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ON THE QUANTUM THEORY OF LINE-SPECTRA

BY

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PART II

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Part II.

On the hydrogen spectrum.

§ 1. The simple theory of the series spectrum of hydrogen.

As well known, the frequencies of the lines of the series spectrum of hydrogen may, if we look apart from the fine structure of the single lines revealed by instruments of high dispersive power, be represented by the formula

$$\nu = K\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right), \tag{35}$$

where K is a constant, and n' and n'' a set of two entire numbers, different for the different lines of the spectrum. According to the general principles of the quantum theory of line spectra discussed in the first section of Part I, we shall therefore expect that this spectrum is emitted by a system which possesses a series of stationary states in which the numerical value of the energy in the n^{th} state, omitting an arbitrary constant, with a high degree of approximation is given by

$$|E_n| = \frac{Kh}{n^2}, \tag{36}$$

where h is Planck's constant which enters in the fundamental relation (1).

Now according to Rutherford's theory of atomic structure, a neutral hydrogen atom must be expected to consist of an electron and a positive nucleus of a mass very large compared with that of the electron, which move under the influence of a mutual attraction inversely proportional to the square of the distance apart. Assuming that the motion in the stationary states may be determined by ordinary mechanics, and neglecting for the moment the small modifications claimed by the theory of relativity, we find that each of the particles will describe an elliptical orbit with their common centre of gravity at one of the foci, and from the well known laws for a Keplerian motion we have that the frequency of revolution ω and the major axis $2a$ of the relative orbit of the particles, quite independent of the degree of eccentricity of this orbit, are given by

$$\omega = \sqrt{\frac{2W^3(M+m)}{\pi^2 N^2 e^4 Mm}}, \quad 2a = \frac{Ne^2}{W}, \tag{37}$$

where W is the work necessary to remove the electron to infinite distance from the nucleus, while Ne and M are the charge and the mass of the nucleus, and $-e$ and m the charge and the mass of the electron.

As explained in Part I, there will in general be no simple connection between the motion of a system in the stationary states and the spectrum emitted during transitions between these states; such a connection, however, must be expected to exist in the limit where the motions in successive stationary states differ comparatively little from each other. In the present case this connection claims in the first place that the frequency of revolution tends to zero for increasing n. According to (36) and (37) we may therefore put the value of W in the n^{th} stationary state equal to

$$W_n = \frac{Kh}{n^2}. \tag{38}$$

Moreover, since (35) can be written in the form

$$\nu = (n' - n'') K \frac{n' + n''}{n'^2 n''^2},$$

it is seen to be a necessary condition that the frequency of revolution for large values of n is asymptotically given by

$$\omega_n \sim \frac{2K}{n^3}, \tag{39}$$

if we wish that the frequency of the radiation emitted during a transition between two stationary states, for which the numbers n' and n'' are large compared with their difference $n' - n''$, shall tend to coincide with one of the frequencies of the spectrum which on ordinary electrodynamics would be emitted from the system in these states. But from (37) and (38) it will be seen that (39) claims the fulfilment of the relation

$$K = \frac{2\pi^2 N^2 e^4 M m}{h^3 (M + m)} = \frac{2\pi^2 N^2 e^4 m}{h^3 (1 + m/M)}. \tag{40}$$

As shown in previous papers, this relation is actually found to be fulfilled within the limit of experimental errors if we put $N = 1$ and for e, m, and h introduce the values deduced from measurements on other phenomena; a result which may be considered as affording a strong support for the validity of the general principles discussed in Part I, as well as for the reality of the atomic model under consideration. Further it was found that, if in formula (35) for the hydrogen spectrum the constant K is replaced by a constant which is four times larger, this formula represents to a high degree of approximation the frequencies of the lines of a spectrum emitted by helium, when this gas is subject to a condensed discharge. This was to be expected on Rutherford's theory, according to which a neutral helium atom contains two electrons and a nucleus of a charge twice that of the nucleus of the hydrogen atom. A helium atom from which one electron is removed will thus form a dynamical system perfectly similar to a neutral hydrogen atom, and may therefore be expected to emit a spectrum represented by (35) if in (40) we put $N = 2$. Moreover a closer comparison of the helium spectrum under consideration with the hydrogen spectrum has shown that the value of the constant K in the former spectrum was not exactly four times as large as that in the latter, but that the ratio between these constants within the limit of experimental errors agreed with the value to be expected from (40), when regard is taken to the different masses of the nuclei of the atoms of hydrogen and helium corresponding to the different atomic weights of these elements[1]).

Introducing the expression for K given by (40) in the formulæ (37) and (38), we find for the values of W, ω and $2a$ in the stationary states

$$W_n = \frac{1}{n^2}\frac{2\pi^2 N^2 e^4 Mm}{h^2(M+m)},\quad \omega_n = \frac{1}{n^3}\frac{4\pi^2 N^2 e^4 Mm}{h^3(M+m)},\quad 2a_n = n^2\frac{h^2(M+m)}{2\pi^2 Ne^2 Mm}. \qquad (41)$$

Now for a mechanical system as that under consideration, for which every motion is periodic independent of the initial conditions, we have that the value of the total energy will be completely determined by the value of the quantity I, defined by equation (5) in Part I. As mentioned this follows directly from relation (8), which shows at the same time that for a system for which every motion is periodic the frequency will be completely determined by I or by the energy only. For the value of I in the stationary states of the hydrogen atom we get by means of (8) from (37) and (41), since in this case I will obviously become zero when W becomes infinite,

$$I = \int_{W_n}^{\infty}\frac{dW}{\omega} = \sqrt{\frac{\pi^2 N^2 e^4 Mm}{2(M+m)}}\int_{W_n}^{\infty} W^{-3/2}dW = \sqrt{\frac{2\pi^2 N^2 e^4 Mm}{W_n(M+m)}} = nh.$$

This result will be seen to be consistent with condition (24) which, as mentioned in Part I, presents itself as a direct generalisation to periodic systems of several degrees of freedom of condition (10) which determines the stationary states of a system of one degree of freedom, and which again on Ehrenfest's principle of the mechanical transformability of the stationary states forms a rational generalisation of Planck's fundamental formula (9) for the possible values of the energy of a linear harmonic vibrator.

In this connection it will be observed, that the relation discussed above between the hydrogen spectrum and the motion of the atom in the limit of small frequencies is completely analogous to the general relation, discussed in § 2 in Part I, between the spectrum which on the quantum theory would be emitted by a system of one degree of freedom, the stationary states of which are determined by (10), and the motion of the system in these states. It will at the same time be noted that, in case of hydrogen, this relation implies that the motion of the particles in the stationary states of the atom will not in general be simply harmonic, or in other words that the orbit of the electron will not in general be circular. In fact if the motion of the particles were simply harmonic, as the motion of a Planck's vibrator,

[1]) For the litterature on this subject the reader is referred to the papers cited in the introduction.

we should expect on the considerations in Part I that no transition between two stationary states of the atom would be possible for which n' and n'' differ by more than one unit; but this would obviously be inconsistent with the observations, since for instance the lines of the ordinary Balmer series, according to the theory, correspond to transitions for which $n'' = 2$ while n' takes the values 3, 4, 5, ... In connection with this consideration it may be remarked that, adopting a terminology well known from acoustics, we may from the point of view of the quantum theory regard the higher members of the Balmer series ($n' = 4, 5, \ldots$) as the "harmonics" of the first member ($n' = 3$), although of course the frequencies of the former lines are by no means entire multipla of the frequency of the latter line.

While in the above way it was possible to obtain a simple interpretation of certain main features of the hydrogen spectrum, it was not found possible in this way to account in detail for such phenomena in which the deviation of the motion of the particles from a simple Keplerian motion plays an essential part. This is the case in the problem of the fine structure of the hydrogen lines, which is due to the effect of the small variation of the mass of the electron with its velocity, as well as in the problems of the characteristic effects of external electric and magnetic fields on the hydrogen lines. As mentioned in the introduction, a progress of fundamental importance in the treatment of such problems was made by Sommerfeld, who obtained a convincing explanation of the fine structure of the hydrogen lines by means of his theory of the stationary states of central systems, in which the single condition $I = nh$ was replaced by the two conditions (16); and the theory was further developed by Epstein and Schwarzschild, who on this line established the general theory, based on the conditions (22), of the stationary states of a conditionally periodic system for which the equations of motion may be solved by means of separation of variables in the Hamilton-Jacobi partial differential equation. If the hydrogen atom is exposed to a homogeneous electric or to a homogeneous magnetic field, the atom forms a system of this class, and, as shown by Epstein and Schwarzschild as regards the Stark effect and by Sommerfeld and Debye as regards the Zeeman effect, the theory under consideration leads to values for the total energy of the atom in the stationary states, which together with relation (1) lead again to values for the frequencies of the radiations emitted during the transitions between these states, which are in agreement with the measured frequencies of the components into which the hydrogen lines are split up in the presence of the fields. As pointed out in Part I, it is possible moreover to throw light on the question of the intensities and polarisations of these components on the basis of the necessary formal relation between the quantum theory of line spectra and the ordinary theory of radiation in the limit where the motions in successive stationary states differ very little from each other. In the following sections the mentioned problems will be discussed in detail. As regards the fixation of the stationary states we shall not, however, follow the same procedure as used by the authors just mentioned, which rests upon the immediate application of the conditions

(22), but it will be shown how the conditions which fix the stationary states of the perturbed atom may be obtained by a direct examination of the small deviations of the motion of the electron from a simple Keplerian motion. In this way it seems possible to obtain a more direct illustration of the principles discussed in Part I; and we shall see moreover that the treatment in question may be used also in cases where the method of separation of variables cannot be applied.

In Part III the problem of the series spectra of other elements will be treated from a similar point of view. As pointed out by the writer in an earlier paper, a simple explanation of the pronounced analogy between these spectra and the hydrogen spectrum is offered by the fact, that the atomic systems, involved in the emission of the spectra under consideration, in a certain sense may be regarded as a perturbed hydrogen atom. On the other hand, a clue to the interpretation of the characteristic difference between the hydrogen spectrum and the spectra of other elements was first obtained by SOMMERFELD's theory of the stationary states of central systems referred to above. As shown by SOMMERFELD, it is possible on this theory to account in general outlines for the well known laws governing the frequencies of the series spectra of the elements; and, as it will be shown in Part III, it is also possible, on the basis of the formal relation between the quantum theory and the ordinary theory of radiation, in this way to obtain a simple interpretation of the laws governing the remarkable differences in the intensities with which the various series of lines appear, which on the combination principle would constitute the complete spectra under consideration. As regards the detailed discussion of these spectra, however, it is necessary to bear in mind that the part played by the inner electrons in the atoms of the elements in question forms a far more intricate problem than the perturbing effect of a fixed external field on the hydrogen atom. For the treatment of this problem the theory of conditionally periodic systems based on the conditions (22) does not seem to suffice, while, as it will be shown in Part III, it appears that the method of perturbations exposed in the following lends itself naturally also to this case.

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§ 2. The stationary states of a perturbed periodic system.

In Part I it was shown that the problem of the fixation of the stationary states of a periodic system of several degrees of freedom, which is subject to the perturbing influence of a small external field, cannot be treated directly on the basis of the general principle of the mechanical transformability of the stationary states by considering the influence, which on ordinary mechanics a slow establishment of the external field would exert on the motion of some arbitrarily chosen stationary state of the undisturbed system (see Part I, p. 23). This is an immediate consequence of the fact, mentioned in the former section, that the stationary states of the perturbed system are characterised by a greater number of extra-mechanical conditions than the stationary states of the undisturbed system. On the other hand, we were led to assume from the general formal relation between the quantum theory of line spectra and the ordinary theory of radiation, that it is possible to obtain information about the stationary states of the perturbed system from a direct consideration of the slow variations which the periodic orbit undergoes as a consequence of the mechanical effect of the external field on the motion. Thus, if these variations are of periodic or conditionally periodic type, we may expect that, in the presence of the external field, the values for the additional energy of the system in the stationary states are related to the small frequency or frequencies of the perturbations, in a manner analogous to the relation between energy and frequency in the stationary states of an ordinary periodic or conditionally periodic system.

If the equations of motion for the perturbed system can be solved by means of separation of variables, it is easily seen that the relation in question is fulfilled if the stationary states are determined by the conditions (22). Consider thus a system for which every orbit is periodic, and let us assume that in the presence of a given small external field a separation of variables is possible in a certain set of coordinates $q_1, \ldots q_s$. For the undisturbed system we have then, according to equation (23), that the quantity I, defined by (5), is equal to $\varkappa_1 I_1 + \ldots\ldots + \varkappa_s I_s$, where $I_1, \ldots I_s$ are defined by (21) and calculated with respect to the set of coordinates just mentioned, and where the $\varkappa$'s are a set of entire positive numbers without a common divisor. For simplicity let us assume that at least one of the $\varkappa$'s, say $\varkappa_s$, is equal to one, and that consequently, as mentioned on page 22, the number n in (24), which characterises the stationary states of the undisturbed system, may take all positive values. This condition will be fulfilled in case of all the applications to spectral problems discussed below; it will be seen, however, that the extension to problems where this condition is not fulfilled will only necessitate small modifications in the following considerations. By use of (29) we get now for the difference in the total energy of two slightly different states of the perturbed system

$$\delta E = \sum_1^s \omega_k \delta I_k = \omega_s \sum_1^s \varkappa_k \delta I_k + \sum_1^{s-1} (\omega_k - \varkappa_k \omega_s) \delta I_k. \tag{42}$$

Since for the undisturbed system $\omega_k = \varkappa_k \omega_s$, the differences $\omega_k - \varkappa_k \omega_s$ appearing in the last term will, for the perturbed system, be small quantities which will just represent the frequencies of the slow variations which the orbit undergoes in the presence of the external field. These quantities will in the following be denoted by ν_k. Consider now the multitude of states of the perturbed system for which $\sum_1^s \varkappa_k I_k$ is equal to nh, where n is a given entire positive number. This multitude will be seen to include all possible stationary states of the perturbed system, which satisfy (22), and the motion of which differs at any moment only slightly from some stationary motion of the undisturbed system, satisfying (24) for the given value of

n. Denoting the value of the energy of the undisturbed system in such a state by E_n, and the value of the energy of the perturbed system in a state belonging to the multitude under consideration by $E_n + \mathfrak{E}$, we get from (42)

$$\delta \mathfrak{E} = \sum_{1}^{s-1} o_k \, \delta I_k \tag{43}$$

for the energy difference between two neighbouring states of this multitude. Since this relation has the same form as (29), we see consequently that by putting $I_1, \ldots I_{s-1}$ equal to entire multipla of h, as claimed by the conditions (22), we obtain exactly the same relation between the additional energy $\mathfrak{E}$ and the small frequencies o_k, impressed on the system by the external field, as that which holds between the total energy and the fundamental frequencies in the stationary states of a conditionally periodic system of $s - 1$ degrees of freedom.

As a simple illustration of these calculations let us consider the system consisting of a particle moving in a plane and subject to an attraction from a fixed point, which varies proportional to the distance apart. If undisturbed, the motion of this system will be periodic independent of the initial conditions, and the particle will describe an elliptical orbit with its centre at the fixed point. Moreover the equations of motion of the undisturbed system may be solved by means of separation of variables in polar coordinates, as well as in any set of rectangular coordinates. In the first case we have, taking for q_1 the length of the radius vector from the fixed point to the particle and for q_2 the angular distance of this radius vector from a fixed direction, $\varkappa_1 = 2$ and $\varkappa_2 = 1$, while in the second case we have $\varkappa_1 = \varkappa_2 = 1$. In the presence of an external field the orbit will in general not remain periodic, but will in the course of time cover a continuous extension of the plane. If the external field is sufficiently small, however, the orbit will at any moment only differ little from a closed elliptical orbit, but in the course of time the lengths and directions of the principal axes of this ellipse will undergo slow variations. In general the perturbed system will not allow of separation of variables, but two cases obviously present themselves in which such a separation is still possible; in the first case the external field is central with the fixed point as centre, and a separation is possible in polar coordinates; in the second case the external field of force is perpendicular to a given line and varies as some function of the distance from this line, and separation is possible in a set of rectangular coordinates with the axes parallel and perpendicular to the given line. In the first case the perturbations will not affect the lengths of the principal axes of the elliptical orbit and will only produce a slow uniform rotation of the directions of these axes, while in the second case the lengths of the principal axes as well as their directions will perform slow oscillations. It will consequently be seen that, by fixing the stationary states of the perturbed system by means of the conditions (22), the cycles of shapes and positions which the orbit of the particle will pass through in the stationary states will be entirely different in the two cases. In both cases, however, it will be seen that the frequency $o = \omega_1 - \varkappa_1 \omega_2$ will be equal to the frequency with which the orbit at regular intervals re-assumes its shape and position. By fixing the stationary states by (22) we obtain therefore, as seen from (43), in both cases that the relation between this frequency and the additional energy of the system due to the presence of the field will be the same as the relation between energy and frequency in the stationary states of a system of one degree of freedom; and it will be seen that the above considerations offer a dynamical interpretation of the characteristic discontinuity involved in the application of the method of separation of variables to the fixation of the stationary states of perturbed periodic systems[1]).

