However, the situation changed when experiments by Geiger and Marsden (1909) on the scattering of α-particles showed that a gold foil of thickness of about 4.10^{-5} cm produced scattering over 90° or more for one α-particle in 20,000. This was incompatible with Thomson's model of the atom and Rutherford (1911; reprinted in this volume on p. 108) deduced from this that the atom should consist of a heavy central mass, concentrated within a very small volume, surrounded by light masses of opposite charge, occupying the outer parts of the atom. We shall briefly discuss the considerations which led Rutherford to this conclusion. In the light of modern nuclear physics and elementary physics experiments, it is interesting to note that Rutherford emphasizes the importance of scattering experiments involving high-energy particles for the study of atomic structure.

In comparing the predictions based upon Thomson's model with those based upon Rutherford's nuclear or planetary atom we must first of all see what the theories predict about single scattering processes, then what the result is of multiple scattering processes and finally discuss why for α-particles one should expect multiple› scattering processes to be unlikely to occur.

Let us consider the scattering of a particle of mass m and charge $Z_1 e$ by a fixed charge $Z_2 e$ (Fig. III.1). Let V be the velocity of m at infinity, and let p be the impact parameter, that is, the distance at which m would pass the fixed charge, if there were no forces acting between the two charges. Let $\pi - 2\theta$ be the scattering angle, that is, the angle over which m is deflected. If we are not interested in the details of the orbit (for such details see, for instance, ter Haar, 1961, chap. I), we can easily find how θ depends on p. To do this, we introduce polar coordinates with the fixed charge as origin (Fig. III.1). We now note, first of all that the angular momentum of m at a point P is equal to $mr^2\dot{\phi}$, since

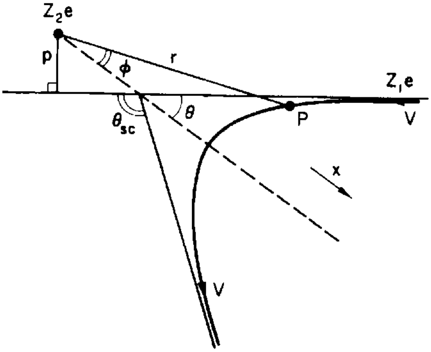

FIG. III.1. Rutherford scattering.

$r\dot{\phi}$ is the transverse velocity, so that the law of conservation of angular momentum reads

$$p\,.\,mV = mr^2\dot{\phi}. \tag{3.1}$$

Consider now the motion of m along the axis of symmetry of the orbit, that is, in the x-direction. From Fig. III.1 we see that the change in linear momentum in the x-direction is equal to $2mV\cos\theta$. As the force acting on m is $Z_1Z_2e^2/r^2$, the force in the x-direction is $Z_1Z_2e^2\cos\phi/r^2$, and from Newton's second law we have thus

$$2mV\cos\theta = \int_{-\infty}^{+\infty} \frac{Z_1Z_2e^2}{r^2}\cos\phi\,dt. \tag{3.2}$$

Using equation (3.1) to replace the integration over t to one over ϕ, we have

$$2mV\cos\theta = 2\int_{\theta}^{0} \frac{Z_1Z_2e^2}{pV}\cos\phi\,d\phi,$$

or

$$\cot\theta = \frac{b}{2p}, \tag{3.3}$$

or

$$\cot\tfrac{1}{2}\theta_{sc} = \frac{2p}{b}, \tag{3.4}$$

where θ_{sc} $(=\pi-2\theta)$ is the scattering angle, and where

$$b=\frac{Z_1 Z_2 e^2}{\frac{1}{2}mV^2} \tag{3.5}$$

is the minimum distance a particle of mass m and charge $Z_1 e$ can approach a charge $Z_2 e$ (assuming the charges to have the same sign) if it is approaching head-on with a velocity V at infinity.†

So far we have taken the charge $Z_2 e$ to be fixed. From classical scattering theory we know that this is only correct, if the mass M of this charge is infinite. If M is finite, the orbit we have considered is the orbit in the centre of mass system, and superposed upon it is the motion of the centre of mass itself. In classical mechanics one proves (see, for instance, ter Haar, 1961, chap. I) that the motion in the centre of mass system is the same as if the scattering centre were fixed and the scattered particle had a mass $mM/(m+M)$, the so-called reduced mass. Let us now investigate the relation between the angle θ in the centre of mass system and the angle θ' in the laboratory system corresponding to θ, which is the angle observed experimentally. If M is at rest in the laboratory system and m moving at a speed V' at infinity, the centre of mass velocity v_{com} will be given by the equation

$$v_{\text{com}}=\frac{mV'}{M+m}, \tag{3.6}$$

while V' is related to the speed V in the centre of mass system as follows

$$V=\frac{M}{M+m}V'=\frac{M}{m}v_{\text{com}}. \tag{3.7}$$

Consider now Fig. III.2. From Fig. III.2(b) we see that θ'_{sc} satisfies the equation (V'' is the velocity of m in the laboratory system after the scattering).

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† We note that our formulae remain unchanged, if the two charges have opposite sign; the only difference lies in Fig. III.1 where the fixed charge lies at the interior rather than the exterior focus of the hyperbolic orbit.

$$\tan\theta'_{sc} = \frac{V''_y}{-V''_x} = \frac{V_y}{-V_x+v_{com}} = \frac{V\sin\theta_{sc}}{V\cos\theta_{sc}+v_{com}}$$

$$= \frac{\sin\theta_{sc}}{\cos\theta_{sc}+(m/M)}. \tag{3.8}$$

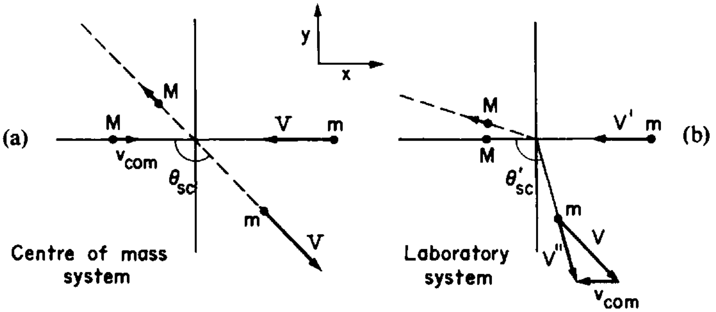

FIG. III.2. Scattering in the centre of mass and laboratory systems.

We note that if $m \ll M$, $\theta'_{sc} \approx \theta_{sc}$, as we would have expected. If $m = M$, we see that although θ'_{sc} and θ_{sc} differ, the scattering angle in the laboratory system can still vary from 0 to π just as the scattering angle in the centre of mass system. However, if $m \gg M$, we see that although the scattering angle in the centre of mass system can become large, in the laboratory system the scattering angle will always be small.

In the Thomson atom, the scattering is due to the corpuscles (electrons), while in the Rutherford atom, it is partly due to the electrons and partly due to the nucleus. In the case of β-rays, we would not expect qualitative differences in the scattering characteristics of the Thomson and Rutherford atoms, as the β-rays are electrons. However, in the case of α-particle scattering, we could not expect scattering over large angles to take place, if the atom had the structure postulated by Thomson and if the observed scattering angle were due to a single scattering process. Provided we can show that multiple scattering is unlikely, the α-particle scattering data and especially the occurrence of large scattering angles prove the untenability of the Thomson atom. Rutherford did not identify the light charges with electrons, but mentioned that a positively charged nucleus might explain the high velocity of the α-particles emitted in radioactive decay processes. We may also mention at this point that Nagaoka (1904) had considered earlier the properties of a "Saturnian" atom, consisting of a central attracting mass surrounded by rings of rotating electrons and that Perrin (1901) had also discussed a similar model.

Before considering multiple scattering, we should note that on the assumption of single-scattering of α-particles by a nucleus of charge $Z_2 e$, Rutherford could determine Z_2 from Geiger and Marsden's data and found that Z_2 was approximately one-half the atomic weight of the scattering atom, in agreement with Barkla's discovery (1911) that the number of electrons scattering X-rays was per atom about one-half the atomic weight.

Let us now consider multiple scattering. First of all, we must note that we may safely neglect the scattering due to the electrons as they will only produce a small correction to the scattering produced by the nucleus. We refer to Section 5 of Rutherford's paper on p. 117 for a discussion of this point. Next, let us determine the probability that a particle is scattered over an angle lying between θ_{sc} and $\theta_{sc}+d\theta_{sc}$, and let us neglect the difference between θ'_{sc} and θ_{sc}, that is, let us assume that $M \gg m$ (in the actual experiments, $M/m \approx 30$ to 50). From equation (3.4), we see that we can find this probability once we know the probability that the scattered particle is incident on the target with an impact parameter lying between p and $p+dp$. If I is the number of incident particles to be scattered per unit area, the number of particles incident with such impact parameters will clearly be $I.2\pi p\,dp$. If n is the number of scattering nuclei per unit volume and t the thickness of the target, and A its area at right angles to the incident beam, the number dN of particles scattered through angles between θ_{sc} and $\theta_{sc}+d\theta_{sc}$ will be

$$dN = IAtn2\pi p\,dp = \tfrac{1}{4}\pi IAtnb^2 \frac{\cos\frac{1}{2}\theta_{sc}}{\sin^3\frac{1}{2}\theta_{sc}}\,d\theta_{sc}. \qquad (3.9)$$

We can find from equation (3.9) the differential cross-section

$$\frac{d\sigma}{d\Omega} = IAt \,.\, 2\pi \sin\theta_{sc}\, d\theta_{sc}$$

and we have

$$\frac{d\sigma}{d\Omega} = \tfrac{1}{16} b^2 \frac{1}{\sin^4 \frac{1}{2}\theta_{sc}}, \tag{3.10}$$

the so-called *Rutherford scattering formula.*

The number f of all particles deflected through an angle greater than θ_{sc} is given by the equation

$$f = \tfrac{1}{4}\pi I A t n b^2 \cot^2 \tfrac{1}{2}\theta_{sc} \tag{3.11}$$

and we see that f decreases rapidly with increasing θ_{sc}. This means that the average scattering angle $\langle\theta_{sc}\rangle$ will be small. In fact, Rutherford (see p. 119) shows that the average scattering angle is $3\pi b/8R$, where R is the radius of the atom which is about 10^{-8} cm, while b for an α-particle of energy 10 MeV and $Z = 100$ is of the order of 10^{-11} to 10^{-12} cm. The average scattering angle θ_t due to multiple scattering in a target of thickness t will be proportional to the square root of the number of scattering processes as follows:

$$\theta_t = \langle\theta_{sc}\rangle \sqrt{(\pi R^2 n t)}, \tag{3.12}$$

or

$$\theta_t = \tfrac{3}{8}\pi b \sqrt{(\pi n t)}. \tag{3.13}$$

The probability p_{multiple} that the deflexion due to multiple scattering will be larger than θ_{sc} will be given by the Gaussian expression $\exp(-\theta_{sc}^2/\theta_t^2)$, or from (3.13)

$$\theta_{sc}^2 = -\tfrac{9}{64}\pi^3 b^2 n t \ln p_{\text{multiple}}, \tag{3.14}$$

while from equation (3.11) we get for the probability p_{single} that the same angle is exceeded in a single scattering process

$$p_{\text{single}} = \tfrac{1}{4}\pi b^2 n t \cot^2 \tfrac{1}{2}\theta_{sc}. \tag{3.15}$$

Combining equations (3.14) and (3.15) and bearing in mind that θ_{sc} for practically all events is small so that $\cot \frac{1}{2}\theta_{sc} \approx 2/\theta_{sc}$ we find†

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† The numerical value on the right-hand side of equation (3.16) is not changed materially when θ_{sc} becomes so large that our approximation becomes invalid.

$$p_{\text{single}} \ln p_{\text{multiple}} = \frac{64}{9\pi^2} = -0{\cdot}7, \qquad (3.16)$$

or

$$p_{\text{multiple}} = e^{-0{\cdot}7/p_{\text{single}}}. \qquad (3.17)$$

From equation (3.15) we can estimate for any given value of θ_{sc} the magnitude of p_{single} for the targets used by Geiger and Marsden. For large angles θ_{sc}, which are the crucial angles in the discussion, p_{single} becomes small. However, as soon as p_{single} becomes small, we see that p_{multiple} becomes very small indeed. For instance, values of 0·1 and 0·01 for p_{single} correspond to values of 0·0004 and less than 10^{-30} for p_{multiple}: the probability for multiple scattering leading to appreciable values of θ_{sc} is completely negligible, as we wanted to show.

CHAPTER IV

Bohr's Atom

THE experimental evidence in support of Rutherford's atom was very extensive, but there were also several severe difficulties. To see what those were, let us consider the simplest of all atoms, the hydrogen atom, consisting of a proton (the name proposed by Rutherford for the hydrogen nucleus in 1920) around which a single electron revolves. It was known that hydrogen produces a line spectrum and that the frequencies of the lines satisfy the relation

$$\nu = Rc\left[\frac{1}{n_1^2}-\frac{1}{n_2^2}\right], \tag{4.1}$$

where c is the velocity of light, n_1 and n_2 are integers, and R is the so-called Rydberg constant ($R = 109\,678\ \mathrm{cm}^{-1}$). The question then arose how one could explain this spectrum on the basis of Rutherford's atom. Classically, one would expect that the frequencies of the various spectral lines would correspond to the characteristic frequencies of the motion of the charged constituents of the atom. However, in the case of hydrogen this would lead to a continuous spectrum stretching over the whole range of wavelengths, as one can see as follows. According to classical electrodynamics (see, for instance, Panofsky and Phillips, 1955) an accelerated charge will radiate and thus lose energy. Hence the electron will slowly spiral into the proton. On the one hand, this means that in a volume of hydrogen gas there would be atoms with the electrons at many different distances from the proton, circling around the nucleus with different frequencies, and thus providing a continuous spectrum. On the other hand, on this picture it is difficult to understand why atoms are such stable entities as it looks as if they should be completely unstable until the electrons have come to rest inside the nucleus. One way out would be to abandon completely classical electrodynamics but, to quote Kramers and Holst (1923):

> It could hardly be expected that physicists in general would be very willing to give up the conceptions of electrodynamics, even if its basis was being seriously damaged by Rutherford's atomic projectiles. Surmounted by its crowning glory—the Lorentz electron theory—the classical electrodynamics stood at the beginning of the twentieth century a structure both solid and spacious, uniting in its construction nearly all the physical knowledge accumulated during the centuries, optics as well as electricity, thermodynamics as well as mechanics. With the collapse of such a structure one might well feel that physics had suddenly become homeless.

The answer, however, was to be found in abandoning classical electrodynamics on the microscopic plane—as has been done by Planck and Einstein in their discussion of radiation phenomena.†

Another difficulty with the Rutherford atom was, as was emphasized by Bohr in the first paper of his "great trilogy" (1913a, b, c; the first of these papers is reprinted in this volume on p. 132), that there is no natural length in the theory, as long as it is treated classically. This is in contrast to the Thomson atom, where the condition of stability of the corpuscle configurations introduces such a length. However, if one decides to invoke quantum theory, one has, apart from the mass m and charge e of the electron, also Planck's constant h, and from those three quantities one can by dimensional analysis construct the combination h^2/me^2, which is a length of the right order of magnitude (compare equation (4.7) below).

Bohr had come to Manchester, joining Rutherford, in March

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† An interesting anecdote told by Sommerfeld (Sommerfeld and Bopp, 1951) may be mentioned here. In a discussion about atomic spectra with the spectroscopist Runge, Helmholtz is quoted as having said "Yes, the planets. How would that be? The planets . . . but no, *it won't do!*" (My italics, D. t. H.) Runge states that Helmholtz clearly thought of orbits of electrons around the nucleus, but saw that these orbits would not be stable.

1912 after a short and not very happy stay at the Cavendish Laboratory in Cambridge. According to Gamow (as told by Condon, 1962), Bohr had not hit it off with J. J. Thomson because he was critical of his model of the atom! During his stay at Manchester, Bohr had started to develop his ideas about ways and means to use the Rutherford atom to explain atomic spectra. In the introduction to a recent reprinting of Bohr's 1913 papers (Bohr, 1963) on the occasion of the fiftieth anniversary of the publication of these papers, Rosenfeld has given a detailed account of how Bohr was led to his theory. From his account we learn that the final—and decisive—touches were not put to the papers until February/March 1913, when Bohr had been back in Copenhagen for about half a year.

Although there are many interesting points in Bohr's second and third papers, in which he discusses heavier atoms and molecules, the first paper is by far the most important one and because of lack of space our discussion will be mainly restricted to this first part which is devoted to a discussion of the hydrogen atom. We have already mentioned how Bohr deduced from the fact that Rutherford's model did not contain a natural length that Planck's quantum of action should enter into the theory. From classical mechanics (see, for instance, ter Haar, 1961), it follows that in the hydrogen atom, where an electron of charge $-e$ is bound to a nucleus of charge $+e$,† the binding energy of the electron E_b, the radius a of the orbit—which we assume to be circular for the sake of simplicity—as was done by Bohr in most of his discussions—and the frequency ω of the electron in its orbit are related by the equations‡

$$E_b = \frac{e^2}{2a}, \tag{4.2}$$

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† It is interesting to note that Bohr states "general evidence indicates that an atom of hydrogen consists simply of a single electron rotating round a positive nucleus of charge e". From the context, it is clear that this result had only just become available when Bohr was writing his paper.

‡ Note that E_b, which is denoted by Bohr simply by E, is the binding energy; the energy of the electron which is negative in a bound state will thus be equal $-E_b$.

$$\omega = \frac{2}{\pi} \frac{E^{\frac{3}{2}}}{e^2 \sqrt{(2m)}}. \tag{4.3}$$

Equation (4.2) follows easily for circular orbits from the fact that (i) the potential energy U is $-e^2/a$ and (ii) the kinetic energy $\mathscr{T}$ is equal to $-\frac{1}{2}U$ by virtue of the virial theorem. Equation (4.3) combined with equation (4.2) expresses Kepler's third law relating the period in a Kepler orbit to its semi-major axis. It follows easily from the fact that $\frac{1}{2}ma^2(2\pi\omega)^2 = \mathscr{T} = E_b$.

Consider now an electron which is brought from infinity to an orbit with frequency ω. As its frequency is zero at infinity, Bohr suggested that the energy lost in binding the electron would be emitted in the form of τ energy quanta $h\nu$ with $\nu = \frac{1}{2}\omega$. We get thus the relation

$$E_b = \tau h \tfrac{1}{2}\omega, \tag{4.4}$$

which together with equations (4.2) and (4.3) leads to the relations

$$E_b = \frac{2\pi^2 me^4}{\tau^2 h^2}, \tag{4.5}$$

$$\omega = \frac{4\pi^2 me^4}{\tau^3 h^3}, \tag{4.6}$$

$$a = \tau^2 \frac{h^2}{4\pi^2 me^2}. \tag{4.7}$$

As Bohr states himself, the basic assumptions involved, if we now identify the states with the parameters given by equations (4.5) to (4.7) as stationary states of the hydrogen atom, are: (a) that the dynamical equilibrium of the systems in the stationary states can be discussed by help of ordinary mechanics, *while the passing of the systems between different stationary states cannot be treated on that basis* (my italics, D. t. H.), and (b) that the latter process is followed by a *homogeneous* (Bohr's italics) radiation, for which the relation between the frequency and the amount of energy is the one given by Planck's theory. We shall return to a discussion of the various main points of Bohr's paper, but first we shall discuss a few more consequences.

Let us consider now the transition from a state with energy E_1 corresponding to $\tau = \tau_1$ to a state with energy E_2 corresponding to $\tau = \tau_2$ $(<\tau_1)$. If we assume that the energy difference $E_2 - E_1$ is emitted in the form of a single light quantum of frequency ν, we have

$$E_1 - E_2 = h\nu, \tag{4.8}$$

or

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right), \tag{4.9}$$

which corresponds both qualitatively *and quantitatively* with relation (4.1). Bohr suggested at the same time that the spectrum of the helium ion He$^+$ would show a similar dependence but with the factor in front of the bracket on the right-hand side of equation (4.9) four times as large and that this spectrum was the one observed by Fowler in a mixture of hydrogen and helium and by Pickering in stellar spectra. This prediction was soon afterwards confirmed by Evans and the slight difference between the coefficients in front of the brackets in equation (4.9) and one-fourth of the analogous constant in the formula for the He$^+$-lines strengthened the identification as the m occurring in that constant should be the reduced mass $mM/(m+M)$, rather than the electronic mass and the nuclear mass M is four times as heavy in the case of helium as it is in the case of hydrogen.

In view of the importance of the so-called correspondence principle (see Chapter VI), which states that quantum systems in the limit of large quantum numbers will behave as classical systems, it is of interest to see how Bohr found a different way to derive equation (4.4). We have seen that equation (4.9) represents the experimental data on the hydrogen spectrum and this is a direct consequence of equation (4.5) which was derived by combining equations (4.3) and (4.4). It is immaterial how equation (4.4) is derived.

Bohr first notes that in writing down equation (4.8) we assume that only one quantum is emitted during the transition. Secondly, he notes that in the region of low frequencies the results obtained from quantum theoretical considerations should be the same as those following from classical considerations (compare Chapter I, where expression (1.48) goes over into the classical expression (1.25) as $h\nu/kT \to 0$). Let us now assume that instead of relation (4.4) we have

$$E_b = f(\tau)h\omega \tag{4.10}$$

where $f(\tau)$ is a so far undetermined function of the quantum number τ. Combining equation (4.10) with equation (4.3) and using equation (4.8), we find that $f(\tau)$ must be proportional to τ: $f(\tau) = K\tau$. Consider now the transition from the state with $\tau = N$ to the state with $\tau = N-1$. From equations (4.3), (4.8), (4.10), and the relation $f(\tau) = K\tau$ we get for the frequency ν of the radiation emitted

$$\nu = \frac{\pi^2 me^4}{2K^2h^3}\frac{2N-1}{N^2(N-1)^2}, \tag{4.11}$$

while we get for the (classical) frequency of the electron in the stationary state corresponding to $\tau = N$

$$\omega_N = \frac{\pi^2 me^4}{2K^3h^3N^3}. \tag{4.12}$$

In the limit as $N \to \infty$, we must have $\omega_N \to \nu$, and, therefore, K must be equal to $\frac{1}{2}$, which means that we have rederived equation (4.4).

From equations (4.6) and (4.7) we find for the angular momentum M of the electron the equation

$$M = ma^2(2\pi\omega) = \tau\hbar, \tag{4.13}$$

where $\hbar$ is Dirac's constant $(=h/2\pi)$. Equation (4.13) expresses the *quantization of angular momentum.*

In Bohr's second paper (1913b) he uses equation (4.13) as a starting point. Indeed, equations (4.5) to (4.7) follow directly from equation (4.13) combined with equations (4.2) and (4.3).

If Bohr's ideas, and especially equation (4.8), are correct, one should expect that controlled electron impact would produce controlled excitation of atoms. In fact, this was found experimentally by Franck and Hertz (1914a, b; the second paper is reprinted in this volume on p. 160) who showed that the mercury resonance line with a wavelength of 2536 Å could be produced when mercury atoms were excited by electrons of the proper energy, and thus gave a direct experimental verification of Bohr's postulate (4.8).

Let us now discuss in a little more detail the many points on which Bohr departs from classical considerations. In doing this, we shall follow Whittaker's exposition (1954). The main points of Bohr's theory are:

(i) Atoms produce spectral lines one at a time and are not responsible for the whole spectrum simultaneously.

(ii) A single electron is responsible for the production of a spectral line.

(iii) The Rutherford nuclear atom provides a satisfactory basis for exact calculations of the frequencies of the spectrum.

(iv) The production of spectra is a quantum process.

(v) A given atom may exist in different stationary states; in such states the atom will not radiate.

(vi) The angular momentum is quantized in units of $\hbar$.

(vii) If a spectral line is produced, two stationary states are involved and the spectral terms can be identified with the energies of the stationary states.

(viii) In both emission and absorption one light quantum is involved and its frequency is determined by the Planck–Einstein relation (4.8).

Finally; (ix) It is impossible to visualize or explain classically the behaviour of the atom when the transition takes place.

Many of these features had been envisaged by earlier workers. For instance, Conway (1907) had suggested that a single atom (and probably a single electron) will produce one spectral line at a time and will do so when it is in an excited state which it will occupy sufficiently long to emit a fairly long wave train. Nicholson in a long series of papers (1911a, b; 1912a, b, c) had tried to explain atomic spectra—with some success which was, however, as we know now, fortuitous—on the basis of the Rutherford atom, invoking the quantum of action, and suggesting that different spectral lines are produced by the atom in different states which are characterized by discrete values of energy and of angular momentum, and he even hinted—without fully grasping what he was doing—that *two* states are involved in the production of a spectral line.† The quantization of angular momentum had been discovered independently by Ehrenfest (1913) in a paper discussing the quantum theory of rotation.‡ From this it is clear—and it is also clear from Rosenfeld's account of how Bohr developed his ideas—that various ideas relevant to Bohr's theory were in the air, but it needed Bohr's genius to put them together and to add to them the essential features of the essential impossibility of describing the emission process and of the stationary states in which the atom will not emit radiation. This combination of those features of the old theory which can be salvaged and those new concepts which are needed to make the theory give results in accordance with experimental facts is characteristic of Bohr's work.

We have noted in earlier chapters how long it took the scientific world to appreciate the importance of Planck's work. It is interesting to note the changed atmosphere in 1913. Although Bohr's theory incorporated ideas which were fully as revolutionary as Planck's introduction of energy quantization, the response was much more positive. It is true that neither J. J. Thomson nor Lorentz accepted the theory immediately and that Lord Rayleigh did not commit himself on the grounds that people over 60 should not judge new developments. However, Sommerfeld (Sommerfeld and Bopp, 1951) recounts how the spectroscopist Paschen commented on Bohr's paper as its being possibly the most important paper in physics for the next decades, while Rosenfeld (1963) tells

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† I feel that Rosenfeld (1963) plays down Nicholson's work too much. Bohr's imaginative step in renouncing a classical description of the emission process so far exceeds the work of any of his predecessors that it is easy to underestimate their contributions.

‡ While Bohr's first paper was submitted in April and published in July, Ehrenfest's paper was submitted in May and published in June.

about the favourable reactions of Hevesy, Oseen, and Sommerfeld himself, and also of Einstein's reaction when he heard that Evans' experiments had confirmed Bohr's interpretation of the spectrum found by Pickering as being due to ionized helium: "It is one of the greatest discoveries." Perhaps we may conclude this chapter by once more quoting Einstein (1951). After noting the serious contradictions between radiative phenomena and classical dynamics, Einstein continues:

> All my attempts to adapt the theoretical foundation of physics to this new type of knowledge failed completely. It was as if the ground had been pulled out from under one, with no firm foundation to be seen anywhere, upon which one could have built. That this insecure and contradictory foundation was sufficient to enable a man of Bohr's unique instinct and tact to discover the major laws of the spectral lines . . . appeared to me like a miracle—and appears to me as a miracle even today. This is the highest form of musicality in the sphere of thought.

CHAPTER V

Atomic Spectra in the Old Quantum Theory

BETWEEN the appearance of Bohr's great trilogy in 1913 and the advent of wave mechanics in 1925, a large number of papers appeared developing Bohr's ideas into an impressive theory of atomic phenomena. It was a collective effort and the names of the physicists contributing to it make up an imposing roll-call: Bohr, Born, Klein, Rosseland, Kramers, Pauli, Sommerfeld, Planck, Einstein, Ehrenfest, Epstein, Debye, Schwarzschild, Wilson. . . .

In the present chapter we shall discuss the theory of atomic spectra, which was first of all based upon the following two postulates (see points (v), (vii), and (viii) in the previous chapter):†

> I. That an atomic system can, and can only, exist permanently in a certain series of states corresponding to a discontinuous series of values for its energy, and that consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states will be denoted as the "stationary states" of the system.
>
> II. That the radiation absorbed or emitted during a transition between two stationary states is "unifrequentic" and possesses a frequency ν, given by the relation
>
> $$E' - E'' = h\nu, \tag{5.1}$$

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† We quote here verbatim from the first of the three comprehensive survey papers by Bohr (1918a, b, 1922a), which were published in the *Proceedings of the Danish Academy*.

where *h* is Planck's constant and where E' and E'' are the values of the energy in the two states under consideration.

These postulates are not by themselves sufficient to determine the stationary states. We saw in the previous chapter how Bohr derived an expression for the energies of the stationary states of the hydrogen atom by requiring that the angular momentum is quantized. The question arises then whether this requirement is sufficient and whether it is always the correct one. First of all, we must emphasize the inner paradox which is inherent to all these considerations. We are trying to find principles and rules to determine the stationary orbits, that is, those *classical* orbits which are quantum-mechanically allowed and which at the same time behave in a most unclassical manner by not changing their energy through the emission of electromagnetic radiation. One should not consider such rules as the adiabatic hypothesis (see below) or the correspondence principle as attempts to make classical and quantum theory compatible; rather, they were attempts to find a way towards a completely quantum-mechanical formulation, such as the one found by Schrödinger and Heisenberg. A similar question arises in connexion with black-body radiation. We have seen how quantum theory can account for the energy density in the radiation field. On the other hand, purely classical arguments (compare Chapter I) lead to both Wien's displacement law (1.1) and the Stefan–Boltzmann law (1.6). The clue to a solution of this apparent paradox, as well as an indication of the path to be followed to find the stationary orbits can be found in our discussion in Chapter I.† The point is that just as the modes of the electromagnetic field are characterized by a set of integers (see equation (1.7)), so are the stationary states. In the latter case, the integers are called *quantum numbers.* If we now subject the system to an (infinitely) slow change—an adiabatic change—it must stay in the same stationary state—or rather it must go from its original stationary state to a new state, which is a

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† The most comprehensive discussion of this point can probably be found in a paper by Ehrenfest (1923; see also Bohr, 1918a, b), where references to earlier literature can be found.

stationary one in the new conditions, but this change must be a continuous, smooth one.† This means that the quantum numbers characterizing the new stationary state must be the same as the ones characterizing the old one. To find the *quantum conditions*, that is, the relations from which the stationary orbits can be derived, we must thus find quantities which do not change when the system is subjected to adiabatic changes. Such quantities are called *adiabatic invariants*. If we are dealing with so-called multiply periodic systems, that is systems where each of the coordinates returns to its original value or is an angular variable, these adiabatic invariants are the *action variables* J_k of classical mechanics.

Let us briefly recapitulate what classical mechanics tell us about action variables (see, for instance, Born, 1927, or ter Haar, 1961). The behaviour of a classical system of s degrees of freedom is completely determined if we know how its s generalized coordinates q_k, which are s parameters fully defining the state of the system, depend on time. If $\mathscr{T}$ is the kinetic energy of the system and U its potential energy, the equations of motion for the q_k can be written in the form

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{q}_k}-\frac{\partial \mathscr{L}}{\partial q_k}=0, \qquad k=1,\ldots,s, \tag{5.2}$$

where $\mathscr{L}$ is the Lagrangian of the system,

$$\mathscr{L}=\mathscr{T}-U. \tag{5.3}$$

Equations (5.2) are s second-order differential equations for the q_k. It is convenient to go over to a set of $2s$ first-order differential equations by introducing the *generalized momenta*, p_k, through the equations

$$p_k=\frac{\partial \mathscr{L}}{\partial \dot{q}_k}. \tag{5.4}$$

The equations of motion now become the canonical or Hamiltonian equation of motion:

$$\dot{p}_k=-\frac{\partial \mathscr{H}}{\partial q_k}, \qquad \dot{q}_k=\frac{\partial \mathscr{H}}{\partial p_k}, \tag{5.5}$$

where $\mathscr{H}$ is the Hamiltonian of the system,

$$\mathscr{H}=\Sigma p_k \dot{q}_k-\mathscr{L}, \tag{5.6}$$

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† The rate of change of the condition must be so slow that the relevant frequencies are all small compared to the frequencies involved in transitions between stationary states.

which, in many cases, is just the total energy, $\mathcal{T}+U$, expressed in terms of the p_k and q_k.

Equations (5.5) are often difficult to solve, and we can use the following method to simplify them. If we introduce a function $S(q_k;\alpha_k)$ of the q_k and of s new variables α_k, and if we perform a transformation from the p_k and q_k to a new set of variables α_k and β_k through the equations

$$p_k = \frac{\partial S}{\partial q_k}, \qquad \beta_k = \frac{\partial S}{\partial \alpha_k}, \tag{5.7}$$

the equations of motion are again in canonical form,

$$\dot{\alpha}_k = -\frac{\partial \overline{\mathscr{H}}}{\partial \beta_k}, \qquad \dot{\beta}_k = \frac{\partial \overline{\mathscr{H}}}{\partial \alpha_k}, \tag{5.8}$$

where $\overline{\mathscr{H}}$ is the Hamiltonian expressed in terms of the α_k and β_k. The function S generating the transformation (5.7) is now chosen in such a way that $\overline{\mathscr{H}}$ does not contain the β_k. In that case, it follows from equation (5.8) that the α_k are constants and the β_k linear functions of the time.

Consider now a one-dimensional case, let the motion be periodic with period τ, and let the solution of the equation for β be written in the form

$$\beta = \gamma(t-t_0). \tag{5.9}$$

The periodicity of the motion can be expressed by the equation†

$$q(\beta+\gamma\tau) = q(\beta). \tag{5.10}$$

Consider now a further transformation from α and β to new variables J and w through a generating function $S' = J\beta/\gamma\tau$. From the equivalent of equations (5.7), we find that

$$J = \alpha\gamma\tau \qquad \text{and} \qquad w = \beta/\gamma\tau, \tag{5.11}$$

while equation (5.10) becomes

$$q(w+1) = q(w). \tag{5.12}$$

As the two transformations together leave the equations of motion invariant, it can be generated by a function $\overline{S}(q,J)$, which connects p and q with J and w as follows

$$p = \frac{\partial \overline{S}}{\partial q}, \qquad w = \frac{\partial \overline{S}}{\partial J}. \tag{5.13}$$

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† We exclude here the case where q is an angle and where the periodic motion is a rotation. In that case, we have instead of equation (5.10) the relation $q(\beta+\gamma\tau) = q(\beta)+2\pi$. The further analysis is completely analogous to the one given here and is left to the reader.

From these equations it follows that

$$\frac{\partial}{\partial J}\oint p\,dq = \frac{\partial}{\partial J}\oint \frac{\partial \bar{S}}{\partial q}\,dq = \oint \frac{\partial w}{\partial q}\,dq = \oint dw = 1, \tag{5.14}$$

where $\oint$ indicates integration over one period. From equation (5.14) we get

$$J = \oint p\,dq. \tag{5.15}$$

As J and w have, respectively, the dimensions of an angular momentum or action and of an angle, they are called the *action and angle variables.*

If we are dealing with systems with more than one degree of freedom, and if the Hamilton–Jacobi equations can be solved by separation of variables, while the system is periodic in each of the q_k, the action variables for the system are given by the equation

$$J_k = \oint p_k\,dq_k, \tag{5.16}$$

where now $\oint$ indicates integration over the period corresponding to q_k.

It was shown by Burgers (1917, 1918) that the action variables given by equation (5.16) are, indeed, adiabatic invariants. We shall not give the proof here, but refer the reader to the literature (for instance, ter Haar, 1961, §6.3; Tomonaga, 1962, §19).

As the J_k are adiabatic invariants, they can be used to determine the stationary orbits. This is done through the Sommerfeld–Wilson quantization rules (Sommerfeld, 1915a, b, 1916; Wilson, 1915):

$$J_k = \oint p_k\,dq_k = n_k\,h, \tag{5.17}$$

where the n_k, the quantum numbers, are integers.

As a first application of the quantum conditions (5.17), let us consider the hydrogen atom. The q_k in this case are the spherical polars, r, θ, and ϕ, the Lagrangian is

$$\mathscr{L} = \tfrac{1}{2}m(\dot{r}^2 + r^2\dot{\theta}^2 + r^2\sin^2\theta\dot{\phi}^2) + \frac{e^2}{r}, \tag{5.18}$$

the p_k are given by the equations

$$p_r = m\dot{r}, \tag{5.19}$$

$$p_\theta = mr^2\dot{\theta}, \tag{5.20}$$

$$p_\phi = mr^2\sin^2\theta\dot{\phi}, \tag{5.21}$$

and the Hamiltonian is

$$\mathscr{H} = \frac{1}{2m}\left(p_r^2+\frac{p_\theta^2}{r^2}+\frac{p_\phi^2}{r^2\sin^2\theta}\right)-\frac{e^2}{r}. \tag{5.22}$$

From equation (5.22) and the equation of motion it follows that p_ϕ is a constant. If we transform from spherical polars to Cartesian coordinates with the z-axis along the polar axis, we see that p_ϕ is the z-component of the angular momentum, M_z. From equation (5.17) it now follows that

$$n_\phi h = \oint p_\phi \, d\phi = 2\pi p_\phi, \tag{5.23}$$

or

$$M_z = p_\phi = n_\phi \hbar, \tag{5.24}$$

showing the quantization of the z-component of the angular momentum; n_ϕ is usually denoted by m, and is called the *magnetic quantum number* (see below for the reason for this terminology).

Consider now the square of the angular momentum, M^2. We find

$$M^2 = ([\mathbf{r}\wedge m\dot{\mathbf{r}}].[\mathbf{r}\wedge m\dot{\mathbf{r}}]) = p_\theta^2+\frac{p_\theta^2}{\sin_\phi^2\theta}, \tag{5.25}$$

and from the equations of motion (5.5) we find that M^2 is a constant of motion. From equation (5.17), we now obtain

$$n_\theta h = J_\theta = 2\int_{\theta_1}^{\theta_2}\left[M^2-\frac{M_z^2}{\sin^2\theta}\right]^{\frac{1}{2}} d\theta, \tag{5.26}$$

where θ_1 and θ_2 are the values of θ for which the radical vanishes. From equations (5.26) and (5.24) we obtain

$$M-|M_z| = n_\theta \hbar, \tag{5.27}$$

or

$$M = (n_\theta+n_\phi)\hbar. \tag{5.28}$$

The sum of n_ϕ and n_θ is usually denoted by k and is called the *auxiliary* or *azimuthal quantum number*. The *orbital quantum number* l of wave mechanics takes the place of the azimuthal quantum number in the old quantum theory. A rough comparison can be made, if we use the relation $l = k-1$.

Using equations (5.22), (5.25) and (5.17), we get for the last quantum condition

$$n_r h = J_r = 2\int_{r_{\min}}^{r_{\max}} \left[2mE + \frac{2me^2}{r} - \frac{M^2}{r^2}\right]^{\frac{1}{2}} dr \qquad (5.29)$$

where E is the energy of the electron, and $r_{\min}$ and $r_{\max}$ are the zeroes of the radical. In Fig. V.1 we have sketched the potential energy, $-e^2/r$, and p_r^2 as functions of r, and in Fig. V.2 we have sketched p_r as function of r. The quantization rule (5.17) thus expresses that the area enclosed by the curve in Fig. V.2 equals an integral multiple of Planck's constant. The fact that h is a measure for the areas in the phase-plane is important in the discussion of *a priori* probabilities in statistical mechanics (see, for instance, ter Haar, 1954, chap. III; for early discussions compare Debye's Wolfskehl lecture (Planck *et al.*, 1914), Bohr, 1918a, b;

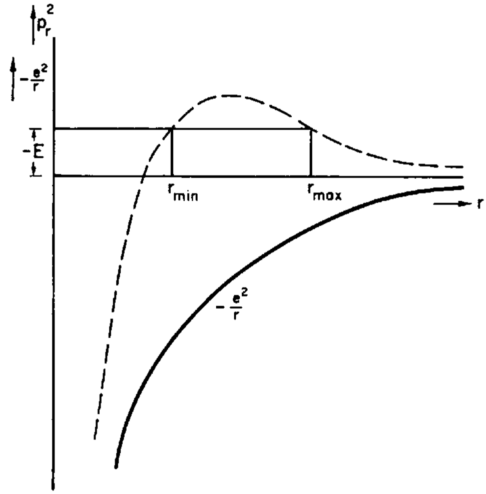

FIG. V.1. The potential energy and p_r^2 as functions of r for the hydrogen atom.

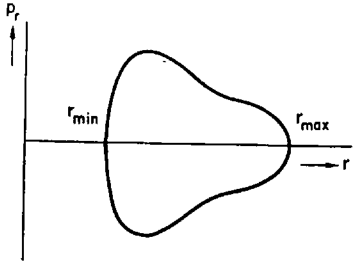

FIG. V.2. The radial momentum p_r as function of r for the hydrogen atom.

Ehrenfest, 1923). From equation (5.29) we get

$$n_r h = -2\pi M + \pi e^2 \sqrt{\left(\frac{2m}{-E}\right)}, \tag{5.30}$$

or, using equation (5.28),

$$E = -\frac{me^4}{2\hbar^2(n_r+n_\theta+n_\phi)^2}, \tag{5.31}$$

which agrees with equation (4.5), if we identify $n_s+n_\theta+n_\phi$ with the *principal quantum number n* (denoted by τ in the preceding chapter).

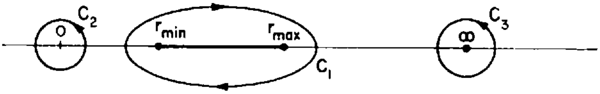

FIG. V.3. The contours in the complex r-plane involved in the evaluation of J_r.

Equations (5.27) and (5.30) can be derived by elementary integration; the integral in (5.29) can be evaluated by introducing a new variable u [$=(2r-r_{min}-r_{max})/(r_{max}-r_{min})$]. A more elegant method, however, is the following one, which is due to Born (1927). We change the integral over r to an integral in the complex plane (see Fig. V.3). As the integrand is a two-valued function, we must thus introduce a cut in the r-plane between the two branch points r_{min} and r_{max}. In Fig. V.3 we have taken the branches such that the positive (negative) square root is taken above (below) the real axis. We then have

$$J_r = \oint_{C_1} p_r\, dr. \tag{5.32}$$

By distorting C_1 into C_2+C_3, we can evaluate the integral by Cauchy's theorem of residues, or

$$J_r = 2\pi i\,(\text{residue at } r = 0 + \text{residue at } r = \infty), \tag{5.33}$$

from which equation (5.30) follows.

Equation (5.27) can be derived in a similar way, but the easiest way is probably by noting that if we split the kinetic energy once into three contributions corresponding to motion in the r-, θ-, and ϕ-directions, respectively, and once into three contributions corresponding to the radial motion, the transverse motion in the orbital plane, and the motion perpendicular to the orbital plane (which does not contribute to the kinetic energy), respectively, we have

$$p_r\dot{r}+p_\theta\dot{\theta}+p_\varphi\dot{\varphi} = p_r\dot{r}+p_\chi\dot{\chi}+0, \tag{5.34}$$

where χ is an angle determining the position of the electron in its orbital plane. The quantity p_χ is clearly the total angular momentum M, so that

$$p_\theta\dot{\theta} = M\quad - p_\varphi\dot{\phi}. \tag{5.35}$$

As χ and ϕ both increase by 2π when θ goes through one period, equation (5.27) follows.

The stationary orbits of the hydrogen atom are determined by the values of n_r, n_θ and n_ϕ—or n, k and m. We have seen that n determines the energy, k the total angular momentum, and m its z-component. In general, the orbit will be an ellipse. As $r_{\min}$ and $r_{\max}$ are the solutions of the equation

$$2mEr^2+2me^2r-M^2 = 0, \tag{5.36}$$

we find for the semi-major axis a $[=\frac{1}{2}(r_{\min}+r_{\max})]$

$$a = -\frac{e^2}{2E} = \frac{\hbar^2}{me^2}n^2, \tag{5.37}$$

which is the same as equation (4.7).

The eccentricity ε of the orbit is given by the equation

$$\varepsilon = \frac{r_{\max}-r_{\min}}{r_{\max}+r_{\min}}, \tag{5.38}$$

and the semi-minor axis b by the equation

$$b = a\sqrt{(1-\varepsilon^2)} = \sqrt{(r_{\min}r_{\max})} = \sqrt{\left(-\frac{M^2}{2mE}\right)} = \frac{\hbar^2}{me^2}nk. \tag{5.39}$$

As $n-k = n_r$, k varies from 1 to n, the value $k = 0$ being excluded as it corresponds to a linear orbit, where the electron would move through the nucleus. This variation corresponds to the limits 0 and $n-1$ for l. As n determines both the energy and the semi-major axis, orbits with the same n, but different k will have the same major axis, but different eccentricities. The orbits are characterized by nk, and $k = 1,2,3,\ldots$ ($l = 0,1,2,\ldots$) corresponds to *s*-, *p*-, *d*-, ... orbits (for an explanation of this nomenclature, see the discussion of the alkali spectra below); for instance, 3*p* corresponds to an orbit with $n = 3$, $k = 2$ ($l = 1$), and so on. In Fig. V.4 we have sketched the 4*s*, 4*p*, 4*d* and 4*f* orbits.

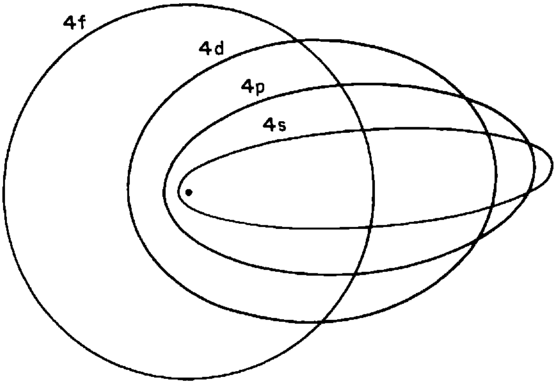

FIG. V.4. The 4*s*, 4*p*, 4*d*, and 4*f* orbits of the hydrogen atom.

Let us now consider the spectrum of an alkali metal atom, such as sodium. The sodium atom consists of a nucleus of charge $+11e$ surrounded by 11 electrons. If we deduce from the experimental data on the sodium spectrum, which bears a strong resemblance to the hydrogen spectrum (compare equation (5.42)) that a single electron is responsible for the spectrum, we must consider the motion of one electron in the combined field of the nucleus and the 10 other electrons. A theoretical justification is afforded by the shell model of the atom which we shall briefly discuss later in this chapter. As there is no preferred direction, we may assume that the field acting upon the electron is spherically symmetric. The potential energy, $U(r)$, will far from the nucleus be simply $-e^2/r$, as the 10 electrons will screen out all but $\frac{1}{11}$ of the nuclear charge. Close to the nucleus, however, the influence of the other electrons will be negligible, and $U(r)$ will behave as $-11e^2/r$. If we apply to the motion of the electron the quantization rules (5.17) and use spherical polars to describe the motion, we can use the results (5.24) and (5.28) as those did not depend on the specific shape of the potential energy. However, instead of equation (5.29) we now have

$$n_r h = 2\int_{r_{\min}}^{r_{\max}} \left[2mE - 2mU(r) - \frac{M^2}{r^2}\right]^{\frac{1}{2}} dr. \tag{5.40}$$

As we do not know the explicit form of $U(r)$, we cannot evaluate the integral. It is, however, possible to reach some general conclusions from equation (5.40). To do this, we consider Fig. V.5. In this figure, we have drawn p_r^2 both for the case (a) when $U(r) = -e^2/r$, and for the case (b) when $U(r)$ has the actual

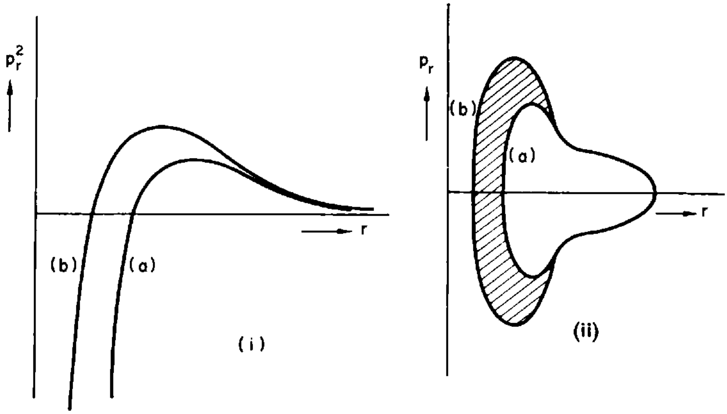

FIG. V.5. The dependence of (i) p_r^2 and (ii) p_r on r for the cases (a) where $U(r) = -e^2/r$ and (b) where $U(r)$ is the potential felt by the optical electron in a sodium atom.

shape occurring in the sodium atom. We have also drawn the corresponding curves in the $p_r - r$ diagram. Equation (5.40) tells us that the area enclosed by the curve (b) in Fig. V.5(ii) is equal to $n_r h$. If the shaded area between the curves (a) and (b) is equal to αh, we have

$$(n_r - \alpha)h = 2\int_{r_{\min}}^{r_{\max}} \left[2mE + \frac{2me^2}{r} - \frac{M^2}{r^2}\right]^{\frac{1}{2}} dr, \tag{5.41}$$

and following step by step the argument which led from equation (5.29) to equation (5.31), we find for the energy of the electron in the stationary orbit characterized by n_s, n_θ and n_ϕ

$$E = -\frac{me^4}{2\hbar^2(n-\alpha)^2}, \tag{5.42}$$

where again $n = n_r + n_\theta + n_\phi$. The quantity α is called the *quantum defect*, and we see that it is a measure for the deviation of the stationary orbit from the corresponding hydrogen orbit, or, put differently, a measure for the penetration of the orbit into the electron shell formed by the other electrons and surrounding the nucleus. We would expect that α will depend strongly on the azimuthal quantum number, because if M varies, so does the centrifugal force and thus the effective potential. Put differently, we would expect that the penetration of an orbit will increase with decreasing k, as can be seen, for instance, from Fig. V.4. The quantity $n - \alpha = n^*$ is called the effective quantum number. We note, by the way, that we can also interpret equation (5.42) by writing e^4/n^{*2} as $Z^{*2}\,e^4/n^2$ and saying that because of penetration, the effective charge acting upon the electron is larger than the charge it feels far away from the nucleus.

Equation (5.42) represents the energy levels of the sodium atom quite well. In fact, the sodium spectrum consists of a number of series of lines, the frequencies of which satisfy the following equation [compare equation (4.1)]:

$$\nu = Rc\left[\frac{1}{(n_1-\alpha_1)^2} - \frac{1}{(n_2-\alpha_2)^2}\right]. \tag{5.43}$$

The so-called principal series corresponded to

$$n_1 = 3, \quad \alpha_1 = 1{\cdot}4; \qquad n_2 = 3, 4, \ldots, \quad \alpha_2 \approx 0{\cdot}9; \tag{5.44}$$

the so-called sharp series to

$$n_1 = 3, \quad \alpha_1 = 0{\cdot}9; \qquad n_2 = 4, 5, \ldots, \quad \alpha_2 \approx 1{\cdot}4; \tag{5.45}$$

the so-called diffuse series to

$$n_1 = 3, \quad \alpha_1 = 0{\cdot}9; \qquad n_2 = 3, 4, \ldots, \quad \alpha_2 \approx 0{\cdot}01; \tag{5.46}$$

and the so-called Bergmann or fundamental series to

$$n_1 = 3, \quad \alpha_1 = 0{\cdot}01; \qquad n_2 = 4, 5\ \ldots, \quad \alpha_2 \approx 0{\cdot}002. \tag{5.47}$$

This suggests a term-diagram or Grotrian diagram of the form given in Fig. V.6. In this diagram we have put the energies given by the equation (5.42) and indicated the appropriate values of n. We have also connected those energies which gave rise to the spectral series (5.44)–(5.47). It turns out that the energies in the

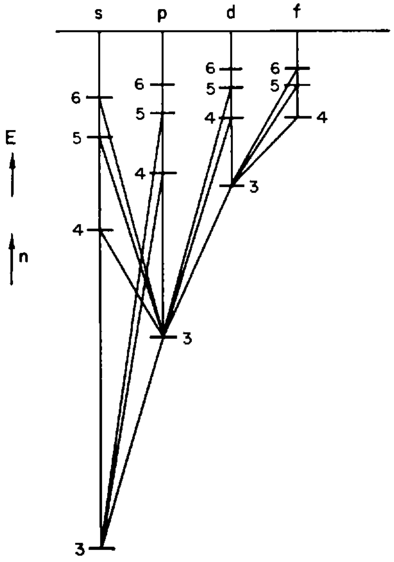

FIG. V.6. Grotrian diagram for sodium.

column marked "*s*" correspond to $n1$ orbits, those in the column marked "*p*" to $n2$ orbits, in the "*d*" column to $n3$ orbits, and in the "*f*" column to $n4$ orbits. The nomenclature *s*, *p*, *d*, *f* was introduced because these levels led to the fundamental, sharp, diffuse, and fundamental series. The fact that only energy-levels in adjacent columns combine is due to so-called *selection rules*, one of which states that in a transition k must either increase or decrease by unity. We shall discuss selection rules in the next chapter. From equations (5.44)–(5.47) we notice that, indeed, α decreases with increasing k, being, respectively, 1·4, 0·9, 0·01 and 0·002 for $k = 1, 2, 3$ and 4.

Before discussing the shell model of the atom, we shall briefly discuss the behaviour of an atom in a magnetic field. Consider the case of a uniform magnetic field **H**. We know from classical mechanics (for instance, ter Haar, 1961) that we can take the influence of a magnetic field into account by changing in the kinetic energy $\mathbf{p}^2$ to $(\mathbf{p}-e\mathbf{A}/c)^2$ where **A** is the vector potential. In the case of a uniform field, we can choose **A** to be of the form

$$\mathbf{A} = \tfrac{1}{2}[\mathbf{H}\wedge\mathbf{r}], \tag{5.48}$$

and if the field is sufficiently weak so that we may neglect terms quadratic in H, we get instead of the equivalent of equation (5.22) for the Hamiltonian the equation

$$\begin{aligned}\mathscr{H} &= \frac{1}{2m}\left(\mathbf{p}-\frac{e\mathbf{A}}{c}\right)^2 + U(r)\\ &= \frac{1}{2m}\left(p_r^2+\frac{p_\theta^2}{r^2}+\frac{p_\phi^2}{r^2\sin^2\theta}\right)-\frac{e}{2mc}Hp_\phi+U(r),\end{aligned} \tag{5.49}$$

where H is the absolute magnitude of **H**. As $\mathscr{H}$ does still not contain ϕ, p_ϕ is again a constant of motion, and equation (5.24) again holds. If we may treat the term involving H as a small perturbation, we see that the energy of the stationary states is changed by an amount ΔE given by the equation

$$\Delta E = -\frac{eH}{2mc}n_\phi\hbar = -n_\phi\mu_B H, \tag{5.50}$$

where μ_B is the so-called Bohr magneton,

$$\mu_B = \frac{e\hbar}{2mc}. \tag{5.51}$$

From equation (5.50) we see the reason why n_ϕ is called the magnetic quantum number. The selection rule for n_ϕ is that it can either increase by unity, or decrease by unity, or remain unchanged in a transition. If we are, therefore, comparing the frequency of a spectral line for the case where there is no magnetic field with the corresponding line for the case where there is a magnetic field present, we find that the line is split in a triplet, the central line of which is undisplaced, while the two other lines are at a distance (in frequency) $\mu_B H/h$ to the left and right of it. This is the normal Zeeman triplet, for which Lorentz gave a simple classical explanation in terms of a precession of the orbital plane (see, for instance, Hindmarsh, 1966).

Let us now conclude this chapter by considering the shell model of the atom. In Fig. V.7 we have given the periodic system of elements up to xenon. In this figure lines connect elements with similar chemical properties in different periods. The first six periods contain, respectively, 2, 8, 8, 18, 18 and 32 elements. Although Bohr (1921, 1922b) was able to explain the structure of the periodic table, starting from the regularities of the atomic spectra, which indicate that only a few of the electrons in the atom are responsible for the spectral lines and from the similarities displayed by the elements connected by lines in Fig. V.7, a satisfactory explanation requires the use of Pauli's exclusion principle (Pauli, 1925b, reprinted in this volume on p. 184). We shall briefly discuss how Pauli was led to this principle (for a more detailed discussion of the history of the Pauli principle see Whittaker, 1954, chap. IV, or Pauli, 1946). The Bohr theory was not able to explain the doublet structure of the alkali atoms, which indicated that there were twice as many quantum states as the Bohr theory predicted. Neither could the theory explain the anomalous Zeeman effect. It was thought for a long time that the doublet was due to the existence of two alternative states of the atom core, but Pauli (1925a) showed that this would lead to a dependence of the Zeeman effect on atomic number which was not observed, and he suggested that the doublet was due to a new

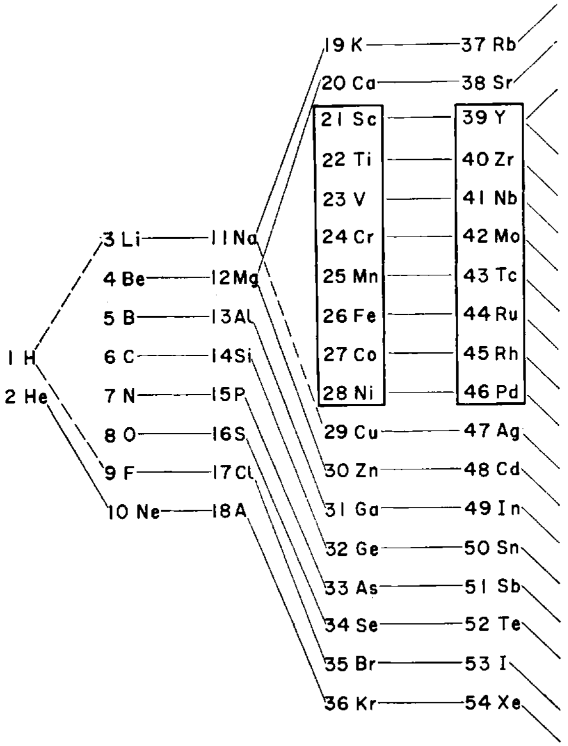

FIG. V.7. The periodic system of elements up to xenon.

quantum theoretical property of the electron, which Pauli called "a two-valuedness not describable classically". The final explanation of this two-valuedness and thus of the doublet structure of the alkali spectra was given by Uhlenbeck and Goudsmit (1926; this paper is reprinted in Hindmarsh, 1966) by their suggestion that the electron possesses an intrinsic angular momentum (spin) and a magnetic moment. In trying to explain the periodic table of elements, Bohr assigned to groups of electrons with given values of the quantum numbers n and l numbers of electrons which varied with the degree of filling of the shells (see Table 1 of Pauli, 1925b, reprinted on p. 194 of this volume), but Stoner (1924) introducing the extra quantum number which was earlier used to characterize X-ray spectra (and which in modern terms is $l \pm \frac{1}{2}$ or j) suggested that each n, j-state could be occupied by $2j+1$ electrons (see Table 2 of Pauli, 1925b, reprinted on p. 194 of this volume). He also suggested that for a given value of n, the number of energy levels of a single electron in the alkali metal spectra in an external magnetic field is equal to the number of electrons in the closed shell of the inert gas which correspond to this value of n. Pauli then suggested that in strong magnetic fields, where we can assign to each electron four quantum numbers, n, l, j, and a magnetic quantum number, m, only one electron can exist with a given set of quantum numbers. Using Bohr's principle of permanence of quantum numbers, Pauli suggested that the number of electrons assigned to a certain subgroup would remain the same also in weak or vanishing fields. We refer to his paper, reprinted in this volume, for Pauli's arguments based on experimental data in favour of his proposal. To construct the periodic system gradually, we shall use instead of n, l, j, and m the equivalent set n, l, m, and m_s (the spin quantum number), where $m_s \hbar$ is the z-component of the electron spin and where $m_s = +\frac{1}{2}$ or $-\frac{1}{2}$. Moreover, we use the fact that for a given value of n, l can take on the values 0, 1, ..., $n-1$, that for a given value of l, m can take on the values $-l$, $-l+1$, ..., $l-1$, l, while m_s can be either $+\frac{1}{2}$ or $-\frac{1}{2}$. We can now construct the periodic table (compare also Pauli's discussion in Pauli, 1925b).

To fix our ideas, let us consider the sodium atom and let us build it up by successively putting the eleven electrons in the field of the nucleus. The first electron will go into a 1s orbit, and so will the second electron. Their quantum numbers will be $n = 1$, $l = 0$, $m = 0$, and $m_s = +\frac{1}{2}$ and $-\frac{1}{2}$. The third electron cannot be accommodated in an $n = 1$ orbit, but must go into an $n = 2$ orbit.

THE ELECTRONIC STRUCTURE OF THE ELEMENTS UP TO XENON

Element	1s	2s	2p	3s	3p	3d	4s	4d	4f	5s	5p
1 H	1										
2 He	2										
3 Li	2	1									
4 Be	2	2									
5 B	2	2	1								
6 C	2	2	2								
7 N	2	2	3								
8 O	2	2	4								
9 F	2	2	5								
10 Ne	2	2	6								
11 Na	2	2	6	1							
12 Mg	2	2	6	2							
13 Al	2	2	6	2	1						
14 Si	2	2	6	2	2						
15 P	2	2	6	2	3						
16 S	2	2	6	2	4						
17 Cl	2	2	6	2	5						
18 A	2	2	6	2	6						
19 K	2	2	6	2	6		1				
20 Ca	2	2	6	2	6		2				
21 Sc	2	2	6	2	6	1	2				
22 Ti	2	2	6	2	6	2	2				
23 V	2	2	6	2	6	3	2				
24 Cr	2	2	6	2	6	5	1				
25 Mn	2	2	6	2	6	5	2				
26 Fe	2	2	6	2	6	6	2				
27 Co	2	2	6	2	6	7	2				
28 Ni	2	2	6	2	6	8	2				
29 Cu	2	2	6	2	6	10	1				
30 Zn	2	2	6	2	6	10	2				
31 Ga	2	2	6	2	6	10	2	1			
32 Ge	2	2	6	2	6	10	2	2			
33 As	2	2	6	2	6	10	2	3			
34 Se	2	2	6	2	6	10	2	4			
35 Br	2	2	6	2	6	10	2	5			
36 Kr	2	2	6	2	6	10	2	6			
37 Rb	2	2	6	2	6	10	2	6		1	
38 Sr	2	2	6	2	6	10	2	6		2	
39 Y	2	2	6	2	6	10	2	6	1	2	
40 Zr	2	2	6	2	6	10	2	6	2	2	
41 Nb	2	2	6	2	6	10	2	6	3	2	
42 Mo	2	2	6	2	6	10	2	6	4	2	
43 Tc	2	2	6	2	6	10	2	6	5	2	
44 Ru	2	2	6	2	6	10	2	6	7	1	
45 Rh	2	2	6	2	6	10	2	6	8	1	
46 Pd	2	2	6	2	6	10	2	6	10		
47 Ag	2	2	6	2	6	10	2	6	10	1	
48 Cd	2	2	6	2	6	10	2	6	10	2	
49 In	2	2	6	2	6	10	2	6	10	2	1
50 Sn	2	2	6	2	6	10	2	6	10	2	2
51 Sb	2	2	6	2	6	10	2	6	10	2	3
52 Te	2	2	6	2	6	10	2	6	10	2	4
53 I	2	2	6	2	6	10	2	6	10	2	5
54 Xe	2	2	6	2	6	10	2	6	10	2	6

We discussed earlier that an *s*-orbit will penetrate more closely to the nucleus than a *p*-orbit and, therefore, if there are already other electrons present, will correspond to a larger binding energy. The third (and fourth) electrons will thus be in 2*s*-orbits ($n = 2$, $l = 0$, $m = 0$, $m_s = \pm\frac{1}{2}$). The fifth electron will go into a 2*p*-orbit, as will the sixth to tenth electrons, corresponding to $n = 2$, $l = 1$, $m = 1, 0, -1$, and $m_s = \pm\frac{1}{2}$. These ten electrons together fill the $n = 1$ and $n = 2$ *shells*, and spectroscopy shows that such filled or closed shells are extremely stable configurations. They are the ground-state configurations of the inert gases which are known to be chemically inactive.

The filling up of the various possible electron orbits continues without any complications until all 3*p*-orbits are filled. The nineteenth electron, however, will go into a 4*s*-orbit rather than a 3*d*-orbit; the reason is that the quantum defect for a 4*s*-orbit is so large that the effective quantum number is smaller for the 4*s*-orbit than for the 3*d*-orbit. However, the 3*d* effective quantum number is smaller than that of the 4*p*-orbit and between scandium and copper, the 3*d*-subshell is filled up. This set of elements form the so-called transition metals. In the table on p. 60 we have given for all the elements up to xenon the electron configurations corresponding to their ground state (compare also Table 2 on p. 194).

The question arises why one may assign quantum numbers which were introduced for the case of a single electron to electrons which are part of a many-electron configuration. This can be done because one may assume that the step-by-step construction of the atom, as we have described it, is an adiabatic process so that, in fact, the quantum numbers remain unchanged from their initial values [compare the discussion by Pauli (1925b; see p. 184 of this volume) of the so-called "Aufbauprinzip"]. In wave mechanics the justification for this is given by the method of the self-consistent field, developed by Hartree and Fock (see, for instance, Davydov, 1965).

Essentially, the reason is because to a good approximation each electron moves in a field due to the average effect of all the others.

If we compare the final wavefunction determined by the self-consistent field method with a wavefunction constructed from single-electron wavefunctions with well-defined quantum numbers, we see that our first guess was a good one.

CHAPTER VI

Radiation Theory

IN THIS last chapter, we shall discuss some aspects of the emission of spectral lines. In the previous chapter our main concern was the determination of the energies corresponding to stationary orbits. We shall now consider such problems as the probabilities with which transitions will take place. This will involve applying Bohr's correspondence principle and we shall see how this principle will enable us to derive expressions for relative intensities of different spectral lines and selection rules.

We shall first of all discuss how Einstein (1917; reprinted in this volume on p. 167) introduced transition probabilities. Einstein showed how one can derive Planck's formula (1.48) for the radiation energy density by assuming that the Boltzmann distribution of atoms over their energy states must be maintained by processes of absorption and emission of light. Moreover, one must require that the interaction between radiation and atoms also leads to the Maxwell velocity distribution for the atoms, and from this it follows that every absorption or emission process has the nature of "needle" radiation, that is, there is a definite direction assigned to it. To some extent one can say that with Einstein's paper the wheel has come full-circle, as it was the consideration of the thermodynamic equilibrium of temperature radiation which led Planck to his radiation law [compare the derivation of equation (1.29)].

Consider a set of atoms, which can be stationary states m and n with energies E_m and E_n. One finds by arguments which are exactly the same as those leading to the Maxwell distribution (see, for instance, ter Haar, 1954, chap. III) that in thermodynamic equilibrium the numbers of atoms, N_m and N_n, in the two states are given by the equation

$$N_m = Ce^{-\beta E_m}, \qquad N_n = Ce^{-\beta E_n}, \tag{6.1}$$

where we have written β for $1/kT$, and where C is a normalizing constant, which if we assume for a moment that there are only two stationary states possible, satisfies the equation

$$C = N\left[e^{-\beta E_m} + e^{-\beta E_n}\right], \tag{6.2}$$

where N is the total number of atoms.†

In order to consider the equilibrium between the radiation field and the atoms,‡ we first of all note that according to Bohr's hypotheses an atom in a stationary state with higher energy can make a transition to a state with lower energy. Assuming, to fix the ideas, that $E_m > E_n$, we find that in the transition from the state m to the state n, a light quantum is emitted with frequency ν equal to $(E_m - E_n)/h$ [see equation (5.1)]. By analogy with radioactive processes, Einstein assumed that there is a probability dW_1 that this spontaneous process will take place during a time interval dt with dW_1 given by the relation

$$dW_1 = A_m^n \, dt. \tag{6.3}$$

From equation (6.3) it follows that if there is no radiation field present which, as we shall see in a moment, influences the transition probabilities, we find for the number N_m of atoms in the state m the equation of motion

$$\frac{dN_m}{dt} = -N_m A_m^n, \tag{6.4}$$

or

$$N_m(t) = N_m(0) \exp(-A_m^n t). \tag{6.5}$$

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† The restriction to the case where there are only two stationary states is not an essential one, and can easily be lifted. We note that we have neglected here all complications due to degeneracies of stationary states; this restriction can also easily be lifted.

‡ The analogous equilibrium between atoms and free electrons has been considered by Klein and Rosseland (1921).

From this equation it follows that we can interpret $1/A^n_m$ as the lifetime of the atom in the excited state m; if there are other transitions to lower-lying states possible for an atom in the state m, we must replace A^n_m by a sum over all relevant lower-lying states.