[1]) In this connection it may be of interest to note that the possibility of a rational interpretation of

In general it will not be possible to solve the equations of motion of the perturbed system by means of separation of variables in a fixed set of positional coordinates, but we shall see that the problem of the fixation of the stationary states of the perturbed system may be attacked by a direct examination of the additional energy of the system and its relation to the slow variations of the orbit, on the basis of the usual theory of perturbations well known from celestial mechanics. Consider a system for which every orbit, if undisturbed, is periodic independent of the initial conditions, and let us assume that the equations of motion for some set of coordinates $q_1, q_2, \dots q_s$ are solved by means of the Hamilton-Jacobi partial differential equation, given by formula (17) in Part I. The motion of the system is then determined by the equations (18), and the orbit is characterised by means of the constants $\alpha_1, \dots \alpha_s, \beta_1, \dots \beta_s$. If now the system is subject to some small external field of force, the motion will no more be periodic, but, defining in the usual way the osculating orbit at a given moment as the periodic orbit which would result if the external forces vanished suddenly at this moment, we find that the constants $\alpha_1, \dots \alpha_s, \beta_1, \dots \beta_s$, characterising the osculating orbit, will vary slowly with the time. Assuming for the present that the external forces possess a constant potential Ω given as a function of the q's, we have according to the theory of perturbations that the rates of variation of the orbital constants of the osculating orbit will be given by[1])

$$\frac{d\alpha_k}{dt} = -\frac{\partial \Omega}{\partial \beta_k}, \quad \frac{d\beta_k}{dt} = \frac{\partial \Omega}{\partial \alpha_k}, \quad (k = 1, \dots s) \tag{44}$$

where Ω is considered as a function of $\alpha_1, \dots \alpha_s, \beta_1, \dots \beta_s$ and t, obtained by introducing for the q's their expressions as functions of these quantities obtained by solving (18). The equations (44) allow to follow completely the perturbing effect of the external field on the motion of the system. For the problem under consideration, however, a detailed examination of the perturbations is not necessary. In fact, we shall not be concerned with the small deformation of the orbit characterised by the small oscillations of the orbital constants within a time interval of the same order of magnitude as the period of the osculating orbit, but only

the discontinuity in question would seem to be essentially connected with the form of the principles of the quantum theory adopted in this paper. If for instance the quantum theory is taken in the form proposed by Planck in his second theory of temperature radiation, the consequent development to periodic systems of several degrees of freedom would seem to involve a serious difficulty as regards the question of the necessary stability of the temperature equilibrium among a great number of systems for small variations of the external conditions. In fact, in connection with the development of his theory of the "physical structure of the phase space", mentioned in Part I on page 18, in which conditions of the same type as (22) are established, Planck has deduced expressions for the total energy of a great number of systems in temperature equilibrium, which, if applied to systems of the same kind as those considered in the above example, show a dependency of this energy on the temperature which is different, according to whether polar coordinates or rectangular coordinates are used as basis for the structure of the phase space.

[1]) See f. inst. C. V. L. Charlier, Die Mechanik des Himmels, Bd. I, Abt. 1, § 10.

with the socalled "secular perturbations" of the orbit, characterised by the total variation of these constants taken over a time interval long compared with the period of the osculating orbit. As we shall see below, these variations may, with an approximation sufficient for our purpose, be obtained directly by taking mean values on both sides of the equations (44). Before entering on these calculations, however, it may be observed that the part played by the constants α_1 and β_1 differs essentially from that played by the other orbital constants $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$. Thus from the formulæ (17) and (18) on page 19, it follows that α_1 is the total energy corresponding to the osculating orbit, while β_1 will represent the moment in which the system would pass some distinguished point in this orbit. If for instance we consider the perturbations of a Keplerian motion, we may for β_1 take the so called time of perihelium passage. When discussing the secular perturbations of the shape and position of the orbit, we see therefore in the first place that the variations of β_1 may be left out of consideration. Further, it follows from the principle of conservation of energy, that $\alpha_1 + \Omega$ will remain constant during the motion, and that consequently during the perturbations α_1 will change only by small quantities of the same order as $\lambda\alpha_1$, where λ denotes a small constant of the same order of magnitude as the ratio between the external forces and the internal forces of the system. Moreover, since the period σ of the undisturbed motion depends on α_1 only, it follows that the period of the osculating orbit will remain constant during the perturbations, with neglect of small quantities of the same order as $\lambda\sigma$. On the other hand it follows from (44) that, in a time interval of the same order as σ/λ, the constants $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$ will in general undergo variations of the same order of magnitude as the values of these constants themselves.

As mentioned above, the total variations of the constants $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$, which characterise the secular perturbations of the shape and position of the orbit, may be obtained by taking mean values on both sides of the equations (44). Introducing a function Ψ of the α's and β's, equal to the mean value of the potential Ω taken over a period σ of the motion of the undisturbed system and defined by the formula

$$\Psi = \frac{1}{\sigma}\int_t^{t+\sigma} \Omega\, dt, \tag{45}$$

it is easily seen, since σ depends only on α_1, that the mean values of the partial differential coefficients of Ω with respect to $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$, taken over an approximate period of the perturbed motion, may, if we look apart from small quantities proportional to λ^2, be replaced by the values of the corresponding partial differential coefficients of Ψ at some moment within this period. With the approximation mentioned we get therefore

$$\frac{D\alpha_k}{Dt} = -\frac{\partial \Psi}{\partial \beta_k}, \quad \frac{D\beta_k}{Dt} = \frac{\partial \Psi}{\partial \alpha_k}, \quad (k = 2, \ldots s) \tag{46}$$

where the differential symbols on the left sides are written to indicate mean values of the rates of variation of the orbital constants during an approximate period of the perturbed motion. From the definition of Ψ it follows that this quantity in general will depend on α_1 as well as on $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$, but that it will not depend upon β_1. From the above considerations it follows further that, with the approximation in question, α_1 may be considered as a constant in the expressions on the right sides of (46), while for $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$ we may take a set of values corresponding to some moment within the period to which the mean values on the left sides refer.

It will be seen that the equations (46) allow to follow the secular perturbations during a time interval sufficiently long for the external forces to produce a considerable change in the shape and position of the original orbit, if in the total variations of the orbital constants $\alpha_2, \ldots \alpha_s, \beta_2 \ldots \beta_s$ we look apart from small quantities of the same order as the small oscillations of these constants within a single period. As a consequence of the secular variations, the orbit will pass through a cycle of shapes and positions, which will depend on its original shape and position and on the character of the perturbing field, but not on the intensity of this field. In fact, as seen from (46), the variations in the shape and position of the orbit will remain the same if Ψ is multiplied by a constant factor, which will only influence the rate at which these variations are performed. It will further be observed that the problem of determining the secular perturbations by means of (46) consists in solving a set of equations of the same type as the Hamiltonian equations of motion for a system of $s-1$ degrees of freedom. In these equations the quantity Ψ plays formally the same part as the total energy in the usual mechanical problem, and in analogy with the principle of conservation of energy it follows directly from (46) that, with neglect of small quantities proportional to λ^2, the value of Ψ will remain constant during the perturbations, even if the external forces act through a time interval of the same order as σ/λ. In fact, with neglect of small quantities proportional to λ^3, we have

$$\frac{D\Psi}{Dt} = \sum_2^s \left(\frac{\partial \Psi}{\partial \alpha_k}\frac{D\alpha_k}{Dt} + \frac{\partial \Psi}{\partial \beta_k}\frac{D\beta_k}{Dt}\right) = \sum_2^s \left(-\frac{\partial \Psi}{\partial \alpha_k}\frac{\partial \Psi}{\partial \beta_k} + \frac{\partial \Psi}{\partial \beta_k}\frac{\partial \Psi}{\partial \alpha_k}\right) = 0.$$

Since at any moment Ψ will differ only by small quantities proportional to λ^2 from the mean value of the potential of the external forces taken over an approximate period of the perturbed motion, it follows from the above that, with neglect of small quantities of this order, also the mean value of the inner energy α_1 of the perturbed system, taken over an approximate period, will remain constant during the perturbations, even if the perturbing forces act through a time interval long enough to produce a considerable change in the shape and position of the orbit. In the special case, where the perturbed system allows of separation of variables, this last result may be shown to follow directly from formula (28) in Part I. Taking for the time interval ϑ in this formula the period σ of the undisturbed motion, we get $N_k = \varkappa_k$, where $\varkappa_1, \ldots \varkappa_s$ are the numbers entering in formula (23). Comparing a given perturbed motion of the system with some undisturbed motion of which it may be regarded as a small variation, we get therefore from (28), with neglect of small quantities proportional to the square of the intensity of the external forces,

$$\int_0^\sigma \delta E\, dt = \sum_1^s \varkappa_k \delta I_k, \tag{47}$$

where the I's are calculated with respect to a set of coordinates in which a separation can be obtained for the perturbed motion, and where δE is the difference between the total energy of the undisturbed motion and the energy which the system would possess in its perturbed state, if the external forces vanished suddenly at the moment under consideration, and which in the above calculations was denoted by α_1. Now the energy E of the undisturbed motion is determined completely by the value of $I = \Sigma \varkappa_k I_k$. If therefore the perturbed motion is all the time compared with a neighbouring undisturbed motion of given constant energy, it follows directly from (47), that, with neglect of small quantities of the same order as the square of the external forces, the integral on the left side, taken over an approximate period of the perturbed motion, will remain unaltered during the perturbations through any time interval, however long.

Before proceeding with the applications of the equations (46) which apply to the case of a constant perturbing field, it will be necessary to consider the effect of a slow and uniform establishment of the external field. Let us assume that, within the interval $0 < t < \vartheta$ where ϑ denotes a quantity of the same order as σ/λ, the intensity of the external field increases uniformly from zero to the value corresponding to the potential Ω. Since the variation in the perturbing field during a single period will only be a small quantity of the same order as λ^2, we see in the first place that the secular variations of the constants $\alpha_2, \ldots \alpha_s, \beta_2, \ldots \beta_s$, with the same approximation as for a constant field, will be given by a set of equations of the same form as (46), with the only difference that Ψ is replaced by $\frac{t}{\vartheta}\Psi$. Moreover it may be shown that in these equations the quantity α_1 may be considered as constant, just as in the equations which hold for a constant perturbing field. In fact the total variation in α_1 at any moment t will be equal to the total work performed by the external forces since the beginning of the establishment of the perturbing field, and will therefore be given by

$$\Delta_t \alpha_1 = -\int_0^t \frac{t}{\vartheta} \sum_1^s \frac{\partial \Omega}{\partial q_k} \dot{q}_k\, dt = \frac{1}{\vartheta}\int_0^t \Omega\, dt - \frac{t}{\vartheta}\Omega_t, \tag{48}$$

where the expression on the right side is obtained by partial integration; but, since both terms in this expression are of the same order of magnitude as $\lambda \alpha_1$, we see that the total variation in α_1 within the interval in question will, just as in case of a constant perturbing field, be only a small quantity of this order. We get therefore the result, that, for the same shape and position of the original orbit, the cycle of shapes and positions passed through by the orbit during the increase of the external field will be the same as that which would appear for a constant perturbing field, and that, with neglect of small quantities proportional to λ^2, the value of the function Ψ will consequently remain constant during the establishment of the field. With this approximation we get therefore from (48), putting $t = \vartheta$,

$$\Delta_\vartheta \alpha_1 + \Omega_\vartheta = \frac{1}{\vartheta}\int_0^\vartheta \Omega \, dt = \Psi,$$

which shows that the change in the total energy of the system, due to the slow and uniform establishment of the external field, is just equal to the value of the function Ψ, and consequently equal to the mean value of the potential of the external forces taken over an approximate period of the perturbed motion. This result may also be expressed by stating, that, with neglect of small quantities proportional to the square of the external forces, the mean value of the inner energy taken over an approximate period of the perturbed motion will be equal to the energy possessed by the system before the establishment of the perturbing field.

Returning now to the problem of the fixation of the stationary states of a periodic system subject to the influence of a small external field of constant potential, we shall base our considerations on the fundamental assumption that these states are distinguished between the continuous multitude of mechanically possible states by a relation between the additional energy of the system due to the presence of the external field and the frequencies of the slow variations of the orbit produced by this field, which is analogous to the relation discussed on page 42 in the special case in which the perturbed system allows of separation of variables in a fixed set of coordinates. On this assumption we shall expect in the first place that, apart from small quantities proportional to λ, the cycles of shapes and positions of the orbit belonging to the stationary states of the perturbed system will depend only on the character of the external field, but not on its intensity. Since now, as shown above, such a cycle will remain unaltered during a slow and uniform increase of the intensity of the external field if the effect of the external forces is calculated by means of ordinary mechanics, we are therefore, with reference to the principle of the mechanical transformability of the stationary states, led to the conclusion that it is possible by direct application of ordinary mechanics, not only to follow the secular perturbations of the orbit in the stationary states corresponding to a constant external field, but also to calculate the variation in the energy of the system in the stationary states which results from a slow and uniform change in the intensity of this field. If we denote the energy in the stationary states of the perturbed system by $E_n + \mathfrak{E}$, where E_n is the value of the energy in the stationary state of the undisturbed system characterised by a given entire value of n in the condition $I = nh$, we may therefore conclude from the above that the additional energy $\mathfrak{E}$ in the stationary states of the perturbed system will be equal to the value in these states of the function Ψ defined by (45), if we look apart from small quantities proportional to the square of the intensity of the external forces. It will be seen that this result is equivalent to the statement, that the mean value of the inner energy taken over an approximate period of the perturbed motion will be equal to the value E_n of the energy in the corresponding stationary state of the undisturbed system. In case of the perturbed system allowing of separation of variables in a fixed set of coordinates, this result may be simply shown to be a direct consequence of the fixation of the stationary states by means of the conditions (22). In fact, if we assume that the undisturbed motion, considered in (47), corresponds to some stationary state, satisfying (24) for a given value of n, and that the perturbed motion is also stationary and satisfies (22), we see that the right side of (47) will be zero, and we get the result that the mean value of the inner energy in the stationary states of the system, with the approximation mentioned, will not be altered in the presence of the external field.

Due to the above result that the additional energy $\mathfrak{E}$ in the stationary states of the perturbed system, with neglect of small quantities proportional to λ^2, may be taken equal to the value in these states of the function Ψ entering in the equations (46) which determine the secular perturbations of the orbits, we are now able to draw further conclusions from the fact, mentioned above, that these equations are of the same type as the Hamiltonian equations of motion for a mechanical system of $s-1$ degrees of freedom. In fact, we see that the fixation of the stationary states of the perturbed system is reduced to a problem which is formally analogous to the fixation of these states for a mechanical system of less degrees of freedom. As it will appear from the following applications this problem may, quite independent of the possibility of separation of variables for the perturbed system, be treated directly on the basis of the fundamental relation between energy and frequency in the stationary states of periodic or conditionally periodic systems, discussed in Part I, if only the solution of the equations (46) is of a periodic or conditionally periodic character. In this connection it may once more be emphasised that these equations, according to the manner in which they were deduced, allow to follow the secular perturbations only through a time interval of the same order of magnitude as that sufficient for the external forces to produce a finite alteration in the shape and position of the orbit. With reference to the necessary stability of the stationary states of an atomic system, it seems justified, however, to conclude that any possible small discrepancy between the motion to be expected from a rigorous application of ordinary mechanics and that determined by a calculation of the secular perturbations, based on the equations (46), cannot cause a material change in the character of the stationary states as fixed by a consideration of the periodicity properties of these perturbations. On the other hand, from the point of view of the general formal relation between the quantum theory and the ordinary theory of radiation, we must be prepared to find that the motion and the energy in the stationary states of a perturbed periodic system, for which we only know that the secular perturbations as determined by (46) are of conditionally periodic type, will not be as sharply defined as the motion and the energy in the stationary states of a conditionally periodic system for which the equations of motion allow of a rigorous solution by means of the method of separation of variables. Thus, if we consider a large number of similar atomic systems of the type in question, we may be prepared to find that the values of the additional energy in a given stationary state will for the different systems deviate from each other by small quantities; but it must be expected that the values of the additional energy for the large majority of systems will differ from the value of Ψ, as determined by the method indicated above, only by small quantities proportional to λ^2, and that only for a small fraction (at most of the same order as λ^2) of the systems the values of the additional energy will show deviations from this value of Ψ, which are of the same order as λ.