Consider now the influence of the radiation field on the atoms. If $\rho(\nu)$ is the radiation energy density at the frequency ν corresponding to the energy difference E_m-E_n, we have first of all the possibility that an atom in the state n will absorb a quantum $h\nu$ and go over to the state m. The probability dW_2 that this will happen during a time interval dt will be proportional to $\rho(\nu)$ and we put, therefore,

$$dW_2 = B^m_n\,\rho(\nu)\,dt. \tag{6.6}$$

From classical electromagnetic theory, we know that a radiation field will stimulate radiation from a charge, and we expect, therefore, by analogy, that the probability that an atom in the state m will make a transition to the state n will be enhanced, if a radiation field is present. Let dW_3 be the probability that such a stimulated or *induced* emission will take place during the time dt; we would expect dW_3 to be proportional to $\rho(\nu)$ and we can write

$$dW_3 = B^n_m\,\rho(\nu)\,dt. \tag{6.7}$$

At equilibrium, the number of transitions $m \to n$ must equal the number of transitions $n \to m$, or

$$N_m[A^n_m+B^n_m\,\rho(\nu)] = N_n\,B^m_n\,\rho(\nu). \tag{6.8}$$

From the requirement that as $\beta \to 0$, that is as the temperature tends to infinity, $\rho(\nu)$ will tend to infinity, and the fact that as $\beta \to 0$, $N_m \to N_n$, we find

$$B^n_m = B^m_n. \tag{6.9}$$

Secondly, one finds from the requirement that at equilibrium $\rho(\nu)$ must satisfy the relation (1.1) that

$$A^n_m = \alpha\nu^3 B^n_m. \tag{6.10}$$

The constant α can be found from the requirement that in the limit as $\beta h\nu \ll 1$, $\rho(\nu)$ must be given by the Rayleigh–Jeans law, so that we find

$$\frac{A_m^n}{B_m^n} = \frac{8\pi h\nu^3}{c^3}, \tag{6.11}$$

while equations (6.1), (6.8), (6.9) and (6.11) together lead to Planck's formula (1.48) for $\rho(\nu)$.

The second conclusion of Einstein's paper on the quantum theory of radiation—and the part he himself considers to be the more important one—deals with the momentum transferred to the atom from the radiation field in an elementary absorption or emission process, that is, the recoil of the atom in such a process. Einstein once again used arguments from the theory of Brownian motion (compare the discussion in Chapter II of the fluctuations in energy and momentum in a radiation field), and the fact that it follows from classical electrodynamics that in a directed beam of light, an energy ε is connected with a momentum ε/c in the direction of the beam. From this fact Einstein drew the conclusion that in absorption process the atom will receive a momentum $(E_m - E_n)/c$ in the direction of the incident radiation while in an induced emission process, it will receive the same momentum, but in the opposite direction. In accordance with the main ideas of the quantum theory of black-body radiation, we must assume that the action of black-body radiation on an atom is equivalent to the simultaneous action of beams isotropically incident from all possible directions, but that in any particular induced emission or absorption process only one of these beams is involved. Finally, we must consider the momentum transfer in a spontaneous emission process. Einstein assumed that also here the atom undergoes a recoil $(E_m - E_n)/c$ and now in a purely random direction. This is in contrast to the classical picture of the emission of radiation which involves the emission of spherical waves.

Consider now the thermodynamic equilibrium between the translational motion of the atom and the radiation. In a time interval τ the momentum Mv of an atom of mass M will be subject to two sources for change. The first one is the frictional force, Rv, acting on the atom which will lead to a change $Rv\tau$, and the second is a change Δ due to the irregularities (fluctuations) in the radiation field. In equilibrium we must have (for the sake of simplicity we consider a one-dimensional motion)

$$\overline{(Mv-Rv\tau+\Delta)^2} = \overline{(Mv)^2} \tag{6.12}$$

where the bar indicates an average over a sufficiently large number of atoms. As $\bar{v} = 0$, we find from equation (6.12)

$$\frac{\overline{\Delta^2}}{\tau} = 2R\overline{Mv^2} = 2RkT, \tag{6.13}$$

where we have used the fact that at equilibrium $\frac{1}{2}\overline{Mv^2} = \frac{1}{2}kT$.

Einstein calculated $\overline{\Delta^2}$ and R (for details, see his paper on p. 167 of the present volume). The first of these quantities follows simply from a consideration of the fluctuations in the momentum transfer, and as this is essentially a random walk process, we expect $\overline{\Delta^2}$ to be proportional to τ, as is the case. The evaluation of R is more complicated, as it involves the calculation of the momentum transfer from the radiation field to an atom which is moving relative to the field, and it is thus necessary to take terms of first order in v/c into account. If one now substitutes the expressions found by Einstein into equation (6.13) it is identically satisfied. It is, however, essential that in evaluating $\overline{\Delta^2}$ one assumes that the atom receives a recoil in each spontaneous emission process, because otherwise equation (6.13), which is the condition for thermal equilibrium, is not satisfied.†

An experimental verification of the recoil for the case of free electrons was given by Compton (1923a), who studied the

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† This is not strictly correct; Jordan (1924) has shown that one can satisfy equation (6.13) without assuming directed spontaneous emission, provided one alters at the same time the assumptions about the momentum transfer in absorption processes. This would, however, lead to results which seem physically unacceptable.

secondary radiation produced by X-rays both theoretically and experimentally. On examining the scattered rays from light elements he found (Compton, 1923b) that apart from lines with the same wavelength as the incident light, there were also lines with a slightly longer wavelength, and the displacement depended on the angle between the incident light and the scattered light. This is the so-called *Compton effect.*

In the scattering of hard X-rays by light elements, $h\nu$ will be large compared to the binding energy of the electron, which scatters the X-ray so that we may consider the electron to be free. If ϑ is the angle over which the X-ray is scattered, and ϕ the angle at which the electron takes off (see Fig. VI.1), conservation of energy and of momentum in the x- and the y-direction gives us three equations from which to calculate ϕ, the frequency ν' of the scattered X-ray, and the momentum p of the electron, as functions of the scattering angle ϑ:†

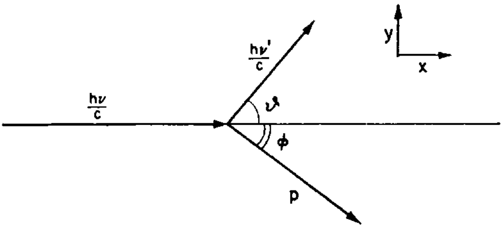

FIG. VI.1. The Compton effect.

$$h\nu+mc^2 = h\nu'+[p^2c^2+m^2c^4]^{\frac{1}{2}}, \qquad (6.14)$$

$$\frac{h\nu}{c} = \frac{h\nu'}{c}\cos\vartheta+p\cos\phi, \qquad (6.15)$$

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† We use here the relativistic expression $[p^2c^2+m^2c^4]^{\frac{1}{2}}$ for the energy. We must note that independent of Compton, Debye (1923) developed the theory of the Compton effect, as did Kramers, who was persuaded by Bohr not to publish his results, as Bohr did not believe them (Bohr was inclined rather to abandon the principles of conservation of energy and momentum; compare the paper by Bohr, Kramers and Slater, 1924).

$$\frac{h\nu'}{c}\sin\vartheta = p\sin\phi, \tag{6.16}$$

Eliminating ϕ from equations (6.15) and (6.16) and then p from the resulting equation and equation (6.14), and introducing the wavelengths $\lambda = c/\nu$ and $\lambda' = c/\nu'$, we find

$$\lambda'-\lambda = \lambda_C(1-\cos\vartheta), \tag{6.17}$$

where λ_C is the so-called Compton wavelength,

$$\lambda_C = \frac{h}{mc} = 0{\cdot}02\,\text{Å U}. \tag{6.18}$$

Relation (6.17) was verified experimentally by Compton.

Let us now consider what we can learn from assuming that in the limit of large quantum numbers classical theory should follow asymptotically. We saw one application of this principle—which was first explicitly stated by Bohr in 1918 (Bohr, 1918a) although the name *correspondence principle* was first used by him in 1920 (Bohr, 1920; see also Bohr, 1922b)—in Chapter IV in the second derivation of equation (4.4). The reasonableness of this principle also follows from equation (5.17) as for a given value of J_k the classical limit $h \to 0$ corresponds to the limit $n_k \to \infty$.

To fix our ideas, we shall first of all consider a system with one degree of freedom. From the quantization rule (5.17), which in this case simply reads

$$J(E) = nh, \tag{6.19}$$

it follows that we can write for the energy, E_n, of the nth stationary orbit

$$E_n = E(nh). \tag{6.20}$$

The classical frequency ν_{cl} of the motion follows from equation (5.8), as w has a period of 1:

$$\nu_{\text{cl}} = \dot{w} = \frac{\partial E}{\partial J}. \tag{6.21}$$

If we consider now a transition from the state n to the state $n-\tau$, we find for the case where n is large,

$$h\nu_{n\to n-\tau} = E_n - E_{n-\tau} = E(nh) - E[(n-\tau)h]$$

$$= \tau h\left(\frac{dE}{dJ}\right)_{J=nh}, \tag{6.22}$$

or

$$\nu_\tau \equiv \nu_{n\to n-\tau} = \tau\nu_{\text{cl}}, \tag{6.23}$$

the frequencies corresponding to transitions between stationary states with large quantum numbers correspond to the classical frequency and the higher harmonics.

To find the transition probabilities which will give us both the selection rules (if we find out which transitions correspond to vanishing A_m^n) and the relative intensities of allowed transitions, we must consider the electrical dipole moment, **P**, of the system. From classical electrodynamics [for instance, Panofsky and Phillips, 1955; compare equation (1.22)] it follows that the rate at which energy is lost through radiation is given by the equation

$$\frac{dE}{dt} = \frac{2}{3c^2}\overline{\ddot{P}^2}, \tag{6.24}$$

where the bar indicates a time average, which for our one-dimensional system can be taken to be the average over a single period. We can compare this with the equation following from equation (6.3):

$$\frac{dE}{dt} = h\nu_\tau A_n^{n-\tau}. \tag{6.25}$$

As our system is periodic, we can expand P in a Fourier series,

$$P = \frac{1}{2}\sum_{\tau=-\infty}^{+\infty} P_\tau e^{2\pi i\tau\nu_{\text{cl}}}, \tag{6.26}$$

where, as P is real,

$$P_\tau = P_{-\tau}^*. \tag{6.27}$$

From equations (6.24), (6.25) and (6.26), we find

$$A_n^{n-\tau} = \frac{(2\pi)^4 \nu_\tau^3}{3hc^3} |P_\tau|^2. \tag{6.28}$$

From this it follows that the transition is forbidden, if P_τ vanishes.†

As a first application, we shall consider the case of a simple harmonic oscillator. In that case, we have for the amplitude x of the oscillator

$$x = x_0 \cos 2\pi\nu_{\text{cl}} t, \tag{6.29}$$

from which it follows that

$$P_1 = P_{-1} = \tfrac{1}{2}ex_0, \quad P_\tau = 0, \quad \tau \neq \pm 1, \tag{6.30}$$

and, therefore,

$$A_n^{n-1} = \frac{(2\pi)^4 e^2 \nu_{\text{cl}}^3}{3hc^3} x_0^2, \tag{6.31}$$

or

$$A_n^{n-1} = \tfrac{8}{3}\pi^2 \frac{e^2 \nu_{\text{cl}}^2}{mc^3} n, \tag{6.32}$$

where we have used the relation [compare equations (1.47) and (1.40)]

$$E_n = nh\nu_{\text{cl}} = \tfrac{1}{2}m(2\pi\nu_{\text{cl}})^2 x_0^2. \tag{6.33}$$

From equation (6.30), it follows that for the case of a harmonic oscillator the selection rule

$$\Delta n = \pm 1 \tag{6.34}$$

holds. The selection rule for n will be different if we consider other potential energies. To find the selection rules for k and m, which are the proper quantum numbers for the case of a central field, we use the fact that the x-, y-, and z-components of the

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† Strictly speaking, this is incorrect. Transitions can occur corresponding to electrical quadrupole, octupole . . . or to magnetic dipole . . . radiations, but the intensities corresponding to such transitions are so much smaller (see, for instance, Panofsky and Phillips, 1955) that to a good approximation we can neglect them.

electrical dipole moment expressed in spherical polars are (e is the charge of the particle moving in the central field)

$$\left.\begin{aligned} P_x &= e\,r\cos\phi\sin\theta, \\ P_y &= e\,r\sin\phi\sin\theta, \\ P_z &= e\,r\cos\theta. \end{aligned}\right\} \tag{6.35}$$

To find how these expressions can lead to selection rules for k and m, we first of all note that it follows from equations (6.35) that the components of **P** contain θ either in the form $e^{i\theta}$ or in the form $e^{-i\theta}$, while they contain ϕ either in the form $e^{i\phi}$ or in the form $e^{-i\phi}$, or not at all. One can prove that these factors as functions of t can be written in the form (for details compare Bohr, 1918a, b, Pauli, 1926, or Tomonaga, 1962)

$$e^{\pm i\phi} = A(t)\,e^{\pm 2\pi i\nu_\phi t}, \tag{6.36}$$

$$e^{\pm i\theta} = B(t)\,e^{\pm 2\pi i\nu_\theta t}, \tag{6.37}$$

where $A(t)$ and $B(t)$ can be written as Fourier series of the same form as (6.26) with ν_{cl} replaced by ν_r. As in equation (6.37) only terms with $\nu_\theta = \pm 1$ occur, we have the selection rule

$$\Delta k = \pm 1, \tag{6.38}$$

while in equation (6.36) only terms with $\nu_\phi = \pm 1$ occur and in P_z only the term with $\nu_\phi = 0$ so that for m the selection rule is

$$\Delta m = 0, \pm 1. \tag{6.39}$$

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1 On an Improvement of Wien's Equation for the Spectrum†

M. PLANCK

THE interesting results of long wave length spectral energy measurements which were communicated by Mr. Kurlbaum at today's meeting, and which were obtained by him and Mr. Rubens, confirm the statement by Mr. Lummer and Mr. Pringsheim, which was based on their observations that Wien's energy distribution law is not as generally valid, as many have supposed up to now, but that this law at most has the character of a limiting case, the simple form of which was due only to a restriction to short wave lengths and low temperatures.‡ Since I myself even in this Society have expressed the opinion that Wien's law must be necessarily true, I may perhaps be permitted to explain briefly the relationship between the electromagnetic radiation theory developed by me and the experimental data.

The energy distribution law is according to this theory determined as soon as the entropy S of a linear resonator which interacts with the radiation is known as function of the vibrational energy U. I have, however, already in my last paper on this subject[1] stated that the law of increase of entropy is by itself not yet sufficient to determine this function completely; my view that Wien's law would be of general validity, was brought about rather by special considerations, namely by the evaluation of an infinitesimal increase of the entropy of a system of n identical

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† *Verh. Dtsch. Phys. Ges. Berlin* **2**, 202 (1900).

‡ Mr. Paschen has written to me that he has also recently found appreciable deviations from Wien's law.

resonators in a stationary radiation field by two different methods which led to the equation

$$dU_n \, . \, \Delta U_n \, . f(U_n) = n \, dU \, . \, \Delta U \, . f(U),$$

where $$U_n = nU \quad \text{and} \quad f(U) = -\frac{3}{5}\frac{d^2S}{dU^2}.$$

From this equation Wien's law follows in the form

$$\frac{d^2S}{dU^2} = \frac{\text{const}}{U}.$$

The expression on the right-hand side of this functional equation is certainly the above-mentioned change in entropy since n identical processes occur independently, the entropy changes of which must simply add up. However, I could consider the possibility, even if it would not be easily understandable and in any case would be difficult to prove, that the expression on the left-hand side would not have the general meaning which I attributed to it earlier, in other words: that the values of U_n, dU_n and ΔU_n are not by themselves sufficient to determine the change of entropy under consideration, but that U itself must also be known for this. Following this suggestion I have finally started to construct completely arbitrary expressions for the entropy which although they are more complicated than Wien's expression still seem to satisfy just as completely all requirements of the thermodynamic and electromagnetic theory.

I was especially attracted by one of the expressions thus constructed which is nearly as simple as Wien's expression and which deserves to be investigated since Wien's expression is not sufficient to cover all observations. We get this expression by putting†

$$\frac{d^2S}{dU^2} = \frac{\alpha}{U(\beta + U)}.$$

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† I use the second derivative of S with respect to U since this quantity has a simple physical meaning.

It is by far the simplest of all expressions which lead to S as a logarithmic function of U—which is suggested from probability considerations—and which moreover reduces to Wien's expression for small values of U. Using the relation

$$\frac{dS}{dU} = \frac{1}{T}$$

and Wien's "displacement" law† one gets a radiation formula with two constants:

$$E = \frac{C\lambda^{-5}}{e^{c/\lambda T} - 1},$$

which, as far as I can see at the moment, fits the observational data, published up to now, as satisfactorily as the best equations put forward for the spectrum, namely those of Thiesen,[2]‡ Lummer–Jahnke,[4] and Lummer–Pringsheim.[5] (This was demonstrated by some numerical examples.) I should therefore be permitted to draw your attention to this new formula which I consider to be the simplest possible, apart from Wien's expression, from the point of view of the electromagnetic theory of radiation.

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† The expression of Wien's displacement law is simply

$$S = f(U/\nu),$$

where ν is the frequency of the resonator, as I shall show elsewhere.

‡ One can see there that Mr. Thiesen had put forward his formula before Mr. Lummer and Mr. Pringsheim had extended their measurements to longer wave lengths. I emphasise this point as I have made a statement to the contrary[3] before this paper was published.

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2 On the Theory of the Energy Distribution Law of the Normal Spectrum†

M. PLANCK

GENTLEMEN: when some weeks ago I had the honour to draw your attention to a new formula which seemed to me to be suited to express the law of the distribution of radiation energy over the whole range of the normal spectrum,[1] I mentioned already then that in my opinion the usefulness of this equation was not based only on the apparently close agreement of the few numbers, which I could then communicate, with the available experimental data,‡ but mainly on the simple structure of the formula and especially on the fact that it gave a very simple logarithmic expression for the dependence of the entropy of an irradiated monochromatic vibrating resonator on its vibrational energy. This formula seemed to promise in any case the possibility of a general interpretation much rather than other equations which have been proposed, apart from Wien's formula which, however, was not confirmed by experiment.

Entropy means disorder, and I thought that one should find this disorder in the irregularity with which even in a completely stationary radiation field the vibrations of the resonator change their amplitude and phase, as long as one considers time intervals long compared to the period of one vibration, but short compared to the duration of a measurement. The constant energy of the

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† *Verh. Dtsch. Phys. Ges. Berlin* **2**, 237 (1900).

‡ In the meantime Mr. H. Rubens and Mr. F. Kurlbaum[2] have given a direct confirmation for very long wave lengths.

stationary vibrating resonator can thus only be considered to be a time average, or, put differently, to be an instantaneous average of the energies of a large number of identical resonators which are in the same stationary radiation field, but far enough from one another not to influence each other. Since the entropy of a resonator is thus determined by the way in which the energy is distributed at one time over many resonators, I suspected that one should evaluate this quantity in the electromagnetic radiation theory by introducing probability considerations, the importance of which for the second law of thermodynamics was first of all discovered by Mr. L. Boltzmann.[3] This suspicion has been confirmed; I have been able to derive deductively an expression for the entropy of a monochromatically vibrating resonator and thus for the energy distribution in a stationary radiation state, that is, in the normal spectrum. To do this it was only necessary to extend somewhat the interpretation of the hypothesis of "natural radiation" which is introduced in electromagnetic theory. Apart from this I have obtained other relations which seem to me to be of considerable importance for other branches of physics and also of chemistry.

I do not wish to give today this deduction—which is based on the laws of electromagnetic radiation, thermodynamics and probability calculus—systematically in all details, but rather to explain as clearly as possible the real core of the theory. This can be done most easily by describing to you a new, completely elementary treatment through which one can evaluate—without knowing anything about a spectral formula or about any theory—the distribution of a given amount of energy over the different colours of the normal spectrum using one constant of nature only and after that also the value of the temperature of this energy radiation using a second constant of nature. You will find many points in the treatment to be presented arbitrary and complicated, but as I said a moment ago I do not want to pay attention to a proof of the necessity and the simple, practical details, but to the clarity and uniqueness of the given prescriptions for the solution of the problem.

Let us consider a large number of monochromatically vibrating resonators—N of frequency ν (per second), N' of frequency ν', N'' of frequency ν'', ..., with all N large numbers—which are at large distances apart and are enclosed in a diathermic medium with light velocity c and bounded by reflecting walls. Let the system contain a certain amount of energy, the total energy E_t (erg) which is present partly in the medium as travelling radiation and partly in the resonators as vibrational energy. The question is how in a stationary state this energy is distributed over the vibrations of the resonators and over the various colours of the radiation present in the medium, and what will be the temperature of the total system.

To answer this question we first of all consider the vibrations of the resonators and assign to them arbitrarily definite energies, for instance, an energy E to the N resonators ν, E' to the N' resonators ν', ... The sum

$$E+E'+E''+\ldots = E_0$$

must, of course, be less than E_t. The remainder E_t-E_0 pertains then to the radiation present in the medium. We must now give the distribution of the energy over the separate resonators of each group, first of all the distribution of the energy E over the N resonators of frequency ν. If E is considered to be a continuously divisible quantity, this distribution is possible in infinitely many ways. We consider, however—this is the most essential point of the whole calculation—E to be composed of a very definite number of equal parts and use thereto the constant of nature $h = 6{\cdot}55\times 10^{-27}$ erg sec. This constant multiplied by the common frequency ν of the resonators gives us the energy element ε in erg, and dividing E by ε we get the number P of energy elements which must be divided over the N resonators. If the ratio is not an integer, we take for P an integer in the neighbourhood.

It is clear that the distribution of P energy elements over N resonators can only take place in a finite, well-defined number of ways. Each of these ways of distribution we call a "complexion", using an expression introduced by Mr. Boltzmann for a similar quantity. If we denote the resonators by the numbers $1, 2, 3, \ldots, N$, and write these in a row, and if we under each resonator put the number of its energy elements, we get for each complexion a symbol of the following form

1	2	3	4	5	6	7	8	9	10
7	38	11	0	9	2	20	4	4	5

We have taken here $N = 10, P = 100$. The number of all possible complexions is clearly equal to the number of all possible sets of numbers which one can obtain for the lower sequence for given N and P. To exclude all misunderstandings, we remark that two complexions must be considered to be different if the corresponding sequences contain the same numbers, but in different order. From the theory of permutations we get for the number of all possible complexions

$$\frac{N(N+1).(N+2)\ldots(N+P-1)}{1.2.3\ldots P} = \frac{(N+P-1)!}{(N-1)!P!}$$

or to a sufficient approximation,

$$= \frac{(N+P)^{N+P}}{N^N P^P}.$$

We perform the same calculation for the resonators of the other groups, by determining for each group of resonators the number of possible complexions for the energy given to the group. The multiplication of all numbers obtained in this way gives us then the total number R of all possible complexions for the arbitrarily assigned energy distribution over all resonators.

In the same way any other arbitrarily chosen energy distribution $E, E', E'', \ldots$ will correspond to a definite number R of all possible complexions which is evaluated in the above manner. Among all energy distributions which are possible for a constant $E_0 = E+E'+E''+\ldots$ there is one well-defined one for which the number of possible complexions R_0 is larger than for any other distribution. We look for this distribution, if necessary by trial, since this will just be the distribution taken up by the resonators in the stationary radiation field, if they together possess the energy E_0. The quantities E, E', E'', ... can then be expressed in terms of E_0. Dividing E by N, E' by N', ... we obtain the stationary value of the energy U_ν, $U'_{\nu'}$, $U''_{\nu''}$, ... of a single resonator of each group, and thus also the spatial density of the corresponding radiation energy in a diathermic medium in the spectral range ν to $\nu+d\nu$,

$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3} \, . \, U_\nu d\nu,$$

so that the energy of the medium is also determined.

Of all quantities which occur only E_0 seems now still to be arbitrary. One sees easily, however, how one can finally evaluate E_0 from the total energy E_t, since if the chosen value of E_0 leads, for instance, to too large a value of E_t, we must decrease it, and the other way round.

After the stationary energy distribution is thus determined using a constant h, we can find the corresponding temperature ϑ in degrees absolute† using a second constant of nature $k = 1{\cdot}346 \times 10^{-6}$ erg degree^{-1} through the equation

$$\frac{1}{\vartheta} = k\frac{d \ln R_0}{dE_0}.$$

The product $k \ln R_0$ is the entropy of the system of resonators; it is the sum of the entropy of all separate resonators.

It would, to be sure, be very complicated to perform explicitly the above-mentioned calculations, although it would not be without some interest to test the truth of the attainable degree of approximation in a simple case. A more general calculation which is performed very simply, using the above prescriptions shows much more directly that the normal energy distribution determined in this way for a medium containing radiation is

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† The original states "degrees centigrade" which is clearly a slip [D. t. H.].

given by the expression

$$u_\nu \, d\nu = \frac{8\pi\nu^3}{c^3}\frac{d\nu}{e^{h\nu/k\vartheta}-1},$$

which corresponds exactly to the spectral formula which I gave earlier

$$E_\lambda \, d\lambda = \frac{c_1 \lambda^{-5}}{e^{c_2/\lambda\vartheta}-1} d\lambda.$$

The formal differences are due to the differences in the definitions of u_ν and E_λ. The first equation is somewhat more general inasfar as it is valid for an arbitrary diathermic medium with light velocity c. The numerical values of h and k which I mentioned were calculated from that equation using the measurements by F. Kurlbaum and by O. Lummer and E. Pringsheim.†

I shall now make a few short remarks about the question of the necessity of the above given deduction. The fact that the chosen energy element ε for a given group of resonators must be proportional to the frequency ν follows immediately from the extremely important Wien displacement law. The relation between u and U is one of the basic equations of the electromagnetic theory of radiation. Apart from that, the whole deduction is based upon the theorem that the entropy of a system of resonators with given energy is proportional to the logarithm of the total number of possible complexions for the given energy. This theorem can be split into two other theorems: (1) The entropy of the system in a given state is proportional to the logarithm of the probability of that state, and (2) The probability of any state is proportional to the number of corresponding complexions, or, in other words, any definite complexion is equally probable as any other complexion. The first theorem is, as far as radiative phenomena are concerned, just a definition of the probability of the state, insofar as we have for energy radiation no other *a priori* way to define the probability than the definition of its entropy. We have here a distinction from

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† F. Kurlbaum[4] gives $S_{100}-S_0 = 0{\cdot}0731$ Watt cm^{-2}, while O. Lummer and E. Pringsheim[5] give $\lambda_m \vartheta = 2940\,\mu$ degree.

the corresponding situation in the kinetic theory of gases. The second theorem is the core of the whole of the theory presented here: in the last resort its proof can only be given empirically. It can also be understood as a more detailed definition of the hypothesis of natural radiation which I have introduced. This hypothesis I have expressed before[6] only in the form that the energy of the radiation is completely "randomly" distributed over the various partial vibrations present in the radiation.† I plan to communicate elsewhere in detail the considerations, which have only been sketched here, with all calculations and with a survey of the development of the theory up to the present.

To conclude I may point to an important consequence of this theory which at the same time makes possible a further test of its reliability. Mr. Boltzmann[7] has shown that the entropy of a monatomic gas in equilibrium is equal to $\omega R \ln P_0$, where P_0 is the number of possible complexions (the "permutability") corresponding to the most probable velocity distribution, R being the well known gas constant ($8{\cdot}31 \times 10^7$ for $\mathrm{O} = 16$), ω the ratio of the mass of a real molecule to the mass of a mole, which is the same for all substances. If there are any radiating resonators present in the gas, the entropy of the total system must according to the theory developed here be proportional to the logarithm of the number of all possible complexions, including both velocities and radiation. Since according to the electromagnetic theory of the radiation the velocities of the atoms are completely independent of the distribution of the radiation energy, the total number of complexions is simply equal to the product of the number

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† When Mr. W. Wien in his Paris report about the theoretical radiation laws did not find my theory on the irreversible radiation phenomena satisfactory since it did not give the proof that the hypothesis of natural radiation is the only one which leads to irreversibility, he surely demanded, in my opinion, too much of this hypothesis. If one could prove the hypothesis, it would no longer be a hypothesis, and one did not have to formulate it. However, one could then not derive anything new from it. From the same point of view one should also declare the kinetic theory of gases to be unsatisfactory since nobody has yet proved that the atomistic hypothesis is the only one which explains irreversibility. A similar objection could with more or less justice be raised against all inductively obtained theories.

relating to the velocities and the number relating to the radiation. For the total entropy we have thus

$$f \ln (P_0 R_0) = f \ln P_0 + f \ln R_0,$$

where f is a factor of proportionality. Comparing this with the earlier expressions we find

$$f = \omega R = k,$$

or
$$\omega = \frac{k}{R} = 1{\cdot}62 \times 10^{-24},$$

that is, a real molecule is $1{\cdot}62 \times 10^{-24}$ of a mole, or, a hydrogen atom weighs $1{\cdot}64 \times 10^{-24}$g, since H = 1·01, or, in a mole of any substance there are $1/\omega = 6{\cdot}175 \times 10^{23}$ real molecules. Mr. O. E. Mayer[8] gives for this number 640×10^{21} which agrees closely.

Loschmidt's number L, that is, the number of gas molecules in 1 cm^3 at 0°C and 1 atm is

$$L = \frac{1\,013\,200}{R\,.\,273\,.\,\omega} = 2{\cdot}76 \times 10^{19}.$$

Mr. Drude[9] finds $L = 2{\cdot}1 \times 10^{19}$.

The Boltzmann–Drude constant α, that is, the average kinetic energy of an atom at the absolute temperature 1 is

$$\alpha = \tfrac{3}{2}\omega R = \tfrac{3}{2}k = 2{\cdot}02 \times 10^{-16}.$$

Mr. Drude[9] finds $\alpha = 2{\cdot}65 \times 10^{-16}$.

The elementary quantum of electricity e, that is, the electrical charge of a positive monovalent ion or of an electron is, if ε is the known charge of a monovalent mole,

$$e = \varepsilon\omega = 4{\cdot}69 \times 10^{-10} \text{ e.s.u.}$$

Mr. F. Richarz[10] finds $1{\cdot}29 \times 10^{-10}$ and Mr. J. J. Thomson[11] recently $6{\cdot}5 \times 10^{-10}$.

If the theory is at all correct, all these relations should be not approximately, but absolutely, valid. The accuracy of the calculated numbers is thus essentially the same as that of the relatively worst known, the radiation constant k, and is thus much better than all determinations up to now. To test it by more direct methods should be both an important and a necessary task for further research.

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3 On a Heuristic Point of View about the Creation and Conversion of Light†

A. EINSTEIN

THERE exists an essential formal difference between the theoretical pictures physicists have drawn of gases and other ponderable bodies and Maxwell's theory of electromagnetic processes in so-called empty space. Whereas we assume the state of a body to be completely determined by the positions and velocities of an, albeit very large, still finite number of atoms and electrons, we use for the determination of the electromagnetic state in space continuous spatial functions, so that a finite number of variables cannot be considered to be sufficient to fix completely the electromagnetic state in space. According to Maxwell's theory, the energy must be considered to be a continuous function in space for all purely electromagnetic phenomena, thus also for light, while according to the present-day ideas of physicists the energy of a ponderable body can be written as a sum over the atoms and electrons. The energy of a ponderable body cannot be split into arbitrarily many, arbitrarily small parts, while the energy of a light ray, emitted by a point source of light is according to Maxwell's theory (or in general according to any wave theory) of light distributed continuously over an ever increasing volume.

The wave theory of light which operates with continuous functions in space has been excellently justified for the representation of purely optical phenomena and it is unlikely ever to be replaced by another theory. One should, however, bear in mind that optical observations refer to time averages and not to

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† *Ann. Physik* **17**, 132 (1905).

instantaneous values and notwithstanding the complete experimental verification of the theory of diffraction, reflexion, refraction, dispersion, and so on, it is quite conceivable that a theory of light involving the use of continuous functions in space will lead to contradictions with experience, if it is applied to the phenomena of the creation and conversion of light.

In fact, it seems to me that the observations on "black-body radiation", photoluminescence, the production of cathode rays by ultraviolet light and other phenomena involving the emission or conversion of light can be better understood on the assumption that the energy of light is distributed discontinuously in space. According to the assumption considered here, when a light ray starting from a point is propagated, the energy is not continuously distributed over an ever increasing volume, but it consists of a finite number of energy quanta, localised in space, which move without being divided and which can be absorbed or emitted only as a whole.

In the following, I shall communicate the train of thought and the facts which led me to this conclusion, in the hope that the point of view to be given may turn out to be useful for some research workers in their investigations.

1. On a Difficulty in the Theory of "Black-body Radiation"

To begin with, we take the point of view of Maxwell's theory and electron theory and consider the following case. Let there be in a volume completely surrounded by reflecting walls, a number of gas molecules and electrons moving freely and exerting upon one another conservative forces when they approach each other, that is, colliding with one another as gas molecules according to the kinetic theory of gases.† Let there further be a number of electrons which are bound to points in space, which are far from one

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† This assumption is equivalent to the preposition that the average kinetic energies of gas molecules and electrons are equal to one another in temperature equilibrium. It is well known that Mr. Drude has theoretically derived in this way the relation between the thermal and electrical conductivities of metals.

another, by forces proportional to the distance from those points and in the direction towards those points. These electrons are also assumed to be interacting conservatively with the free molecules and electrons as soon as the latter come close to them. We call the electrons bound to points in space "resonators"; they emit and absorb electromagnetic waves with definite periods.

According to present-day ideas on the emission of light, the radiation in the volume considered—which can be found for the case of dynamic equilibrium on the basis of the Maxwell theory—must be identical with the "black-body radiation"—at least provided we assume that resonators are present of all frequencies to be considered.

For the time being, we neglect the radiation emitted and absorbed by the resonators and look for the condition for dynamic equilibrium corresponding to the interaction (collisions) between molecules and electrons. Kinetic gas theory gives for this the condition that the average kinetic energy of a resonator electron must equal the average kinetic energy corresponding to the translational motion of a gas molecule. If we decompose the motion of a resonator electron into three mutually perpendicular directions of oscillation, we find for the average value $\bar{E}$ of the energy of such a linear oscillatory motion

$$\bar{E} = \frac{R}{N} T,$$

where R is the gas constant, N the number of "real molecules" in a gramme equivalent and T the absolute temperature. This follows as the energy $\bar{E}$ is equal to $\frac{2}{3}$ of the kinetic energy of a free molecules of a monatomic gas since the time averages of the kinetic and the potential energy of a resonator are equal to one another. If, for some reason—in our case because of radiation effects—one manages to make the time average of a resonator larger or smaller than $\bar{E}$, collisions with the free electrons and molecules will lead to an energy transfer to or from the gas which has a non-vanishing average. Thus, for the case considered by us, dynamic equilibrium will be possible only if each resonator has the average energy $\bar{E}$.

We can now use a similar argument for the interaction between the resonators and the radiation which is present in space. Mr. Planck[1] has derived for this case the condition for dynamic equilibrium under the assumption that one can consider the radiation as the most random process imaginable.† He found

$$\bar{E}_\nu = \frac{L^3}{8\pi\nu^2}\rho_\nu,$$

where $\bar{E}_\nu$ is the average energy of a resonator with eigenfrequency ν (per oscillating component), L the velocity of light, ν the frequency and $\rho_\nu d\nu$ the energy per unit volume of that part of the radiation which has frequencies between ν and $\nu + d\nu$.

If the radiation energy of frequency ν is not to be either decreased or increased steadily, we must have

$$\frac{R}{N}T = \bar{E} = \bar{E}_\nu = \frac{L^3}{8\pi\nu^2}\rho_\nu,$$

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† One can formulate this assumption as follows. We expand the z-component of the electrical force (Z) at a given point in space between the time $t = 0$ and $t = T$ (where T indicates a time which is large compared to all oscillation periods considered) in a Fourier series

$$Z = \sum_{\nu=1}^{\infty} A_\nu \sin\left(2\pi\nu\frac{t}{T} + \alpha_\nu\right),$$

where $A_\nu \geqq 0$ and $0 \leqq \alpha_\nu \leqq 2\pi$. For the same point in space, one considers to have made such an expansion arbitrarily often with arbitrarily chosen initial times. In that case, we have for the frequency of different combinations of values for the quantities A_ν and α_ν (statistical) probabilities dW of the form

$$dW = f(A_1, A_2, \ldots, \alpha_1, \alpha_2, \ldots)\, dA_1\, dA_2 \ldots d\alpha_1\, d\alpha_2 \ldots.$$

Radiation is now the most random process imaginable, if

$$f(A_1, A_2, \ldots, \alpha_1, \alpha_2, \ldots) = F_1(A_1)F_2(A_2)\ldots f_1(\alpha_1)f_2(\alpha_2)\ldots,$$

that is, when the probability for a given value of one of the A or the α is independent of the values of the other A and α. The more closely the condition is satisfied that the separate pairs of quantities A_ν and α_ν depend on the emission and absorption processes of *special* groups of resonators, the more definitely can we thus say in the case treated by us that the radiation can be considered to be the most random imaginable one.

$$\rho_\nu = \frac{R}{N}\frac{8\pi\nu^2}{L^3}T.$$

This relation, which we found as the condition for dynamic equilibrium does not only lack agreement with experiment, but it also shows that in our picture there can be no question of a definite distribution of energy between aether and matter. The greater we choose the range of frequencies of the resonators, the greater becomes the radiation energy in space and in the limit we get

$$\int_0^\infty \rho_\nu \, d\nu = \frac{R}{N}\frac{8\pi}{L^3}T\int_0^\infty \nu^2 \, d\nu = \infty.$$

2. On Planck's Determination of Elementary Quanta

We shall show in the following that determination of elementary quanta given by Mr. Planck is, to a certain extent, independent of the theory of "black-body radiation" constructed by him.

Planck's formula[2] for ρ_ν which agrees with all experiments up to the present is

$$\rho_\nu = \frac{\alpha\nu^3}{e^{\beta\nu/T}-1},$$

where $\alpha = 6{\cdot}10 \times 10^{-56}$, $\beta = 4{\cdot}866 \times 10^{-11}$.

For large values of T/ν, that is, for long wavelengths and high radiation densities, this formula has the following limiting form

$$\rho_\nu = \frac{\alpha}{\beta}\nu^2 T.$$

One sees that this formula agrees with the one derived in section 1 from Maxwell theory and electron theory. By equating the coefficients in the two formulae, we get

$$\frac{R}{N}\frac{8\pi}{L^3} = \frac{\alpha}{\beta}$$

or
$$N = \frac{\beta}{\alpha}\frac{8\pi R}{L^3} = 6{\cdot}17 \times 10^{23},$$

that is, one hydrogen atom weighs $1/N = 1{\cdot}62 \times 10^{-24}$ g. This is exactly the value found by Mr. Planck, which agrees satisfactorily with values of this quantity found by different means.

We thus reach the conclusion: the higher the energy density and the longer the wavelengths of radiation, the more usable is the theoretical basis used by us; for short wavelengths and low radiation densities, however, the basis fails completely.

In the following, we shall consider "black-body radiation", basing ourselves upon experience without using a picture of the creation and propagation of the radiation.

3. On the Entropy of the Radiation

The following considerations are contained in a famous paper by Mr. W. Wien and are only mentioned here for the sake of completeness.

Consider radiation which takes up a volume v. We assume that the observable properties of this radiation are completely determined if we give the radiation energy $\rho(\nu)$ for all frequencies.† As we may assume that radiations of different frequencies can be separated without work or heat, we can write the entropy of the radiation in the form

$$S = v\int_0^\infty \phi(\rho, \nu)\, d\nu,$$

where ϕ is a function of the variables ρ and ν. One can reduce ϕ to a function of one variable only by formulating the statement that the entropy of radiation between reflecting walls is not changed by an adiabatic compression. We do not want to go into this, but at once investigate how one can obtain the function ϕ from the radiation law of a black body.

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† This is an arbitrary assumption. Of course, one sticks to this simplest assumption until experiments force us to give it up.

In the case of "black-body radiation", ρ is such a function of ν that the entropy is a maximum for a given energy, that is,

$$\delta \int_0^\infty \phi(\rho, \nu)\, d\nu = 0,$$

if

$$\delta \int_0^\infty \rho\, d\nu = 0.$$

From this it follows that for any choice of $\delta\rho$ as function of ν

$$\int_0^\infty \left(\frac{\partial \phi}{\partial \rho} - \lambda\right) \delta\rho\, d\nu = 0,$$

where λ is independent of ν. In the case of black-body radiation, $\partial\phi/\partial\rho$ is thus independent of ν.

If the temperature of a black-body radiation in a volume $v = 1$ increases by dT, we have the equation

$$dS = \int_{\nu=0}^{\nu=\infty} \frac{\partial \phi}{\partial \rho}\, d\rho\, d\nu,$$

or, as $\partial\phi/\partial\rho$ is independent of ν:

$$dS = \frac{\partial \phi}{\partial \rho}\, dE.$$

As dE is equal to the heat transferred and as the process is reversible, we have also

$$dS = \frac{1}{T}\, dE.$$

Through comparing, we get

$$\frac{\partial \phi}{\partial \rho} = \frac{1}{T}.$$

This is the black-body radiation law. One can thus from the function ϕ obtain the black-body radiation law and conversely from the latter the function ϕ through integration, bearing in mind that ϕ vanishes for $\rho = 0$.

4. Limiting Law for the Entropy of Monochromatic Radiation for Low Radiation Density

From the observation made so far on "black-body radiation", it is clear that the law

$$\rho = \alpha \nu^3 e^{-\beta \nu / T}$$

put forward originally for "black-body radiation" by Mr. W. Wien is not exactly valid. However, for large values of ν/T, it is in complete agreement with experiment. We shall base our calculations on this formula, though bearing in mind that our results are valid only within certain limits.

First of all, we get from this equation

$$\frac{1}{T} = -\frac{1}{\beta \nu} \ln \frac{\rho}{\alpha \nu^3},$$

and then, if we use the relation found in the preceding section

$$\phi(\rho, \nu) = -\frac{\rho}{\beta \nu}\left[\ln \frac{\rho}{\alpha \nu^3} - 1\right].$$

Let there now be radiation of energy E with a frequency between ν and $\nu + d\nu$ and let the volume of the radiation be v. The entropy of this radiation is

$$S = v \phi(\rho, \nu)\, d\nu = -\frac{E}{\beta \nu}\left[\ln \frac{E}{v \alpha \nu^3\, d\nu} - 1\right].$$

If we restrict ourselves to investigating the dependence of the entropy on the volume occupied by the radiation, and if we denote the entropy of the radiation by S_0 if it occupies a volume v_0, we get

$$S - S_0 = \frac{E}{\beta \nu} \ln \frac{v}{v_0}.$$

This equation shows that the entropy of a monochromatic radiation of sufficiently small density varies with volume according to the same rules as the entropy of a perfect gas or of a dilute solution. The equation just found will in the following be interpreted on the basis of the principle, introduced by Mr. Boltzmann into physics, according to which the entropy of a system is a function of the probability of its state.

5. Molecular–Theoretical Investigation of the Volume-dependence of the Entropy of Gases and Dilute Solutions

When calculating the entropy in molecular gas theory one often uses the word "probability" in a sense which is not the same as the definition of probability given in probability theory. Especially, often "cases of equal probability" are fixed by hypothesis under circumstances where the theoretical model used is sufficiently definite to deduce probabilities rather than fixing them by hypothesis. I shall show in a separate paper that when considering thermal phenomena it is completely sufficient to use the so-called "statistical probability", and I hope thus to do away with a logical difficulty which is hampering the consistent application of Boltzmann's principle. At the moment, however, I shall give its general formulation and the application to very special cases.

If it makes sense to talk about the probability of a state of a system and if, furthermore, any increase of entropy can be considered as a transition to a more probable state, the entropy S_1 of a system will be a function of the probability W_1 of its instantaneous state. If, therefore, one has two systems which do not interact with one another, one can write

$$S_1 = \phi_1(W_1), \quad S_2 = \phi_2(W_2).$$

If one considers these two systems as a single system of entropy S and probability W we have

$$S = S_1 + S_2 = \phi(W) \quad \text{and} \quad W = W_1 \,.\, W_2.$$

This last relation states that the states of the two systems are independent.

From these equations it follows that

$$\phi(W_1 . W_2) = \phi_1(W_1)+\phi_2(W_2),$$

and hence finally

$$\phi_1(W_1) = C \ln W_1 + \text{const},$$

$$\phi_2(W_2) = C \ln W_2 + \text{const},$$

$$\phi(W) = C \ln W + \text{const}.$$

The quantity C is thus a universal constant; it follows from kinetic gas theory that it has the value R/N where the constants R and N have the same meaning as above. If S_0 is the entropy of a certain initial state of the system considered and W the relative probability of a state with entropy S, we have in general

$$S - S_0 = \frac{R}{N} \ln W.$$

We now consider the following special case. Let us consider a number, n, moving points (e.g., molecules) in a volume v_0. Apart from those, there may be in this space arbitrarily many other moving points of some kind or other. We do not make any assumptions about the laws according to which the points considered move in space, except that as far as their motion is concerned no part of space—and no direction—is preferred above others. The number of the (first-mentioned) points which we are considering be moreover so small that we can neglect their mutual interaction.

There corresponds a certain entropy S_0 to the system under consideration, which may be, for instance, a perfect gas or a dilute solution. Consider now the case where a part v of the volume v_0 contains all n moving points while otherwise nothing is changed in the system. This state clearly corresponds to a different value, S_1 of the entropy, and we shall now use Boltzmann's principle to determine the entropy difference.

We ask: how large is the probability of this state relative to the original state? Or: how large is the probability that at an arbitrary moment all n points moving independently of one another in a given volume v_0 are (accidentally) in the volume v?

One gets clearly for this probability, which is a "statistical probability":

$$W = \left(\frac{v}{v_0}\right)^n;$$

one obtains from this, applying Boltzmann's principle:

$$S - S_0 = R\frac{n}{N}\ln\frac{v}{v_0}.$$

It must be noted that it is unnecessary to make any assumptions about the laws, according to which the molecules move, to derive this equation from which one can easily derive thermodynamically the Boyle–Gay–Lussac law and the same law for the osmotic pressure.†

6. Interpretation of the Expression for the Volume-dependence of the Entropy of Monochromatic Radiation according to Boltzmann's Principle

In Section 4, we found for the volume-dependence of the entropy of monochromatic radiation the expression

$$S - S_0 = \frac{E}{\beta\nu}\ln\frac{v}{v_0}.$$

If we write this equation in the form

$$S - S_0 = \frac{R}{N}\ln\left[\left(\frac{v}{v_0}\right)^{NE/R\beta\nu}\right],$$

and compare it with the general formula which expresses

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† If E is the energy of the system, we have

$$-d(E-TS) = p\,dv = T\,dS = RT\frac{n}{N}\frac{dv}{v}$$

or

$$pv = R\frac{n}{N}T.$$

Boltzmann's principle,

$$S-S_0=\frac{R}{N}\ln W,$$

we arrive at the following conclusion:

If monochromatic radiation of frequency ν and energy E is enclosed (by reflecting walls) in a volume v_0, the probability that at an arbitrary time the total radiation energy is in a part v of the volume v_0 will be

$$W=\left(\frac{v}{v_0}\right)^{NE/R\beta\nu}.$$

From this we then conclude:

Monochromatic radiation of low density behaves—as long as Wien's radiation formula is valid—in a thermodynamic sense, as if it consisted of mutually independent energy quanta of magnitude $R\beta\nu/N$.

We now wish to compare the average magnitude of the "black-body" energy quanta with the average kinetic energy of the translational motion of a molecule at the same temperature. The latter is $\frac{3}{2}RT/N$, while we get from Wien's formula for the average magnitude of the energy quantum

$$\frac{\int_0^\infty \alpha\nu^3 e^{-\beta\nu/T}\,d\nu}{\int_0^\infty \frac{N}{R\beta\nu}\alpha\nu^3 e^{-\beta\nu/T}\,d\nu}=3\frac{R}{N}T.$$

If monochromatic radiation—of sufficiently low density—behaves, as far as the volume-dependence of its entropy is concerned, as a discontinuous medium consisting of energy quanta of magnitude $R\beta\nu/N$, it is plausible to investigate whether the laws on creation and transformation of light are also such as if light consisted of such energy quanta. This question will be considered in the following.

7. On Stokes' Rule

Consider monochromatic light which is changed by photoluminescence to light of a different frequency; in accordance with the result we have just obtained, we assume that both the original and the changed light consist of energy quanta of magnitude $(R/N)\beta\nu$, where ν is the corresponding frequency. We must then interpret the transformation process as follows. Each initial energy quantum of frequency ν_1 is absorbed and is—at least when the distribution density of the initial energy quanta is sufficiently low—by itself responsible for the creation of a light quantum of frequency ν_2; possibly in the absorption of the initial light quantum at the same time also light quanta of frequencies ν_3, ν_4, ... as well as energy of a different kind (e.g. heat) may be generated. It is immaterial through what intermediate processes the final result is brought about. Unless we can consider the photoluminescing substance as a continuous source of energy, the energy of a final light quantum can, according to the energy conservation law, not be larger than that of an initial light quantum; we must thus have the condition

$$\frac{R}{N}\beta\nu_2 \leqq \frac{R}{N}\beta\nu_1, \quad \text{or} \quad \nu_2 \leqq \nu_1$$

This is the well-known Stokes' rule.

We must emphasise that according to our ideas the intensity of light produced must—other things being equal—be proportional to the incident light intensity for weak illumination, as every initial quantum will cause one elementary process of the kind indicated above, independent of the action of the other incident energy quanta. Especially, there will be no lower limit for the intensity of the incident light below which the light would be unable to produce photoluminescence.

According to the above ideas about the phenomena deviations from Stokes' rule are imaginable in the following cases:

1. When the number of the energy quanta per unit volume

involved in transformations is so large that an energy quantum of the light produced may obtain its energy from several initial energy quanta.

2. When the initial (or final) light energetically does not have the properties characteristic for "black-body radiation" according to Wien's law; for instance, when the initial light is produced by a body of so high a temperature that Wien's law no longer holds for the wavelengths considered.

This last possibility needs particular attention. According to the ideas developed here, it is not excluded that a "non-Wienian radiation", even highly-diluted, behaves energetically differently than a "black-body radiation" in the region where Wien's law is valid.

8. On the Production of Cathode Rays by Illumination of Solids

The usual idea that the energy of light is continuously distributed over the space through which it travels meets with especially great difficulties when one tries to explain photo-electric phenomena, as was shown in the pioneering paper by Mr. Lenard.[3]

According to the idea that the incident light consists of energy quanta with an energy $R\beta\nu/N$, one can picture the production of cathode rays by light as follows. Energy quanta penetrate into a surface layer of the body, and their energy is at least partly transformed into electron kinetic energy. The simplest picture is that a light quantum transfers all of its energy to a single electron; we shall assume that that happens. We must, however, not exclude the possibility that electrons only receive part of the energy from light quanta. An electron obtaining kinetic energy inside the body will have lost part of its kinetic energy when it has reached the surface. Moreover, we must assume that each electron on leaving the body must produce work P, which is characteristic for the body. Electrons which are excited at the surface and at right angles to it will leave the body with the greatest normal velocity. The kinetic energy of such electrons is

$$\frac{R}{N}\beta\nu - P$$

If the body is charged to a positive potential Π and surrounded by zero potential conductors, and if Π is just able to prevent the loss of electricity by the body, we must have

$$\Pi\varepsilon = \frac{R}{N}\beta\nu - P,$$

where ε is the electrical mass of the electron, or

$$\Pi E = R\beta\nu - P',$$

where E is the charge of a gram equivalent of a single-valued ion and P' is the potential of that amount of negative electricity with respect to the body.†

If we put $E = 9{\cdot}6 \times 10^3$, $\Pi \times 10^{-8}$ is the potential in Volts which the body assumes when it is irradiated in a vacuum.

To see now whether the relation derived here agrees, as to order of magnitude, with experiments, we put $P' = 0$, $\nu = 1{\cdot}03 \times 10^{15}$ (corresponding to the ultraviolet limit of the solar spectrum) and $\beta = 4{\cdot}866 \times 10^{-11}$. We obtain $\Pi \times 10^7 = 4{\cdot}3$ Volt, a result which agrees, as to order of magnitude, with Mr. Lenard's results.[3]

If the formula derived here is correct, Π must be, if drawn in Cartesian coordinates as a function of the frequency of the incident light, a straight line, the slope of which is independent of the nature of the substance studied.

As far as I can see, our ideas are not in contradiction to the properties of the photoelectric action observed by Mr. Lenard. If every energy quantum of the incident light transfers its energy to electrons independently of all other quanta, the velocity distribution of the electrons, that is, the quality of the resulting cathode radiation, will be independent of the intensity of the incident light; on the other hand, ceteris paribus, the number of

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† If one assumes that it takes a certain amount of work to free a single electron by light from a neutral molecule, one has no need to change this relation; one only must consider P' to be the sum of two terms.

electrons leaving the body should be proportional to the intensity of the incident light.[3]

As far as the necessary limitations of these rules are concerned, we could make remarks similar to those about the necessary deviations from the Stokes rule.

In the preceding, we assumed that the energy of at least part of the energy quanta of the incident light was always transferred completely to a single electron. If one does not make this obvious assumption, one obtains instead of the earlier equation the following one

$$\Pi E + P' \leqq R\beta\nu.$$

For cathode-luminescence, which is the inverse process of the one just considered, we get by a similar argument

$$\Pi E + P' \geqq R\beta\nu.$$

For the substances investigated by Mr. Lenard, ΠE is always considerably larger than $R\beta\nu$, as the voltage which the cathode rays must traverse to produce even visible light is, in some cases a few hundred, in other cases thousands of volts.[3] We must thus assume that the kinetic energy of an electron is used to produce many light energy quanta.

9. On the Ionisation of Gases by Ultraviolet Light

We must assume that when a gas is ionised by ultraviolet light, always one absorbed light energy quantum is used to ionise just one gas molecule. From this follows first of all that the ionisation energy (that is, the energy theoretically necessary for the ionisation) of a molecule cannot be larger than the energy of an effective, absorbed light energy quantum. If J denotes the (theoretical) ionisation energy per gram equivalent, we must have

$$R\beta\nu \geqq J.$$

According to Lenard's measurements, the largest effective wavelength for air is about $1{\cdot}9 \times 10^{-5}$ cm, or

$$R\beta\nu = 6{\cdot}4 \times 10^{12}\,\mathrm{erg} \geqq J.$$

An upper limit for the ionisation energy can also be obtained from ionisation voltages in dilute gases. According to J. Stark[4] the smallest measured ionisation voltage (for platinum anodes) in air is about 10 Volt.† We have thus an upper limit of $9{\cdot}6 \times 10^{12}$ for J which is about equal to the observed one. There is still another consequence, the verification of which by experiment seems to me to be very important. If each light energy quantum which is absorbed ionises a molecule, the following relation should exist between the absorbed light intensity L and the number j of moles ionised by this light:

$$j = \frac{L}{R\beta\nu}.$$

This relation should, if our ideas correspond to reality, be valid for any gas which—for the corresponding frequency—does not show an appreciable absorption which is not accompanied by ionisation.

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† In the interior of the gas, the ionisation voltage for negative ions is anyhow five times larger.

References

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2. M. Planck, *Ann. Physik* **4**, 561 (1901); this paper contains essentially the results of the two papers, reprinted as 1 and 2 in the present volume.
3. P. Lenard, *Ann. Physik* **8**, 149 (1902).
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4 The Scattering of α and β Particles by Matter and the Structure of the Atom†

E. RUTHERFORD

§1. It is well known that the α and β particles suffer deflexions from their rectilinear paths by encounters with atoms of matter. This scattering is far more marked for the β than for the α particle on account of the much smaller momentum and energy of the former particle. There seems to be no doubt that such swiftly moving particles pass through the atoms in their path, and that the deflexions observed are due to the strong electric field traversed within the atomic system. It has generally been supposed that the scattering of a pencil of α or β rays in passing through a thin plate of matter is the result of a multitude of small scatterings by the atoms of matter traversed. The observations, however, of Geiger and Marsden[1] on the scattering of α rays indicate that some of the α particles must suffer a deflexion of more than a right angle at a single encounter. They found, for example, that a small fraction of the incident α particles, about 1 in 20,000, were turned through an average angle of 90° in passing through a layer of gold foil about 0·00004 cm thick, which was equivalent in stopping power of the α particle to 1·6 millimetres of air. Geiger[2] showed later that the most probable angle of deflexion for a pencil of α particles traversing a gold-foil of this thickness was about 0·87°. A simple calculation based on the theory of probability shows that the chance of an α particle being deflected through 90° is vanishingly small. In addition, it will be seen later that the

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† *Phil. Mag.* **21**, 669 (1911). A brief account of this paper was communicated to the Manchester Literary and Philosophical Society in February, 1911.

distribution of the α particles for various angles of large deflexion does not follow the probability law to be expected if such large deflexions are made up of a large number of small deviations. It seems reasonable to suppose that the deflexion through a large angle is due to a single atomic encounter, for the chance of a second encounter of a kind to produce a large deflexion must in most cases be exceedingly small. A simple calculation shows that the atom must be a seat of an intense electric field in order to produce such a large deflexion at a single encounter.

Recently Sir J. J. Thomson[3] has put forward a theory to explain the scattering of electrified particles in passing through small thicknesses of matter. The atom is supposed to consist of a number N of negatively charged corpuscles, accompanied by an equal quantity of positive electricity uniformly distributed throughout a sphere. The deflexion of a negatively electrified particle in passing through the atom is ascribed to two causes—(1) the repulsion of the corpuscles distributed through the atom, and (2) the attraction of the positive electricity in the atom. The deflexion of the particle in passing through the atom is supposed to be small, while the average deflexion after a large number m of encounters was taken as $\sqrt{m} . \theta$, where θ is the average deflexion due to a single atom. It was shown that the number N of the electrons within the atom could be deduced from observations of the scattering of electrified particles. The accuracy of this theory of compound scattering was examined experimentally by Crowther[4] in a later paper. His results apparently confirmed the main conclusions of the theory, and he deduced, on the assumption that the positive electricity was continuous, that the number of electrons in an atom was about three times its atomic weight.

The theory of Sir J. J. Thomson is based on the assumption that the scattering due to a single atomic encounter is small, and the particular structure assumed for the atom does not admit of a very large deflexion of an α particle in traversing a single atom, unless it be supposed that the diameter of the sphere of positive electricity is minute compared with the diameter of the sphere of influence of the atom.

Since the α and β particles traverse the atom, it should be possible from a close study of the nature of the deflexion to form some idea of the constitution of the atom to produce the effects observed. In fact, the scattering of high-speed charged particles by the atoms of matter is one of the most promising methods of attack of this problem. The development of the scintillation method of counting single α particles affords unusual advantages of investigation, and the researches of H. Geiger by this method have already added much to our knowledge of the scattering of α rays by matter.

§2. We shall first examine theoretically the single encounters† with an atom of simple structure, which is able to produce large deflexions of an α particle, and then compare the deductions from the theory with the experimental data available.

Consider an atom which contains a charge $\pm Ne$ at its centre surrounded by a sphere of electrification containing a charge $\pm Ne$ supposed uniformly distributed throughout a sphere of radius R. e is the fundamental unit of charge, which in this paper is taken as $4{\cdot}65 \times 10^{-10}$ e.s.u. We shall suppose that for distances less than 10^{-12} cm the central charge and also the charge on the α particle may be supposed to be concentrated at a point. It will be shown that the main deductions from the theory are independent of whether the central charge is supposed to be positive or negative. For convenience, the sign will be assumed to be positive. The question of the stability of the atom proposed need not be considered at this stage, for this will obviously depend upon the minute structure of the atom, and on the motion of the constituent charged parts.

In order to form some idea of the forces required to deflect an α particle through a large angle, consider an atom containing a positive charge Ne at its centre, and surrounded by a distribution

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† The deviation of a particle throughout a considerable angle from an encounter with a single atom will in this paper be called "single" scattering. The deviation of a particle resulting from a multitude of small deviations will be termed "compound" scattering.

of negative electricity Ne uniformly distributed within a sphere of radius R. The electric force X and the potential V at a distance r from the centre of an atom for a point inside the atom, are given by

$$X = Ne\left(\frac{1}{r^2}-\frac{r}{R^3}\right)$$

$$V = Ne\left(\frac{1}{r}-\frac{3}{2R}+\frac{r^2}{2R^3}\right).$$

Suppose an α particle of mass m and velocity u and charge E shot directly towards the centre of the atom. It will be brought to rest at a distance b from the centre given by

$$\tfrac{1}{2}mu^2 = NeE\left(\frac{1}{b}-\frac{3}{2R}+\frac{b^2}{2R^3}\right).$$

It will be seen that b is an important quantity in later calculations. Assuming that the central charge is $100e$, it can be calculated that the value of b for an α particle of velocity $2{\cdot}09\times10^9$ cm per second is about $3{\cdot}4\times10^{-12}$ cm. In this calculation b is supposed to be very small compared with R. Since R is supposed to be of the order of the radius of the atom, viz. 10^{-8} cm, it is obvious that the α particle before being turned back penetrates so close to the central charge, that the field due to the uniform distribution of negative electricity may be neglected. In general, a simple calculation shows that for all deflexions greater than a degree, we may without sensible error suppose the deflexion due to the field of the central charge alone. Possible single deviations due to the negative electricity, if distributed in the form of corpuscles, are not taken into account at this stage of the theory. It will be shown later that its effect is in general small compared with that due to the central field.

Consider the passage of a positive electrified particle close to the centre of an atom. Supposing that the velocity of the particle is not appreciably changed by its passage through the atom, the path of the particle under the influence of a repulsive force varying inversely as the square of the distance will be an hyperbola with the centre of the atom S as the external focus. Suppose the particle to enter the atom in the direction PO (Fig. 4.1), and that the direction of motion on escaping the atom is OP′. OP and OP′ make equal angles with the line SA, where A is the apse of the hyperbola. $p = \text{SN}$ = perpendicular distance from centre on direction of initial motion of particle.

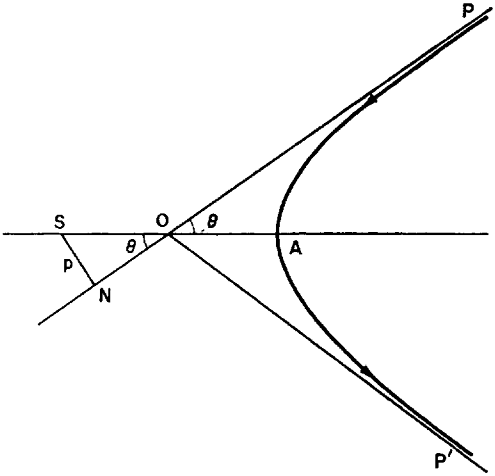

FIG. 4.1

Let angle POA $= \theta$.

Let V = velocity of particle on entering the atom, v its velocity at A, then from consideration of angular momentum

$$pV = \text{SA}\, v.$$

From conservation of energy

$$\tfrac{1}{2}mV^2 = \tfrac{1}{2}mv^2 + \frac{NeE}{\text{SA}},$$

$$v^2 = V^2\left(1 - \frac{b}{\text{SA}}\right).$$

Since the eccentricity is $\sec\theta$,

$$\mathrm{SA} = \mathrm{SO}+\mathrm{OA} = p\operatorname{cosec}\theta(1+\cos\theta)$$

$$= p\cot\tfrac{1}{2}\theta,$$

$$p^2 = \mathrm{SA}(\mathrm{SA}-b) = p\cot\tfrac{1}{2}\theta(\mathrm{p}\cot\tfrac{1}{2}\theta-b),$$

or

$$b = 2p\cot\theta.$$

The angle of deviation ϕ of the particle is $\pi-2\theta$ and

$$\cot\tfrac{1}{2}\phi = \frac{2p}{b}\text{[†]} \qquad (1)$$

This gives the angle of deviation of the particle in terms of b, and the perpendicular distance of the direction of projection from the centre of the atom.

For illustration, the angle of deviation ϕ for different values of p/b are shown in the following table:

p/b	10	5	2	1	0·5	0·25	0·125
ϕ	5·7°	11·4°	28°	53°	90°	127°	152°

§ 3. Probability of Single Deflexion through any Angle

Suppose a pencil of electrified particles to fall normally on a thin screen of matter of thickness t. With the exception of the few particles which are scattered through a large angle, the particles are supposed to pass nearly normally through the plate with only a small change of velocity. Let n = number of atoms in unit volume of material. Then the number of collisions of the particle with the atom of radius R is $\pi R^2 nt$ in the thickness t.

The probability m of entering an atom within a distance p of its centre is given by

$$m = \pi p^2 nt.$$

[†] A simple consideration shows that the deflexion is unaltered if the forces are attractive instead of repulsive.

Chance dm of striking within radii p and $p+dp$ is given by

$$dm = 2\pi pnt\,dp = \tfrac{1}{4}\pi ntb^2 \cot\tfrac{1}{2}\phi \operatorname{cosec}^2\tfrac{1}{2}\phi\,d\phi, \tag{2}$$

since
$$\cot\tfrac{1}{2}\phi = 2p/b.$$

The value of dm gives the *fraction* of the total number of particles which are deviated between the angles ϕ and $\phi+d\phi$.

The fraction ρ of the total number of particles which are deflected through an angle greater than ϕ is given by

$$\rho = \tfrac{1}{4}\pi ntb^2 \cot^2\tfrac{1}{2}\phi. \tag{3}$$

The fraction ρ which is deflected between the angles ϕ_1 and ϕ_2 is given by

$$\rho = \tfrac{1}{4}\pi ntb^2(\cot^2\tfrac{1}{2}\phi_1 - \cot^2\tfrac{1}{2}\phi_2). \tag{4}$$

It is convenient to express the equation (2) in another form for comparison with experiment. In the case of the α rays, the number of scintillations appearing on a *constant* area of a zinc sulphide screen are counted for different angles with the direction of incidence of the particles. Let r = distance from point of incidence of α rays on scattering material, then if Q be the total number of particles falling on the scattering material, the number y of α particles falling on unit area which are deflected through an angle ϕ is given by

$$y = \frac{Q\,dm}{2\pi r^2 \sin\phi\,d\phi} = \frac{ntb^2 Q \operatorname{cosec}^4\tfrac{1}{2}\phi}{16r^2}. \tag{5}$$

Since $b = 2NeE/mu^2$, we see from this equation that the number of α particles (scintillations) per unit area of zinc sulphide screen at a given distance r from the point of incidence of the rays is proportional to

(1) $\operatorname{cosec}^4\tfrac{1}{2}\phi$ or $1/\phi^4$ if ϕ be small;
(2) thickness of scattering material t provided this is small;
(3) square of the magnitude of central charge Ne;†

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† The original has "magnitude" rather than "square of the magnitude" which is clearly a slip [D. t. H.].

(4) and is inversely proportional to $(mu^2)^2$, or to the fourth power of the velocity if m be constant.

In these calculations, it is assumed that the α particles scattered through a large angle suffer only one large deflexion. For this to hold, it is essential that the thickness of the scattering material should be so small that the change of a second encounter involving another large deflexion is very small. If, for example, the probability of a single deflexion ϕ in passing through a thickness t is $\frac{1}{1000}$, the probability of two successive deflexions each of value ϕ is $1/10^6$, and is negligibly small.

The angular distribution of the α particles scattered from a thin metal sheet affords one of the simplest methods of testing the general correctness of this theory of single scattering. This has been done recently for α rays by Dr. Geiger,[5] who found that the distribution for particles deflected between 30° and 150° from a thin gold-foil was in substantial agreement with the theory. A more detailed account of these and other experiments to test the validity of the theory will be published later.

§ 4. Alteration of Velocity in an Atomic Encounter

It has so far been assumed that an α or β particle does not suffer an appreciable change of velocity as the result of a single atomic encounter resulting in a large deflexion of the particle. The effect of such an encounter in altering the velocity of the particle can be calculated on certain assumptions. It is supposed that only two systems are involved, viz., the swiftly moving particle and the atom which it traverses supposed initially at rest. It is supposed that the principle of conservation of momentum and of energy applies, and that there is no appreciable loss of energy or momentum by radiation.

Let m be mass of the particle,
v_1 = velocity of approach,
v_2 = velocity of recession,
M = mass of atom,
V = velocity communicated to atom as result of encounter.

Let OA (Fig. 4.2) represent in magnitude and direction the momentum mv_1 of entering particle, and OB the momentum of the receding particle which has been turned through an angle AOB $= \phi$. Then BA represents in magnitude and direction the momentum MV of the recoiling atom.

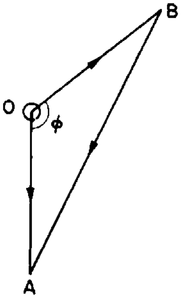

FIG. 4.2

$$(MV)^2 = (mv_1)^2 + (mv_2)^2 - 2m^2 v_1 v_2 \cos\phi. \tag{1}$$

By the conservation of energy

$$MV^2 = mv_1^2 - mv_2^2. \tag{2}$$

Suppose $M/m = K$ and $v_2 = \rho v_1$, where ρ is <1.
From (1) and (2),

$$(K+1)\rho^2 - 2\rho\cos\phi = K-1,$$

or
$$\rho = \frac{\cos\phi}{K+1} + \frac{1}{K+1}\sqrt{(K^2 - \sin^2\phi)}.$$

Consider the case of an α particle of atomic weight 4, deflected through an angle of 90° by an encounter with an atom of gold of atomic weight 197.