As to the application of the preceding considerations to special problems, it will be seen in the first place that in case of a perturbed periodic system possessing two degrees of freedom, as for instance that considered in the example on page 43, the problem of the fixation of the stationary states of the perturbed system in the presence of a small external field allows of a general solution on the basis of the method developed above, because in this case the secular perturbations will in general be simply periodic. In fact, in this case the shape and position of the orbit are characterised by two constants α_2 and β_2, and from the equations (46), which will be analogous to the equations of motion of a system of one degree of freedom, it follows directly that during the perturbations α_2 will be a function of β_2 and that in general these quantities will be periodic functions of the time with a period σ which, besides on α_1, will depend on the value of Ψ only. Considering two slightly different states of the perturbed system for which the corresponding states of the undisturbed system (i. e. the states which would appear if the external forces vanished at a slow and uniform rate) possess the same energy and consequently the same value for the quantity I defined by (5), we get therefore by a calculation completely analogous to that leading to relation (8) in Part I, which was deduced directly from the Hamiltonian equations, for the difference in the values of the function Ψ for these two states

$$\delta \Psi = \mathfrak{o} \delta \mathfrak{J}, \tag{49}$$

where $\mathfrak{o} = \frac{1}{\sigma}$ is the frequency of the secular perturbations, and where the quantity $\mathfrak{J}$ is defined by

$$\mathfrak{J} = \int_0^{\sigma} \alpha_2 \frac{D\beta_2}{Dt} dt = \int \alpha_2 D\beta_2, \tag{50}$$

where the latter integral is taken over a complete oscillation of β_2. In order to fix the stationary states, it will now be seen in the first place that, among the multitude of states of the perturbed system for which the value of I in the corresponding states of the undisturbed system is equal to nh where n is a given positive integer, the state for which $\mathfrak{J} = 0$ must beforehand be expected to be a stationary state. In fact, for this value of $\mathfrak{J}$, the shape and position of the orbit will not undergo secular perturbations but will remain unaltered for a constant external field as well as during a slow and uniform establishment of this field. In contrast to what in general will take place during a slow establishment of the external field, we may therefore expect that, for this special shape and position of the orbit, a direct application of ordinary mechanics will be legitimate in calculating the effect of the establishment of the field, since there will in this case obviously be nothing to cause the coming into play of some non-mechanical process, connected with the mechanism of a transition between two stationary states accompanied by the emission or absorption of a radiation of small frequency. With reference to relation (49) we see therefore that, by fixing the stationary states of the perturbed system by means of the condition

$$\mathfrak{J} = \mathfrak{n}h, \qquad (51)$$

where $\mathfrak{n}$ is an entire number, we obtain a relation between the additional energy $\mathfrak{E} = \Psi$ of the system in the presence of the field and the frequency $\mathfrak{o}$ of the secular perturbations, which is exactly of the same type as that which holds between the energy and frequency in the stationary states of a system of one degree of freedom, and which is expressed by (8) and (10). By means of (51) it is possible, with neglect of small quantities proportional to the square of the perturbing forces, directly to determine the value of the additional energy in the stationary states of a periodic system of two degrees of freedom subject to an arbitrarily given small external field of force, and consequently with this approximation, by use of the fundamental relation (1), to determine the effect of this field on the frequencies of the spectrum of the undisturbed periodic system. In general this effect will consist in a splitting up of each of the spectral lines into a number of components which are displaced from the original position of the line by small quantities proportional to the intensity of the external forces.

When we pass to perturbed periodic systems of more than two degrees of freedom, the general problem is more complex. For a given external field, however, it may be possible to choose a set of orbital constants $\alpha_2, \ldots \alpha_s$, $\beta_2, \ldots \beta_s$ in such a way, that during the motion every of the α's will depend on the corresponding β only, while every of the β's will oscillate between two fixed limits. From analogy with the theory of ordinary conditionally periodic systems which allow of separation of variables, the perturbations may in such a case be said to be conditionally periodic, and, from a calculation quite analogous to that leading to equation (29) in Part I which is based entirely on the use of the Hamiltonian equations, we get for the difference in Ψ for two slightly different states of the perturbed system, for which the value of I in the corresponding states of the undisturbed system is the same,

$$\delta \Psi = \sum_{1}^{s-1} \mathfrak{v}_k \, \delta \mathfrak{J}_k, \tag{52}$$

where $\mathfrak{v}_k$ is the mean frequency of oscillation of β_{k+1} between its limits, and where the quantities $\mathfrak{J}_k$ are defined by

$$\mathfrak{J}_k = \int \alpha_{k+1} \, D\beta_{k+1}, \quad (k = 1, \ldots s-1) \tag{53}$$

where the integral is taken over a complete oscillation of β_{k+1}. In analogy with the expression (31) for the displacements of the particles of an ordinary conditionally periodic system which allows of separation of variables, we get further in the present case that every of the α's and β's may be expressed as a function of the time by a sum of harmonic vibrations of small frequencies

$$\left.\begin{matrix}\alpha \\ \beta\end{matrix}\right\} = \Sigma \mathfrak{C}_{\mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}} \cos 2\pi \left\{ (\mathfrak{t}_1 \mathfrak{v}_1 + \ldots \mathfrak{t}_{s-1} \mathfrak{v}_{s-1}) \, t + \mathfrak{c}_{\mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}} \right\}, \tag{54}$$

where the $\mathfrak{C}$'s and $\mathfrak{c}$'s are constants, the former of which, besides on I, depend on the $\mathfrak{J}$'s only, and where the summation is to be extended over all positive and negative entire values of the $\mathfrak{t}$'s. If therefore the secular perturbations are conditionally periodic, we may conclude that the stationary states of the perturbed system, corresponding to a given stationary state of the undisturbed system, will be characterised by the $s-1$ conditions

$$\mathfrak{J}_k = \mathfrak{n}_k h, \quad (k = 1, \ldots s-1) \tag{55}$$

where $\mathfrak{n}_1, \ldots \mathfrak{n}_{s-1}$ form a set of entire numbers. In fact, as seen from (52), we obtain in this way a relation between the additional energy and the frequencies of the secular perturbations of exactly the same type as that holding for the energy and frequencies of ordinary conditionally periodic systems and expressed by (22) and (29); moreover we may conclude beforehand that the state in which every of the quantities $\mathfrak{J}_k$, defined by (53), is equal to zero must belong to the stationary states of the perturbed system, because in this case the orbit will not undergo secular perturbations for a constant external field, nor during a slow and uniform establishment of this field. Since the conditions (55), with neglect of small quantities proportional to the square of the intensities of the external forces, allow to determine the additional energy of the system due to the presence of the external field, we see therefore that the effect of this field on the spectrum of the undisturbed system, if the secular perturbations are conditionally periodic, will consist in a splitting up of each spectral line in a number of components, in analogy with the effect of a perturbing field on the spectrum of a periodic system of two degrees of freedom. In general, however, the perturbations, which a periodic system of more than two degrees of freedom undergoes in the presence of a given external field, cannot be expected to be conditionally periodic and to exhibit periodicity properties of the type expressed by formula (54). In such cases it seems impossible to define stationary states in a way which leads to a complete fixation of the total energy in these states, and we are therefore led to the conclusion, that the effect of the external field on the spectrum will not consist in the splitting up of the spectral lines of the original system into a number of sharp components, but in a diffusion of these lines over spectral intervals of a width proportional to the intensity of the external forces.

In special cases in which the secular perturbations of a perturbed periodic system of more than two degrees of freedom are of conditionally periodic type, it may occur that these perturbations are characterised by a number of fundamental frequencies, which is less than $s-1$. In such cases, in which the perturbed periodic system from analogy with the terminology used in Part I may be said to be degenerate, the necessary relation between the additional energy and the frequencies of the secular perturbations is secured by a number of conditions less than that given by (55), and the stationary states are consequently characterised by a number of conditions less than s. With a typical example of such systems we meet if, for a perturbed periodic system of more than two degrees of freedom, the secular perturbations are simply periodic independent of the initial shape and position of the orbit. In direct analogy to what holds for perturbed periodic systems of two degrees of freedom, the difference between the values of Ψ in two slightly different states of the perturbed system, corresponding to the same value of I, will in the present case be given by

$$\delta \Psi = \mathfrak{o} \delta \mathfrak{J}, \tag{56}$$

where $\mathfrak{o}$ is the frequency of the secular perturbations, and where $\mathfrak{J}$ is defined by

$$\mathfrak{J} = \int_0^{\sigma} \sum_2^s \alpha_k \frac{D\beta_k}{Dt} dt, \tag{57}$$

where $\sigma = \frac{1}{\mathfrak{o}}$ is the period of the perturbations. We may therefore conclude that the stationary states of the perturbed system, corresponding to a given stationary state of the undisturbed system, will be characterised by the single condition

$$\mathfrak{J} = \mathfrak{n} h, \tag{58}$$

in which $\mathfrak{n}$ is an entire number, and which will be seen to be completely analogous to the condition which fixes the stationary states of ordinary periodic systems of several degrees of freedom.

In the following sections we shall apply the preceding considerations to the problem of the fixation of the stationary states of the hydrogen atom, when the relativity modifications are taken into account, and when the atom is exposed to small external fields. In this discussion we shall for the sake of simplicity consider the mass of the nucleus as infinite in the calculations of the perturbations of the orbit of the electron. This involves, in the expression for the additional energy of the system, the neglect of small terms of the same order as the product of the intensity of the external forces with the ratio between the mass of the electron and the mass of the nucleus, but due to the smallness of the latter ratio the error introduced by this simplification will be of no importance in the comparison of the results with the measurements. Since in the case under consideration the system possesses three degrees of freedom, the equations which determine the secular perturbations of the orbit of the electron will correspond to the equations of motion of a system of two degrees of freedom, and it will therefore not be possible to give a general treatment of the problem of the stationary states. Thus, for any given external field, we meet with the question whether the perturbations are conditionally periodic and, if so, in what set of orbital constants this periodicity may be conveniently expressed. Now, in many spectral problems, the external field possesses axial symmetry round an axis through the nucleus, and in this case it is easily shown that the problem of the fixation of the stationary states allows of a general solution. A choice of orbital constants which is suitable for the discussion of this problem, and which is well known from the astronomical theory of planetary perturbations, is obtained by choosing for α_2 the total angular momentum of the electron round the nucleus and for α_3 the component of this angular momentum round the axis of the field. For the set of β's, corresponding to this set of α's, we may take β_2 equal to the angle, which the major axis makes with the line in which the plane of the orbit cuts the plane through the nucleus perpendicular to the axis of the field, and β_3 equal to the angle between this line and a fixed direction in the latter plane. For the problem under consideration it will be seen that, with this choice of constants, the mean value Ψ of the potential of the perturbing field will, besides on α_1, generally depend on α_2 and β_2 as well as on α_3, but due to the symmetry round the axis it will obviously not depend on β_3. In consequence of this, the equations (46), which determine the secular perturbations, will possess the same form as the Hamiltonian equations of motion for a particle moving in a plane and subject to a central field of force. Thus corresponding to the conservation of angular momentum for central systems, we get in the first place from (46) that α_3 will remain unaltered during the perturbations. Next corresponding to the simple periodicity of the radial motion in central systems, we see from (46), if α_3 as well as α_1 is considered as a constant, that during the perturbations α_2 will be a function of β_2 and vary in a simple periodic way with the time. The perturbations of the orbit of the electron produced by an external field which possesses axial symmetry will therefore always be of conditionally periodic type, quite independent of the possibility of separation of variables for the perturbed system. As regards the form of the conditions which fix the stationary states, it may be noted, however, that with the choice of orbital constants under consideration the β's will not, as it was assumed for the sake of simplicity in the general discussion on page 52, oscillate between fixed limits, but it will be seen that β_2 during the perturbations may either oscillate between two such limits or increase (or decrease) continuously, while β_3 will always vary in the latter manner. This constitutes, however, only a formal difficulty of the same kind as that mentioned in Part I in connection with the discussion of the conditions (16), which fix the stationary states of a system consisting of a particle moving in a central field of force. Thus from a simple consideration it will be seen that, in complete analogy to the relations (52) and (53), we get in the present case for the difference between the energy of two slightly different states of the perturbed system, which correspond to the same value of I,

$$\delta \Psi = \omega_1 \delta \mathfrak{J}_1 + \omega_2 \delta \mathfrak{J}_2, \tag{59}$$

where ω_1 is the frequency with which the shape of the orbit and its position relative to the axis of the field repeats itself at regular intervals and which is characterised by the variation of α_2 and β_2, while ω_2 is the mean frequency of rotation of the plane of the orbit round this axis characterised by the variation of β_3, and where $\mathfrak{J}_1$ and $\mathfrak{J}_2$ are defined by the equations

$$\mathfrak{J}_1 = \int \alpha_2 D \beta_2, \qquad \mathfrak{J}_2 = \int_0^{2\pi} \alpha_3 D \beta_3 = 2\pi \alpha_3. \tag{60}$$

In case β_2 varies in an oscillating manner with the time, the first integral must be taken over a complete oscillation of this orbital constant, while, if β_2 during the perturbations increases or decreases continuously, the integral in the expression for $\mathfrak{J}_1$ must be taken over an interval of 2π, just as the integral in the expression for $\mathfrak{J}_2$. By fixing the stationary states of the perturbed system by means of the two conditions[1])

$$\mathfrak{J}_1 = n_1 h, \qquad \mathfrak{J}_2 = n_2 h, \tag{61}$$

where n_1 and n_2 are entire numbers, it will therefore be seen that we obtain the right relation between the additional energy $\mathfrak{E} - \Psi$ of the perturbed atom and the fre-

[1]) Quite apart from the problem of perturbed periodic systems, the second of these conditions would also follow directly from certain interesting considerations of EPSTEIN (Ber. d. D. Phys. Ges. XIX. p. 116 (1917)) about the stationary states of systems which allow of what may be called "partial separation of variables". In this case it is possible to choose a set of positional coordinates $q_1, \ldots q_s$ in such a way that, for some of the coordinates, the conjugated momenta may be considered as functions of the corresponding q's only, so that, for these coordinates, quantities I may be defined by (21) in the same way as for systems for which a complete separation of variables can be obtained. From analogy with the theory of the stationary states of the latter systems, EPSTEIN proposes therefore the assumption, that some of the conditions to be fulfilled in the stationary states of the systems in question may be obtained by putting the I's thus defined equal to entire multipla of h. It will be seen that, in case of systems possessing an axis of symmetry, this leads to the second of the conditions (61), which expresses the condition that in the stationary states the total angular momentum round the axis must be equal to an entire multiple of $h/2\pi$. As pointed out in Part I on page 34, this condition would also seem to obtain an independent support from considerations of conservation of angular momentum during a transition between two stationary states.

quencies of the secular perturbations of the orbit of the electron. It will moreover be seen that a state in which the electron moves in a circular orbit perpendicular to the axis of the field, and which beforehand must be expected to belong to the stationary states of the perturbed atom since this orbit will not undergo secular perturbations during a uniform establishment of the external field, will be included among the states determined by (61). In fact, if n is the number which characterises the corresponding stationary state of the undisturbed system, this state of the perturbed system will correspond to $\mathfrak{n}_1 = 0$, $\mathfrak{n}_2 = n$ or to $\mathfrak{n}_1 = n$, $\mathfrak{n}_2 = n$, according to whether β_2 during the perturbations oscillates between fixed limits, or increases (or decreases) continuously. As regards the application of the conditions (61) it is of importance to point out that, from considerations of the invariance of the a-priori probability of the stationary states of an atomic system during continuous transformations of the external conditions (see Part I, page 9 and 27), it seems necessary to conclude that no stationary state exists corresponding to $\mathfrak{n}_2 = 0$. For this value of $\mathfrak{n}_2$ the motion of the electron would take place in a plane through the axis, but for certain external fields such motions cannot be regarded as physically realisable stationary states of the atom, since in the course of the perturbations the electron would collide with the nucleus (compare page 68).