Since $K = 49$ nearly,

$$\rho = \sqrt{\frac{K-1}{K+1}} = 0{\cdot}979,$$

or the velocity of the particle is reduced only about 2 per cent. by the encounter.

In the case of aluminium $K = \frac{27}{4}$ and for $\phi = 90^\circ$ $\rho = 0{\cdot}86$.

It is seen that the reduction of velocity of the α particle becomes marked on this theory for encounters with the lighter atoms. Since the range of an α particle in air or other matter is approximately proportional to the cube of the velocity, it follows that an α particle of range 7 cm has its range reduced to 4·5 cm after incurring a single deviation of 90° in traversing an aluminium atom. This is of a magnitude to be easily detected experimentally. Since the value of K is very large for an encounter of a β particle with an atom, the reduction of velocity on this formula is very small.

Some very interesting cases of the theory arise in considering the changes of velocity and the distribution of scattered particles when the α particle encounters a light atom, for example a hydrogen or helium atom. A discussion of these and similar cases is reserved until the question has been examined experimentally.

§ 5. Comparison of Single and Compound Scattering

Before comparing the result of theory with experiment, it is desirable to consider the relative importance of single and compound scattering in determining the distribution of the scattered particles. Since the atom is supposed to consist of a central charge surrounded by a uniform distribution of the opposite sign through a sphere of radius R, the chance of encounters with the atom involving small deflexions is very great compared with the chance of a single large deflexion.

This question of compound scattering has been examined by Sir J. J. Thomson in the paper previously discussed (§ 1). In the notation of this paper, the average deflexion ϕ_1 due to the field of the sphere of positive electricity of radius R and quantity Ne was found by him to be

$$\phi_1 = \tfrac{1}{4}\pi \frac{NeE}{mu^2}\frac{1}{R}.$$

The average deflexion ϕ_2 due to the N negative corpuscles supposed distributed uniformly throughout the sphere was found to be

$$\phi_2 = \frac{16}{5}\frac{eE}{mu^2}\frac{1}{R}\sqrt{(\tfrac{3}{2}N)}.$$

The mean deflexion due to both positive and negative electricity was taken as

$$(\phi_1^2+\phi_2^2)^{\frac{1}{2}}.$$

In a similar way, it is not difficult to calculate the average deflexion due to the atom with a central charge discussed in this paper.

Since the radial electric field X at any distance r from the centre is given by

$$X = Ne\left(\frac{1}{r^2}-\frac{r}{R^3}\right),$$

it is not difficult to show that the deflexion (supposed small) of an electrified particle due to this field is given by

$$\theta = \frac{b}{p}\left(1-\frac{p^2}{R^2}\right)^{\frac{3}{2}},$$

where p is the perpendicular from the centre on the path of the particle and b has the same value as before. It is seen that the value of θ increases with diminution of p and becomes great for small values of ϕ.

Since we have already seen that the deflexions become very large for a particle passing near the centre of the atom, it is obviously not correct to find the average value by assuming θ is small.

Taking R of the order 10^{-8} cm, the value of p for a large deflexion is for α and β particles of the order 10^{-11} cm. Since the chance of an encounter involving a large deflexion is small compared with the chance of small deflexions, a simple consideration shows that the average small deflexion is practically unaltered if the large deflexions are omitted. This is equivalent to integrating over that part of the cross section of the atom where the deflexions are small and neglecting the small central area. It can in this way be simply shown that the average small deflexion is given by

$$\phi_1 = \tfrac{3}{8}\pi\frac{b}{R}.$$

This value of ϕ_1 for the atom with a concentrated central charge is three times the magnitude of the average deflexion for the same value of Ne in the type of atom examined by Sir J. J. Thomson. Combining the deflexions due to the electric field and to the corpuscles, the average deflexion is

$$(\phi_1^2+\phi_2^2)^{\frac{1}{2}} \quad \text{or} \quad \frac{b}{2R}\left(5{\cdot}54+\frac{15{\cdot}4}{N}\right)^{\frac{1}{2}}.$$

It will be seen later that the value of N is nearly proportional to the atomic weight, and is about 100 for gold. The effect due to scattering of the individual corpuscles expressed by the second term of the equation is consequently small for heavy atoms compared with that due to the distributed electric field.

Neglecting the second term, the average deflexion per atom is $3\pi b/8R$. We are now in a position to consider the relative effects on the distribution of particles due to single and to compound scattering. Following J. J. Thomson's argument, the average deflexion θ_t after passing through a thickness t of matter is proportional to the square root of the number of encounters and is given by

$$\theta_t = \frac{3\pi b}{8R}\sqrt{(\pi R^2 nt)} = \tfrac{3}{8}\pi b\sqrt{(\pi nt)},$$

where n as before is equal to the number of atoms per unit volume.

The probability p_1 for compound scattering that the deflexion of the particle is greater than ϕ is equal to $e^{-\phi^2/\theta_t^2}$. Consequently

$$\phi^2 = -\tfrac{9}{64}\pi^3 b^2 nt \ln p_1.$$

Next suppose that single scattering alone is operative. We have seen (§3) that the probability p_2 of a deflexion greater than ϕ is given by

$$p_2 = \tfrac{1}{4}\pi b^2 nt \cot^2 \tfrac{1}{2}\phi.$$

By comparing these two equations

$$p_2 \ln p_1 = -0{\cdot}181\phi^2 \cot^2 \tfrac{1}{2}\phi,$$

ϕ is sufficiently small that

$$\tan \tfrac{1}{2}\phi = \tfrac{1}{2}\phi, \quad p_2 \ln p_1 = -0{\cdot}72.$$

If we suppose $p_2 = 0{\cdot}5$, then $p_1 = 0{\cdot}24$.

If $p_2 = 0{\cdot}1$, $p_1 = 0{\cdot}0004$.

It is evident from this comparison, that the probability for any given deflexion is always greater for single than for compound scattering. The difference is especially marked when only a small fraction of the particles are scattered through any given angle. It follows from this result that the distribution of particles due to encounters with the atoms is for small thicknesses mainly governed by single scattering. No doubt compound scattering produces some effect in equalizing the distribution of the scattered particles; but its effect becomes relatively smaller, the smaller the fraction of the particles scattered through a given angle.

§6. Comparison of Theory with Experiments

On the present theory, the value of the central charge *Ne* is an important constant, and it is desirable to determine its value for different atoms. This can be most simply done by determining the small fraction of α or β particles of known velocity falling on a thin metal screen, which are scattered between ϕ and $\phi + d\phi$ where ϕ is the angle of deflexion. The influence of compound scattering should be small when this fraction is small.

Experiments in these directions are in progress, but it is desirable at this stage to discuss in the light of the present theory the data already published on scattering of α and β particles.

The following points will be discussed:

(*a*) The "diffuse reflexion" of α particles, i.e. the scattering of α particles through large angles (Geiger and Marsden).
(*b*) The variation of diffuse reflexion with atomic weight of the radiator (Geiger and Marsden).
(*c*) The average scattering of a pencil of α rays transmitted through a thin metal plate (Geiger).
(*d*) The experiments of Crowther on the scattering of β rays of different velocities by various metals.

(*a*) In the paper of Geiger and Marsden[1] on the diffuse reflexion of α particles falling on various substances it was shown that about $\frac{1}{8000}$ of the α particles from radium C falling on a thick plate of platinum are scattered back in the direction of the incidence. This fraction is deduced on the assumption that the α particles are uniformly scattered in all directions, the observations being made for a deflexion of about 90°. The form of experiment is not very suited for accurate calculation, but from the data available it can be shown that the scattering observed is about that to be expected on the theory if the atom of platinum has a central charge of about $100\,e$.

(*b*) In their experiments on this subject, Geiger and Marsden gave the relative number of α particles diffusely reflected from thick layers of different metals, under similar conditions. The numbers obtained by them are given in the table below, where z represents the relative number of scattered particles, measured by the number of scintillations per minute on a zinc sulphide screen.

On the theory of single scattering, the fraction of the total number of α particles scattered through any given angle in passing through a thickness t is proportional to nA^2t, assuming that the central charge is proportional to the atomic weight A. In the present case, the thickness of matter from which the scattered α particles are able to emerge and affect the zinc sulphide screen depends on the metal. Since Bragg has shown that the stopping

Metal	Atomic weight	z	$\frac{z}{A^{3/2}}$
Lead	207	62	208
Gold	197	67	242
Platinum	195	63	232
Tin	119	34	226
Silver	108	27	241
Copper	64	14·5	225
Iron	56	10·2	250
Aluminium	27	3·4	243
		Average	233

power of an atom for an α particle is proportional to the square root of its atomic weight, the value of nt for different elements is proportional to $1/\sqrt{A}$. In this case t represents the greatest depth from which the scattered α particles emerge. The number z of α particles scattered back from a thick layer is consequently proportional to $A^{3/2}$ or $z/A^{3/2}$ should be a constant.

To compare this deduction with experiment, the relative values of the latter quotient are given in the last column. Considering the difficulty of the experiments, the agreement between theory and experiment is reasonably good.†

The single large scattering of α particles will obviously affect to some extent the shape of the Bragg ionization curve for a pencil of α rays. This effect of large scattering should be marked when the α rays have traversed screens of metals of high atomic weight, but should be small for atoms of light atomic weight.

(*c*) Geiger made a careful determination of the scattering of α particles passing through thin metal foils, by the scintillation method, and deduced the most probable angle through which the α particles are deflected in passing through known thicknesses of different kinds of matter.

A narrow pencil of homogeneous α rays was used as a source. After passing through the scattering foil, the total number of

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† The effect of change of velocity in an atomic encounter is neglected in this calculation.

α particles deflected through different angles was directly measured. The angle for which the number of scattered particles was a maximum was taken as the most probable angle. The variation of the most probable angle with thickness of matter was determined, but calculation from these data is somewhat complicated by the variation of velocity of the α particles in their passage through the scattering material. A consideration of the curve of distribution of the α particles given in the paper[2] shows that the angle through which half the particles are scattered is about 20 per cent greater than the most probable angle.

We have already seen that compound scattering may become important when about half the particles are scattered through a given angle, and it is difficult to disentangle in such cases the relative effects due to the two kinds of scattering. An approximate estimate can be made in the following way: From (§ 5) the relation between the probabilities p_1 and p_2 for compound and single scattering respectively is given by

$$p_2 \ln p_1 = -0{\cdot}721.$$

The probability q of the combined effects may as a first approximation be taken as

$$q = (p_1^2 + p_2^2)^{\frac{1}{2}}.$$

If $q = 0{\cdot}5$, it follows that

$$p_1 = 0{\cdot}2 \quad \text{and} \quad p_2 = 0{\cdot}46.$$

We have seen that the probability p_2 of a single deflexion greater than ϕ is given by

$$p_2 = \tfrac{1}{4}\pi n t b^2 \cot^2 \tfrac{1}{2}\phi.$$

Since in the experiments considered ϕ is comparatively small

$$\frac{\phi \sqrt{p_2}}{\sqrt{(\pi n t)}} = b = \frac{2NeE}{mu^2}.$$

Geiger found that the most probable angle of scattering of the α rays in passing through a thickness of gold equivalent in stopping power to about 0·76 cm of air was 1° 40′. The angle ϕ through which half the α particles are turned thus corresponds to 2° nearly.

$$t = 0{\cdot}00017\,\text{cm}; \quad n = 6{\cdot}07 \times 10^{22};$$

$$u\,(\text{average value}) = 1{\cdot}8 \times 10^{9}.$$

$$E/m = 1{\cdot}5 \times 10^{14}\,\text{e.s.u.}; \quad e = 4{\cdot}65 \times 10^{-10}.$$

Taking the probability of single scattering $= 0{\cdot}46$ and substituting the above values in the formula, the value of N for gold comes out to be 97.

For a thickness of gold equivalent in stopping power to 2·12 cm of air, Geiger found the most probable angle to be 3° 40′. In this case $t = 0{\cdot}00047$, $\phi = 4{\cdot}4°$, and average $u = 1{\cdot}7 \times 10^{9}$, and N comes out to be 114.

Geiger showed that the most probable angle of deflexion for an atom was nearly proportional to its atomic weight. It consequently follows that the value of N for different atoms should be nearly proportional to their atomic weights, at any rate for atomic weights between gold and aluminium.

Since the atomic weight of platinum is nearly equal to that of gold, it follows from these considerations that the magnitude of the diffuse reflexion of α particles through more than 90° from gold and the magnitude of the average small angle scattering of a pencil of rays in passing through gold-foil are both explained on the hypothesis of single scattering by supposing the atom of gold has a central charge of about 100 e.

(*d*) *Experiments of Crowther on scattering of β rays.* We shall now consider how far the experimental results of Crowther on scattering of β particles of different velocities by various materials can be explained on the general theory of single scattering. On this theory, the fraction of β particles p turned through an angle greater than ϕ is given by

$$p = \tfrac{1}{4}\pi n t b^{2} \cot^{2} \tfrac{1}{2}\phi.$$

In most of Crowther's experiments ϕ is sufficiently small that

$\tan \frac{1}{2}\phi$ may be put equal to $\frac{1}{2}\phi$ without much error. Consequently

$$\phi^2 = 2\pi ntb^2 \qquad \text{if } p = \tfrac{1}{2}.$$

On the theory of compound scattering, we have already seen that the chance p_1 that the deflexion of the particles is greater than ϕ is given by

$$\phi^2/\ln p_1 = -\tfrac{9}{64}\pi^3 ntb^2.$$

Since in the experiments of Crowther the thickness t of matter was determined for which $p_1 = \frac{1}{2}$,

$$\phi^2 = 0{\cdot}96\pi ntb^2.$$

For a probability of $\frac{1}{2}$, the theories of single and compound scattering are thus identical in general form, but differ by a numerical constant. It is thus clear that the main relations on the theory of compound scattering of Sir J. J. Thomson, which were verified experimentally by Crowther, hold equally well on the theory of single scattering.

For example, if t_m be the thickness for which half the particles are scattered through an angle ϕ, Crowther showed that $\phi/\sqrt{t_m}$ and also $(mu^2/E)\sqrt{t_m}$ were constants for a given material when ϕ was fixed. These relations hold also on the theory of single scattering. Notwithstanding this apparent similarity in form, the two theories are fundamentally different. In one case, the effects observed are due to cumulative effects of small deflexions, while in the other the large deflexions are supposed to result from a single encounter. The distribution of scattered particles is entirely different on the two theories when the probability of deflexion greater than ϕ is small.

We have already seen that the distribution of scattered α particles at various angles has been found by Geiger to be in substantial agreement with the theory of single scattering, but cannot be explained on the theory of compound scattering alone. Since there is every reason to believe that the laws of scattering of α and β particles are very similar, the law of distribution of scattered β particles should be the same as for α particles for small thicknesses of matter. Since the value of mu^2/E for the β particles is in most cases much smaller than the corresponding value for the α particles, the chance of large single deflexions for β particles in passing through a given thickness of matter is much greater than for α particles. Since on the theory of single scattering the fraction of the number of particles which are deflected through a given angle is proportional to kt, where t is the thickness supposed small and k a constant, the number of particles which are undeflected through this angle is proportional to $1-kt$. From considerations based on the theory of compound scattering, Sir J. J. Thomson deduced that the probability of deflexion less than ϕ is proportional to $1-e^{-\mu/t}$ where μ is a constant for any given value of ϕ.

The correctness of this latter formula was tested by Crowther by measuring electrically the fraction I/I_0 of the scattered β particles which passed through a circular opening subtending an angle of 36° with the scattering material. If

$$I/I_0 = 1-e^{-\mu/t},$$

the value of I should decrease very slowly at first with increase of t. Crowther, using aluminium as scattering material, states that the variation of I/I_0 was in good accord with this theory for small values of t. On the other hand, if single scattering be present, as it undoubtedly is for α rays, the curve showing the relation between I/I_0 and t should be nearly linear in the initial stages. The experiments of Madsen[6] on scattering of β rays, although not made with quite so small a thickness of aluminium as that used by Crowther, certainly support such a conclusion. Considering the importance of the point at issue, further experiments on this question are desirable.

From the table given by Crowther of the value $\phi/\sqrt{t_m}$ for different elements for β rays of velocity $2{\cdot}68\times10^{10}$ cm per second, the values of the central charge Ne can be calculated on the theory of single scattering. It is supposed, as in the case of the α rays, that for the given value of $\phi/\sqrt{t_m}$ the fraction of the β particles deflected by single scattering through an angle greater than ϕ is 0·46 instead of 0·5.

The values of N calculated from Crowther's data are given below.

Element	Atomic weight	$\frac{\phi}{\sqrt{t_m}}$	N
Aluminium	27	4·25	22
Copper	63·2	10·0	42
Silver	108	15·4	78
Platinum	194	29·0	138

It will be remembered that the values of N for gold deduced from scattering of the α rays were in two calculations 97 and 114. These numbers are somewhat smaller than the values given above for platinum (viz. 138), whose atomic weight is not very different from gold. Taking into account the uncertainties involved in the calculation from the experimental data, the agreement is sufficiently close to indicate that the same general laws of scattering hold for the α and β particles, notwithstanding the wide differences in the relative velocity and mass of these particles.

As in the case of the α rays, the value of N should be most simply determined for any given element by measuring the small fraction of the incident β particles scattered through a large angle. In this way, possible errors due to small scattering will be avoided.

The scattering data for the β rays, as well as for the α rays, indicate that the central charge in an atom is approximately proportional to its atomic weight. This falls in with the experimental deductions of Schmidt.[7] In his theory of absorption of β rays, he supposed that in traversing a thin sheet of matter, a small fraction α of the particles are stopped, and a small fraction β are reflected or scattered back in the direction of incidence. From comparison of the absorption curves of different elements, he deduced that the value of the constant β for different elements is proportional to nA^2 where n is the number of atoms per unit volume and A the atomic weight of the element. This is exactly the relation to be expected on the theory of single scattering if the central charge on an atom is proportional to its atomic weight.

§ 7. General Considerations

In comparing the theory outlined in this paper with the experimental results, it has been supposed that the atom consists of a central charge supposed concentrated at a point, and that the large single deflexions of the α and β particles are mainly due to their passage through the strong central field. The effect of the equal and opposite compensating charge supposed distributed uniformly throughout a sphere has been neglected. Some of the evidence in support of these assumptions will now be briefly considered. For concreteness, consider the passage of a high speed α particle through an atom having a positive central charge Ne, and surrounded by a compensating charge of N electrons. Remembering that the mass, momentum, and kinetic energy of the α particle are very large compared with the corresponding values for an electron in rapid motion, it does not seem possible from dynamic considerations that an α particle can be deflected through a large angle by a close approach to an electron, even if the latter be in rapid motion and constrained by strong electrical forces. It seems reasonable to suppose that the chance of single deflexions through a large angle due to this cause, if not zero, must be exceedingly small compared with that due to the central charge.

It is of interest to examine how far the experimental evidence throws light on the question of the extent of the distribution of the central charge. Suppose, for example, the central charge to be composed of N unit charges distributed over such a volume that the large single deflexions are mainly due to the constituent charges and not to the external field produced by the distribution. It has been shown (§ 3) that the fraction of the α particles scattered through a large angle is proportional to $(NeE)^2$, where Ne is the central charge concentrated at a point and E the charge on the deflected particle. If, however, this charge is distributed in single units, the fraction of the α particles scattered through a given angle is proportional to Ne^2 instead of N^2e^2. In this calculation, the influence of mass of the constituent particle has been neglected, and account has only been taken of its electric field. Since it has been shown that the value of the central point charge for gold must be about 100, the value of the distributed charge required to produce the same proportion of single deflexions through a large angle should be at least 10,000. Under these conditions the mass of the constituent particle would be small compared with that of the α particle, and the difficulty arises of the production of large single deflexions at all. In addition, with such a large distributed charge, the effect of compound scattering is relatively more important than that of single scattering. For example, the probable small angle of deflexion of a pencil of α particles passing through a thin gold-foil would be much greater than that experimentally observed by Geiger (§ 6 *b*–*c*). The large and small angle scattering could not then be explained by the assumption of a central charge of the same value. Considering the evidence as a whole, it seems simplest to suppose that the atom contains a central charge distributed through a very small volume, and that the large single deflexions are due to the central charge as a whole, and not to its constituents. At the same time, the experimental evidence is not precise enough to negative the possibility that a small fraction of the positive charge may be carried by satellites extending some distance from the centre. Evidence on this point could be obtained by examining whether the same central charge is required to explain the large single deflexions of α and β particles; for the α particle must approach much closer to the centre of the atom than the β particle of average speed to suffer the same large deflexion.

The general data available indicate that the value of this central charge for different atoms is approximately proportional to their atomic weights, at any rate for atoms heavier than aluminium. It will be of great interest to examine experimentally whether such a simple relation holds also for the lighter atoms. In cases where the mass of the deflecting atom (for example, hydrogen, helium, lithium) is not very different from that of the α particle, the general theory of single scattering will require modification, for it is necessary to take into account the movements of the atom itself (see §4).

It is of interest to note that Nagaoka[8] has mathematically considered the properties of a "Saturnian" atom which he supposed to consist of a central attracting mass surrounded by rings of rotating electrons. He showed that such a system was stable if the attractive force was large. From the point of view considered in this paper, the chance of large deflexion would practically be unaltered, whether the atom is considered to be a disk or a sphere. It may be remarked that the approximate value found for the central charge of the atom of gold ($100\,e$) is about that to be expected if the atom of gold consisted of 49 atoms of helium, each carrying a charge $2\,e$. This may be only a coincidence, but it is certainly suggestive in view of the expulsion of helium atoms carrying two unit charges from radioactive matter.

The deductions from the theory so far considered are independent of the sign of the central charge, and it has not so far been found possible to obtain definite evidence to determine whether it be positive or negative. It may be possible to settle the question of sign by consideration of the difference of the laws of absorption of the β particle to be expected on the two hypotheses, for the effect of radiation in reducing the velocity of the β particle should be far more marked with a positive than with a negative centre. If the central charge be positive, it is easily seen that a positively charged mass if released from the centre of a heavy atom, would acquire a great velocity in moving through the electric field. It may be possible in this way to account for the high velocity of expulsion of α particles without supposing that they are initially in rapid motion within the atom.

Further consideration of the application of this theory to these and other questions will be reserved for a later paper, when the main deductions of the theory have been tested experimentally. Experiments in this direction are already in progress by Geiger and Marsden.

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5 On the Constitution of Atoms and Molecules†

N. Bohr

Introduction

In order to explain the results of experiments on scattering of α rays by matter Prof. Rutherford[1] has given a theory of the structure of atoms. According to this theory, the atoms consist of a positively charged nucleus surrounded by a system of electrons kept together by attractive forces from the nucleus; the total negative charge of the electrons is equal to the positive charge of the nucleus. Further, the nucleus is assumed to be the seat of the essential part of the mass of the atom, and to have linear dimensions exceedingly small compared with the linear dimensions of the whole atom. The number of electrons in an atom is deduced to be approximately equal to half the atomic weight. Great interest is to be attributed to this atom-model; for, as Rutherford has shown, the assumption of the existence of nuclei, as those in question, seems to be necessary in order to account for the results of the experiments on large angle scattering of the α rays.[2]

In an attempt to explain some of the properties of matter on the basis of this atom-model we meet, however, with difficulties of a serious nature arising from the apparent instability of the system of electrons: difficulties purposely avoided in atom-models previously considered, for instance, in the one proposed by Sir J. J. Thomson.[3] According to the theory of the latter the atom consists of a sphere of uniform positive electrification, inside which the electrons move in circular orbits.

† *Phil. Mag.* **26**, 1 (1913).

The principal difference between the atom-models proposed by Thomson and Rutherford consists in the circumstance that the forces acting on the electrons in the atom-model of Thomson allow of certain configurations and motions of the electrons for which the system is in a stable equilibrium; such configurations, however, apparently do not exist for the second atom-model. The nature of the difference in question will perhaps be most clearly seen by noticing that among the quantities characterizing the first atom a quantity appears—the radius of the positive sphere—of dimensions of a length and of the same order of magnitude as the linear extension of the atom, while such a length does not appear among the quantities characterizing the second atom, viz. the charges and masses of the electrons and the positive nucleus; nor can it be determined solely by help of the latter quantities.

The way of considering a problem of this kind has, however, undergone essential alterations in recent years owing to the development of the theory of the energy radiation, and the direct affirmation of the new assumptions introduced in this theory, found by experiments on very different phenomena such as specific heats, photoelectric effect, Röntgen-rays, etc. The result of the discussion of these questions seems to be a general acknowledgment of the inadequacy of the classical electrodynamics in describing the behaviour of systems of atomic size.[4] Whatever the alteration in the laws of motion of the electrons may be, it seems necessary to introduce in the laws in question a quantity foreign to the classical electrodynamics, i.e. Planck's constant, or as it often is called the elementary quantum of action. By the introduction of this quantity the question of the stable configuration of the electrons in the atoms is essentially changed, as this constant is of such dimensions and magnitude that it, together with the mass and charge of the particles, can determine a length of the order of magnitude required.

This paper is an attempt to show that the application of the above ideas to Rutherford's atom-model affords a basis for a theory of the constitution of atoms. It will further be shown that from this theory we are led to a theory of the constitution of molecules.

In the present first part of the paper the mechanism of the binding of electrons by a positive nucleus is discussed in relation to Planck's theory. It will be shown that it is possible from the point of view taken to account in a simple way for the law of the line spectrum of hydrogen. Further, reasons are given for a principal hypothesis on which the considerations contained in the following parts are based.

I wish here to express my thanks to Prof. Rutherford for his kind and encouraging interest in this work.

PART I.—BINDING OF ELECTRONS BY POSITIVE NUCLEI

§ 1. General Considerations

The inadequacy of the classical electrodynamics in accounting for the properties of atoms from an atom-model as Rutherford's, will appear very clearly if we consider a simple system consisting of a positively charged nucleus of very small dimensions and an electron describing closed orbits around it. For simplicity, let us assume that the mass of the electron is negligibly small in comparison with that of the nucleus, and further, that the velocity of the electron is small compared with that of light.

Let us at first assume that there is no energy radiation. In this case the electron will describe stationary elliptical orbits. The frequency of revolution ω and the major-axis of the orbit $2a$ will depend on the amount of energy W which must be transferred to the system in order to remove the electron to an infinitely great distance apart from the nucleus. Denoting the charge of the electron and of the nucleus by $-e$ and E respectively and the mass of the electron by m, we thus get

$$\omega = \frac{2^{\frac{1}{2}}}{\pi}\frac{W^{\frac{3}{2}}}{eEm^{\frac{1}{2}}}, \quad 2a = \frac{eE}{W}. \tag{1}$$

Further, it can easily be shown that the mean value of the kinetic energy of the electron taken for a whole revolution is equal to W.

We see that if the value of W is not given, there will be no values of ω and a characteristic for the system in question.

Let us now, however, take the effect of the energy radiation into account, calculated in the ordinary way from the acceleration of the electron. In this case the electron will no longer describe stationary orbits. W will continuously increase, and the electron will approach the nucleus describing orbits of smaller and smaller dimensions, and with greater and greater frequency; the electron on the average gaining in kinetic energy at the same time as the whole system loses energy. This process will go on until the dimensions of the orbit are of the same order of magnitude as the dimensions of the electron or those of the nucleus. A simple calculation shows that the energy radiated out during the process considered will be enormously great compared with that radiated out by ordinary molecular processes.

It is obvious that the behaviour of such a system will be very different from that of an atomic system occurring in nature. In the first place, the actual atoms in their permanent state seem to have absolutely fixed dimensions and frequencies. Further, if we consider any molecular process, the result seems always to be that after a certain amount of energy characteristic for the systems in question is radiated out, the systems will again settle down in a stable state of equilibrium, in which the distances apart of the particles are of the same order of magnitude as before the process.

Now the essential point in Planck's theory of radiation is that the energy radiation from an atomic system does not take place in the continuous way assumed in the ordinary electrodynamics, but that it, on the contrary, takes place in distinctly separated emissions, the amount of energy radiated out from an atomic vibrator of frequency ν in a single emission being equal to $\tau h\nu$, where τ is an entire number, and h is a universal constant.[5]

Returning to the simple case of an electron and a positive nucleus considered above, let us assume that the electron at the beginning of the interaction with the nucleus was at a great distance apart from the nucleus, and had no sensible velocity relative to the latter. Let us further assume that the electron after the interaction has taken place has settled down in a stationary orbit around the nucleus. We shall, for reasons referred to later, assume that the orbit in question is circular; this assumption will, however, make no alteration in the calculations for systems containing only a single electron.

Let us now assume that, during the binding of the electron, a homogeneous radiation is emitted of a frequency ν, equal to half the frequency of revolution of the electron in its final orbit; then, from Planck's theory, we might expect that the amount of energy emitted by the process considered is equal to $\tau h\nu$, where h is Planck's constant and τ an entire number. If we assume that the radiation emitted is homogeneous, the second assumption concerning the frequency of the radiation suggests itself, since the frequency of revolution of the electron at the beginning of the emission is 0. The question, however, of the rigorous validity of both assumptions, and also of the application made of Planck's theory, will be more closely discussed in §3.

Putting

$$W = \tau h \tfrac{1}{2}\omega, \tag{2}$$

we get by help of the formula (1)

$$W = \frac{2\pi^2 m e^2 E^2}{\tau^2 h^2}, \quad \omega = \frac{4\pi^2 m e^2 E^2}{\tau^3 h^3}, \quad 2a = \frac{\tau^2 h^2}{2\pi^2 m e E}. \tag{3}$$

If in these expressions we give τ different values, we get a series of values for W, ω, and a corresponding to a series of configurations of the system. According to the above considerations, we are led to assume that these configurations will correspond to states of the system in which there is no radiation of energy; states which consequently will be stationary as long as the system is not disturbed from outside. We see that the value of W is greatest if τ has its smallest value 1. This case will therefore correspond to the most stable state of the system, i.e. will correspond to the binding of the electron for the breaking up of which the greatest amount of energy is required.

Putting in the above expressions $\tau = 1$ and $E = e$, and introducing the experimental values

$$e = 4{\cdot}7 \times 10^{-10}, \quad e/m = 5{\cdot}31 \times 10^{17}, \quad h = 6{\cdot}5 \times 10^{-27},$$

we get

$$2a = 1{\cdot}1 \times 10^{-8}\,\text{cm}, \quad \omega = 6{\cdot}2 \times 10^{15}\,\text{sec}^{-1}, \quad W/e = 13\,\text{V}.$$

We see that these values are of the same order of magnitude as the linear dimensions of the atoms, the optical frequencies, and the ionization-potentials.

The general importance of Planck's theory for the discussion of the behaviour of atomic systems was originally pointed out by Einstein.[6] The considerations of Einstein have been developed and applied on a number of different phenomena, especially by Stark, Nernst, and Sommerfeld. The agreement as to the order of magnitude between values observed for the frequencies and dimensions of the atoms, and values for these quantities calculated by considerations similar to those given above, has been the subject of much discussion. It was first pointed out by Haas[7] in an attempt to explain the meaning and the value of Planck's constant on the basis of J. J. Thomson's atom-model, by help of the linear dimensions and frequency of an hydrogen atom.

Systems of the kind considered in this paper, in which the forces between the particles vary inversely as the square of the distance, are discussed in relation to Planck's theory by J. W. Nicholson.[8] In a series of papers this author has shown that it seems to be possible to account for lines of hitherto unknown origin in the spectra of the stellar nebulae and that of the solar corona, by assuming the presence in these bodies of certain hypothetical elements of exactly indicated constitution. The atoms of these elements are supposed to consist simply of a ring of a few electrons surrounding a positive nucleus of negligibly small dimensions. The ratios between the frequencies corresponding to the lines in question are compared with the ratios between the frequencies corresponding to different modes of vibration of the ring of electrons. Nicholson has obtained a relation to Planck's theory showing that the ratios between the wave-length of different sets of lines of the coronal spectrum can be accounted for with great accuracy by assuming that the ratio between the energy of the system and the frequency of rotation of the ring is equal to an entire multiple of Planck's constant. The quantity Nicholson refers to as the energy is equal to twice the quantity which we have denoted above by *W*. In the latest paper cited Nicholson has found it necessary to give the theory a more complicated form, still, however, representing the ratio of energy to frequency by a simple function of whole numbers.

The excellent agreement between the calculated and observed values of the ratios between the wave-lengths in question seems a strong argument in favour of the validity of the foundation of Nicholson's calculations. Serious objections, however, may be raised against the theory. These objections are intimately connected with the problem of the homogeneity of the radiation emitted. In Nicholson's calculations the frequency of lines in a line-spectrum is identified with the frequency of vibration of a mechanical system in a distinctly indicated state of equilibrium. As a relation from Planck's theory is used, we might expect that the radiation is sent out in quanta; but systems like those considered, in which the frequency is a function of the energy, cannot emit a finite amount of a homogeneous radiation; for, as soon as the emission of radiation is started, the energy and also the frequency of the system are altered. Further, according to the calculation of Nicholson, the systems are unstable for some modes of vibration. Apart from such objections—which may be only formal (see end of the present paper)—it must be remarked, that the theory in the form given does not seem to be able to account for the well-known laws of Balmer and Rydberg connecting the frequencies of the lines in the line-spectra of the ordinary elements.

It will now be attempted to show that the difficulties in question disappear if we consider the problems from the point of view taken in this paper. Before proceeding it may be useful to restate briefly the ideas characterizing the calculations leading to equation (3). The principal assumptions used are:

(1) That the dynamical equilibrium of the systems in the stationary states can be discussed by help of the ordinary mechanics, while the passing of the systems between different stationary states cannot be treated on that basis.

(2) That the latter process is followed by the emission of a *homogeneous* radiation, for which the relation between the frequency and the amount of energy emitted is the one given by Planck's theory.

The first assumption seems to present itself; for it is known that the ordinary mechanics cannot have an absolute validity, but will only hold in calculations of certain mean values of the motion of the electrons. On the other hand, in the calculations of the dynamical equilibrium in a stationary state in which there is no relative displacement of the particles, we need not distinguish between the actual motions and their mean values. The second assumption is in obvious contrast to the ordinary ideas of electrodynamics, but appears to be necessary in order to account for experimental facts.

In our calculations we have further made use of the more special assumptions, viz. that the different stationary states correspond to the emission of a different number of Planck's energy-quanta, and that the frequency of the radiation emitted during the passing of the system from a state in which no energy is yet radiated out to one of the stationary states, is equal to half the frequency of revolution of the electron in the latter state. We can, however (see § 3), also arrive at the expressions (3) for the stationary states by using assumptions of somewhat different form. We shall, therefore, postpone the discussion of the special assumptions, and first show how by the help of the above principal assumptions, and of the expressions (3) for the stationary states, we can account for the line-spectrum of hydrogen.