A special case of an external field possessing axial symmetry, in which the secular perturbations are very simple, presents itself if the external forces form a central field with the nucleus at the centre. In this case the solution of the problem of the fixation of the stationary states is given by SOMMERFELD's general theory of central systems, discussed i Part I, which rests upon the fact that these systems allow of separation of variables in polar coordinates. In connection with the above considerations it may be of interest, however, to consider the problem in question directly from the point of view of perturbed periodic systems, because it presents a characteristic example of a degenerate perturbed system. In the present case Ψ will, besides on α_1, depend on α_2 only, and from the equations (46) we get therefore the well known result, that the angular momentum of the electron and the plane of its orbit will not vary during the perturbations, and that the only secular effect of the perturbing field will consist in a slow uniform rotation of the direction of the major axis. For the frequency of this rotation we get from (46)

$$\mathfrak{o} = \frac{1}{2\pi}\frac{D\beta_2}{Dt} = \frac{1}{2\pi}\frac{\partial\Psi}{\partial\alpha_2}, \tag{62}$$

from which we get directly for the difference between the values of Ψ for two neighbouring states of the perturbed system, for which the corresponding value of I is the same,

$$\delta\Psi = 2\pi\mathfrak{o}\,\delta\alpha_2. \tag{63}$$

This relation, which corresponds to (56), is seen to coincide with (59), since in the present case $\mathfrak{o}_2 = 0$ and $\mathfrak{I}_1 = 2\pi\alpha_2$. From (63) it follows that the necessary relation between the additional energy of the atom and the frequency of the perturbations is secured if the stationary states in the presence of a small external central field are characterised by the condition

$$\mathfrak{J} = 2\pi\alpha_2 = \mathfrak{n}h, \tag{64}$$

where $\mathfrak{n}$ is an entire number. This condition, which is equivalent with the second of SOMMERFELD's conditions (16), corresponds to (58) and is seen to coincide with the first of the conditions (61), while the second of the latter conditions in the special case under consideration looses its validity corresponding to the fact that the orientation of the plane of the orbit in space is obviously arbitrary. Since, for a Keplerian motion, the major axis of the orbit depends on the total energy only while the minor axis is proportional to the angular momentum, it will be seen from (64) that the presence of a small external field imposes the restriction on the motion of the atom in the stationary states, that the minor axis ot the orbit of the electron must be equal to an entire multiple of the n^{th} part of the major axis, which was given by $2a_n$ in (41). This result has been pointed out by SOMMERFELD as a consequence of the application of the conditions (16).

In the preceding it has been shown how it is possible to attack the problem of the stationary states of a perturbed periodic system by an examination of the secular perturbations of the shape and position of the orbit, and to fix these states if the perturbations are of periodic or conditionally periodic type. While these considerations allow to determine the possible values for the total energy of the perturbed system and thereby the frequencies of the components into which the lines of the spectrum of the undisturbed system are split up in the presence of the external field, it is necessary, however, for the discussion of the intensities and polarisations of these components to consider more closely the motion of the particles in the perturbed system and the relation of the total energy of this system to the fundamental frequencies which characterise the motion. In the first place it will be seen that, if the secular perturbations as determined by the equations (46) are of conditionally periodic type, the displacements of the particles of the system in any given direction may, with neglect of small quantities proportional to the intensity of the external forces, be represented, within a time interval sufficiently large for these forces to produce a considerable change in the shape and position of the orbit, as a sum of harmonic vibrations by expressions of the type:

$$\xi = \Sigma C_{\tau, \mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}} \cos 2\pi \{ (\tau\omega_P + \mathfrak{t}_1 \mathfrak{v}_1 + \ldots \mathfrak{t}_{s-1} \mathfrak{v}_{s-1}) t + c_{\tau, \mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}} \}, \tag{65}$$

where the summation is to be extended over all positive and negative entire values of $\tau, \mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}$, and where the C's and c's are two sets of constants, the former of which depend only on the values of the quantities $\mathfrak{J}_1, \ldots \mathfrak{J}_{s-1}$ defined by (53) and on the value of the quantity I, which characterises the corresponding state of the undisturbed system which would appear if the external field vanished at a slow and uniform rate. While the quantities $\mathfrak{v}_1, \ldots \mathfrak{v}_{s-1}$ are the same as those which appear in the formula (54), and represent the small frequencies of the secular perturbations of the shape and position of the orbit, the quantity ω_p may be considered as representing the mean frequency of revolution of the particles in their approximately periodic orbit. As regards the total energy of the perturbed system, it may next be proved that, looking apart from small quantities proportional to the square of the intensity of the external forces, the difference in the total energy in two slightly different states of the perturbed system, for which the values of $I, \mathfrak{I}_1, \ldots \mathfrak{I}_{s-1}$ differ by $\delta I, \delta\mathfrak{I}_1, \ldots \delta\mathfrak{I}_{s-1}$ respectively, is given by the relation.[1])

$$\delta E = \omega_p \delta I + \sum_1^{s-1} \mathfrak{o}_k \delta \mathfrak{I}_k, \tag{66}$$

which coincides with (52) if $\delta I = 0$, and which will be seen to be completely analogous with formula (29) in Part I, holding for an ordinary conditionally periodic system which allows of separation of variables in a fixed set of positional coordinates; just as (65) is analogous to formula (31) representing the displacements of the par-

[1]) From a comparison with formula (8), holding for the energy difference between two neighbouring states of the undisturbed system, and with formula (52), it will be seen that (66) implies the condition $\omega_p = \omega + \partial\Psi/\partial I$, where ω is the frequency of revolution in the corresponding state of the undisturbed system characterised by the given value of I, and where, in the partial differential coefficient, Ψ is considered as a function of I and $\mathfrak{I}_1, \ldots \mathfrak{I}_{s-1}$. This relation can be verified by means of a consideration based on the perturbation equations (44), which takes into account the simple relation between α_1 and I for the undisturbed system, as well as the relation between the mean rate of variation of β_1 with the time and the difference between ω_p and ω. We shall not enter, however, on the details of the rather intricate calculations involved in such a consideration, since the problems in question allow of a more elegant treatment by means of another analytical method. Thus it will be shown by Mr. H. A. Kramers, in the paper mentioned in the end of § 4, that, quite independent of the possibility of separation of variables for the perturbed system in a fixed set of positional coordinates, the theory of secular perturbations exposed in this section offers — if these perturbations as determined by (46) are of conditionally periodic type — a means of disclosing a set of angle variables, which may be used to describe the motion of the perturbed system with the same degree of approximation as that involved in the preceding calculations. According to the definition of angle variables, mentioned in the Note on page 29 in Part I, this means that it is possible, in stead of the positional coordinates $q_1, \ldots q_s$ of the perturbed system and their conjugated momenta $p_1, \ldots p_s$, to introduce a new set of s variables in such a way, that the q's and p's are periodic in every of the new variables with period 1, when they are considered as functions of these variables and of their canonically conjugated momenta. These momenta will just coincide with the quantities denoted above by $I, \mathfrak{I}_1, \ldots \mathfrak{I}_{s-1}$, and the corresponding angle variables may conveniently be denoted by $w, \mathfrak{w}_1, \ldots \mathfrak{w}_{s-1}$ respectively. Introducing the new variables, the total energy of the perturbed system will be a function of $I, \mathfrak{I}_1, \ldots \mathfrak{I}_{s-1}$ only, if we look apart from small quantities proportional to λ^2. With this approximation we get consequently by a calculation, analogous to that given in the Note referred to, that the angle variables $w, \mathfrak{w}_1, \ldots \mathfrak{w}_{s-1}$ may be represented as linear functions of the time within an interval of the same order as σ/λ. Denoting the rates of variation of $w, \mathfrak{w}_1, \ldots \mathfrak{w}_{s-1}$ by $\omega_p, \mathfrak{o}_1, \ldots \mathfrak{o}_{s-1}$ respectively, the formulae (65) and (66) are therefore directly obtained, just as the corresponding formulae (31) and (29) in Part I. In this connection it will be observed that, due to the possibility of introduction of angle variables, the conditions (67) appear in the same form as that in which the conditions, which fix the stationary states of ordinary conditionally periodic systems which allow of separation of variables, have been formulated by Schwarzschild, and which, as mentioned in the Note in Part I, has already been applied by Burgers to certain systems for which such a separation cannot be obtained.

ticles for such a system. Since moreover, in complete analogy to the conditions (22), the stationary states of the perturbed system are characterised by

$$I = nh, \qquad \mathfrak{J}_k = \mathfrak{n}_k h, \qquad (k = 1, \ldots s-1) \tag{67}$$

we see consequently that, for sufficiently small intensity of the external forces, we obtain in the region of large values of n and of the $\mathfrak{n}$'s a connection between the frequencies of the components of the spectral lines, determined on the quantum theory by means of relation (1), and those to be expected on ordinary electrodynamics, which is of exactly the same type as the analogous connection, discussed in Part I, in case of ordinary conditionally periodic systems which allow of separation of variables. In perfect analogy with the general considerations in Part I, we are therefore led directly to certain simple conclusions as regards the intensities and polarisations of the components into which the lines of the spectrum of the undisturbed periodic system are split up in the presence of the external field. Thus we shall expect that there will exist an intimate connection between the probability of spontaneous transition between two stationary states of the perturbed system, for which $n = n'$, $\mathfrak{n}_k = \mathfrak{n}'_k$ and $n = n''$, $\mathfrak{n}_k = \mathfrak{n}''_k$ respectively, and the values in these states of the coefficient $C_{\tau, \mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}}$ in the expressions for the displacements of the particles, for which $\tau = n' - n''$ and $\mathfrak{t}_k = \mathfrak{n}'_k - \mathfrak{n}''_k$. If for instance, for a certain set of values of τ and $\mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}$, the coefficient $C_{\tau, \mathfrak{t}_1, \ldots \mathfrak{t}_{s-1}}$ in the expressions for the displacements in every direction will be equal to zero for all motions of the perturbed system, we shall expect that the corresponding transitions between two stationary states will be impossible in the presence of the given external field; and if this coefficient is zero for the displacements of the particles in a certain direction only, we shall expect that the corresponding transitions will give rise to the emission of a radiation which is polarised in a plane perpendicular to this direction.

With a characteristic example of these considerations we meet in the case of the spectrum of a hydrogen atom exposed to an external field of force which possesses axial symmetry round an axis through the nucleus. In analogy with the resolution of the motion of an ordinary conditionally periodic system which possesses an axis of symmetry in its constituent harmonic vibrations, discussed in Part I on page 33, it follows from the discussion of the general character of the secular perturbations on page 54 that the motion of the electron in the perturbed atom in this case can be resolved in a number of linear harmonic vibrations parallel to the axis with frequencies $\tau\omega_p + \mathfrak{t}_1 \mathfrak{o}_1$ and in a number of circular harmonic rotations perpendicular to the axis with frequencies $\tau\omega_p + \mathfrak{t}_1 \mathfrak{o}_1 + \mathfrak{o}_2$. In complete analogy with the considerations in Part I, we are therefore led to conclude that in the present case only two types of transitions between the stationary states of the perturbed atom are possible. In the transitions of the first type $\mathfrak{n}_2$ will remain unaltered and the emitted radiation will give rise to components of the hydrogen lines which will show linear polarisation parallel to the axis. In the transitions of the second type $\mathfrak{n}_2$ will change by one unit and the emitted radiation will show circular polarisation when viewed in the direction of the axis. Remembering that, according to the conditions (61), the angular momentum of the system round the axis in the stationary states is equal to $n_2 \frac{h}{2\pi}$, it will be seen moreover that, also in the present case, these conclusions obtain an independent support from a consideration of conservation of angular momentum during the transitions (Compare Part I page 34)[1]. In the following we will meet with applications of these considerations when discussing the effect of electric and magnetic fields on the hydrogen lines. In the latter case, however, the preceding considerations need some modifications due to the fact, that the external forces acting on the electron cannot be derived from a potential expressed as a function of its positional coordinates; to this point we shall come back in § 5.

Before leaving the general theory of perturbed periodic systems we shall still consider the problem of the effect on the spectrum of a periodic system, undergoing secular perturbations of conditionally periodic type under the influence of a given small external field, if this system is further subject to the influence of a second external field which is small compared with the first field, but the perturbing effect of which is yet large compared with the small effects on the motion, proportional to the square of the intensity of the first perturbing field, which were neglected in the preceding calculations. This problem is closely analogous to the problem, briefly discussed in Part I, of the effect of a small perturbing field on the spectrum of an ordinary conditionally periodic system which allows of separation of variables. As mentioned on page 34, we have in this case, quite independent of the possibility of separation of variables for the perturbed system, that in general the motion under the influence of the external field may still be represented as a sum of harmonic vibrations by a formula of the type (31), if we look apart from small terms proportional to the square of the perturbing forces. Corresponding to this we have in the case under consideration that, independent of the nature of the second external field, the resultant secular perturbations may in general be expressed as a sum of harmonic vibrations of small frequencies of the type (54), if we look apart from small terms of the same order as the product of the secular perturbations produced by the first external field with the square of the ratio between the intensities of the forces due to the first and those due to the second external field. Let us denote this ratio by μ and let, as above, λ represent a small constant of the same order as the ratio between the ex-

[1]) Note added during the proof. In an interesting paper by A. Rubinowicz (Phys. Zeitschr. XIX, p. 441 and p. 465 (1918)) which has just been published, a similar consideration of conservation of angular momentum has been used to draw conclusions, as regards the possibility of transitions between the stationary states of a conditionally periodic system possessing an axis of symmetry, and as regards the character of the polarisation of the radiation accompanying these transitions. In this way Rubinowicz has arrived at several of the results discussed in the present paper; in this connection, however, it may be remarked that, from a consideration of conservation of angular momentum, it is not possible, even for systems possessing axial symmetry, to obtain as complete information, as regards the number and polarisation of the possible components, as from a consideration based on the resolution of the motion of the electron in harmonic vibrations.

ternal forces due to the first field and the internal forces of the system. On the basis of the general relation between energy and frequency in the stationary states, we may then expect that it is possible to fix the motion in these states for the perturbed periodic system in the presence of both external fields with neglect of small terms of the same order as the largest of the quantities μ^2 and λ, and to fix the corresponding values for the energy with neglect of small terms of the same order as the largest of the quantities $\lambda\mu^2$ and λ^2.[1] In general, however, the effect on the spectrum of the perturbed system, produced by the second external field, may be calculated without considering the perturbing effect of this field in detail. In fact, it is in general possible, by means of the principle of the mechanical transformability of the stationary states, with the approximation mentioned to determine the alteration of the energy of the system, due to the presence of the second external field, directly from the character of the secular perturbations produced by the first external field only. Thus let us assume that the second field is slowly established at a uniform rate within a time interval of the same order of magnitude as that in which the system will pass approximately through any state belonging to the cycle of shapes and positions, which the orbit passes through in the stationary states in the presence of the first external field only. Denoting a time interval of this order by ϑ and the potential of the first perturbing field by Ω and that of the second by $\Delta\Omega$, we get then, by a calculation quite analogous to that given in Part I on page 11 for the alteration in the mean value of the energy of a periodic system during a slow establishment of a small external field, that the alteration in the mean value of $\alpha_1 + \Omega$ taken over a time interval of the same order as ϑ, due to the establishment of the second external field, will be a small quantity of the same order of magnitude as $\vartheta\ (\Delta\Omega)^2$; but with the notation used above this means, in general, a small quantity of the same order as $\lambda\mu^2$. It follows consequently that, with this approximation, the alteration in the energy in a given stationary state, due to the presence of the second perturbing field, is equal to the mean value of the potential of this field taken over the cycle of shapes and positions, which the orbit would pass through in the corresponding stationary state of the perturbed system under the influence of the first external field only. In general, the effect on the spectrum will therefore consist in a small displacement of the original components proportional to the intensity of the forces due to the second perturbing field; and as regards the degree of approximation with which these displacements are defined, it will be seen from the above that, if μ is smaller than $\sqrt{\lambda}$, the fixation of the energy in the stationary states in the presence of the second external field, and therefore also the determination of the frequencies of the spectral

[1]) In analogy with the considerations on page 50 it may be expected, however, that these limits for the definition of the energy in the stationary states will hold only for the great majority among a large number of atomic systems. Thus in the present case we must be prepared to find that for a small fraction of the systems of the same order as μ^2 (if $\mu^2 > \lambda$) the energy will differ from that fixed by the method under consideration by small quantities of the same order as $\mu\lambda$.

lines by means of (1), allow of the same degree of approximation as the fixation of the energy in the stationary states of the original perturbed periodic system. If μ is larger than $\sqrt{\lambda}$, however, the stationary states will in general not be as well defined as for the original system, and from relation (1) we may therefore expect that the components will be diffuse, although, as long as μ remains small compared with unity, the width of the components will remain small compared with the displacements from their positions in the presence of the first external field alone. Only when μ becomes of the same order as unity, the simultaneous effect of both perturbing fields may be expected to consist in a diffusion of the lines of the undisturbed periodic system; unless of course the secular perturbations due to the simultaneous presence of both fields are still of conditionally periodic type, as it may happen in special problems. In certain cases the second external field will not only give rise to small displacements of the original components but also to the appearance of new components of small intensities proportional to μ^2. This occurs if for the original perturbed periodic system, due to some pecularity of the motion, some of the coefficients $C_{\tau, t_1, \ldots t_{s-1}}$ in the expressions (65) for the displacements of the particles as a sum of harmonic vibrations, corresponding to certain combinations of the numbers $\tau, t_1, \ldots t_{s-1}$, are equal to zero, while in the presence of the second external field these coefficients are small quantities proportional to μ (Compare Part I, page 34).[1] In the preceding considerations it has been assumed that the perturbed system in the presence of the first external field is non-degenerate. In case, however, this system is degenerate, it is obviously impossible, by a direct application of the principle of the mechanical transformability of the stationary states, to determine the alteration in the energy in the stationary states of the system, which will be due to the presence of a second external field small compared with the first field; because, as mentioned, the stationary states of the system, in the presence of this field only, will be determined by a number of conditions which is less than the number s of degrees of freedom, and that consequently the cycles of shapes and positions, which the orbit will pass through in these states, will not be completely determined. For the calculation of the energy in the stationay states it will therefore be necessary to consider the secular perturbing effect of the second external field on these cycles. In the special case where the secular perturbations due to the first field are simply periodic, it will in this way be seen that the problem of the fixation of the stationary states in the presence of the second external field, by means of the method exposed in this section, may be reduced to the problem of the fixation of the stationary states of a system of $s-2$ degrees of freedom. If, as in the applications considered below, s is equal to 3, this problem allows of a general solution, and we must therefore expect that in this case the

[1]) As regards the degree of definition with which the positions of the new components will be determined, we must be prepared to find that the frequencies of these components are only defined with neglect of small quantities proportional to $\lambda\mu$. Compare the detailed discussion of the example in § 5 on page 97.

effect on the spectrum of the perturbed system produced by an arbitrary second external field, which is small compared with the first, will consist in the splitting up of every component into a number of separate components, just as the effect of an arbitrary small external field on the lines of the spectrum of a simple periodic system of two degrees of freedom. We will meet with applications of the above considerations when considering the effect on the hydrogen spectrum of the combined action of different external fields and when considering the effect of an external field on the spectra of other elements, which latter problem will be discussed in Part III.

§ 3. The fine structure of the hydrogen lines.

An instructive application of the calculations in the last section may be made in connection with the fine structure of the hydrogen lines, which, according to SOMMERFELD's theory mentioned in Part I on page 18, may be explained by taking into account the small variation of the mass of the electron with its velocity, claimed by the theory of relativity. In this connection it must first of all be remarked that all the general considerations in the preceding sections, as regards relations between energy and frequency and as regards the mechanical transformability of the stationary states, hold unaltered if the relativity modifications are taken into account. This follows from the fact that the Hamiltonian equations (4), which are taken as a basis for all the previous calculations, may be used to describe the motion also in this case. If, when the relativity modifications are taken into account, the motion of the system is simply periodic independent of the initial conditions, we shall consequently expect that the stationary states are characterised by the condition $I = nh$ only, and that the energy and frequency are the same for all states corresponding to a given value of n in this equation. Further the stationary states will also in the relativity case be fixed by (22), if the system is conditionally periodic and allows of separation of variables; while the stationary states of a perturbed periodic system, also in the relativity case, will be characterised by the conditions (67), if the secular perturbations are of conditionally periodic type.

Now, when the relativity modifications are taken into account, the motion of the particles in the hydrogen atom will not, as assumed in § 1, be exactly periodic, but the orbit of the electron will be of the same type as that, which would appear on ordinary Newtonian mechanics, if the law of attraction between the particles differed slightly from that of the inverse square. If, for the moment, we consider the mass of the nucleus as infinite, the system will allow of a separation of variables in polar coordinates, and the stationary states may consequently be fixed by the conditions (16). In this way SOMMERFELD obtained an expression for the total energy in the stationary states, which, with neglect of small quantities of higher order than the square of the ratio of the velocity of the electron and the velocity of light c, is given by[1])

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2 (n_1 + n_2)^2} \left[1 + \frac{\pi^2 N^2 e^4}{c^2 h^2 (n_1 + n_2)^2} \left(1 + 4 \frac{n_1}{n_2} \right) \right], \tag{68}$$

where, as in the calculations in § 1, the charge and the mass of the electron are denoted by $-e$ and m, and for sake of generality the charge of the nucleus by Ne. Further n_1 and n_2 are the integers appearing on the right side of the conditions (16) as factors to PLANCK's constant. While n_1 may take the values 0, 1, 2, ..., it will be seen that n_2 can only take the values 1, 2, ..., because in the present case there will obviously not correspond any stationary state to $n_2 = 0$, since in such a state the electron would collide with the nucleus. Introducing the experimental values for e, h and c, it is found that e^2/hc is a small quantity of the same order as 10^{-3}; and, unless N is large number, the second term within the bracket on the right side of (68) will consequently be very small compared with unity. Putting $n_1 + n_2 = n$, it will further be seen that the factor outside the bracket will coincide with the expression for W_n given by (41) in § 1, if we look apart from the small correction due to the finite mass of the nucleus. Due to the presence of the second term within the bracket, we thus see that, for any value of n, formula (68) gives a set of values for E which differ slightly from each other and from $-W_n$. SOMMERFELD's theory leads therefore to a direct explanation of the fact, that the hydrogen lines, when observed by instruments of high dispersive power, are split up in a number of components situated closely to each other; and, by means of formula (68) in connection with relation (1), it was actually found possible, within the limits of experimental errors, to account for the frequencies of the components of this socalled *fine structure* of the hydrogen lines. Moreover the theory was supported in the most striking way by PASCHEN's[2]) recent investigation of the fine structure of the lines of the analogous helium spectrum, the frequencies of which are represented approximately by formula (35), if in the expression for K, given by (40), we put $N = 2$. As it should be expected from (68), the components of these lines were found to show frequency differences several times larger than those of the hydrogen lines, and from his measurements PASCHEN concluded, that it was possible on SOMMERFELD's theory to account completely for the frequencies of all the components observed.

We shall not enter here on the details of the calculation leading to (68), but shall only show how this formula may be simply interpreted from the point of

[1]) A. SOMMERFELD, Ann. d. Phys. LI, p. 53 (1916). Compare also P. DEBYE, Phys. Zeitschr., XVII, p. 512 (1916). In the special case of circular orbits ($n_1 = 0$), this expression coincides with an expression previously deduced by the writer (Phil. Mag. XXIX p. 332 (1915)), by a direct application of the condition $I = nh$ to these periodic motions.

[2]) F. PASCHEN, Ann. d. Phys. L, p. 901 (1916). See also E. J. EVANS and C. CROXSON, Nature, XCVII, p. 56 (1916).

view of perturbed periodic systems. Thus, by a simple application of relativistic mechanics, it is found that, if the equation of a Keplerian ellipse in polar coordinates is given by $r = f(\vartheta)$, the equation of the orbit of the electron in the case under consideration will be given by $r = f(\gamma\vartheta)$ where γ is a constant given by $\gamma^2 = 1 - \left(\frac{Ne^2}{pc}\right)^2$, in which expression p denotes the angular momentum of the electron round the nucleus.[1]) Now in the stationary states the quantity in the bracket, which is of the same order of magnitude as the ratio between the velocity of the electron and the velocity of light, will be very small, unless N is a large number, and it will therefore be seen that the orbit of the electron can be described as a periodic orbit on which a slow uniform rotation is superposed. Denoting the frequency of revolution in the periodic orbit by ω and the frequency of the superposed rotation by σ_R, we have, with neglect of small quantities of higher order than the square of the ratio between the velocity of the electron and the velocity of light,

$$\sigma_R = \omega(1-\gamma) = \frac{1}{2}\,\omega\left(\frac{Ne^2}{pc}\right)^2. \tag{69}$$

Comparing this formula with equation (62) and remembering that, with the approximation in question, p may be replaced by the quantity denoted in § 2 by α_2, we see that the frequency of the secular rotation of the orbit will be the same as that which would appear, if the variation of the mass of the electron was neglected, but if the atom was subject to a small external central force the mean value of the potential of which, taken over a revolution of the electron, was equal to

$$\Psi = -\omega\frac{\pi N^2 e^4}{c^2 \alpha_2}. \tag{70}$$

This is simply shown, however, to be equal to the expression for Ψ corresponding to a small attractive force varying as the inverse cube of the distance. In fact, let the potential of such a force be given by $\Omega = C/r^2$, where C is a constant and r the length of the radius vector from the nucleus to the electron. By means of the relation $\alpha_2 = mr^2\dot{\vartheta}$, where ϑ is the angular distance of the radius vector from a fixed line in the plane of the orbit, we get then

$$\Psi = \frac{1}{\sigma}\int_0^\sigma \frac{C}{r^2}\,dt = \frac{\omega m C}{\alpha_2}\int_0^{2\pi} d\vartheta = \frac{2\pi\omega m C}{\alpha_2},$$

which expression is seen to coincide with (70), if $C = -\frac{N^2 e^4}{2c^2 m}$.

If the relativity modifications are taken into account, and if for a moment we would imagine that the nucleus, in addition to its usual attraction, exerted

[1]) See f. inst. A. Sommerfeld, loc. cit. p. 47.

a small repulsion on the electron, proportional to the inverse cube of the distance and equal and opposite to the attraction just mentioned, we would therefore obtain a system for which, with neglect of small quantities of higher order than the square of the ratio between the velocity of the electron and the velocity of light, every orbit would be periodic independent of the initial conditions, and for which consequently the stationary states would be fixed by the single condition $I = nh$. Now the actual hydrogen atom may obviously be considered as a perturbed system, formed by this periodic system, when it is exposed to a small central field for which the value of Ψ is given by (70). With the approximation mentioned, we get therefore for the total energy in the stationary states of the atom

$$E = E'_n - \frac{8\pi^4 N^4 e^8 m}{h^4 c^2} \frac{1}{n^3 \mathrm{n}}, \tag{71}$$

where E'_n is the energy in the stationary states of the periodic system just mentioned, and where the last term is obtained by introducing in (70) the value of a_2 given by (64) and the value of ω_n given by (41), neglecting the small correction due to the finite mass of the nucleus. Remembering that in our notation $n_1 + n_2 = n$ and $n_2 = \mathrm{n}$, it will be seen that, as regards the small differences in the energy of the different stationary states corresponding to the same value of n, formula (71) gives the same result as SOMMERFELD's formula (68). In fact, comparing (68) and (71), we get

$$E'_n = -\frac{2\pi^2 N^2 e^4 m}{h^2 n^2}\left(1 - \frac{3\pi^2 N^2 e^4}{c^2 h^2 n^2}\right), \tag{72}$$

which is seen to be a function of n only. This expression might also have been deduced directly from the condition $I = nh$ by considering, for instance, a circular orbit, in which case the calculation can be very simply performed.

In connection with the above calculations, it may be remembered that the fixation of the stationary states, leading to the formulæ (68) or (71), is based on the assumption, that the motion of the electron can be determined as that of a mass point which moves in a conservative field of force, according to the laws of ordinary relativistic mechanics, and that we have looked apart from all such forces which, according to the ordinary theory of electrodynamics, would act on an accellerated charged particle, and which constitute the reaction from the radiation which on this theory would accompany the motion of the electron. Some procedure of this kind, which means a radical departure from the ordinary theory of electrodynamics, is obviously necessary in the quantum theory in order to avoid dissipation of energy in the stationary states. Since we are entirely ignorant as regards the mechanism of radiation, we must be prepared, however, to find that the above treatment will allow to determine the motion in the stationary states, only with an approximation which looks apart from small quantities of the same order as the ratio between the radiation forces in ordinary electrodynamics and the main forces on the electron due to the attraction from the nucleus.[1]) Now it is easily shown that this ratio will be a small quantity of the same order of magnitude as $N^2 \left(\frac{e^2}{pc}\right)^3$, and it would therefore beforehand seem justified in the expression for the total energy in the stationary states to retain small terms of the same order as the second term in (71), while at the same time it might appear highly questionable, whether, in the complete expression for the total energy in the stationary states deduced by Sommerfeld and Debye on the basis of the conditions (16), it has a physical meaning to retain terms of higher order than those retained in formula (68); unless N is a large number, as in the theory of the Röntgenspectra to be discussed in Part III.

While the preceding considerations, which deal with the determination of the energy in the stationary states of the hydrogen atom, allow to determine the frequency of the radiation which would be emitted during a transition between two such states, they leave quite untouched the problem of the actual occurrence of these transitions in the luminous gas, and therefore give no direct information about the number and relative intensities of the components into which the hydrogen lines may be expected to split up as a consequence of the relativity modifications. This problem has recently been discussed by Sommerfeld[2]), who in this connection emphasises the importance of the different a-priori probabilities of the stationary states, characterised by different sets of values of the n's in the conditions (16). Thus Sommerfeld attempts to obtain a measure for the relative intensities of the components of the fine structure of a given line, by comparing the intensities observed with the products of the values of the a-priori probabilities of the two states, involved in the emission of the components under consideration; and he tries in this connection to test different expressions for these a-priori probabilities (See Part I, pag. 26). In this way, however, it was not found possible to account in a satisfactory manner for the observations; and the difficulty in obtaining an explanation of the intensities on this basis was also strikingly brought out by the fact, that the number and relative intensities of the components observed varied in a remarkable way with the experimental conditions under which the lines were

[1]) Compare Part I, p. 6. It may in this connection be noted that the degree of approximation, involved in the determination of the frequencies of an atomic system by means of relation (1 if in the fixation of the stationary states we look apart from small forces of the same order of magnitude as the radiation forces in ordinary electrodynamics, would appear to be intimately connected with the limit of sharpness of the spectral lines, which depends on the total number of waves contained in the radiation emitted during the transition between two stationary states. In fact, from a consideration based on the general connection between the quantum theory and the ordinary theory of radiation, it seems natural to assume that the rate, at which radiation is emitted during a transition between two stationary states, is of the same order of magnitude as the rate, at which radiation would be emitted from the system in these states according to ordinary electrodynamics. But this will be seen to imply that the total number of waves in question will just be of the same order as the ratio between the main forces acting on the particles of the system and the reaction from the radiation in ordinary electrodynamics.

[2]) A. Sommerfeld, Ber. Akad. München, 1917, p. 83.

excited. Thus PASCHEN found a greater number of components in the fine structure of the helium lines, mentioned above, when the gas was subject to a condensed interrupted discharge, than when a continuous voltage was applied. It would seem, however, that all the facts observed obtain a simple interpretation on the basis of the general considerations about the relation between the quantum theory of line spectra and the ordinary theory of radiation discussed in Part I. According to this relation, we shall assume that the probability, for a transition between two given stationary states to take place, will depend not only on the a-priori probability of these states, which is determining for their occurrence in a distribution of statistical equilibrium, but will also depend essentially on the motion of the particles in these states, characterised by the harmonic vibrations in which this motion can be resolved. Now, in the absence of external forces, the motion of the electron in the hydrogen atom forms a special simple case of the motion of a conditionally periodic system possessing an axis of symmetry, and may therefore be represented by trigonometric series of the type deduced for such motions in Part I. Taking a line through the nucleus perpendicular to the plane of the orbit as z-axis, we get from the calculations on page 32

$$z = \text{const.}$$

and

$$x = \Sigma C_\tau \cos 2\pi \{ (\tau\omega_1 + \omega_2)t + c_\tau \}, \quad \pm y = \Sigma C_\tau \sin 2\pi \{ (\tau\omega_1 + \omega_2)t + c_\tau \}, \quad (73)$$

where ω_1 is the frequency of the radial motion and ω_2 is the mean frequency of revolution, and where the summation is to be extended over all positive and negative entire values of τ. It will thus be seen that the motion may be considered as a superposition of a number of circular harmonic vibrations, for which the direction of rotation is the same as, or the opposite of, that of the revolution of the electron round the nucleus, according as the expression $\tau\omega_1 + \omega_2$ is positive or negative respectively. From the relation just mentioned between the quantum theory of line spectra and the ordinary theory of radiation, we shall therefore in the present case expect that, if the atom is not disturbed by external forces, only such transitions between stationary states will be possible, in which the plane of the orbit remains unaltered, and in which the number n_2 in the conditions (16) decreases or increases by one unit; i. e. where the angular momentum of the electron round the nucleus decreases or increases by $h/2\pi$. From the relation under consideration, we shall further expect that there will be an intimate connection between the probability of a spontaneous transition of this type between two stationary states, for which n_1 is equal to n'_1 and n''_1 respectively, and the intensity of the radiation of frequency $(n'_1 - n''_1)\,\omega_1 \pm \omega_2$, which on ordinary electrodynamics would be emitted by the atom in these states, and which would depend on the value C_τ of the amplitude of the harmonic rotation, corresponding to $\tau = \pm(n'_1 - n''_1)$, which appears in the motion of the electron. Without entering upon a closer examination of the numerical values of these amplitudes, it will directly be seen that the amplitudes of the harmonic rotations, which have the same direction as the revolution of the electron, in general, are considerably larger than the amplitudes of the rotations in the opposite direction, and we shall accordingly expect that the probability of spontaneous transition will in general be much larger for transitions, in which the angular momentum decreases, than for transitions in which it increases. This expectation is verified by PASCHEN's observations of the fine structure of the helium lines, which show that, for a given line, the components corresponding to the transitions of the former kind are by far the strongest. On PASCHEN's photographs, however, especially in the case of the application of a condensed discharge to the vacuum tube containing the gas, there appear, in addition to the main components corresponding to transitions for which the angular momentum changes by $h/2\pi$, a number of weaker components, corresponding to transitions for which the angular momentum remains unchanged or changes by higher multipla of $h/2\pi$. This fact obtains a simple interpretation on the considerations in Part I on page 34 about the influence of small external forces on the spectrum of a conditionally periodic system. Thus, in the presence of small perturbing forces, the motion will generally not remain in a plane, and in the trigonometric series representing the displacement of the electron in space, there will occur small terms corresponding to frequencies $(\tau_1 \omega_1 + \tau_2 \omega_2)$, where τ_2 may be different from one. In the presence of such forces, we shall therefore expect that, in addition to the regular probabilities of the above mentioned main transitions, there will appear small probabilities for other transitions.[1] A detailed discussion of these problems will be given in a later paper by Mr. H. A. KRAMERS, who on my proposal has kindly undertaken to examine the resolution of the motion of the electron in its constituent harmonic vibrations more closely, and who has deduced explicite expressions for the amplitudes of these vibrations, not only for the motion of the electron in the undisturbed atom, but also for the perturbed motion in the presence of a small external homogeneous electric field. As it will be shown by KRAMERS, these calculations allow to account in particulars for the observations of the relative intensities of the components of the fine structure of the hydrogen lines and the analogous helium lines, as well as for the characteristic way in which this phenomenon is influenced by the variation of the experimental conditions.