§ 2. Emission of Line-spectra

Spectrum of Hydrogen.—General evidence indicates that an atom of hydrogen consists simply of a single electron rotating round a positive nucleus of charge e.[9]† The reformation of a hydrogen atom, when the electron has been removed to great distances away from the nucleus—e.g. by the effect of electrical discharge in a vacuum tube—will accordingly correspond to the binding of an electron by a positive nucleus considered in § 1. If in (3) we put $E = e$, we get for the total amount of energy radiated out by the formation of one of the stationary states,

$$W_\tau = \frac{2\pi^2 me^4}{h^2\tau^2}.$$

The amount of energy emitted by the passing of the system from a state corresponding to $\tau = \tau_1$ to one corresponding to $\tau = \tau_2$, is consequently

$$W_{\tau_2} - W_{\tau_1} = \frac{2\pi^2 me^4}{h^2}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right).$$

If now we suppose that the radiation in question is homogeneous, and that the amount of energy emitted is equal to $h\nu$, where ν is the frequency of the radiation, we get

$$W_{\tau_2} - W_{\tau_1} = h\nu,$$

and from this

$$\nu = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2} - \frac{1}{\tau_1^2}\right). \tag{4}$$

We see that this expression accounts for the law connecting the lines in the spectrum of hydrogen. If we put $\tau_2 = 2$ and let τ_1 vary, we get the ordinary Balmer series. If we put $\tau_2 = 3$, we get the series in the ultra-red observed by Paschen[11] and previously suspected by Ritz. If we put $\tau_2 = 1$ and $\tau_2 = 4, 5, \ldots$, we get series respectively in the extreme ultra-violet and the extreme ultra-red, which are not observed, but the existence of which may be expected.

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† The conclusion drawn in ref. 9 is strongly supported by the fact that hydrogen, in the experiments on positive rays of Sir J. J. Thomson,[10] is the only element which never occurs with a positive charge corresponding to the loss of more than one electron.

The agreement in question is quantitative as well as qualitative. Putting

$$e = 4{\cdot}7 \times 10^{-10}, \quad e/m = 5{\cdot}31 \times 10^{17}, \quad \text{and} \quad h = 6{\cdot}5 \times 10^{-27},$$

we get

$$\frac{2\pi^2 me^4}{h^3} = 3{\cdot}1 \times 10^{15}.$$

The observed value for the factor outside the bracket in the formula (4) is

$$3{\cdot}290 \times 10^{15}.$$

The agreement between the theoretical and observed values is inside the uncertainty due to experimental errors in the constants entering in the expression for the theoretical value. We shall in § 3 return to consider the possible importance of the agreement in question.

It may be remarked that the fact, that it has not been possible to observe more than 12 lines of the Balmer series in experiments with vacuum tubes, while 33 lines are observed in the spectra of some celestial bodies, is just what we should expect from the above theory. According to the equation (3) the diameter of the orbit of the electron in the different stationary states is proportional to τ^2. For $\tau = 12$ the diameter is equal to $1{\cdot}6 \times 10^{-6}$ cm, or equal to the mean distance between the molecules in a gas at a pressure of about 7 mm mercury; for $\tau = 33$ the diameter is equal to $1{\cdot}2 \times 10^{-5}$ cm, corresponding to the mean distance of the molecules at a pressure of about 0·02 mm mercury. According to the theory the necessary condition for the appearance of a great number of lines is therefore a very small density of the gas; for simultaneously to obtain an intensity sufficient for observation the space filled with the gas must be very great. If the theory is right, we may therefore never expect to be able in experiments with vacuum tubes to observe the lines corresponding to high numbers of the Balmer series of the emission spectrum of hydrogen; it might, however, be possible to observe the lines by investigation of the absorption spectrum of this gas (see § 4).

It will be observed that we in the above way do not obtain other series of lines, generally ascribed to hydrogen; for instance, the series first observed by Pickering[12] in the spectrum of the star ζ Puppis, and the set of series recently found by Fowler[13] by experiments with vacuum tubes containing a mixture of hydrogen and helium. We shall, however, see that, by help of the above theory, we can account naturally for these series of lines if we ascribe them to helium.

A neutral atom of the latter element consists, according to Rutherford's theory, of a positive nucleus of charge $2e$ and two electrons. Now considering the binding of a single electron by a helium nucleus, we get, putting $E = 2e$ in the expressions (3) of § 1, and proceeding in exactly the same way as above,

$$\nu = \frac{8\pi^2 me^4}{h^3}\left(\frac{1}{\tau_2^2}-\frac{1}{\tau_1^2}\right) = \frac{2\pi^2 me^4}{h^3}\left(\frac{1}{(\frac{1}{2}\tau_2)^2}-\frac{1}{(\frac{1}{2}\tau_1)^2}\right).$$

If we in this formula put $\tau_2 = 1$ or $\tau_2 = 2$, we get series of lines in the extreme ultra-violet. If we put $\tau_2 = 3$, and let τ_1 vary, we get a series which includes 2 of the series observed by Fowler, and denoted by him as the first and second principal series of the hydrogen spectrum. If we put $\tau_2 = 4$, we get the series observed by Pickering in the spectrum of ζ Puppis. Every second of the lines in this series is identical with a line in the Balmer series of the hydrogen spectrum; the presence of hydrogen in the star in question may therefore account for the fact that these lines are of a greater intensity than the rest of the lines in the series. The series is also observed in the experiments of Fowler, and denoted in his paper as the Sharp series of the hydrogen spectrum. If we finally in the above formula put $\tau_2 = 5, 6, \ldots$, we get series, the strong lines of which are to be expected in the ultra-red.

The reason why the spectrum considered is not observed in ordinary helium tubes may be that in such tubes the ionization of helium is not so complete as in the star considered or in the experiment of Fowler, where a strong discharge was sent through a mixture of hydrogen and helium. The condition for the appearance of the spectrum is, according to the above theory, that helium atoms are present in a state in which they have lost both their electrons. Now we must assume that the amount of energy to be used in removing the second electron from a helium atom is much greater than that to be used in removing the first. Further, it is known from experiments on positive rays, that hydrogen atoms can acquire a negative charge; therefore the presence of hydrogen in the experiments of Fowler may effect that more electrons are removed from some of the helium atoms than would be the case if only helium were present.

Spectra of other substances.—In case of systems containing more electrons we must—in conformity with the result of experiments—expect more complicated laws for the line-spectra than those considered. I shall try to show that the point of view taken above allows, at any rate, a certain understanding of the laws observed.

According to Rydberg's theory—with the generalization given by Ritz[14]—the frequency corresponding to the lines of the spectrum of an element can be expressed by

$$\nu = F_r(\tau_1) - F_s(\tau_2),$$

where τ_1 and τ_2 are entire numbers, and $F_1, F_2, F_3, \ldots$ are functions of τ which approximately are equal to

$$\frac{K}{(\tau + a_1)^2}, \quad \frac{K}{(\tau + a_2)^2}, \quad \ldots$$

K is a universal constant, equal to the factor outside the bracket in the formula (4) for the spectrum of hydrogen. The different series appear if we put τ_1 or τ_2 equal to a fixed number and let the other vary.

The circumstance that the frequency can be written as a difference between two functions of entire numbers suggests an origin of the lines in the spectra in question similar to the one we have assumed for hydrogen; i.e. that the lines correspond to a radiation emitted during the passing of the system between two different stationary states. For systems containing more than one electron the detailed discussion may be very complicated, as there will be many different configurations of the electrons which can be taken into consideration as stationary states. This may account for the different sets of series in the line spectra emitted from the substances in question. Here I shall only try to show how, by help of the theory, it can be simply explained that the constant K entering in Rydberg's formula is the same for all substances.

Let us assume that the spectrum in question corresponds to the radiation emitted during the binding of an electron; and let us further assume that the system including the electron considered is neutral. The force on the electron, when at a great distance apart from the nucleus and the electrons previously bound, will be very nearly the same as in the above case of the binding of an electron by a hydrogen nucleus. The energy corresponding to one of the stationary states will therefore for τ great be very nearly equal to that given by the expression (3) in § 1, if we put $E = e$. For τ great we consequently get

$$\lim\left(\tau^2 F_1(\tau)\right) = \lim\left(\tau^2 F_2(\tau)\right) = \ldots = \frac{2\pi^2 m e^4}{h^3},$$

in conformity with Rydberg's theory.

§ 3. General Considerations continued

We shall now return to the discussion of the special assumptions used in deducing the expressions (3) for the stationary states of a system consisting of an electron rotating round a nucleus.

For one, we have assumed that the different stationary states correspond to an emission of a different number of energy-quanta. Considering systems in which the frequency is a function of the energy, this assumption, however, may be regarded as improbable; for as soon as one quantum is sent out the frequency is altered. We shall now see that we can leave the assumption used and still retain equation (2), and thereby the formal analogy with Planck's theory.

Firstly, it will be observed that it has not been necessary, in order to account for the law of the spectra by help of the expressions (3) for the stationary states, to assume that in any case a radiation is sent out corresponding to more than a single energy-quantum, $h\nu$. Further information on the frequency of the radiation may be obtained by comparing calculations of the energy radiation in the region of slow vibrations based on the above assumptions with calculations based on the ordinary mechanics. As is known, calculations on the latter basis are in agreement with experiments on the energy radiation in the named region.

Let us assume that the ratio between the total amount of energy emitted and the frequency of revolution of the electron for the different stationary states is given by the equation $W = f(\tau)h\omega$, instead of by the equation (2). Proceeding in the same way as above, we get in this case instead of (3)

$$W = \frac{\pi^2 m e^2 E^2}{2h^2 f^2(\tau)}, \quad \omega = \frac{\pi^2 m e^2 E^2}{2h^3 f^3(\tau)}.$$

Assuming as above that the amount of energy emitted during the passing of the system from a state corresponding to $\tau = \tau_1$ to one for which $\tau = \tau_2$ is equal to $h\nu$, we get instead of (4)

$$\nu = \frac{\pi^2 m e^2 E^2}{2h^3}\left(\frac{1}{f^2(\tau_2)} - \frac{1}{f^2(\tau_1)}\right).$$

We see that in order to get an expression of the same form as the Balmer series we must put $f(\tau) = c\tau$.

In order to determine c let us now consider the passing of the system between two successive stationary states corresponding to $\tau = N$ and $\tau = N-1$; introducing $f(\tau) = c\tau$, we get for the frequency of the radiation emitted

$$\nu = \frac{\pi^2 m e^2 E^2}{2c^2 h^3} \frac{2N-1}{N^2(N-1)^2}.$$

For the frequency of revolution of the electron before and after the emission we have

$$\omega_N = \frac{\pi^2 m e^2 E^2}{2c^3 h^3 N^3} \quad \text{and} \quad \omega_{N-1} = \frac{\pi^2 m e^2 E^2}{2c^3 h^3 (N-1)^3}.$$

If N is great the ratio between the frequency before and after the emission will be very near equal to 1; and according to the ordinary electrodynamics we should therefore expect that the ratio between the frequency of radiation and the frequency of revolution also is very nearly equal to 1. This condition will only be satisfied if $c = \frac{1}{2}$. Putting $f(\tau) = \frac{1}{2}\tau$, we, however, again arrive at the equation (2) and consequently at the expression (3) for the stationary states.

If we consider the passing of the system between two states corresponding to $\tau = N$ and $\tau = N-n$, where n is small compared with N, we get with the same approximation as above, putting $(\tau) = \frac{1}{2}\tau$,

$$\nu = n\omega.$$

The possibility of an emission of a radiation of such a frequency may also be interpreted from analogy with the ordinary electrodynamics, as an electron rotating round a nucleus in an elliptical orbit will emit a radiation which according to Fourier's theorem can be resolved into homogeneous components, the frequencies of which are $n\omega$, if ω is the frequency of revolution of the electron.

We are thus led to assume that the interpretation of the equation (2) is not that the different stationary states correspond to an emission of different numbers of energy-quanta, but that the frequency of the energy emitted during the passing of the system from a state in which no energy is yet radiated out to one of the different stationary states, is equal to different multiples of $\frac{1}{2}\omega$, where ω is the frequency of revolution of the electron in the state considered. From this assumption we get exactly the same expressions as before for the stationary states, and from these by help of the principal assumptions of § 1 the same expression for the law of the hydrogen spectrum. Consequently we may regard our preliminary considerations of § 1 only as a simple form of representing the results of the theory.

Before we leave the discussion of this question, we shall for a moment return to the question of the significance of the agreement between the observed and calculated values of the constant entering in the expressions (4) for the Balmer series of the hydrogen spectrum. From the above consideration it will follow that, taking the starting-point in the form of the law of the hydrogen spectrum and assuming that the different lines correspond to a homogeneous radiation emitted during the passing between different stationary states, we shall arrive at exactly the same expression for the constant in question as that given by (4), if we only assume (1) that the radiation is sent out in quanta $h\nu$, and (2) that the frequency of the radiation emitted during the passing of the system between successive stationary states will coincide with the frequency of revolution of the electron in the region of slow vibrations.

As all the assumptions used in this latter way of representing the theory are of what we may call a qualitative character, we are justified in expecting—if the whole way of considering is a sound one—an absolute agreement between the values calculated and observed for the constant in question, and not only an approximate agreement. The formula (4) may therefore be of value in the discussion of the results of experimental determinations of the constants e, m, and h.

While there obviously can be no question of a mechanical foundation of the calculations given in this paper, it is, however, possible to give a very simple interpretation of the result of the calculation in § 1 by help of symbols taken from the ordinary mechanics. Denoting the angular momentum of the electron round the nucleus by M, we have immediately for a circular orbit $\tau M = T/\omega$, where ω is the frequency of revolution and T the kinetic energy of the electron; for a circular orbit we further have $T = W$ and from (2), we consequently get

$$M = \tau M_0,$$

where

$$M_0 = \frac{h}{2\pi} = 1{\cdot}04 \times 10^{-27}.$$

If we therefore assume that the orbit of the electron in the stationary states is circular, the result of the calculation in § 1 can be expressed by the simple condition: that the angular momentum of the electron round the nucleus in a stationary state of the system is equal to an entire multiple of a universal value, independent of the charge on the nucleus. The possible importance of the angular momentum in the discussion of atomic systems in relation to Planck's theory is emphasized by Nicholson.[8]

The great number of different stationary states we do not observe except by investigation of the emission and absorption of radiation. In most of the other physical phenomena, however, we only observe the atoms of the matter in a single distinct state, i.e. the state of the atoms at low temperature. From the preceding considerations we are immediately led to the assumption that the "permanent" state is the one among the stationary states during the formation of which the greatest amount of energy is emitted. According to equation (3), this state is the one which corresponds to $\tau = 1$.

§4. Absorption of Radiation

In order to account for Kirchhoff's law it is necessary to introduce assumptions on the mechanism of absorption of radiation which correspond to those we have used considering the emission. Thus we must assume that a system consisting of a nucleus and an electron rotating round it under certain circumstances can absorb a radiation of a frequency equal to the frequency of the homogeneous radiation emitted during the passing of the system between different stationary states. Let us consider the radiation emitted during the passing of the system between two stationary states A_1 and A_2 corresponding to values for τ equal to τ_1 and τ_2, $\tau_1 > \tau_2$. As the necessary condition for an emission of the radiation in question was the presence of systems in the state A_1, we must assume that the necessary condition for an absorption of the radiation is the presence of systems in the state A_2.

These considerations seem to be in conformity with experiments on absorption in gases. In hydrogen gas at ordinary conditions for instance there is no absorption of a radiation of a frequency corresponding to the line-spectrum of this gas; such an absorption is only observed in hydrogen gas in a luminous state. This is what we should expect according to the above. We have in §2 assumed that the radiation in question was emitted during the passing of the systems between stationary states corresponding to $\tau \geqq 2$. The state of the atoms in hydrogen gas at ordinary conditions should, however, correspond to $\tau = 1$; furthermore, hydrogen atoms at ordinary conditions combine into molecules, i.e. into systems in which the electron have frequencies different from those in the atoms (see Part III). From the circumstance that certain substances in a non-luminous state, as, for instance, sodium vapour, absorb radiation corresponding to lines in the line-spectra of the substances, we may, on the other hand, conclude that the lines in question are emitted during the passing of the system between two states, one of which is the permanent state.

How much the above considerations differ from an interpretation based on the ordinary electrodynamics is perhaps most clearly shown by the fact that we have been forced to assume that a system of electrons will absorb a radiation of a frequency different from the frequency of vibration of the electron calculated in the ordinary way. It may in this connexion be of interest to mention a generalization of the considerations to which we are led by experiments on the photo-electric effect, and which may be able to throw some light on the problem in question. Let us consider a state of the system in which the electron is free, i.e. in which the electron possesses kinetic energy sufficient to remove to infinite distances from the nucleus. If we assume that the motion of the electron is governed by the ordinary mechanics and that there is no (sensible) energy radiation, the total energy of the system—as in the above considered stationary states—will be constant. Further, there will be perfect continuity between the two kinds of states, as the difference between frequency and dimensions of the systems in successive stationary states will diminish without limit if τ increases. In the following considerations we shall for the sake of brevity refer to the two kinds of states in question as "mechanical" states; by this notation only emphasizing the assumption that the motion of the electron in both cases can be accounted for by the ordinary mechanics.

Tracing the analogy between the two kinds of mechanical states, we might now expect the possibility of an absorption of radiation, not only corresponding to the passing of the system between two different stationary states, but also corresponding to the passing between one of the stationary states and a state in which the electron is free; and as above, we might expect that the frequency of this radiation was determined by the equation $E = h\nu$, where E is the difference between the total energy of the system in the two states. As it will be seen, such an absorption of radiation is just what is observed in experiments on ionization by ultra-violet light and by Röntgen rays. Obviously, we get in this way the same expression for the kinetic energy of an electron ejected from an atom by photo-electric effect as that deduced by Einstein,[15] i.e. $T = h\nu - W$, where T is the kinetic energy of the electron ejected, and W the total amount of energy emitted during the original binding of the electron.

The above considerations may further account for the result of some experiments of R. W. Wood[16] on absorption of light by sodium vapour. In these experiments, an absorption corresponding to a very great number of lines in the principal series of the sodium spectrum is observed, and in addition a continuous absorption which begins at the head of the series and extends to the extreme ultra-violet. This is exactly what we should expect according to the analogy in question, and, as we shall see, a closer consideration of the above experiments allows us to trace the analogy still further. As mentioned in §2 the radii of the orbits of the electrons will for stationary states corresponding to high values for τ be very great compared with ordinary atomic dimensions. This circumstance was used as an explanation of the non-appearance in experiments with vacuum-tubes of lines corresponding to the higher numbers in the Balmer series of the hydrogen spectrum. This is also in conformity with experiments on the emission spectrum of sodium; in the principal series of the emission spectrum of this substance rather few lines are observed. Now in Wood's experiments the pressure was not very low, and the states corresponding to high values for τ could therefore not appear; yet in the absorption spectrum about 50 lines were detected. In the experiments in question we consequently observe an absorption of radiation which is not accompanied by a complete transition between two different stationary states. According to the present theory we must assume that this absorption is followed by an emission of energy during which the systems pass back to the original stationary state. If there are no collisions between the different systems this energy will be emitted as a radiation of the same frequency as that absorbed, and there will be no true absorption but only a scattering of the original radiation; a true absorption will not occur unless the energy in question is transformed by collisions into kinetic energy of free particles. In analogy we may now from the above experiments conclude that a bound electron—also in cases in which there is no ionization—will have an absorbing (scattering) influence on a homogeneous radiation, as soon as the frequency of the radiation is greater than W/h, where W is the total amount of energy emitted during the binding of the electron. This would be highly in favour of a theory of absorption as the one sketched above, as there can in such a case be no question of a coincidence of the frequency of the radiation and a characteristic frequency of vibration of the electron. It will further be seen that the assumption, that there will be an absorption (scattering) of any radiation corresponding to a transition between two different mechanical states, is in perfect analogy with the assumption generally used that a free electron will have an absorbing (scattering) influence on light of any frequency. Corresponding considerations will hold for the emission of radiation.

In analogy to the assumption used in this paper that the emission of line-spectra is due to the re-formation of atoms after one or more of the lightly bound electrons are removed, we may assume that the homogeneous Röntgen radiation is emitted during the settling down of the systems after one of the firmly bound electrons escapes, e.g. by impact of cathode particles.[17] In the next part of this paper, dealing with the constitution of atoms, we shall consider the question more closely and try to show that a calculation based on this assumption is in quantitative agreement with the results of experiments: here we shall only mention briefly a problem with which we meet in such a calculation.

Experiments on the phenomena of X-rays suggest that not only the emission and absorption of radiation cannot be treated by the help of the ordinary electrodynamics, but not even the result of a collision between two electrons of which the one is bound in an atom. This is perhaps most clearly shown by some very instructive calculations on the energy of β-particles emitted from radioactive substances recently published by Rutherford.[18] These calculations strongly suggest that an electron of great velocity in passing through an atom and colliding with the bound electrons will loose energy in distinct finite quanta. As is immediately seen, this is very different from what we might expect if the result of the collisions was governed by the usual mechanical laws. The failure of the classical mechanics in such a problem might also be expected beforehand from the absence of anything like equipartition of kinetic energy between free electrons and electrons bound in atoms. From the point of view of the "mechanical" states we see, however, that the following assumption—which is in accord with the above analogy—might be able to account for the result of Rutherford's calculation and for the absence of equipartition of kinetic energy: two colliding electrons, bound or free, will, after the collision as well as before, be in mechanical states. Obviously, the introduction of such an assumption would not make any alteration necessary in the classical treatment of a collision between two free particles. But, considering a collision between a free and a bound electron, it would follow that the bound electron by the collision could not acquire a less amount of energy than the difference in energy corresponding to successive stationary states, and consequently that the free electron which collides with it could not lose a less amount.

The preliminary and hypothetical character of the above considerations needs not to be emphasized. The intention, however, has been to show that the sketched generalization of the theory of the stationary states possibly may afford a simple basis of representing a number of experimental facts which cannot be explained by help of the ordinary electrodynamics, and that the assumptions used do not seem to be inconsistent with experiments on phenomena for which a satisfactory explanation has been given by the classical dynamics and the wave theory of light.

§ 5. The Permanent State of an Atomic System

We shall now return to the main object of this paper—the discussion of the "permanent" state of a system consisting of nuclei and bound electrons. For a system consisting of a nucleus and an electron rotating round it, this state is, according to the above, determined by the condition that the angular momentum of the electron round the nucleus is equal to $h/2\pi$.

On the theory of this paper the only neutral atom which contains a single electron is the hydrogen atom. The permanent state of this atom should correspond to the values of a and ω calculated in § 1. Unfortunately, however, we know very little of the behaviour of hydrogen atoms on account of the small dissociation of hydrogen molecules at ordinary temperatures. In order to get a closer comparison with experiments, it is necessary to consider more complicated systems.

Considering systems in which more electrons are bound by a positive nucleus, a configuration of the electrons which presents itself as a permanent state is one in which the electrons are arranged in a ring round the nucleus. In the discussion of this problem on the basis of the ordinary electrodynamics, we meet—apart from the question of the energy radiation—with new difficulties due to the question of the stability of the ring. Disregarding for a moment this latter difficulty, we shall first consider the dimensions and frequency of the systems in relation to Planck's theory of radiation.

Let us consider a ring consisting of n electrons rotating round a nucleus of charge E, the electrons being arranged at equal angular intervals around the circumference of a circle of radius a.

The total potential energy of the system consisting of the electrons and the nucleus is

$$P = -\frac{ne}{a}\ (E-es_n),$$

where
$$s_n = \frac{1}{4}\sum_{s=1}^{s=n-1} \operatorname{cosec}\frac{s\pi}{n}.$$

For the radial force exerted on an electron by the nucleus and the other electrons we get

$$F = -\frac{1}{n}\frac{dP}{da} = -\frac{e}{a^2}(E-es_n).$$

Denoting the kinetic energy of an electron by T and neglecting the electromagnetic forces due to the motion of the electrons (see Part II), we get, putting the centrifugal force on an electron equal to the radial force,

$$\frac{2T}{a} = \frac{e}{a^2}(E-es_n), \quad \text{or} \quad T = \frac{e}{2a}(E-es_n).$$

From this we get for the frequency of revolution

$$\omega = \frac{1}{2\pi}\sqrt{\left(\frac{e(E-es_n)}{ma^3}\right)}.$$

The total amount of energy W necessary to be transferred to the system in order to remove the electrons to infinite distances apart from the nucleus and from each other is

$$W = -P-nT = \frac{ne}{2a}(E-es_n) = nT,$$

equal to the total kinetic energy of the electrons.

We see that the only difference in the above formula and those holding for the motion of a single electron in a circular orbit round a nucleus is the exchange of E for $E-es_n$. It is also immediately seen that corresponding to the motion of an electron in an elliptical orbit round a nucleus, there will be a motion of the n electrons in which each rotates in an elliptical orbit with the nucleus in the focus, and the n electrons at any moment are situated at equal angular intervals on a circle with the nucleus as the centre. The major axis and frequency of the orbit of the single electrons will for this motion be given by the expressions (1) if we replace E by $E-es_n$ and W by W/n. Let us now suppose that the system of n electrons rotating in a ring round a nucleus is formed in a way analogous to the one assumed for a single electron rotating round a nucleus. It will thus be assumed that the electrons, before the binding by the nucleus, were at a great distance apart from the latter and possessed no sensible velocities, and also that during the binding a homogeneous radiation is emitted. As in the case of a single electron, we have here that the total amount of energy emitted during the formation of the system is equal to the final kinetic energy of the electrons. If we now suppose that during the formation of the system the electrons at any moment are situated at equal angular intervals on the circumference of a circle with the nucleus in the centre, from analogy with the considerations in § 1 we are here led to assume the existence of a series of stationary configurations in which the kinetic energy per electron is equal to $\tau h \frac{1}{2} \omega$, where τ is an entire number, h Planck's constant, and ω the frequency of revolution. The configuration in which the greatest amount of energy is emitted is, as before, the one in which $\tau = 1$. This configuration we shall assume to be the permanent state of the system if the electrons in this state are arranged in a single ring. As for the case of a single electron we get that the angular momentum of each of the electrons is equal to $h/2\pi$. It may be remarked that instead of considering the single electrons we might have considered the ring as an entity. This would, however, lead to the same result, for in this case the frequency of revolution ω will be replaced by the frequency $n\omega$ of the radiation from the whole ring calculated from the ordinary electrodynamics, and T by the total kinetic energy nT.

There may be many other stationary states corresponding to other ways of forming the system. The assumption of the existence of such states seems necessary in order to account for the line-spectra of systems containing more than one electron; it is also suggested by the theory of Nicholson mentioned in § 1, to which we shall return in a moment. The consideration of the spectra, however, gives, as far as I can see, no indication of the existence of stationary states in which all the electrons are arranged in a ring and which correspond to greater values for the total energy emitted than the one we above have assumed to be the permanent state.

Further, there may be stationary configurations of a system of n electrons and a nucleus of charge E in which all the electrons are not arranged in a single ring. The question, however, of the existence of such stationary configurations is not essential for our determination of the permanent state, as long as we assume that the electrons in this state of the system are arranged in a single ring. Systems corresponding to more complicated configurations will be discussed below.

Using the relation $T = h\frac{1}{2}\omega$ we get, by help of the above expressions for T and ω, values for a and ω corresponding to the permanent state of the system which only differ from those given by equations (3), by exchange of E for $E - es_n$.

The question of stability of a ring of electrons rotating round a positive charge is discussed in great detail by Sir J. J. Thomson.[3] An adaption of Thomson's analysis for the case here considered of a ring rotating round a nucleus of negligibly small linear dimensions is given by Nicholson.[8] The investigation of the problem in question naturally divides in two parts: one concerning the stability for displacements of the electrons in the plane of the ring; one concerning displacements perpendicular to this plane. As Nicholson's calculations show, the answer to the question of stability differs very much in the two cases in question. While the ring for the latter displacements in general is stable if the number of electrons is not great, the ring is in no case considered by Nicholson stable for displacements of the first kind.

According, however, to the point of view taken in this paper, the question of stability for displacements of the electrons in the plane of the ring is most intimately connected with the question of the mechanism of the binding of the electrons, and like the latter cannot be treated on the basis of the ordinary dynamics. The hypothesis of which we shall make use in the following is that the stability of a ring of electrons rotating round a nucleus is secured through the above condition of the universal constancy of the angular momentum, together with the further condition that the configuration of the particles is the one by the formation of which the greatest amount of energy is emitted. As will be shown, this hypothesis is, concerning the question of stability for a displacement of the electrons perpendicular to the plane of the ring, equivalent to that used in ordinary mechanical calculations.

Returning to the theory of Nicholson on the origin of lines observed in the spectrum of the solar corona, we shall now see that the difficulties mentioned in § 1 may be only formal. In the first place, from the point of view considered above the objection as to the instability of the systems for displacements of the electrons in the plane of the ring may not be valid. Further, the objection as to the emission of the radiation in quanta will not have reference to the calculations in question, if we assume that in the coronal spectrum we are not dealing with a true emission but only with a scattering of radiation. This assumption seems probable if we consider the conditions in the celestial body in question; for on account of the enormous rarefaction of the matter there may be comparatively few collisions to disturb the stationary states and to cause a true emission of light corresponding to the transition between different stationary states; on the other hand there will in the solar corona be intense illumination of light of all frequencies which may excite the natural vibrations of the systems in the different stationary states. If the above assumption is correct, we immediately understand the entirely different form for the laws connecting the lines discussed by Nicholson and those connecting the ordinary line-spectra considered in this paper.

Proceeding to consider systems of a more complicated constitution, we shall make use of the following theorem, which can be very simply proved:

"In every system consisting of electrons and positive nuclei, in which the nuclei are at rest and the electrons move in circular orbits with a velocity small compared with the velocity of light, the kinetic energy will be numerically equal to half the potential energy."

By help of this theorem we get—as in the previous cases of a single electron or of a ring rotating round a nucleus—that the total amount of energy emitted, by the formation of the systems from a configuration in which the distances apart of the particles are infinitely great and in which the particles have no velocities relative to each other, is equal to the kinetic energy of the electrons in the final configuration.

In analogy with the case of a single ring we are here led to assume that corresponding to any configuration of equilibrium a series of geometrically similar, stationary configurations of the system will exist in which the kinetic energy of every electron is equal to the frequency of revolution multiplied by $\frac{1}{2}\tau h$ where τ is an entire number and h Planck's constant. In any such series of stationary configurations the one corresponding to the greatest amount of energy emitted will be the one in which τ for every electron is equal to 1. Considering that the ratio of kinetic energy to frequency for a particle rotating in a circular orbit is equal to π times the angular momentum round the centre of the orbit, we are therefore led to the following simple generalization of the hypotheses mentioned in §3 and earlier in the present section.

"*In any molecular system consisting of positive nuclei and electrons in which the nuclei are at rest relative to each other and the electrons move in circular orbits, the angular momentum of every electron round the centre of its orbit will in the permanent state of the system be equal to $h/2\pi$, where h is Planck's constant.*"†

In analogy with the considerations given a moment ago, we shall

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† In the considerations leading to this hypothesis we have assumed that the velocity of the electrons is small compared with the velocity of light. The limits of the validity of this assumption will be discussed in Part II.

assume that a configuration satisfying this condition is stable if the total energy of the system is less than in any neighbouring configuration satisfying the same condition of the angular momentum of the electrons.

As mentioned in the introduction, the above hypothesis will be used in a following communication as a basis for a theory of the constitution of atoms and molecules. It will be shown that it leads to results which seem to be in conformity with experiments on a number of different phenomena.

The foundation of the hypothesis has been sought entirely in its relation with Planck's theory of radiation; by help of considerations given later it will be attempted to throw some further light on the foundation of it from another point of view.

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6 On the Excitation of the 2536 Å Mercury Resonance Line by Electron Collisions†

J. FRANCK AND G. HERTZ

IT WAS shown in our experiments on collisions between electrons and molecules of an inert gas or of a metal vapour that the electrons are reflected in such collisions without loss of energy, as long as their kinetic energy does not exceed a certain critical magnitude, but that as soon as their energy becomes equal to the critical value, they lose all of it on collision. The critical velocity is a quantity, characteristic for each gas and is in the cases studied so far equal to the ionisation energy.[1] This result is completely in agreement with quantum theory since according to that theory the vibrations of the electrons in an atom can receive energy only in certain quanta and not in arbitrary amounts. The question whether, indeed, as follows also from quantum theory, the smallest amount of energy which can be transmitted is equal to the product of Planck's constant h and the frequency ν of the electron receiving the energy‡ could only be decided with a certain amount of certainty for the case of mercury vapour. In the case of this vapour one has not only measured with relatively high accuracy the critical kinetic energy, but one also knows very probably the frequency of the vibrating electron as Wood's experiments[2] on the mercury resonance radiation have proved that there is in every mercury atom an electron which can vibrate with a frequency

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† *Verh. Dtsch. Phys. Ges. Berlin* **16**, 512 (1914).

‡ The hypothesis that the ionisation energy is equal to the product $h\nu$ has first been made by J. Stark.

corresponding to a wavelength of 2536 Å. It turned out that the value measured by us corresponding to the smallest energy quantum which can be transferred agreed within the limits of accuracy with the product $h\nu$.

To conclude with certainty from our results that the phenomena studied take place in agreement with quantum theory, we can, however, not restrict ourselves to proving that the energy is transferred only in certain quanta. Rather, it is still necessary to prove that the total energy quantum transferred, $h\nu$, is given to a single electron which can vibrate with frequency ν. The aim of the present paper is to give this proof.

As we emphasised in our earlier paper[1] the majority of collisions which transfer to the vibrating electron an energy $h\nu$ do not lead to ionisation. In the atoms which have undergone such collisions, there is thus an electron of energy $h\nu$, vibrating with frequency ν. One should, therefore, expect that such collisions which do not lead to ionisation but just to an energy loss $h\nu$ should be accompanied by an emission of light of frequency ν, that is, that one should be able to observe the emission of resonance radiation. This means that if one introduces electrons in mercury vapour and enables them to attain a velocity corresponding to a voltage difference of 4·9 Volt, one should be able to observe light emission corresponding exclusively to the emission of the mercury 2536 Å resonance line. Experiments have fully confirmed this expectation.