§ 4. The effect of an external electric field on the hydrogen lines.

As mentioned in the introduction, a detailed theory of the characteristic effect of an external homogeneous electric field on the hydrogen spectrum, discovered by

[1] Note added during the proof. As remarked in Part I, this consideration obtains a striking confirmation by the observation of the appearance of new series of lines in the ordinary series spectra of helium and other elements, when the atoms are exposed to an intense external electric field. As it will be discussed more closely in Part III, it is possible in this way to account in detail for the manifold results, regarding the appearance of such series in the helium spectrum, which have been published quite recently by J. STARK (Ann. d. Phys. LVI, p. 577 (1918)) and by G. LIEBERT (ibid. LVI, p. 589 and p. 610 (1918)).

Stark, has been given by Epstein and Schwarzschild on the basis of the general theory of conditionally periodic systems which allow of separation of variables. Before we enter on the discussion of the results of the calculations of these authors, we shall first, however, show how the problem may be treated in a simple way by means of the considerations about perturbed periodic systems, developed in § 2.

Consider an electron of mass m and charge $-e$, rotating round a positive nucleus of infinite mass and of charge Ne, and subject to a homogeneous electric field of intensity F, and let us for the present neglect the small effect of the relativity modifications. Using rectangular coordinates, and taking the nucleus as origin and the z-axis parallel to the external field, we get for the potential of the system relative to the external field, omitting an arbitrary constant,

$$\Omega = eFz.$$

Calculating now the mean value of Ω over a period σ of the undisturbed motion, we see at once, from considerations of symmetry, that this mean value Ψ will depend only on the component of the external electric force in the direction of the major axis of the orbit. We have therefore

$$\Psi = eF\cos\varphi \frac{1}{\sigma}\int_0^\sigma r\cos\vartheta\, dt,$$

where φ is the angle between the z-axis and the major axis, taken in the direction from the nucleus to the aphelium, and where r is the length of the radius-vector from the nucleus to the electron, and ϑ the angle between this radius-vector and the major axis. By means of the well known equations for a Keplerian motion

$$r\cos\vartheta = a(\cos u + \varepsilon), \quad \frac{dt}{\sigma} = (1 + \varepsilon\cos u)\frac{du}{2\pi},$$

where $2a$ is the major axis, ε the eccentricity and u the socalled eccentric anomaly, this gives

$$\Psi = eF\cos\varphi \frac{1}{2\pi}\int_0^{2\pi} a(\cos u + \varepsilon)(1 + \varepsilon\cos u)\, du = \frac{3}{2}\varepsilon a eF\cos\varphi. \tag{74}$$

We see thus that Ψ is equal to the potential energy relative to the external field, which the system would possess, if the electron was placed at a point, situated on the major axis of the ellipse and dividing the distance $2\varepsilon a$ between the foci in the ratio 3:1. This point may be denoted as the "electrical centre" of the orbit. From the approximate constancy of Ψ during the motion, proved in § 2, it follows therefore in the first place that, with neglect of small quantities of the same order of magnitude as the ratio between the external force and the attraction from the nucleus, the electrical centre will during the perturbations of the orbit remain in a fixed plane perpendicular to the direction of the external force. From the considerations in § 2 it follows further, that the total energy in the stationary states of the system in the presence of the field, with neglect of small quantities proportional to F^2, will be equal to $E_n + \Psi$, where E_n is the energy of the hydrogen atom in its undisturbed stationary state. Since both ε and cos φ are numerically smaller than one, we obtain therefore at once from (74) a lower and an upper limit for the possible variations of the energy in the stationary states, due to the field. Introducing from (41) the values of E_n and a_n, and neglecting, here as well as in the following calculations in this section, the small correction due to the finite mass of the nucleus — not only in the expression for the additional energy but, for the sake of brevity, also in the main term — we get for these limits

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2 n^2} \pm \frac{3h^2 n^2}{8\pi^2 N e m} F, \tag{75}$$

which formula coincides with the expression previously deduced by the writer by applying the condition $I = nh$ to the two (physically not realisable) limiting cases, corresponding to $\varepsilon = 1$ and cos $\varphi = \pm 1$, in which the orbit remains periodic in the presence of the field.[1]

In order to obtain further information as to the values of the energy in the stationary states in the presence of the field, it is necessary to consider more closely the variation of the orbit during the perturbations. Since the external forces possess axial symmetry, the problem of the stationary states might be treated by means of the procedure indicated in § 2 on page 55. In the present special case, however, the stationary states of the atom may be very simply determined, due to the fact that the secular perturbations are simply periodic independent of the initial shape and position of the orbit, so that we are concerned with a degenerate case of a perturbed periodic system. This property of the perturbations follows already from some calculations given by Schwarzschild[2]) in a previous attempt to explain the Stark effect of the hydrogen lines, without the help of the quantum theory, by means of a direct consideration of the harmonic vibrations into which the motion may be resolved, according to the analytical theory of conditionally periodic systems. Starting from the above result, that the electrical centre moves in a plane perpendicular to the direction of the external field, the periodicity of the perturbations may also be proved in the following way, by means of a simple consideration of the variation of the angular momentum of the electron round the nucleus, due to the effect of the external electric force.

Using again rectangular coordinates with the nucleus at the origin and the z-axis parallel to the direction of the electric force, and calling the coordinates of the electrical centre ξ, η, ζ, we have according to formula (74)

[1]) See N. Bohr, Phil. Mag. XXVII, p. 506 (1914) and XXX, p. 394 (1915). Compare also E. Warburg, Verh. d. D. Phys. Ges. XV, p. 1259 (1913), where it was pointed out, for the first time, that the effect of an electric field on the hydrogen lines to be expected on the quantum theory was of the same order of magnitude as the effect observed by Stark.

[2]) K. Schwarzschild, Verh. d. D. Phys. Ges. XVI, p. 20 (1914).

$$\xi^2 + \eta^2 + \zeta^2 = \left(\frac{3}{2}\varepsilon a\right)^2, \qquad \zeta = \text{const.} \tag{1*}$$

Denoting the components parallel to the x, y and z-axis of the angular momentum of the electron round the nucleus, considered as a vector, by P_x, P_y and P_z, we have next

$$P_x^2 + P_y^2 + P_z^2 = (1-\varepsilon^2)(2\pi m a^2 \omega)^2, \qquad P_z = \text{const.} \tag{2*}$$

Since the angular momentum is perpendicular to the plane of the orbit, we have further

$$\xi P_x + \eta P_y + \zeta P_z = 0. \tag{3*}$$

Now we have for the mean values of the rates of variation of P_x and P_y with the time

$$\frac{DP_x}{Dt} = eF\eta, \quad \frac{DP_y}{Dt} = -eF\xi. \tag{4*}$$

From this we get, differentiating (1*) and (2*) with respect to the time, and remembering that a and ω remain constant during the perturbations,

$$\xi\frac{D\xi}{Dt} + \eta\frac{D\eta}{Dt} = -K^2\left(P_x\frac{DP_x}{Dt} + P_y\frac{DP_y}{Dt}\right) = -eFK^2(\eta P_x - \xi P_y), \tag{5*}$$

where

$$K = \frac{3}{4\pi m a \omega}. \tag{6*}$$

On the other hand we have, differentiating (3*) and introducing (4*),

$$P_x\frac{D\xi}{Dt} + P_y\frac{D\eta}{Dt} = 0,$$

which together with (5*) gives

$$\frac{D\xi}{Dt} = eFK^2P_y, \quad \frac{D\eta}{Dt} = -eFK^2P_x,$$

from which we get, by means of (4*),

$$\frac{D^2\xi}{Dt^2} = -e^2F^2K^2\xi, \quad \frac{D^2\eta}{Dt^2} = -e^2F^2K^2\eta,$$

the solution of which is

$$\xi = \mathfrak{A}\cos 2\pi(\mathfrak{o}t + \mathfrak{a}), \quad \eta = \mathfrak{B}\cos 2\pi(\mathfrak{o}t + \mathfrak{b}), \tag{7*}$$

where $\mathfrak{A}$, $\mathfrak{a}$, $\mathfrak{B}$ and $\mathfrak{b}$ are constants, and where, introducing (6*), we have

$$\mathfrak{o} = \frac{eFK}{2\pi} = \frac{3eF}{8\pi^2 m a \omega}. \tag{8*}$$

During the perturbations the electrical centre will thus perform slow harmonic vibrations perpendicular to the direction of the electric force, with a frequency which is proportional to the intensity of the electric field, but, for a given value of F, quite independent of the initial shape of the orbit and its position relative to the direction of the field. For the value of this frequency in the multitude of states of the perturbed system, for which the mean value of the inner energy is equal to the energy E_n in a stationary state of the undisturbed system corresponding to a given value of n, we get from the above calculation, introducing for a and ω the values of a_n and ω_n given by (41),

$$\upsilon_F = \frac{3hn}{8\pi^2 Nem} F. \tag{76}$$

Now from the periodic motion of the electrical centre we may conclude that, in the presence of the field, the system will be able to emit or absorb a radiation of frequency υ_F, and that accordingly the possible values of the additional energy of the system in the presence of the field will be given directly by PLANCK's fundamental formula (9), holding for the possible values of the total energy of a linear harmonic vibrator, if in this formula ω is replaced by the above frequency υ_F. Since further a circular orbit, perpendicular to the direction of the electric force, will not undergo secular perturbations during a slow establishment of the field, and therefore must be included among the stationary states of the perturbed system, we get for the total energy of the atom in the presence of the field

$$E = E_n + \mathfrak{n}\,\upsilon_F h = -\frac{2\pi^2 N^2 e^4 m}{n^2 h^2} + \frac{3h^2 n \mathfrak{n}}{8\pi^2 Nem} F, \tag{77}$$

where $\mathfrak{n}$ is an entire number which in the present case may be taken positive as well as negative. From a comparison between (75) and (77), we see that the presence of the external field imposes the restriction on the motion of the atom in the stationary states, that the plane in which the electrical centre of the orbit moves must have a distance from the nucleus equal to an entire multiple of the n^{th} part of its maximum distance $\frac{3}{2} a_n$.

The result, contained in formula (77), is in agreement with the expression for the total energy in the stationary states, deduced by EPSTEIN and SCHWARZSCHILD by means of the general theory of conditionally periodic systems based on the conditions (22). The treatment of these authors rests upon the fact, that, as mentioned in Part I, the equations of motion for the electron in the present problem may be solved by means of separation of variables in parabolic coordinates (compare page 21). Taking for q_1 and q_2 the parameters of the two paraboloids of revolution, which pass through the instantaneous position of the electron and which have their foci at the nucleus and their axes parallel to the direction of the field, and for q_3 the angular distance between the plane through the electron and the axis of the system and a fixed plane through this axis, the momenta p_1, p_2, p_3 will during the motion depend on the corresponding q's only, and the stationary states will be fixed by three conditions of the type (22). With neglect of small quantities proportional to higher powers of F, the final formula for the total energy, obtained by EPSTEIN in this way, is given by

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2 (n_1 + n_2 + n_3)^2} - \frac{3h^2 (n_1 + n_2 + n_3)(n_1 - n_2)}{8\pi^2 Nem} F, \text{ [1]} \tag{78}$$

[1]) P. EPSTEIN, Ann. d. Phys. L, p. 508 (1916).

where n_1, n_2, n_3 are the positive entire numbers which occur as factors to PLANCK's constant on the right sides of the mentioned three conditions.

As regards the possible values of the total energy of the hydrogen atom in the presence of the electric field, it will be seen that (78) coincides with (77) if we put $n_1 + n_2 + n_3 = n$ and $n_2 - n_1 = n$. At the same time it will be observed, however, that the motion in the stationary states, as fixed by the procedure followed by EPSTEIN, is more restricted than was necessary in order to secure the right relation between the additional energy and the frequency of the secular perturbations. Thus, in addition to the condition which fixes the plane in which the electrical centre moves, EPSTEIN's theory involves the further condition, that the angular momentum of the electron round the axis of the perturbed system is equal to an entire multiple of $h/2\pi$; which multiple is seen to be even or uneven, according as $n + n$ is an even or an uneven number respectively. This circumstance is intimately connected with the fact that, although the perturbed system under consideration is degenerate if we look apart from small quantities proportional to the square of the intensity of the external force, the degenerate character of the system does not reveal itself from the point of view of the theory of stationary states based on the conditions (22), because the system under consideration allows of separation of variables only in one set of positional coordinates. On the other hand, this degenerate character of the system has been emphasised by SCHWARZSCHILD[1]) on the basis of the theory of stationary states based on the introduction of angle variables, in which the periodicity properties of the motion play an essential part. In a later discussion of this point EPSTEIN[2]) calls attention to the fact that, if small quantities proportional to the square of the electric force are taken into account, the system appears no more as degenerate; and he finds therein a justification of the fixation of the stationary states by means of (22). From the point of view of perturbed systems, this would mean that the motion in the stationary states of the system in question, as fixed by (22), would certainly be stable for infinitely small disturbances, but that we should expect finite deviations from the motion in these states, already if the system was exposed to a second perturbing field, the intensity of which was only of the same order as the product of the external electric force with the ratio between this force and the attraction from the nucleus. A closer consideration, however, in which regard is taken to the influence of the relativity modifications, learns that the degree of stability of the motion in the stationary states, as determined by (22), actually is often much higher, the order of magnitude of the external force, necessary to cause finite deviations from this motion, being of the same order as the product of the attraction from the nucleus with the square of the ratio of the velocity of the electron and the velocity of light. To this point we shall come back at the end of this section, when considering the simultaneous perturbing influence on the

[1]) K. SCHWARZSCHILD, Ber. Akad. Berlin, 1916, p. 548.
[2]) P. EPSTEIN, Ann. d. Phys. LI, p. 168 (1916).

motion of the electron in the hydrogen atom, due to the relativity modifications and an external electric field.