In Fig. 6.1 we give the apparatus used. The vessel was made of quartz; the bottom part and the two tubes at the bottom were filled with mercury. A circular gas flame heated the apparatus to about 150°. The platinum wire D, which was heated by an electric current served as electron source. The platinum mesh N at the other side was connected to earth via a galvanometer, and we put a voltage to accelerate the electrons between the wire and the mesh. The soldering places which could not be avoided were, as far as possible, away from the heated parts of the apparatus and were cooled with water. We used a Fuess ultraviolet spectrograph kindly put at our disposal by Professor Goldstein to study the emitted radiation.

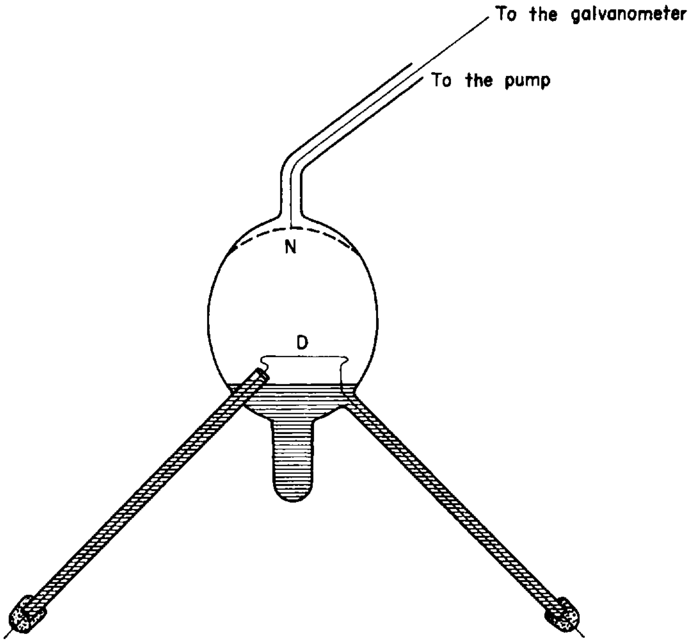

FIG. 6.1

We know from our earlier investigations that as soon as the applied voltage exceeds 4·9 Volt† for carefully chosen values of pressure and voltage electrons occur with a velocity corresponding to a voltage of 4·9 Volt, but not with higher velocities. We can, however, not state with any certainty that no electrons of that velocity are present when the applied voltage is lower than 4·9 Volt as the electrons leave the platinum wire with a certain

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† A pressure of about 1 mm and a field gradient of 2 V/cm completely satisfy these conditions as is shown by the measurements on the velocity distribution of the electrons discussed in our earlier paper.[1] As soon as the electrons have attained a velocity corresponding to 4·9 Volt, one of the subsequent collisions will certainly lead to a complete loss of energy; along the few mean free paths which the electron can still traverse with the critical velocity, the increase of velocity is small compared to the critical velocity,

initial velocity which for the wires used goes up to about 1 Volt. The photographs obtained after exposing for one or two hours showed a continuous spectrum, stretching into the violet, caused by the light emitted by the incandescent wire, and then, a long distance away from it, clearly the 2536 Å line; however, in no case was there even a suspicion of the other mercury lines which in the mercury arc spectrum have partially far greater intensities than the resonance line. The identification of the line was made by comparison with a wavelength scale built for the apparatus and also by imposing upon the spectrum the arc spectrum of mercury as a comparison spectrum.

Figure 6.2 is such a photograph,† taken when the potential applied to the electrons was 8 Volt. It shows clearly (we hope also in the reproduction) the appearance of the 2536 Å resonance line. The intensity of the emitted light depends essentially on the value of the vapour pressure, as can be understood from Wood's results on the scattering and absorption of resonance radiation in mercury vapour. The best results were obtained for a temperature of about 150° so that the vapour pressure of the mercury vapour is more than 1 mm. We have followed the appearance of the line, varying the experimental conditions for different applied voltages and we never saw a suspicion of the line for a potential less than the critical one; for instance, under the same conditions for 4 Volt there is no indication of the line, while it is clearly visible already for 6 Volt.

As we have now shown that the energy quantum transferred is indeed exactly equal to $h\nu$, we can use an accurate measurement of this energy quantum for a determination of the value of the constant h which should not be less accurate than the determinations of this constant based upon measurements of radiation. As apart from the measured potential difference, traversed by the electrons, only the elementary quantum and the wavelength of the resonance radiation enter into the calculations, one can in this way determine the quantity h with the same accuracy with which we can measure the critical velocity of the electrons. From our

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† Figure 6.2 is reproduced as a drawing, sketched from the original [D. t. H.].

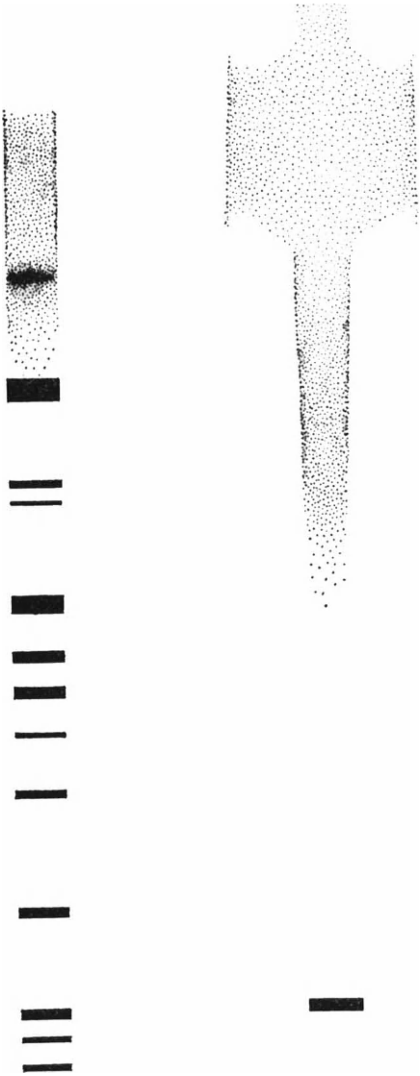

Fig. 6.2

measurements we find $h = 6{\cdot}59 \times 10^{-27}$ erg sec with a possible error of 2 percent, whereas the values of the radiation constant found by several observers differ by far more than 2 percent. If we use the Warburg[3] value of the constant c_2 of the radiation law, $c_2 = 1{\cdot}437$ cm degree and the Westphal[4] value of the constant σ in Stefan's law, $\sigma = 5{\cdot}57 \times 10^{-12}$ Watt cm^{-2} degree^{-4}, we find $h = 6{\cdot}47 \times 10^{-27}$ erg sec. Using for σ the average value of the latest measurements, $\sigma = 5{\cdot}70 \times 10^{-12}$, we find $h = 6{\cdot}62 \times 10^{-27}$. Both values agree with ours within the limits given.

These results lead to new questions, the answers to which will have to be given by later experiments, which we are to some extent preparing. The interesting experiments of Gehrcke and Seeliger[5] and of Holm[6] show that the situation is far less simple for higher electron velocities. According to Gehrcke and Seeliger, even electrons of about 10 Volt excite visible light in mercury vapour. It would be of great interest to extend these investigations to the ultraviolet region. One should also investigate whether for other metal vapours and for the inert gases a similar radiation occurs the wavelength of which can be evaluated from the energy of the electrons which transfer the energy in inelastic collisions. The easiest would probably be to study alkali metal vapours.

Summary

The results of our two papers on the collisions between electrons and mercury atoms can be summarised as follows:

1. The electrons are reflected by the mercury atoms without energy loss, as long as their kinetic energy is less than the amount $h\nu$, where ν is the frequency corresponding to the resonance line.

2. As soon as the kinetic energy of an electron has reached the value $h\nu$, this energy quantum is transferred in one of the subsequent collisions to the spectrum of frequency ν, present in the atom.

3. The energy transferred is partly used for ionisation and partly emitted as radiation of light with a frequency ν.

4. The quantity *h* turns out to be according to these experiments equal to $6{\cdot}59 \times 10^{-27}$ erg sec with a possible error of 2 percent.

Part of the apparatus used was bought from a grant from the Solvay Foundation, for which we express our gratitude.

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7 On the Quantum Theory of Radiation†

A. EINSTEIN

THE formal similarity of the curve of the chromatic distribution of black-body radiation and the Maxwell velocity-distribution is too striking to be hidden for long. Indeed, already Wien in his important theoretical paper in which he derived his displacement law

$$\rho = \nu^3 f(\nu/T) \tag{1}$$

was led by this similarity to a further determination of the radiation formula. It is well known that he then found the formula

$$\rho = \alpha\nu^3 e^{-h\nu/kT}, \tag{2}$$

which is also nowadays accepted as being correct as a limiting law for large values of ν/T (Wien's radiation law). We know nowadays that no considerations based on classical mechanics and electrodynamics can give us a usable radiation formula, and that classical theory necessarily leads to the Rayleigh formula

$$\rho = \frac{k\alpha}{h}\nu^2 T. \tag{3}$$

As soon as Planck in his classical investigation based his radiation formula

$$\rho = \alpha\nu^3 \frac{1}{e^{h\nu/kT} - 1} \tag{4}$$

on the assumption of discrete elements of energy, from which very

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† *Physikalische Zeitschrift* **18**, 121 (1917).

quickly quantum theory developed, it was natural that Wien's discussion which led to equation (2) became forgotten.

Recently[1]† I found a derivation of Planck's radiation formula which is based upon the basic assumption of quantum theory and which is related to Wien's original considerations; in this derivation, the relationship between the Maxwell distribution and the chromatic black-body distribution plays a role. This derivation is of interest not only because it is simple, but especially because it seems to clarify somewhat the at present unexplained phenomena of emission and absorption of radiation by matter. I have shown, on the basis of a few assumptions about the emission and absorption of radiation by molecules, which are closely related to quantum theory, that molecules distributed in temperature equilibrium over states in a way which is compatible with quantum theory are in dynamic equilibrium with the Planck radiation. In this way, I deduced in a remarkably simple and general manner Planck's formula (4). It was a consequence of the condition that the distribution of the molecules over the states of their internal energy, which is required by quantum theory, must be established solely through the absorption and emission of radiation.

If the assumptions about the interaction between radiation and matter which we have introduced are essentially correct, they must, however, yield more than the correct statistical distribution of the internal energy of the molecules. In fact, in absorption and emission of radiation, momentum is transferred to the molecules; this entails that merely through the interaction of radiation and molecules the velocities of the molecules will acquire a certain distribution. This must clearly be the same velocity distribution as the one which the molecules attain through the action of their mutual collisions alone, that is, it must be the same as the Maxwell distribution. We must require that the average kinetic energy (per degree of freedom) which a molecule acquires in the Planck radiation field of temperature T is equal to $\frac{1}{2}kT$; this must be true independent of the nature of the molecules considered and independent of the frequencies of the light emitted or absorbed by

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† The considerations given in that paper are repeated in the present one.

them. In the present paper, we want to show that our simple hypotheses about the elementary processes of emission and absorption obtain another support.

In order to obtain the above-mentioned result we must, however, complete to some extent the hypotheses upon which our earlier work was based, as the earlier hypotheses were concerned only with the exchange of energy. The question arises: does the molecule receive an impulse when it absorbs or emits the energy ε? Let us, for instance, consider the emission from the point of view of classical electrodynamics. If a body emits the energy ε, it receives a recoil (momentum) ε/c if all of the radiation ε is emitted in the same direction. If, however, the emission takes place as an isotropic process, for instance, in the form of spherical waves, no recoil at all occurs. This alternative also plays a role in the quantum theory of radiation. When a molecule during a transition from one quantum-theoretically possible state to another absorbs or emits energy ε in the form of radiation, such an elementary process can be thought of either as being a partially or completely directed or as being a symmetrical (non-directional) process. *It now turns out that we arrive at a consistent theory only, if we assume each elementary process to be completely directional.* This is the main result of the following considerations.

1. Basic Hypothesis of Quantum Theory.
Canonical Distribution over States

According to quantum theory, a molecule of a given kind can take up—apart from its orientation and its translational motion—only a discrete set of states $Z_1, Z_2, \ldots, Z_n, \ldots$ with (internal) energies $\varepsilon_1, \varepsilon_2, \ldots, \varepsilon_n, \ldots$. If molecules of this kind form a gas of temperature T, the relative occurrence W_n of these states Z_n is given by the formula giving the canonical distribution of statistical mechanics:

$$W_n = p_n e^{-\varepsilon_n/kT}. \tag{5}$$

In this equation $k = R/N$ is the well-known Boltzmann constant, and p_n a number which is characteristic for the molecule and its

nth quantum state and which is independent of T; it can be called the statistical "weight" of the state. One can derive equation (5) either from Boltzmann's principle or by purely thermodynamic means. Equation (5) expresses the greatest generalisation of Maxwell's velocity distribution law.

Recent important progress in quantum theory relates to the theoretical determination of quantum theoretically possible states Z_n and their weight p_n. For our considerations of the principles involved in radiation, we do not need a detailed determination of the quantum states.

2. Hypotheses about Energy Exchange through Radiation

Let Z_n and Z_m be two quantum-theoretically possible states of the gas molecule, and let their energies ε_n and ε_m satisfy the inequality $\varepsilon_m > \varepsilon_n$. Let the molecule be able to make a transition from the state Z_n to the state Z_m by absorbing radiative energy $\varepsilon_m - \varepsilon_n$; similarly let a transition from Z_m to Z_n be possible in which this radiative energy is emitted. Let the frequency of the radiation absorbed or emitted by the molecule in such transitions be ν; it is characteristic for the combination (m, n) of the indices.

We make a few hypotheses about the laws valid for this transition; these are obtained by using the relations known from classical theory for a Planck resonator, as the quantum-theoretical relations which are as yet unknown.

(a) *Spontaneous emission.*† It is well known that a vibrating Planck resonator emits according to Hertz energy independent of whether it is excited by an external field or not. Accordingly, let it be possible for a molecule to make without external stimulation a transition from the state Z_m to the state Z_n while emitting the radiation energy $\varepsilon_m - \varepsilon_n$ of frequency ν. Let the probability dW that this will in fact take place in the time interval dt be

$$dW = A_m^n \, dt, \tag{A}$$

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† Einstein uses *Ausstrahlung* and *Einstrahlung* for spontaneous emission and induced radiation [D. t. H.].

where A_m^n denotes a constant which is characteristic for the combination of indices considered.

The statistical law assumed here corresponds to the law of a radioactive reaction, and the elementary process assumed here corresponds to a reaction in which only γ-rays are emitted. It is not necessary to assume that this process takes place instantaneously; it is only necessary that the time this process takes is negligible compared with the time during which the molecule is in the state $Z_1, \ldots$.

(b) *Induced radiation processes.* If a Planck resonator is in a radiation field, the energy of the resonator can be changed by the transfer of energy from the electromagnetic field to the resonator; this energy can be positive or negative depending on the phases of the resonator and of the oscillating field. Accordingly we introduce the following quantum-theoretical hypothesis. Under the influence of a radiation density ρ of frequency ν a molecule can make a transition from the state Z_n to the state Z_m by absorbing the radiative energy $\varepsilon_m - \varepsilon_n$ and the probability law for this process is

$$dW = B_n^m \rho \, dt. \tag{B}$$

Similarly, a transition $Z_m \rightarrow Z_n$ may also be possible under the influence of the radiation; in this process the radiative energy $\varepsilon_m - \varepsilon_n$ will be freed according to the probability law

$$dW = B_m^n \rho \, dt. \tag{B'}$$

The B_n^m and B_m^n are constants. These two processes we shall call "changes in state, induced by radiation".

The question now arises: what is the momentum transferred to the molecule in these changes in state? Let us begin with the induced processes. If a radiation beam with a well-defined direction does work on a Planck resonator, the corresponding energy is taken from the beam. According to the law of conservation of momentum, this energy transfer corresponds also to a momentum transfer from the beam to the resonator. The resonator is thus subject to the action of a force in the direction of the beam. If the energy transferred is negative, the action of the force on the resonator is also in the opposite direction. This means clearly the following in the case of the quantum hypothesis. If through the irradiation by a beam of light a transition $Z_n \rightarrow Z_m$ is induced, the momentum $(\varepsilon_m - \varepsilon_n)/c$ is transferred to the molecule in the direction of propagation of the beam. In the induced transition $Z_m \rightarrow Z_n$ the transferred momentum has the same magnitude but is in the opposite direction. We assume that in the case where the molecule is simultaneously subjected to several radiation beams, the total energy $\varepsilon_m - \varepsilon_n$ of an elementary process is absorbed from or added to *one* of these beams, so that also in that case the momentum $(\varepsilon_m - \varepsilon_n)/c$ is transferred to the molecule.

In the case of a Planck resonator, when the energy is emitted through a spontaneous emission process, no momentum is transferred to the resonator, since according to classical theory the emission is in the form of a spherical wave. We have, however, already noted that we can only obtain a consistent quantum theory by assuming that the spontaneous emission process is also a directed one. In that case, in each spontaneous emission elementary process $(Z_m \rightarrow Z_n)$ momentum of magnitude $(\varepsilon_m - \varepsilon_n)/c$ is transferred to the molecule. If the molecule is isotropic, we must assume that all directions of emission are equally probable. If the molecule is not isotropic, we arrive at the same statement if the orientation changes in a random fashion in time. We must, of course, make a similar assumption for the statistical laws (B) and (B′) for the induced processes, as otherwise the constants should depend on direction, but we can avoid this through the assumption of isotropy or pseudo-isotropy (through time-averaging) of the molecule.

3. Derivation of the Planck Radiation Law

We now ask for that radiation density ρ which must be present in order that the exchange of energy between radiation and molecules according to the statistical laws (A), (B), and (B′) does not perturb the distribution (5) of the molecules. For this it is necessary and sufficient that on the average per unit time as many elementary processes of type (B) take place as of types (A) and (B′) combined. This combination leads, because of (5), (A), (B), and (B′), to the following equation for the elementary processes corresponding to the index combination (m, n):

$$p_n e^{-\varepsilon_n/kT} B_n^m \rho = p_m e^{-\varepsilon_m/kT} (B_m^n \rho + A_m^n).$$

If, furthermore, ρ will increase to infinity with T, as we shall assume, the following relation must exist between the constants B_n^m and B_m^n:

$$p_n B_n^m = p_m B_m^n. \tag{6}$$

We then obtain from our equation the following condition for dynamic equilibrium:

$$\rho = \frac{A_m^n / B_m^n}{e^{(\varepsilon_m - \varepsilon_n)/kT} - 1}. \tag{7}$$

This is the temperature-dependence of the radiation density of the Planck law. From Wien's displacement law (1) it follows from this immediately that

$$\frac{A_m^n}{B_m^n} = \alpha \nu^3, \tag{8}$$

and

$$\varepsilon_m - \varepsilon_n = h\nu, \tag{9}$$

where α and h are constants. To find the numerical value of the constant α, we should have an exact theory of the electrodynamic and mechanic processes; for the time being we must use the Rayleigh limit of high temperatures, for which the classical theory is valid as a limiting case.

Equation (9) is, of course, the second main hypothesis of Bohr's theory of spectra of which we can now state after Sommerfeld's and Epstein's extensions that it belongs to those parts of our science which are sure. It contains implicitly, as I have shown, also the photochemical equivalence rule.

4. Method of Calculating the Motion of Molecules in the Radiation Field

We now turn to the investigation of the motions which our molecules execute under the influence of the radiation. To do this, we use a method which is well known from the theory of Brownian motion, and which I have used already many times for numerical calculations of motion in radiation. To simplify the calculations, we only perform them for the case where the motion takes place only in one direction, the X-direction of our system or coordinates. We shall moreover restrict ourselves to calculating the average value of the kinetic energy of the translational motion, and thus do not give the proof that these velocities v are distributed according to Maxwell's law. Let the mass M of the molecule be sufficiently large that we can neglect higher powers of v/c in comparison with lower ones; we can then apply ordinary mechanics to the molecule. Moreover, without any real loss of generality, we can perform our calculations as if the states with indices m and n were the only ones which the molecule can take on.

The momentum Mv of a molecule is changed in two ways in the short time τ. Although the radiation is the same in all directions, because of its motion the molecule will feel a force acting in the opposite direction of its motion which comes from the radiation. Let this force be Rv, where R is a constant to be evaluated later on. This force would bring the molecule to rest, if the irregularity of the action of the radiation did not have as a consequence that during the time τ a momentum Δ of varying sign and varying magnitude is transferred to the molecule; this unsystematic influence will against the earlier mentioned force maintain a certain motion of the molecule. At the end of the short time τ, which we are considering, the momentum of the molecule will have the value

$$Mv - Rv\tau + \Delta.$$

As the velocity distribution must remain the same in time, this quantity must have the same average absolute magnitude as Mv; therefore, the average squares of those two quantities, averaged over a long period or over a large number of molecules, must be equal to one another:

$$\overline{(Mv-Rv\tau+\Delta)^2} = \overline{(Mv)^2}.$$

As we have separately taken into account the systematic influence of v on the momentum of the molecule, we must neglect the average $\overline{\Delta v}$. Expanding the left-hand side of the equation, we get then

$$\overline{\Delta^2} = 2RM\overline{v^2}\tau. \tag{10}$$

The average $\overline{v^2}$ for our molecules, which is caused by radiation of temperature T through its interaction with the molecules must be equal to the average value $\overline{v^2}$, which according to the kinetic theory of gases a molecule in the gas would have according to the gas laws at the temperature T. Otherwise, the presence of our molecules would disturb the thermodynamic equilibrium between black-body radiation and any gas of the same temperature. We must then have

$$\tfrac{1}{2}\overline{Mv^2} = \tfrac{1}{2}kT. \tag{11}$$

Equation (10) thus becomes

$$\frac{\overline{\Delta^2}}{\tau} = 2RkT. \tag{12}$$

The investigation must now proceed as follows. For given radiation $[\rho(\nu)]$ we can calculate Δ^2 and R with our hypotheses about the interaction between radiation and molecules. Inserting these results into (12), this equation must be satisfied identically if ρ as function of ν and T is expressed by the Planck equation (4).

5. Calculation of R

Let a molecule of the kind considered move uniformly with velocity v along the X-axis of the system of coordinates K. We ask for the average momentum transferred by the radiation to the molecule per unit time. To be able to evaluate this, we must consider the radiation in a system of coordinates K' which is at rest relative to the molecule under consideration, because we have only formulated our hypotheses about emission and absorption for molecules at rest. The transformation to the system K' has often been given in the literature and especially accurately in Mosengeil's Berlin thesis.[2] For the sake of completeness, I shall, however, repeat the simple considerations.

In K the radiation is isotropic, that is, we have for the radiation per unit volume in a frequency range $d\nu$ and propagating in a direction within a given infinitesimal solid angle $d\kappa$:

$$\rho\, d\nu \frac{d\kappa}{4\pi}, \tag{13}$$

where ρ depends only on the frequency ν, but not on the direction. This particular radiation corresponds in the coordinate system K' to a particular radiation, which is also characterised by a frequency range $d\nu'$ and a certain solid angle $d\kappa'$. The volume density of this particular radiation is

$$\rho'(\nu', \phi')\, d\nu' \frac{d\kappa'}{4\pi}. \tag{13'}$$

This defines ρ'. It depends on the direction which is defined in the usual way by the angle ϕ' with the X'-axis and the angle ψ' between the projection in the $Y'Z'$-plane with the Y'-axis. These angles correspond to the angles ϕ and ψ which in a similar manner fix the direction of $d\kappa$ with respect to K.

First of all it is clear that the same transformation law must be valid between (13) and (13′) as between the squares of the amplitude A^2 and A'^2 of a plane wave of the appropriate direction of propagation. Therefore in the approximation we want, we have

$$\frac{\rho'(\nu', \phi')\, d\nu'\, d\kappa'}{\rho(\nu)\, d\nu\, d\kappa} = 1 - 2\frac{v}{c}\cos\phi, \tag{14}$$

or

$$\rho'(\nu', \phi') = \rho(\nu) \frac{d\nu}{d\nu'} \frac{d\kappa}{d\kappa'} \left(1 - 2\frac{v}{c}\cos\phi\right). \tag{14'}$$

The theory of relativity further gives the following formulae, valid in the approximation needed here,

$$\nu' = \nu\left(1-\frac{v}{c}\cos\phi\right), \tag{15}$$

$$\cos\phi' = \cos\phi-\frac{v}{c}+\frac{v}{c}\cos^2\phi, \tag{16}$$

$$\psi' = \psi. \tag{17}$$

From (15) in the same approximation it follows that

$$\nu = \nu'\left(1+\frac{v}{c}\cos\phi'\right).$$

Therefore, also in the same approximation,

$$\rho(\nu) = \rho\left(\nu'+\frac{v}{c}\nu'\cos\phi'\right),$$

or

$$\rho(\nu) = \rho(\nu')+\frac{\partial\rho(\nu')}{\partial\nu}\frac{v}{c}\nu'\cos\phi'. \tag{18}$$

Furthermore from (15), (16), and (17) we have

$$\frac{d\nu}{d\nu'} = 1+\frac{v}{c}\cos\phi',$$

$$\frac{d\kappa}{d\kappa'} = \frac{\sin\phi\, d\phi\, d\psi}{\sin\phi'\, d\phi'\, d\psi'} = \frac{d(\cos\phi)}{d(\cos\phi')} = 1-2\frac{v}{c}\cos\phi'.$$

Using these two relations and (18), we get from (14′)

$$\rho(\nu',\phi') = \left[\rho(\nu)+\frac{v}{c}\nu'\cos\phi'\frac{\partial\rho(\nu)}{\partial\nu}\right]\left(1-3\frac{v}{c}\cos\phi'\right). \tag{19}$$

From (19) and our hypothesis about the spontaneous emission and the induced processes of the molecule, we can easily calculate the average momentum transferred per unit time to the molecule. Before doing this we must, however, say something to justify the method used. One can object that the equations (14), (15), and (16) are based upon Maxwell's theory of the electromagnetic field which is incompatible with quantum theory. This objection, however, touches the form rather than the essence of the matter. Whatever the form of the theory of electromagnetic processes, surely in any case the Doppler principle and the aberration law will remain valid, and thus also equations (15) and (16). Furthermore, the validity of the energy relation (14) certainly extends beyond that of the wave theory; this transformation law is, for instance, also valid according to the theory of relativity for the energy density of a mass having an infinitesimal rest mass and moving with (quasi-) light-velocity. We can thus claim the validity of equation (19) for any theory of radiation.

The radiation corresponding to the spatial angle $d\kappa'$ will according to (B) lead per second to

$$B_n^m \rho'(\nu', \phi') \frac{d\kappa'}{4\pi}$$

induced elementary processes of the type $Z_n \rightarrow Z_m$, provided the molecule is brought back to the state Z_n immediately after each such elementary process. In reality, however, the time spent per second in the state Z_n is according to (5) equal to

$$\frac{1}{S} p_n e^{-\varepsilon_n/kT},$$

where we used the abbreviation

$$S = p_n e^{-\varepsilon_n/kT} + p_m e^{-\varepsilon_m/kT}. \tag{20}$$

In actual fact the number of these processes per second is thus

$$\frac{1}{S} p_n e^{-\varepsilon_n/kT} B_n^m \rho'(\nu', \phi') \frac{d\kappa'}{4\pi}.$$

In each process the momentum

$$\frac{\varepsilon_m - \varepsilon_n}{c} \cos \phi'$$

is transferred to the molecule in the direction of the positive X'-axis. Similarly, we find, using (B') that the corresponding number of induced elementary processes of the kind $Z_m \rightarrow Z_n$ per second is

$$\frac{1}{S} p_m e^{-\varepsilon_m/kT} B_m^n \rho'(\nu', \phi') \frac{d\kappa'}{4\pi},$$

and in each such elementary process the momentum

$$-\frac{\varepsilon_m - \varepsilon_n}{c} \cos\phi'$$

is transferred to the molecule. The total momentum transferred per unit time to the molecule through induced processes is thus, taking (6) and (9) into account,

$$\frac{h\nu'}{cS} p_n B_n^m (e^{-\varepsilon_n/kT} - e^{-\varepsilon_m/kT}) \int \rho'(\nu', \phi') \cos\phi' \frac{d\kappa'}{4\pi},$$

where the integration is over all elements of solid angle. Performing the integration we get, using (19), the value

$$-\frac{h\nu}{c^2 S}\left(\rho - \tfrac{1}{3}\nu \frac{\partial \rho}{\partial \nu}\right) p_n B_n^m (e^{-\varepsilon_n/kT} - e^{-\varepsilon_m/kT}) v.$$

Here we have denoted the frequency involved by ν (instead of ν').

This expression represents, however, the total average momentum transferred per unit time to a molecule moving with a velocity v; because it is clear that the spontaneous emission processes which take place without the action of radiation do not have a preferential direction, considered in the system K', so that they can on average not transfer any momentum to the molecule. We obtain thus as the final result of our considerations:

$$R = \frac{h\nu}{c^2 S}\left(\rho - \tfrac{1}{3}\nu \frac{\partial \rho}{\partial \nu}\right) p_n B_n^m e^{-\varepsilon_n/kT} (1 - e^{-h\nu/kT}). \qquad (21)$$

6. Calculation of $\overline{\Delta^2}$

It is much simpler to calculate the influence of the irregularity of the elementary processes on the mechanical behaviour of the molecule, as we can base this calculation on a molecule at rest in the approximation which we have used from the start.

Let some event lead to the transfer of a momentum λ in the X-direction to a molecule. Let this momentum have varying sign and varying magnitude in different cases, but let there be such a statistical law for λ that the average value of λ vanishes. Let now $\lambda_1, \lambda_2, \ldots$ be the values of the momentum in the X-direction transferred to the molecule through several, independently acting causes so that the resultant transfer of momentum Δ is given by

$$\Delta = \Sigma \lambda_v.$$

As the average value $\overline{\lambda_v}$ vanishes for the separate λ_v, we must have

$$\overline{\Delta^2} = \Sigma \overline{\lambda_v^2}. \tag{22}$$

If the averages $\overline{\lambda_v^2}$ of the separate momenta are equal to one another ($= \overline{\lambda^2}$), and if l is the total number of momentum transferring processes, we have the relation

$$\overline{\Delta^2} = l \overline{\lambda^2}. \tag{22a}$$

According to our hypothesis in each elementary process, induced or spontaneous, the momentum

$$\lambda = \frac{h\nu}{c} \cos \phi$$

is transferred to the molecule. Here ϕ is the angle between the X-axis and a direction chosen randomly. Therefore we have

$$\overline{\lambda^2} = \frac{1}{3}\left(\frac{h\nu}{c}\right)^2. \tag{23}$$

As we assume that we may take all elementary processes which take place to be independent of one another, we may apply (22a). In that case, l is the number of all elementary processes taking place during the time τ. This is twice the number of the number of induced processes $Z_n \rightarrow Z_m$ during the time τ. We have thus

$$l = \frac{2}{S} p_n B_n^m e^{-\varepsilon_n/kT} \rho\tau. \tag{24}$$

We get from (23), (24), and (22)

$$\frac{\overline{\Delta^2}}{\tau} = \frac{2}{3S}\left(\frac{h\nu}{c}\right)^2 p_n B_n^m e^{-\varepsilon_n/kT} \rho. \tag{25}$$

7. Results

To prove now that the momenta transferred by the radiation to the molecules in accordance with our hypotheses never disturb the thermodynamic equilibrium, we only need to substitute the values (25) and (21) for $\overline{\Delta^2}/\tau$ and R which we have calculated after we have used (4) to replace in (21) the quantity

$$\left(\rho - \tfrac{1}{3}\nu\frac{\partial\rho}{\partial\nu}\right)(1 - e^{-h\nu/kT})$$

by $\rho h\nu/3kT$. It then turns out immediately that our fundamental equation (12) is identically satisfied.

The considerations which are now finished give strong support for the hypotheses given in Section 2 about the interaction between matter and radiation through absorption and emission processes, that is, through spontaneous and induced radiation processes. I was led to these hypotheses by my attempt to postulate as simply as possible a quantum theoretical behaviour of the molecules which would be similar to the behaviour of a Planck resonator of the classical theory. I obtained then in a natural fashion from the general quantum assumption for matter the second Bohr rule (equation (9)) as well as the Planck radiation formula.

The most important result seems to me, however, to be the one about the momentum transferred to the molecule in spontaneous or induced radiation processes. If one of our assumptions about this momentum transfer is changed, this would lead to a violation of equation (12); it seems hardly possible to remain in agreement with this relation which is required by the theory of heat otherwise than on the basis of our assumptions. We can thus consider the following as rather certainly proved.

If a ray of light causes a molecule hit by it to absorb or emit through an elementary process an amount of energy $h\nu$ in the form of radiation (induced radiation process), the momentum $h\nu/c$ is always transferred to the molecule, and in such a way that the momentum is directed along the direction of propagation of the ray if the energy is absorbed, and directed in the opposite direction, if the energy is emitted. If the molecule is subjected to the action of several directed rays of light, always only one of them will participate in an induced elementary process; this ray alone defines then the direction of the momentum transferred to the molecule.

If the molecule undergoes a loss of energy of magnitude $h\nu$ without external influence, by emitting this energy in the form of radiation (spontaneous emission), this process is also a *directed one*. There is no emission in spherical waves. The molecule suffers in the spontaneous elementary process a recoil of magnitude $h\nu/c$ in a direction which is in the present state of the theory determined only by "chance".

These properties of the elementary processes required by equation (12) make it seem practically unavoidable that one must construct an essentially quantum theoretical theory of radiation. The weakness of the theory lies, on the one hand, in the fact that it does not bring any nearer the connexion with the wave theory and, on the other hand, in the fact that it leaves moment and direction of the elementary processes to "chance"; all the same, I have complete confidence in the reliability of the method used here.

Still one more general remark may be made here. Practically all theories of black-body radiation are based on a consideration of the interaction between radiation and molecules. However, in general one restricts oneself to considering energy-exchange, without taking momentum-exchange into account. One feels easily justified in this as the smallness of the momenta transferred by the radiation entails that these momenta are practically always in reality negligible compared to other processes causing a change in motion. However, for the *theoretical* discussion, these small actions must be considered to be completely as important as the obvious actions of the *energy*-exchange through radiation, as energy and momentum are closely connected; one can, therefore, consider a theory to be justified only when it is shown that according to it the momenta transferred by the radiation to the matter lead to such motion as is required by the theory of heat.

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8 On the Connexion between the Completion of Electron Groups in an Atom with the Complex Structure of Spectra[†]

W. PAULI

ESPECIALLY in connexion with Millikan and Landé's observation that the alkali doublet can be represented by relativistic formulae and with results obtained in an earlier paper, it is suggested that this doublet and its anomalous Zeeman effect expresses a classically non-describable two-valuedness of the quantum theoretical properties of the optically active electron,[‡] without any participation of the closed rare gas configuration of the atom core in the form of a core angular momentum or as the seat of the magneto-mechanical anomaly of the atom. We then attempt to pursue this point of view, taken as a temporary working hypothesis, as far as possible in its consequences also for atoms other than the alkali atoms, notwithstanding its difficulties from the point of view of principle. First of all it turns out that it is possible, in contrast to the usual ideas, to assign for the case of a strong external magnetic field, which is so strong that we can neglect the coupling between the atomic core and the optically active electrons, to those two systems, as far as the number of their stationary states, the values of their quantum numbers, and their magnetic energy is concerned, no other properties than those of the free atomic core of the optically active electron of the alkalis. On the basis of these results one is also led to a general classification of every electron in the atom by the principal quantum number n and *two* auxiliary quantum numbers k_1 and k_2 to which is added a further quantum number m_1 in the presence of an external field. In conjunction with a recent paper by E. C. Stoner this classification leads to a general quantum theoretical formulation of the completion of electron groups in atoms.

[†] *Z. Physik* **31**, 765 (1925). A few footnotes have been omitted in this translation.

[‡] In German: *Leuchtelektron*.

1. The Permanence of Quantum Numbers (Principle of Gradual Construction)† in Complex Structures and the Zeeman Effect

In a previous paper[1] it was emphasised that the usual ideas, according to which the inner, completed electron shells of an atom play an essential part in the complex structure of optical spectra and their anomalous Zeeman effect in the shape of core angular momenta and as the real seat of the magneto-mechanical anomaly, are subject to several serious difficulties. It seems therefore plausible to set against these ideas that especially the doublet structure of the alkali spectra and their anomalous Zeeman effect are caused by a classically undescribable two-valuedness of the quantum theoretical properties of the optically active electron. This idea is particularly based upon the results of Millikan and Landé that the optical doublets of the alkalis are similar to the relativity doublets in X-ray spectra and that their magnitude is determined by a relativistic formula.

If we now pursue this point of view, we shall assign—as was done by Bohr and Coster for the X-ray spectra—to the stationary states of the optically active electron involved in the emission of the alkali spectra two auxiliary quantum numbers k_1 and k_2 as well as the principal quantum number n. The first quantum number k_1 (usually simply denoted by k) has the values $1, 2, 3, \ldots$ for the $s, p, d, \ldots$ terms and changes by unity in the allowed transition processes; it determines the magnitude of the central force interaction forces of the valence electron with the atom core. The second quantum number k_2 is for the two terms of a doublet (e.g., p_1 and p_2) equal to $k_1 - 1$ and k_1, in the transition processes it changes by ± 1 or 0 and determines the magnitude of the relativity correction (which is modified according to Landé to take into account the penetration of the optically active electron in the atom core). If we follow Sommerfeld to define the total angular momentum quantum number j of an atom in general as

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† In German: *Aufbauprinzip*.

the maximum value of the quantum number m_1 (usually simply denoted by m) which determines the component of the angular momentum along an external field, we must put $j = k_2 - \frac{1}{2}$ for the alkalis. The number of stationary states in a magnetic field for given k_1 and k_2 is $2j+1 = 2k_2$, and the number of these states for both doublet terms with given k_1 is altogether $2(2k_1 - 1)$.

If we now consider the case of strong field (Paschen–Back effect), we can introduce apart from k_1 and the just mentioned quantum number m_1, instead of k_2 also a magnetic quantum number m_2 which determines directly the energy of the atom in the magnetic field, that is, the component of the magnetic moment of the valence electron parallel to the field. For the two terms of the doublet it has, respectively, the values $m_1 + \frac{1}{2}$ and $m_1 - \frac{1}{2}$. Just as in the doublet structure of the alkali spectra the "anomaly of the relativity correction" is expressed (the magnitude of which is mainly determined by another quantum number, as is the magnitude of the central force interaction energy of the optically active electron and the atom core), so appears in the deviations of Zeeman structure from the normal Lorentz triplet the "magneto-mechanical anomaly" which is similar to the other anomaly (the magnitude of the magnetic moment of the optically active electron is mainly determined by another quantum number, as is the angular momentum). Clearly, the appearance of half-odd-integral (effective) quantum numbers and the thereby formally caused value $g = 2$ of the splitting factor of the s-term of the alkalis is closely connected with the two-foldness of the energy level. We shall here, however, not attempt a more detailed theoretical analysis of this state of affairs and use the following considerations of the Zeeman effect of the alkalis as empirical data.

Without worrying about the difficulties encountered by our point of view, which we shall mention presently, we now try to extend this formal classification of the optically active electron by four quantum numbers n, k_1, k_2, m_1 to atoms, more complex than the alkalis. *It now turns out that we can retain completely on the basis of this classification the principle of permanence of quantum numbers* (*Aufbauprinzip*) *also for the complex structure of the* *spectra and the anomalous Zeeman effect in contrast to the usual ideas.* This principle, due to Bohr, states that when a further electron is added to a—possibly charged—atom, the quantum numbers of the electrons which are already bound to the atom retain the same values as correspond to the appropriate state of the free atom core.

Let us first of all consider the alkaline earths. The spectrum consists in this case of a singlet and a triplet system. The quantum states with a well-defined value of the quantum number k_1 of the optically active electron correspond then for the first system to altogether $1(2k_1-1)$ and in the last system to $3(2k_1-1)$ stationary states in an external magnetic field. Up to now this was interpreted as meaning that in strong fields the optically active electron in each case could take up $2k_1-1$ positions, while the atom core was able to take up in the first case one, and in the last case three positions. The number of these positions is clearly different from the number 2 of the positions of the free atom core (alkali-like s-term) in a field. Bohr[2] called this state of affairs a "constraint"† which is not analogous to the action of external fields of force. Now, however, we can simply interpret the total $4(2k_1-1)$ states of the atom as meaning that the atom core always has two positions in a field, and the optically active electron as for the alkalis $2(2k_1-1)$ states.

More generally, a branching rule formulated by Heisenberg and Landé[3] states that a stationary state of the atom core with N states in a field leads through the addition of one more electron to two systems of terms, corresponding to altogether $(N+1)(2k_1-1)$ and $(N-1)(2k_1-1)$ states in a field, respectively, for a given value of the quantum number k_1 of the last electron. According to our interpretation, the $2N(2k_1-1)$ states of the complete atom in a strong field come about through N states of the atom core and $2(2k_1-1)$ states of the optically active electron. In the present quantum theoretical classification of the electrons the term multiplicity required by the branching rule is simply a consequence of the "Aufbauprinzip". According to the ideas presented here

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† In German: *Zwang.*

Bohr's constraint expresses itself not in a violation of the permanence of quantum numbers when the series electron is coupled to the atom core, but only in the peculiar two-valuedness of the quantum theoretical properties of each electron in the stationary states of an atom.

We can, however, from this point of view use the "Aufbauprinzip" to calculate not only the number of stationary states, but also *the energies in the case of strong fields* (at least that part which is proportional to the field) *additively from those of the free atom core and of the optically active electron,* where the latter can be taken from the alkali spectra. Because, in this case, both the total component $\overline{m_1}$ of the angular momentum of the atom along the field (in units $\hbar$) as well as the component $\overline{m_2}$ of the magnetic moment of the atom in the same direction (in Bohr magnetons) are equal to the sum of the quantum numbers m_1 and m_2 of the single electrons:

$$\overline{m_1} = \Sigma m_1, \qquad \overline{m_2} = \Sigma m_2. \tag{1}$$

The latter can independently run through all values corresponding to the values of the angular momentum quantum numbers k_1 and k_2 of the electrons in the stationary state of the atom considered. ($\overline{m_2}\, oh$ is here thus the part of the energy of the atom proportional to the field strength; o = Larmor frequency.)

Let us consider as an example the two s-terms (singlet- and triplet S-term) of the alkaline earths. To begin with it is sufficient to consider only the two valence electrons, as the contribution of the other electrons to the sums in (1) vanish when taken together. According to our general assumption we must for each of the two valence electrons take (independently of the other electron) the values $m_1 = -\frac{1}{2}$, $m_2 = -1$ and $m_1 = \frac{1}{2}$, $m_2 = 1$ of the s-terms of the alkalis. According to (1) we then get the following values for the quantum numbers $\overline{m_1}$ and $\overline{m_2}$ of the total atom:

$$\overline{m_1} = -\tfrac{1}{2}-\tfrac{1}{2},\ -\tfrac{1}{2}+\tfrac{1}{2},\ +\tfrac{1}{2}-\tfrac{1}{2},\ +\tfrac{1}{2}+\tfrac{1}{2}$$

$$\overline{m_2} = -1-1,\ -1+1,\ 1-1,\ 1+1,$$

or

$\overline{m_1} = -1$	0	1
$\overline{m_2} = -2$	0, 0	2

,

[Corresponding to one term with $j = 0$ and one with $j = 1$ in weak fields.]† To obtain the *p*-, *d*-, ... terms of the alkaline earths, one must combine in (1) the unchanged contribution of the first valence electron (*S*-term) in an appropriate manner with the m_1- and m_2-values of the *p*-, *d*-, ... terms of the alkalis for the second electron.

The rule (1) leads in general exactly to the procedure for calculating the energy values in strong field proposed recently by Landé[4] which has been shown by this author to give correct results also in complicated cases. According to Landé this procedure leads, for instance, to the correct Zeeman terms of neon (at least in the case of strong fields) if one assumes‡ that in the atom core there is one active electron in a *p*-term (instead of in an *s*-term as above) and if one lets the optically active electron go through *s*-, *p*-, *d*-, *f*-, ... terms.

This result now suggests that we *characterise in general each electron in an atom not only by a principal quantum number n, but also by the two auxiliary quantum numbers k_1 and k_2*, even when several equivalent electrons or completed electron groups are present. Moreover, we shall allow (also in the just-mentioned cases) in our thoughts *such a strong magnetic field that we can assign to each electron, independently of the other electrons not only the quantum numbers n and k_1, but also the two quantum numbers m_1 and m_2* (where the last one determines the contribution of the

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† One notes that one must assign to the two cases $m_1 = -\frac{1}{2}$ for the first and $m_2 = \frac{1}{2}$ for the second electron, or $m_1 = +\frac{1}{2}$ for the first and $m_2 = -\frac{1}{2}$ for the second electron two different terms (as far as the part of the energy independent of the field is concerned). This is perhaps a blemish of the classification given here. It will later on, however, turn out that if the inner and the outer valence electron are equivalent, these two terms are in fact identical.

‡ The replacement here of a seven-shell (atom core of neon) by *one* electron will be given a theoretical basis in the next section.

electron to the magnetic energy of the atom). The connexion between k_2 and m_2 for given k_1 and m_1 must be taken from the alkali spectra.

Before we apply in the next section this quantum theoretical classification of the electrons in an atom to the problem of the completion of the electron groups, we must discuss in more detail the difficulties encountered by the here-proposed ideas of the complex structure and the anomalous Zeeman effect and the limitations of the meaning of our ideas.

First of all, these ideas do not pay proper regard to the, in many respects independent, separate appearance of the different term systems (e.g., the singlet and the triplet systems of the alkaline earths), which also play a role in the position of the terms of these systems and in the Landé interval rule. Certainly, one cannot assume two different causes for the energy differences of the triplet levels of the alkaline earths, both the anomaly of the relativity correction of the optically active electron and the dependence of the interaction between the electron and the atom core on the relative orientation of these two systems.

A more serious difficulty, raising a matter of principle, is however the connexion of these ideas with the correspondence principle which is well known to be a necessary means to explain the selection rules for the quantum numbers k_1, j, and m and the polarisation of the Zeeman components. It is, to be sure, not necessary according to this principle to assign in a definite stationary state to each electron an orbit uniquely determined in the sense of usual kinematics; however, it is necessary that the totality of the stationary states of an atom corresponds to a collection (class) of orbits with a definite type of periodicity properties. In our case, for instance, the above-mentioned selection and polarisation rules require according to the correspondence principle a kind of motion corresponding to a central force orbit on which is superposed a precession of the orbital plane around a definite axis of the atom to which is added in weak external magnetic fields also a precession around an axis through the nucleus in the direction of the field. The dynamic explanation of this kind of motion of the optically active electron, which was based upon the assumption of deviations of the forces between the atom core and the electron from central symmetry, seems to be incompatible with the possibility to represent the alkali doublet (and thus also the magnitude of the corresponding precession frequency) by relativistic formulae. The situation with respect to the kind of motion in the case of strong fields is similar.

The difficult problem thus arises *how to interpret the appearance of the kind of motion of the optically active electron which is required by the correspondence principle independently of its special dynamic interpretation which has been accepted up to now but which can hardly be retained.* There also seems to be a close connexion between this problem and the question of the magnitude of the term values of the Zeeman effect (especially of the alkali spectra).

As long as this problem remains unsolved, the ideas about the complex structure and the anomalous Zeeman effect suggested here can certainly not be considered to be a sufficient physical basis for the explanation of these phenomena, especially as they were in many respects better reproduced in the usually accepted point of view. It is not impossible that in the future one will succeed in merging these two points of view. In the present state of the problem it seemed of interest to us to pursue as far as possible also the first point of view to see what its consequences are. This is the sense in which one must consider our discussions in the next section of the application of the tentative point of view presented here to the problem of the completion of electron groups in an atom, notwithstanding the objections which can be made against it. We shall here draw conclusions only about the number of possible stationary states of an atom when several equivalent electrons are present, but not about the position and relative order of the term values.

2. On a General Quantum Theoretical Rule for the Possibility of the Occurrence of Equivalent Electrons in an Atom

It is well known that the appearance of several equivalent electrons, that is, electrons which are fully equivalent both with respect to their quantum numbers and with respect to their binding energies, in an atom is possible only under special circumstances which are closely connected with the regularities of the complex structure of spectra. For instance, the ground state of the alkaline earths in which the two valence electrons are equivalent corresponds to a singlet S-term, while in those stationary states of the atom which belong to the triplet system the valence electrons are never bound equivalently, as the lowest triplet s-term has a principal quantum number exceeding that of the ground state by unity. Let us now as second example consider the neon spectrum. This consists of two groups of terms with different series limits, corresponding to different states of the atom core. The first group, belonging to the removal of an electron with the quantum numbers $k_1 = 2$, $k_2 = 1$ from the atom core can be considered to be composed of a singlet and a triplet system, while the second group, belonging to the removal of an electron with $k_1 = k_2 = 2$ from the atom core, can be said to be a triplet and quintet system. The ultraviolet resonance lines of neon have not yet been observed, but there can hardly be any doubt that the ground state of a Ne-atom must be considered to be a p-term as far as its combination with the known excited states of the atom is concerned; in accordance with the unique definiteness and the diamagnetic behaviour of the inert gas configuration there can be only *one* such term, namely with the value $j = 0$.† As the only p-terms with $j = 0$ are the (lowest) triplet terms of the two groups, we can thus conclude that for Ne for the value 2 of the principal quantum number only those two triplet terms exist and moreover are identical for both groups of terms.

In general we can thus expect *that for those values of the quantum*

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† As already indicated, the value of j is defined here and henceforth as the maximum value of the quantum number m_1.

numbers n and k_1 for which already some electrons are present in the atom, certain multiplet terms of spectra are absent or coincide. The question arises what quantum theoretical rules decide this behaviour of the terms.

As is already clear from the example of the neon spectrum, this question is closely connected with the problem of the completion of electron groups in an atom, which determines the lengths 2, 8, 18, 32, ... of the periods in the periodic table of the elements. This completion consists in that an n-quantum electron group neither through emission or absorption of radiation nor through other external influences is able to accept more than $2n^2$ electrons.

It is well known that Bohr in his theory of the periodic table, which contains a unified summary of spectroscopic and chemical data and especially a quantum theoretical basis for the occurrence of chemically similar elements such as the platinum and iron metals and the rare earths in the later period of the table, has introduced a subdivision of these electron groups into subgroups. By characterising each electron in the stationary states of the atom by analogy with the stationary states of a central force motion by a symbol n_k with $k \leqq n$, he obtained in general for an electron group with a value n of the principal quantum number n subgroups. In this way Bohr was led to the scheme of the structure of the inert gases given in Table 1. He has, however, emphasised himself[5] that the equality, assumed here, of the number of electrons in the different subgroups of a maingroup is highly hypothetical and that for the time being no complete and satisfying theoretical explanation of the completion of the electron groups in the atom, and especially of the period lengths 2, 8, 18, 32, ... in the periodic table could be given.

Recently essential progress was made in the problem of the completion of the electron groups in an atom by the considerations of E. C. Stoner.[6] This author suggests first of all a scheme for the atomic structure of the inert gases in which in contrast to Bohr no opening of a completed subgroup is allowed by letting other electrons of the same main group be added to it, so that the number of electrons in a closed subgroup depends only on the

TABLE 1. ORIGINAL BOHR SCHEME OF INERT GAS CONFIGURATIONS

Element	Atomic number	Number of n_k electrons														
		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2	5_3	6_1	6_2
Helium	2	2	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Neon	10	2	4	4	–	–	–	–	–	–	–	–	–	–	–	–
Argon	18	2	4	4	4	4	–	–	–	–	–	–	–	–	–	–
Krypton	36	2	4	4	6	6	6	4	4	–	–	–	–	–	–	–
Xenon	54	2	4	4	6	6	6	6	6	6	–	4	4	–	–	–
Emanation	86	2	4	4	6	6	6	8	8	8	8	6	6	6	4	4

TABLE 2. SCHEME OF INERT GAS CONFIGURATIONS ACCORDING TO STONER

Element	Atomic number	Number of $n_{k_1 k_2}$ electrons														
		1_1	2_1	$2_{2,(1+2)}$	3_1	$3_{2,(1+2)}$	$3_{3,(2+3)}$	4_1	$4_{2,(1+2)}$	$4_{3,(2+3)}$	$4_{4,(3+4)}$	5_1	$5_{2,(1+2)}$	$5_{3,(2+3)}$	6_1	$6_{2,(1+2)}$
Helium	2	2	–	–	–	–	–	–	–	–	–	–	–	–	–	–
Neon	10	2	2	2+4	–	–	–	–	–	–	–	–	–	–	–	–
Argon	18	2	2	2+4	2	2+4	–	–	–	–	–	–	–	–	–	–
Krypton	36	2	2	2+4	2	2+4	4+6	2	2+4	–	–	–	–	–	–	–
Xenon	54	2	2	2+4	2	2+4	4+6	2	2+4	4+6	–	2	2+4	–	–	–
Emanation	86	2	2	2+4	2	2+4	4+6	2	2+4	4+6	6+8	2	2+4	4+6	2	2+4

value of k, but not on the value of n, that is, on the existence of other subgroups in the same main group. This means already a large simplification which could, moreover, be supported by several experimental data. One must here assume for $k = 1$ two, for $k = 2$ six, for $k = 3$ ten, and in general for a given value of k $2(2k-1)$ electrons in the closed state of the corresponding subgroup to remain in agreement with the empirically known numbers of electrons in the inert gases.

Stoner remarked further that *these numbers of electrons agree with the number of the stationary states of the alkali atoms in an external field for the given value of k*. He therefore pushes further the analogy with the stationary states of the alkali spectra by assuming a further subdivision of the subgroups, corresponding to the complex structure of these spectra (and of the X-ray spectra), which are characterised by the two numbers k_1 and k_2, where k_1 is the same as Bohr's k, while we must put $k_2 = k_1 - 1$ or $k_2 = k_1$ (except for $k_1 = 1$, where in accordance with the simple nature of the s-term, $k_2 = 1$ only). Corresponding to the number $2k_2$ of the stationary states into which a stationary state of an alkali atom with given values of the quantum numbers k_1 and k_2 decomposes in an external field, Stoner assumes $2k_2$ electrons in a completed part-subgroup corresponding to the quantum numbers n, k_1, k_2. Table 2 gives the scheme of the atomic structure of the inert gases, to which Stoner was led in this way.

We can now make this idea of Stoner's more precise and more general, if we apply the ideas about the complex structure of the spectra and the anomalous Zeeman effect, discussed in the previous section, to the case where equivalent electrons are present in an atom. In that case we arrived, on the basis of an attempt to retain the permanence of quantum numbers, at a characterisation of each electron in an atom by both the principal quantum number n and the two auxiliary quantum numbers k_1 and k_2. In strong magnetic fields also an angular momentum quantum number m_1 was added to this for each electron and, furthermore, one can use apart from k_1 and m_1 also a magnetic moment quantum number m_2, instead of k_2. First of all, we see that the use of the two quantum numbers k_1 and k_2 for each electron is in excellent agreement of Stoner's subdivision of Bohr's subgroup.† Secondly, by considering the case of strong magnetic fields we can reduce Stoner's result, that the number of electrons in a completed subgroup is the same as the number of the corresponding terms of the Zeeman effect of the alkali spectra, to the following more general rule about the occurrence of equivalent electrons in an atom:

There can never be two or more equivalent electrons in an atom for which in strong fields the values of all quantum numbers n, k_1, k_2, m_1 *(or, equivalently,* n, k_1, m_1, m_2*) are the same. If an electron is present in the atom for which these quantum numbers (in an external field) have definite values, this state is "occupied".*

We must bear in mind that the principal quantum number occurs in an essential way in this rule; of course, several (not equivalent) electrons may occur in an atom which have the same values of the quantum numbers k_1, k_2, m_1, but have different values of the principal quantum number n.

We cannot give a further justification for this rule, but it seems to be a very plausible one. It refers, as mentioned, first of all to the case of strong fields. However, from thermodynamic arguments (invariance of statistic weights under adiabatic transformations of the system)‡ it follows that the number of stationary states of an atom must be the same in strong and weak fields for given values of the numbers k_1 and k_2 of the separate electrons and a value of $\overline{m_1} = \Sigma m_1$ (see (1)) for the whole atom. We can therefore also in the latter case make definite statements about the number of stationary states and the corresponding values of j (for a given

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† It follows directly from Millikan and Landé's results about the relativistic doublets of the X-ray spectra that this subdivision and the question about the number of electrons in the part-subgroups also makes sense for completed electron groups. These numbers appear clearly in the expression for the energy of the whole groups as function of the order number in the shape of factors of the Moseley–Sommerfeld expressions involving definite values of the screening numbers (determined by k_1) and the relativity correction (determined by k_2).

‡ This invariance is independent of the validity of classical mechanics under the transformation.

number of equivalent electrons belonging to different values of k_1 and k_2). We can thus find the number of possibilities of realising various incomplete electron shells and give an unambiguous answer to the question posed at the beginning of this section about the absence or coincidence of certain multiplet terms in spectra for values of the principal quantum number for which several equivalent electrons are present in an atom. We can, however, only say something about the number of terms and the values of their quantum numbers, but not about their magnitude and about interval relations.

We must now show that the consequences of our rule agree with experiment in the simplest cases. We must wait and see whether it will also prove itself in comparison with experiment in more complicated cases or whether it will need modifications in that case; this will become clear when complicated spectra are sorted out.

First of all, we see that Stoner's result and with it the period lengths 2, 8, 18, 32, ... are immediately included in a natural way in our rule. Clearly, for given k_1 and k_2 there cannot be more equivalent electrons in an atom than the appropriate value of m_1 (that is, $2k_2$) and in the completed group there corresponds exactly *one* electron to each of these values of m_1.

Secondly, it turns out that our rule has an immediate consequence that the triplet s-term with the same principal quantum number as the ground state is absent for the alkaline earths. If we investigate the possibilities for the equivalent binding of two electrons in s-terms (in that case we have thus $k_1 = 1$ and k_2 can also only have the value 1), according to our rule the cases are excluded in strong fields where both electrons have $m_1 = \frac{1}{2}$ or both have $m_1 = -\frac{1}{2}$; rather, we can only have $m_1 = \frac{1}{2}$ for the first electron and $m_1 = -\frac{1}{2}$ for the second electron, or the other way round† so that the quantum number $\overline{m_1} = \Sigma m_1$ for the total atom

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† The second case corresponds to an interchange of the two equivalent electrons and gives us therefore here no new stationary state (compare the footnote on p. 189). However, in this two-fold realisability of the quantum state considered is contained the fact that its statistical weight with respect to the exchangeability of the two electrons must be multiplied by two (compare also the discussion of statistical weights by Stoner)[6].

can only have the value 0. Therefore also in weak fields (or when there is no field) only the value $j = 0$ is possible (singlet S-term).

We now investigate the case that *one* electron is removed from a closed shell, as will occur in X-ray spectra. Clearly when an electron is missing from one of Stoner's part-subgroups, the case is always possible that *no* electron is present with the value m_1; we call this the "hole-value" of m_1. The other electrons are then uniquely divided over the other values of m_1 so that for each of those values we have one electron. The sum of these other values of m_1 and thus the quantum number $\overline{m_1}$ of the total atom is clearly in each case equal to the opposite of the hole-value of m_1. If we let it go through all possible values and take into account that an electron can be removed from every part-subgroup, we see that in strong fields the multiplicity of the hole-values of m_1 and thus also that of the values of $\overline{m_1}$ is the same as that of the m_1 value of a single electron. Due to the invariance of statistical weights it follows thus also for weak fields that the numbers of stationary states and of j-values of single ionised closed electron shells (X-ray spectra) are the same as in the alkali spectra, in accordance with experiment.

This is a special case of a general *reciprocity law: For each arrangement of electrons there exists a conjugate arrangement in which the hole-values of* m_1 *and the occupied values of* m_1 *are interchanged.* This interchange may refer to a single part-subgroup while the other part-subgroups are unchanged, or to a Bohr subgroup, or to the whole of a main group, since the different part-subgroups are completely independent of one another as far as possible arrangements are concerned. *The electron numbers of the two conjugate arrangements add up to the number of electrons in the completed state of the group (or subgroup) considered, while the j-values of the two arrangements are the same.* The latter follows from the fact that the sum of the hole-values of m_1 of an arrangement always is the opposite of the sum of the occupied m_1-values. Therefore, the quantum numbers $\overline{m_1}$ of the whole atom are the opposite of one another for conjugate arrangements. As the j-values are defined as the upper limit of the set of $\overline{m_1}$-values, and as this set is symmetric around zero, it follows that the j-values are the same (compare the examples discussed below). Because of this periodicity law to some extent the relations at the end of a period of the periodic table reflect those at the beginning of a period. We must emphasise, however, that this for the time being refers only to the number of stationary states of the shell in question and the values of their quantum numbers, whereas we can say nothing about the magnitude of their energies or about interval relations.†

As an application of our rule we shall discuss now the special case of the gradual formation of the eight-shell (where of the principal quantum number considered no electrons with $k = 2$ are present in the ground state); this gives us at the same time another example of the just-derived reciprocity rule. The binding of the first two electrons in this shell has already been discussed and in what follows we shall assume for the sake of simplicity that no electron is missing from the $k_1 = 1$ subgroup so that it is closed (compare Table 2 with Stoner's scheme). According to Stoner, for the following elements until the completion of the eight-shell (e.g., from B to Ne) the ground state will always be a p-term, in agreement with all experimental data up to now. Especially follows the alkali-like spectrum, corresponding to the binding of the third electron of the eight-shell, with the well-known absence of the s-term with the same principal quantum number as the ground state.

We can thus immediately go over to the binding of the fourth electron of the eight-shell, which appears in the not-yet analysed arc spectrum of carbon and the partially already unraffled arc spectrum of lead. According to the Landé–Heisenberg branching rule (see previous section) the corresponding spectrum should have in general the same structure as the neon spectrum, that is, consist of a singlet–triplet group and a triplet–quintet group with different series limits, corresponding to the $2p_1$- and the $2p_2$-doublet term

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† However, because of the equality of the number of m_2-values for conjugate arrangements it follows that also in weak fields the "g-sums" (taken over terms with the same j) of the appropriate terms are the same.

of the ion considered. We shall show, however, that according to our rules these spectra must differ essentially, as far as the number and j-values of the p-terms of the maximum principal quantum number ($n = 2$ for C, $n = 6$ for Pb) is concerned, from the Ne-spectrum (where, as we mentioned at the beginning of this section, apart from the ground state with $j = 0$ no further p-term exists with principal quantum number 2); this is in contrast to the structure of the excited states which we expect to be similar.

We must distinguish three cases, according to the number of electrons in the two part-subgroups with $k_1 = 2$, $k_2 = 1$ and with $k_1 = 2$, $k_2 = 2$ over which we must distribute two electrons (we have already assumed that the first two electrons are bound in s-terms, $k_1 = k_2 = 1$).

(a) Two equivalent n_{21}-electrons: Corresponding to the p_1-term of the alkalis m_1 can for this part-subgroup only take on the two values $m_1 = \pm\frac{1}{2}$. It is thus closed in this case with $\overline{m_1} = 0$ and $j = 0$.

(b) One n_{21}- and one n_{22}-electron: For the second part-subgroup m_1 can, corresponding to the p_2-term of the alkalis take on the four values $\pm\frac{1}{2}$, $\pm\frac{3}{2}$ and these can be combined in all possible ways with the above-mentioned values $m_1 = +\frac{1}{2}$ of the first electron, since the two electrons are in different part-subgroups and are thus not equivalent.† We have thus

$$\begin{aligned}\overline{m_1} &= (-\tfrac{3}{2}, -\tfrac{1}{2}, \tfrac{1}{2}, \tfrac{3}{2}) + (-\tfrac{1}{2}, \tfrac{1}{2}) \\ &= \pm(\tfrac{3}{2}+\tfrac{1}{2}), \pm(\tfrac{3}{2}-\tfrac{1}{2}), \pm(\tfrac{1}{2}+\tfrac{1}{2}), \pm(\tfrac{1}{2}-\tfrac{1}{2}) \\ &= \pm 2, \pm 1, \pm 1, 0, 0.\end{aligned}$$

From this we see immediately that the terms split in two series with $|\overline{m_1}| \leqq 2$ and with $|\overline{m_1}| \leqq 1$. In the field free case these correspond clearly to two terms: one with $j = 2$, and one with $j = 1$.

(c) Two equivalent n_{22}-electrons: According to our rule the

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† Because of this we must count the case $m_1 = +\frac{1}{2}$ for the first and $m_1 = -\frac{1}{2}$ for the second electron different from the case $m_1 = -\frac{1}{2}$ for the first and $m_1 = +\frac{1}{2}$ for the second electron. Compare the footnote on p. 189.

m_1-values of the two electrons must be different and we find for the possible values of $\overline{m_1}$:

$$\overline{m_1} = \pm(\tfrac{3}{2}+\tfrac{1}{2}), \pm(\tfrac{3}{2}-\tfrac{1}{2}), (\tfrac{3}{2}-\tfrac{3}{2}), (\tfrac{1}{2}-\tfrac{1}{2}) = \pm 2, \pm 1, 0, 0.$$

If there is no magnetic field we find thus one term with $j = 2$ and one with $j = 0$.

Altogether we find thus for the four-shell five different p-terms with maximum principal quantum number, of which two have $j = 2$, *one* $j = 1$, *and two* $j = 0$.

We can say nothing about the energies or the interval relations of this group of terms. However, we can make definite statements about the Zeeman splittings of these terms to be expected.

By substituting the m_2-values (taken from the Zeeman terms of the alkalis in strong fields) for the separate electrons corresponding to the given m_1-values, we find from rule (1) the Zeeman splittings for the five p-terms of the four-shell in strong fields:

$\overline{m_1}$	-2	-1	0	1	2
$\overline{m_2}$	$-3, -2$	$-2, -1, -1$	$0, 0, 0, 0, 0$	$1, 1, 2$	$2, 3$

Using the same rule applied by Landé[4] to higher-order multiplets, one obtains from this for the determination of the sum of the g-values for the two $j = 2$ terms (denoted by Σg_2) and for the g-value for the $j = 1$ term (denoted by g_1) the equations

$$2\Sigma g_2 = 2+3 = 5, \qquad \Sigma g_2 + g_1 = 1+1+2 = 4,$$

or

$$\Sigma g_2 = \tfrac{5}{2}, \qquad g_1 = \tfrac{3}{2}.$$

The earliest test of this theoretical result for the four-shell is possible for lead. Observations certainly show four p-terms, while the existence of a fifth p-term is doubtful.[7] So far unpublished measurements by E. Back of a few lead lines make it, moreover, very likely that the first four p-terms have j-values 2, 2, 1, 0, and that the g-values of these terms also agree with the theoretically expected ones.

Let us now return to the discussion of the gradual construction of the eight-shell. By means of the reciprocity rule, applied to the whole of the Bohr subgroup with $k = 2$, which contains in its closed state six electrons, we can immediately apply the results obtained for the four-shell to the number of possibilities to realise the six-shell (from electrons with $k_1 = 2$), which occurs, for instance, for O. The following cases of the six-shell are clearly conjugate to the cases (a), (b), and (c):

(a) Four equivalent n_{22}-electrons (two empty spaces in the n_{21}-group). This part-subgroup is closed; hence as before sub (a) one term with $j = 0$.

(b) One n_{21}-, three equivalent n_{22}-electrons (one empty space in the n_{21}-, and one empty space in the n_{22}-group). As before: one term with $j = 2$ and one term with $j = 1$.

(c) Two equivalent n_{21}- and two equivalent n_{22}-electrons (two empty spaces in the n_{22}-group). The first part-subgroup is closed. As before: one term with $j = 2$, one term with $j = 0$.

We must thus also here, for instance for oxygen, expect five p-terms with the smallest principal quantum number. So far only three such terms have been observed for O and S, with j-values of 2, 1, 0.[8] We must wait and see whether two more p-terms of the same principal quantum number can be found from the observations, or whether our rule must be modified in this case.

As yet there are no observations about the five-shell (3 electrons with $k_1 = 2$) and we shall therefore give only the result of the discussion; according to our rule this shell gives rise to five p-terms, one term with $j = \frac{5}{2}$, three terms with $j = \frac{3}{2}$, and one term with $j = \frac{1}{2}$. For the seven-shell, realised in x-ray spectra we get—as we mentioned before—terms similar to the alkalis.

We shall not discuss here further special cases, before experimental data are available, but it should be clear from the examples given that in each case our rule is able to give a unique answer to the question about the possibilities of realising the different shells for a given number of equivalent electrons. To be sure, only in the simplest cases was it possible to verify that the results obtained in this way are in agreement with experiment.

In general we may note that the discussions given here are in principle based, as far as the transition from strong to weak or vanishing fields is concerned, upon the invariance of the statistical weights of quantum states. However, on the basis of the results obtained there seem to be no reasons for a connexion between the problem of the completion of electron groups in an atom and the correspondence principle, as Bohr suspected to be the case. It is probably necessary to improve the basic principles of quantum theory before we can successfully discuss the problem of a better foundation of the general rules, suggested here, for the occurrence of equivalent electrons in an atom.

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