In the deduction of formula (78) there is looked apart, not only from the effect on the motion of the electron due to the small modifications in the laws of mechanics claimed by the theory of relativity, but also from the effect of possible forces which might act on the electron, corresponding to the reaction from the radiation in ordinary electrodynamics. If, however, for the moment we exclude all stationary states for which the angular momentum round the axis of the system would be equal to zero ($n_3 = 0$), the total angular momentum of the electron round the nucleus will during the perturbations always remain larger than or equal to $h/2\pi$, just as in the stationary states considered in the theory of the fine structure; and, according to the considerations on page 66, we shall therefore expect that the effect of the neglect of possible "radiation" forces will be small compared with the effect of the relativity modifications. On the other hand, if the intensity of the electric field is of the same order of magnitude as that applied in Stark's experiments, the effect of these modifications must again be expected to be very small compared with the total effect of the electric force on the hydrogen lines, since the perturbing effect of this force on the Keplerian motion of the electron will be very large compared with the corresponding effects of the relativity modifications. If, on the contrary, we would consider a state of the atom for which n_3 was equal to zero, the orbit would be plane and would during the perturbations assume shapes, for which the total angular momentum round the nucleus was very small, and in which the electron during the revolution would pass within a very short distance from the nucleus. In such a state the effect of the relativity modifications on the motion of the electron would be considerable, but quite apart from this a rough calculation shows that the amount of energy, which, on ordinary electrodynamics, would be emitted during the intervals in which the angular momentum during the perturbations of the orbit remains small, is so large that it would hardly seem justifiable to calculate the motion and the energy in these states by neglecting all forces corresponding to the radiation forces in ordinary electrodynamics. We need not, however, enter more closely on these difficulties, because, on the general considerations in Part I about the a-priori probability of the different stationary states, we are forced to conclude that, for any value of the external electric field, no state which would correspond to $n_3 = 0$ will be physically possible; since any such state might be transformed continuously, and without passing through a degenerate system, into a state which obviously cannot represent a physically realisable stationary state (compare pag. 27). In fact, if we imagine that an external central field of force, varying as the inverse cube of the distance from the nucleus, is slowly established, it would be possible to compensate the secular effect of the relativity modifications and to obtain orbits in which the electron would pass within any given, however small, distance from the nucleus. As regards the other stationary states fixed by (22), which correspond to $n_3 > 1$, we shall according to the considerations in Part I expect that their a-priori probabilities are all equal.[1])

As regards the comparison between the theory and the experiments, it will be remembered that STARK found that every hydrogen line in the presence of an electric field was split up in a number of polarised components, in a way different for the different lines. When viewed parallel to the direction of the field, there appeared a number of components polarised parallel to the field and a number of components polarised perpendicular to the field; when viewed in the direction of the field, only the latter components appeared, but without showing characteristic polarisation. Apart from the marked symmetry of the resolution of every line, the distances between successive components and their relative intensities varied in an apparently irregular way from component to component. As pointed out by EPSTEIN and SCHWARZSCHILD, however, it is possible by means of (78), in connection with relation (1), to account in a convincing way for STARK's measurements as regards the frequencies of the components. Especially a closer examination of these measurements showed that all the differences between the frequencies of the components were equal to entire multipla of a certain quantity, which was the same for all lines in the spectrum and, within the limits of experimental errors, equal to the theoretical value $\frac{3hF}{8\pi^2 Nem}$. On the other hand, the theories of EPSTEIN and SCHWARZSCHILD gave no direct information as regards the question of the polarisation and intensity of the different components. Comparing formula (78) with STARK's observations, EPSTEIN pointed out, however, that the polarisation of the different components observed could apparently be accounted for by the rule: that a transition between two stationary states gives rise to a component polarised parallel to the field, if n_3 remains unchanged or is changed by an even number of units; while a component, corresponding to a transition in which n_3 is changed by an uneven number of units,

[1]) By a simple enumeration it follows from this result, that the total number of different stationary states of the hydrogen atom, subject to a small homogeneous electric field, which corresponds to a stationary states of the undisturbed atom, characterised by a given value of n in the condition $I = nh$, is equal to $n(n+1)$. This expression is directly obtained, if we remember that $n = n_1 + n_2 + n_3$ and if we count each state, characterised by a given combination of the positive integers n_1, n_2, n_3, as double, corresponding to the two possible opposite directions of rotation of the electron round the axis of the field. With reference to the necessary stability for a small variation of the external conditions of the statistical distribution of the values of the energy among a large number of atoms in temperature equilibrium (see Note on page 43), it will be seen that the expression $n(n+1)$ may be taken as a measure for the relative value of the a-priori probability of the different stationary states of the undisturbed hydrogen atom, corresponding to different values of n. The problem of the determination of this a-priori probability has been discussed by K. HERZFELD (Ann. d. Phys. LI, p. 261 (1916)) who, by an examination of the volumes of the different extensions in the phase space which might be considered as belonging to the different stationary states of the hydrogen atom, has arrived at an expression for the a-priori probability of these states which differs from the above. From the point of view, as regards the principles of the quantum theory, taken in the present paper, a consideration of this kind, however, does not, as explained in Part I on page 26, afford a rational means of determining the a-priori probability of the stationary states of an atomic system.

is polarised perpendicular to the field. This result may be simply interpreted on the basis of the general formal relation between the quantum theory of line spectra and the ordinary theory of radiation. In fact, it was shown in Part I that, for a conditionally periodic system possessing an axis of symmetry, we shall expect only two types of transitions to be possible. In transitions of the first type n_3 remains unchanged, and the emitted radiation is polarised parallel to the axis of symmetry, while the transitions of the second type, in which n_3 varies by one unit, give rise to a radiation of circular polarisation in a plane perpendicular to this axis (see page 34). In order to show that this agrees with the empirical rule of Epstein, it may be noted in the first place that, for any component which might be ascribed to a certain transition in which n_3 changes by a given entire number of units, there exists always another transition which will give rise to a radiation of the same frequency but in which n_3 remains unchanged or changes by one unit, according to whether the given number is even or uneven. Next it will be seen that, in case of the effect of an electric field on the hydrogen spectrum, we cannot detect by means of direct observations the circular polarisation of the radiation corresponding to transitions of the second type; because, for each transition giving rise to a radiation of circular polarisation in one direction, there will exist another transition giving rise to a radiation which possesses the same frequency but is polarised in the opposite direction. Besides on the problem of the polarisations of the different components into which the hydrogen lines are split up in the presence of the electric field, the general considerations in Part I allow also to throw light on the question of the relative intensities of these components, by considering the harmonic vibrations into which the motion of the electron in the stationary states can be resolved. Compared with the problem of the relative intensities of the components of the fine structure of the hydrogen lines, the present problem is simpler in that respect, that the stationary states may be assumed to be a-priori equally probable. Since the different components, into which a given hydrogen line is split up in the electric field, correspond to transitions between pairs of states which for all components have very nearly the same values for the total energy, these states may therefore be expected to be of approximately equal occurrence in the luminous gas. According to the considerations in Part I, we shall consequently assume that for a given hydrogen line the relative intensities of the different Stark effect components, corresponding to transitions between different pairs of stationary states characterised by $n_1 = n'_1$, $n_2 = n'_2$, $n_3 = n'_3$ and $n_1 = n''_1$, $n_2 = n''_2$, $n_3 = n''_3$ respectively, will be intimately connected with the intensities of the radiations of frequency $(n'_1 - n''_1)\,\omega_1 + (n'_2 - n''_2)\,\omega_2 + (n'_3 - n''_3)\,\omega_3$, which on ordinary electrodynamics would be emitted by the atom in the two states involved in the transition in question; ω_1, ω_2 and ω_3 being the fundamental frequencies entering in the expression (31) for the displacement of the electron. In order to test how far such a connection is actually brought out by the observations, it is necessary to determine the numerical values of the amplitudes of the harmonic vibrations into which the motion of the electron can be resolved. The examination of this problem has been undertaken by Mr. H. A. KRAMERS, who has deduced complete expressions for these amplitudes, by means of which it was found possible, for each of the hydrogen lines H_α, H_β, H_γ and H_δ, to account in a convincing way for the apparently capricious laws which govern the intensities of the components observed by STARK.[1]) This agreement offered at the same time a direct experimental support for the conclusions mentioned above: that there exist no stationary states corresponding to $n_3 = 0$, while the stationary states corresponding to other values of n_3 are a-priori equally probable; and that transitions can only take place between pairs of stationary states for which n_3 is the same or differs by one unit. A general discussion of these problems will be given by KRAMERS in the paper, mentioned on page 69 in the last section, in which also the problem of the intensity of the fine structure components is treated in detail.

In the former section and in the present we have seen, how the problems of the influence of the relativity modifications on the lines of the hydrogen spectrum and of the influence of an external electric field on this spectrum can be treated, by regarding the motion of the electron as a perturbed periodic motion, and by fixing the stationary states on the basis of the relation between the energy and the frequencies of the secular perturbations. As it was done originally by SOMMERFELD and EPSTEIN, both these problems can also be treated by means of the theory of the stationary states of conditionally periodic systems which allow of separation of variables in a fixed set of positional coordinates. If, however, we consider the problem of the simultaneous influence on the hydrogen spectrum of the relativity modifications and a homogeneous electric field of any given intensity, there does not exist a set of coordinates for which a separation of variables can be obtained. On the other hand it is possible, also in this case, to apply the general considerations about perturbed periodic systems developed in the preceding. In fact, with reference to the treatment given in § 3 of the problem of the fine structure of the hydrogen lines, it will be seen that the deviations of the orbit of the electron from a Keplerian ellipse in the problem under consideration

[1]) Note added during the proof. In recent papers H. NYQUIST (Phys. Rev. X, p. 226 (1917)) and J. STARK (Ann. d. Physik, LVI, p. 569 (1918)) have published measurements on the effect of an electric field on certain lines of the helium spectrum which is given by (35), if in (40) we put $N = 2$. As will be seen from (78), the differences between the frequencies of the components into which these lines are split up will, for the same intensity of the external electric field, be smaller than for the hydrogen lines. In conformity with this it was not possible, with the experimental arrangement used by the authors mentioned, to observe separately the numerous components to be expected on the theory, but only to obtain certain rough features of the resolution of the lines in question. For the interpretation of these observations a detailed consideration of the relative intensities to be expected for the different theoretical components is therefore essential; and, as it will be shown in KRAMERS' paper, it is possible, on the basis of the calculation of the amplitudes of the harmonic vibrations into which the motion of the electron in the stationary states can be resolved, to account satisfactorily for NYQUIST's and STARK's results.

will be the same as the secular perturbations produced on a Keplerian motion by the simultaneous influence of an external homogeneous field of force and an external central force proportional to the inverse cube of the distance from the nucleus. Since these two fields together form a perturbing field possessing axial symmetry, it follows therefore that the secular perturbations, when the relativity modications are taken into account, will be conditionally periodic and that the problem of the stationary states may be treated by means of the method mentioned in § 2 on page 55. In this way we obtain in the first place the result, that, for any value of the intensity of the external electric field, we must expect that the hydrogen lines will be split up in a number of sharp components. Next, since for any value of this intensity different from zero the system will be non-degenerate, it follows from the conditions (61), that we must assume that the angular momentum round the axis of the field is always equal to an entire multiple of $h/2\pi$; in consistence with the assumption of the validity of the analogous condition involved in the fixation of the stationary states by means of the method of separation of variables, when applied to an explanation of the Stark effect with neglect of the relativity modifications (compare page 74). On the basis of the conditions (61) it is possible to predict in detail, how the fine structure of the hydrogen lines will be influenced by an increasing electric field until, for a sufficiently large intensity of this field, the phenomenon develops gradually into the ordinary Stark effect. The problem of this transmutation will be treated in a later paper by Mr. H. A. Kramers[1]), who has kindly drawn my attention to this interesting application of the method of perturbations, and has thereby given a valuable impetus to the detailed elaboration of this method as regard the treatment of more complicate problems.

§ 5. The effect of a magnetic field on the hydrogen spectrum.

A theory of the Zeeman effect of the hydrogen lines based on the quantum theory of line spectra has, as mentioned in the introduction, been given independently by Sommerfeld and by Debye. The calculations of these authors rest upon the fact, that it is possible, also in the presence of a magnetic field, to write the equations of motion of the electron in the canonical Hamiltonian form given by (4), if the momenta p_1, p_2, p_3, which are conjugated to the positional coordinates of the electron q_1, q_2, q_3, are defined in a suitable way. In complete analogy to the problem of the fixation of the stationary states of an atomic system when the relativity modifications are taken into account, it follows therefore that, if these equations

[1]) Besides the discussion of this problem, the paper in question will contain a general treatment of the theory of perturbed periodic systems from the point of view of the possibility of describing the motion by means of angle variables (compare Note on page 58).

can be solved by the method of separation of variables, we obtain, by fixing the stationary states by means of the conditions (22), a relation between the total energy of the atom in the presence of a magnetic field and the fundamental frequencies characterising the motion of the electron, which is exactly the same as that holding between the energy and frequencies in the stationary states of an ordinary conditionally periodic system. By a procedure analogous to that applied by Burgers in his proof of the mechanical invariance of the relations (22) for slow changes of the external conditions, mentioned in Part I on page 21, it may further be proved that also in the presence of a magnetic field these relations are invariant, when regard is taken to the effect of the induced electric forces which, according to the ordinary theory of electrodynamics, will accompany a variation of the magnetic field. In the following, however, we shall not treat the problem of the influence of an external magnetic field on the hydrogen spectrum by means of the method of separation of variables, but in analogy to the treatment of the problems of the fine structure and of the Stark effect of the hydrogen lines, given in the preceding sections, we shall treat the problem from the point of view of the theory of perturbed periodic systems. Before entering on the detailed discussion of the necessary modifications to be introduced in the general considerations in § 2, in order that they may be applied also to the problem of the fixation of the stationary states of the atom in the presence of external magnetic forces, we shall for the sake of illustration first show how it is possible in certain cases to treat the problem of the effect of a homogeneous magnetic field on the hydrogen spectrum in a simple way, which will be seen to present a close formal analogy with the theory originally devised by Lorentz on the basis of the classical theory of electrons.

In these considerations we shall make use of a well known theorem of Larmor, which states that, if we look apart from small quantities proportional to the square of the intensity of the magnetic field, the motion of a system of electrons moving in a conservative field of force possessing axial symmetry round a fixed axis will, in the presence of an external homogeneous magnetic field parallel to this axis, differ from a mechanically possible motion of the system without field, only by a superposed uniform rotation of the entire system round the axis, the frequency of which is given by

$$\omega_H = \frac{e}{4\pi m c} H, \tag{79}$$

where H is the intensity of the magnetic field and c the velocity of light, while $-e$ and m represent the charge and the mass of an electron.[1]) If the magnetic field

[1]) J. Larmor, Aether & Matter, Cambridge 1900, p. 341. This theorem, which was established in connection with an attempt to develop a general theory of the Zeeman effect based on the ordinary theory of electrodynamics, is directly proved by observing that, with the degree of approximation in question, the accellerations of the electrons due to the presence of the magnetic field are equal to the changes in the accellerations of the particles due to the superposed rotation of the system.

is not constant, but if its intensity increases slowly and uniformly from zero, it is further simply shown that the electric induction forces, which will accompany the change in the intensity of the magnetic force, will just effect that a rotation as that described will be impressed on the original motion of the system.[1]) Moreover, as regards the effect of the magnetic field on the total energy of the system,[2]) it will be observed that the superposed rotation under consideration will not affect the mutual potential energy of the particles, while, with neglect of small quantities proportional to H^2, it will produce a change in the kinetic energy equal to $2\pi P o_H$,

[1]) Compare P. Langevin, Ann. de Chim. et de Phys. V, p. 70 (1905), who has deduced this result in connection with his well known theory of the magnetic properties of atomic systems based on the classical theory of electrons.

[2]) In an earlier paper (Phil. Mag. XXVII, p. 506 (1914)) the writer had assumed that the total energy in the stationary states of the hydrogen atom in the presence of a magnetic field would not be different from the energy in the corresponding states without field, as far as small quantities proportional to the intensity of the magnetic force are concerned; the effect on the kinetic energy of the electron due to the superposed rotation being assumed to be compensated by some kind of "potential" energy of the whole atom relative to the magnetic field. This assumption seemed not only suggested by the absence of paramagnetism in many elements, the atoms and molecules of which, according to the theory to be discussed in Part IV, must be expected to possess a resultant angular momentum, but it was especially thought to be supported by the fact, that the spectrum, emitted by hydrogen in the presence of a magnetic field, apparently did not form a combination spectrum of the type which should be expected, if the frequency of the radiation, emitted during a transition between two stationary states of the atom in the presence of the field, could be calculated directly from the values of the energy in these states by means of relation (1). As remarked by Debye (Phys. Zeitschr. XVII, p. 511 (1916)), this view, however, would not be reconcilable with Einstein's theory of temperature radiation (see Part I, page 7) which implies the general validity of relation (1); and, moreover, as will be shown in the following, the Zeeman effect of the hydrogen lines may actually be considered, not as involving a deviation from the combination principle, but rather as affording an instructive example of a systematic disappearance of certain possible combination lines, for which a simple explanation can be obtained from a consideration based on the general formal relation between the quantum theory of line spectra and the ordinary theory of radiation. Further, with reference to this relation — and remembering that on ordinary electrodynamics the magnetic field will not directly influence the exchange of energy during a process of radiation, since the forces due to this field, being always perpendicular to the direction of the velocity, will not perform work on the moving electron — it seems also natural to assume that it is possible, simply from the effect of the superposed rotation on the kinetic energy of the electron, to determine the effect of the magnetic field, as regards the differences between the values of the energy in the different stationary states of the atom. Now, in a discussion of the spectrum to be expected on the quantum theory, we are concerned only with these differences and not with the absolute values of the additional energy of the system due to the presence of the magnetic field. It would therefore be possible to escape from the difficulty, mentioned above, as regards the absence of paramagnetism, by assuming that only the energy in the socalled "normal" state of an atomic system (i. e. the stationary state of the system which possesses the smallest value for the total energy; see Part IV) is not altered in the presence of a magnetic field, as far as small quantities proportional to the intensity of the magnetic force are concerned. On this view, the absence of paramagnetism would thus be a special property of the normal state, connected with the impossibility of spontaneous transitions from this state to other stationary states of the system. To this question we shall come back in the following parts of this paper; for the sake of simplicity, however, we shall not, in the considerations of this section, enter more closely on the consequences of the mentioned hypothesis, which would imply small modifications in the form of the following considerations, but would not affect the results.

where P represents the total angular momentum of the system round the axis, taken in the same direction as that of the superposed rotation.

From these results it follows that the motion of the electron in any stationary state of a hydrogen atom, which is exposed to a homogeneous magnetic field, will — if we look apart from small quantities proportional to the square of the intensity of the magnetic force and to the product of this intensity with the ratio between the mass of the electron and that of the nucleus — differ from the motion in some stationary state of the atom in the absence of the field, only by a superposed uniform rotation round an axis through the nucleus parallel to the magnetic force with a frequency given by (79). Due to the degenerate character of the system formed by the atom in the absence of the magnetic field, it is not possible, however, from a consideration of the mechanical effect produced on the motion of the electron by a slow and uniform establishment of the magnetic field, to fix the stationary states of the perturbed atom completely, but in order to fix these states we must consider more closely the relation between the additional energy of the system due to the presence of the magnetic field and the character of the secular perturbations produced by this field on the orbit of the electron. On the basis of LARMOR's theorem the discussion of this problem is very simple. In fact, since the frequency $\mathfrak{o}_H$ is independent of the shape and position of the orbit, we may proceed in a manner which is completely analogous to that applied in the fixation of the stationary states of the hydrogen atom in the presence of a homogeneous electric field. Thus, looking apart from the effect of the relativity modifications, we may conclude at once that the total energy in the stationary states of the atom will be given by

$$E = E_n + \mathfrak{n}\,\mathfrak{o}_H h, \tag{80}$$

where $\mathfrak{n}$ is an entire number which can be positive as well as negative, while E_n will be equal to the energy in the corresponding stationary state of the undisturbed atom, which is given by $-W_n$ in (41). As in the case of the STARK effect, it will moreover be seen that this formula includes the values of the energy in such states of the atom, in which the electron moves in a circular orbit perpendicular to the direction of the field, and which beforehand must be expected to be included among the stationary states of the perturbed system, since such orbits during a slow and uniform establishment of the external field will not undergo secular perturbations as regards shape and position (compare page 73). In fact, since in these cases we have $P = \pm nh/2\pi$, where n is the entire number characterising the stationary states of the undisturbed hydrogen atom, it follows from the above that the total energy in the special stationary states under consideration will just be represented by the formula (80), if we put $\mathfrak{n} = \pm n$. From this formula it will be seen at the same time, that the presence of the external magnetic field imposes the restriction on the motion in the stationary states of the hydrogen atom, that, with neglect of small quantities proportional to H, the angular momentum of the electron round the axis of the field will be equal to an entire multiple of $h/2\pi$.

As regards the expression for the total energy of the hydrogen atom in the presence of the magnetic field, formula (80) is in agreement with the formulæ obtained by SOMMERFELD and DEBYE on the basis of the conditions (22), holding for conditionally periodic systems which allow of separation of variables. As shown by these authors, a system, which consists of an electron moving under the influence of the attraction from a fixed nucleus and of a homogeneous magnetic field, allows of separation of variables in polar coordinates, if the polar axis is chosen parallel to the magnetic field. Looking apart from the effect of the relativity modifications, and choosing for q_1, q_2 and q_3 the length of the radius vector from the nucleus to the electron, the angle between this radius vector and the axis of the system, and the angle which the plane through the electron and this axis makes with a fixed plane through the axis respectively, they obtain the following expression for the total energy: [1])

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2(n_1 + n_2 + n_3)^2} \pm \frac{e h n_3}{4\pi m c} H, \tag{81}$$

where n_1, n_2 and n_3 are the integers which appear as factors to PLANCK's constant on the right side of the conditions (22). As mentioned this formula gives the same result as (80); in fact, if we put $n = n_1 + n_2 + n_3$ and if we look apart from the small correction due to the finite mass of the nucleus, the first term in (81) is seen to coincide with the expression for $-W_n$ given by (41), while the last term in (81) coincides with the last term in (80), if we put $\mathrm{n} = n_3$. It will be observed, however, that, while in the theories of SOMMERFELD and DEBYE the stationary states are characterised by three conditions, only two conditions were necessary on the above considerations in order to secure the right relation between the energy and frequencies of the system in the stationary states. Thus, besides the conditions which prescribe the length of the major axis of the rotating orbit and the value of the angular momentum of the system round the axis of the field, the theories of the mentioned authors involve the further condition, that the value of the total angular momentum of the electron round the nucleus must be equal to an entire multiple of $h/2\pi$; and that consequently the minor axis of the orbit has the same values as in a hydrogen atom perturbed by a small external central field (compare page 57). This is due to the circumstance, that the perturbed atom forms a degenerate system if we look apart from the effect of the relativity modifications, because the secular per-

[1]) A. SOMMERFELD, Phys. Zeitschr. XVII, p. 491 (1916) and P. DEBYE, Phys. Zeitschr. XVII, p. 507 (1916). While DEBYE proceeds directly by the application of the conditions (22) in a fixed set of positional polar coordinates, SOMMERFELD determines the stationary states by applying these conditions to the motion of the system relative to a set of coordinates which rotates uniformly round the polar axis with the frequency o_H; a procedure which in the special case under consideration is simply shown to give the same result as the direct application of (22) to fixed polar coordinates.

turbations are simply periodic. From the point of view of separation of variables, this degenerate character of the system is in the present case, in contrast to the analogous case of the STARK effect, also directly revealed by the fact, that a separation can be obtained, not only in polar coordinates, but in any set of axial elliptical coordinates for which one focus is placed at the nucleus and the other at some point on the axis of the field. Just as in the case of the STARK effect, however, the system is no more degenerate as soon as the relativity modifications are taken into account, in which case a separation of variables will still be possible but only in polar coordinates. To this point we shall come back below.

The observations on the ZEEMAN effect of the hydrogen lines show that, if the fine structure is neglected, each line is in the presence of a magnetic field split up in a normal LORENTZ triplet; i. e. each line is resolved in three components of which the one is undisplaced and polarised parallel to the direction of the field, while the two other components possess frequencies, which differ from that of the original line by $\mathfrak{o}_H$, and are circularly polarised in opposite directions in a plane perpendicular to the direction of the field. As pointed out by SOMMERFELD and by DEBYE, the frequencies of a LORENTZ triplet are included among the frequencies of the components deduced from (81) by application of relation (1). In addition to the observed components, however, we might from (81) and (1) expect the appearance of a number of components, displaced from the original positions of the lines by higher multipla of $\mathfrak{o}_H$. For the non-appearance of these components the theories of SOMMERFELD and DEBYE offered no explanation, no more than for the polarisation of the components observed; except that SOMMERFELD in this connection draws attention to the fact, that the law governing the observed polarisations exhibits a certain analogy to the emperical rule of EPSTEIN concerning the observed polarisations of the components of the STARK effect of the hydrogen lines (see page 76). On the other hand, just as in case of the latter effect, an explanation of the number of the components observed and their characteristic polarisations is directly obtained on the basis of the general formal relation between the quantum theory of line spectra and the ordinary theory of radiation. In the first place we have at once from LARMOR's theorem, denoting the frequency of revolution of the electron in a stationary state of the undisturbed hydrogen atom by ω, that the motion of the electron, in a corresponding stationary state of the atom in the presence of the field, may be resolved in a number of linear harmonic vibrations parallel to the direction of the magnetic force with frequencies $\tau\omega$, where τ is a positive integer, and in a number of circular harmonic rotations perpendicular to this direction with frequencies $\tau\omega + \mathfrak{o}_H$ or $\tau\omega - \mathfrak{o}_H$, according as the direction of rotation is the same as or the opposite of that of the superposed rotation. Next, with neglect of small quantities proportional to H^2, we have for the difference in the total energy between two neighbouring states of the perturbed system under consideration

$$\delta E = \delta E_0 + \delta \mathfrak{E} = \omega \delta I + \mathfrak{o}_H \delta \mathfrak{J}, \qquad (82)$$

where E_0 and ω are the values of the energy and frequency and I is the value of the quantity defined by (5), all corresponding to the state of the undisturbed system which would appear if the magnetic force vanished at a slow and uniform rate, while $\mathfrak{E}$ is the additional energy due to the presence of the magnetic field and $\mathfrak{J}$ the angular momentum of the system round the axis of the field multiplied by 2π and taken in the same direction as that of the superposed rotation. Since (82) has exactly the same form as relation (66), and since in the stationary states we have $I = nh$ and $\mathfrak{J} = \mathfrak{n}h$, we are therefore from a consideration, quite analogous to that given in § 2 on page 59, led to the conclusion, that, in the presence of the magnetic field, only two types of transitions between stationary states are possible. For both types of transitions the integer n may change by any number of units, but in transitions of the first type the integer $\mathfrak{n}$ will remain constant and the emitted radiation will be polarised parallel to the direction of the field, while in transitions of the second type $\mathfrak{n}$ will decrease or increase by one unit and the emitted radiation will be circularly polarised in a plane perpendicular to the field, the direction of the polarisation being the same as or the opposite of that of the superposed rotation respectively. Remembering that, with neglect of small quantities proportional to the magnetic force, the angular momentum of the system round the axis of the field remains unaltered in transitions of the first type and changes by $h/2\pi$ in transitions of the second type, it will be seen that this conclusion is independently supported by a consideration of conservation of angular momentum during the transitions, like that given in Part I on page 34.

With reference to formula (80), it will be seen that the above results are in complete agreement with the experiments on the Zeeman effect of the hydrogen lines, as regards the frequencies and polarisations of the observed components. On the other hand, the observed intensities are directly accounted for, independent of any special theory about the origin of the lines. In fact, from a consideration of the necessary "stability" of spectral phenomena, it follows that the total radiation of the components, in which a spectral line, which originally is unpolarised, is split up in the presence of a small external field, cannot show characteristic polarisation with respect to any direction. In case of the Zeeman effect of the hydrogen lines, it is therefore necessary beforehand to expect that the intensity of the radiation, summed over all directions, corresponding to each of the three components in which every line is split up must be the same. From the point of view of the quantum theory of line spectra, it will be seen that by means of considerations of this kind we may inversely obtain a certain amount of direct quantitative information as regards the probabilities of spontaneous transition between different sets of stationary states, holding also in the region where the integers characterising these states are not large and where consequently the estimate of the values of these probabilities, based on the formal relation between the quantum theory and the ordinary theory of radiation, gives results which are only of an approximative character. This point will be discussed more closely in Kramers' paper on the relative intensities of the components of the fine structure and the STARK effect of the hydrogen lines.

A procedure quite analogous to that applied above may be used to treat the problem of the effect of a homogeneous magnetic field on the hydrogen spectrum, also when the relativity modifications are taken into account, and when the atoms at the same time are exposed to a small external field of force of constant potential, which possesses axial symmetry round an axis through the nucleus parallel to the magnetic force; because also in this case we can obviously make direct use of LARMOR's theorem. We shall not, however, proceed in this way, but shall come back to these questions when we have shown how, by a simple modification of the general considerations of perturbed periodic systems given in § 2, it is possible to represent the theory of the stationary states of the hydrogen atom in the presence of a small magnetic field on a form, which allows to discuss the effect on the hydrogen spectrum also if the atom is exposed to a magnetic field which is not homogeneous, or to discuss the effect of a homogeneous magnetic field if electric forces, which do not possess axial symmetry round an axis through the nucleus parallel to the magnetic field, are acting on the atom at the same time.

In order to examine the general problem of the secular perturbations of the orbit of the electron in the hydrogen atom which take place if the atom is exposed to small external forces which, entirely or partly, are of magnetic origin, we shall, as in the usual theory of planetary perturbations, take our starting point in the equations of motion in their canonical form. Now the equations of motion of an electron of charge $-e$, which besides by an electric field of potential V is acted upon by a magnetic field of vector potential $\mathfrak{A}$ (defined by div $\mathfrak{A} = 0$ and curl $\mathfrak{A} = \mathfrak{H}$, where $\mathfrak{H}$ is the magnetic force considered as a vector), can be written in the Hamiltonian form given by (4), if, just as in the absence of the magnetic field, E is taken equal to the sum of the kinetic energy T of the electron and its potential energy $-eV$ relative to the electric field, while the momenta which are conjugated to the positional coordinates q_2, q_2, q_3 of the electron in space are defined by the equations[1])

$$p'_k = p_k - \frac{e}{c}\frac{\partial(\mathfrak{v}\mathfrak{A})}{\partial \dot{q}_k}, \quad (k = 1, 2, 3) \tag{83}$$

where the p's are the momenta defined in the usual way (compare page 10), and where $(\mathfrak{v}\mathfrak{A})$ represents the scalar product of the velocity of the electron $\mathfrak{v}$ and the vector potential $\mathfrak{A}$, considered as a function of the q's and of the generalised velocities $\dot{q}_1$, $\dot{q}_2$, $\dot{q}_3$. If we now assume that the effect of the magnetic forces on the motion of the electron is so small compared with the effect of the electric forces, that in the calculations we may look apart from all terms proportional to $\mathfrak{H}^2$, it is simply seen that the energy function E in (4), obtained by introducing the momenta defined by (83), will differ from the corresponding function, holding in

[1]) See f. inst. G. A. SCHOTT: Electromagnetic Radiation, App. F (Cambridge, 1912).

the absence of the magnetic field, only by the addition of a term which is linear in the momenta and equal to $\frac{e}{c}(\mathfrak{v}\mathfrak{A})$. In fact, denoting E expressed as a function of the q's and p's by $\varphi(p, q)$, we get from (83) together with (4), with the approximation under consideration,

$$E - \varphi(p', q) = -\sum_1^3 \frac{\partial \varphi}{\partial p'_k}(p'_k - p_k) = \sum_1^3 \frac{\partial E}{\partial p'_k}\frac{e}{c}\frac{\partial(\mathfrak{v}\mathfrak{A})}{\partial \dot{q}_k} = \frac{e}{c}\sum_1^3 \dot{q}_k \frac{\partial(\mathfrak{v}\mathfrak{A})}{\partial \dot{q}_k} = \frac{e}{c}(\mathfrak{v}\mathfrak{A}).$$

From this it follows that, with neglect of small quantities proportional to the square of the magnetic forces, the perturbations of the orbit of the electron in a hydrogen atom, which besides to a small external electric field of potential Φ is exposed to a small external magnetic field of vector potential $\mathfrak{A}$, are given by a set of equations of the same form as (44) in § 2, but where the α's and β's are replaced by a set of quantities $\alpha'_1, \alpha'_2, \alpha'_3, \beta'_1, \beta'_2, \beta'_3$, which are related to the q's and p''s and the time in the same way as the orbital constants $\alpha_1, \alpha_2, \alpha_s, \beta_1, \beta_2, \beta_3$ for the undisturbed atom are related to the q's and p's and the time through the equations (18), and where Ω is replaced by the expression $-e\Phi + \frac{e}{c}(\mathfrak{v}\mathfrak{A})$, considered as a function of the α''s and β''s and the time. Since now, at any moment, the quantities $\alpha'_1, \alpha'_2, \alpha'_3, \beta'_1, \beta'_2, \beta'_3$ differ from the corresponding orbital constants α_1, $\alpha_2, \alpha_3, \beta_1, \beta_2, \beta_3$ only by small terms proportional to the intensity of the magnetic field, we see therefore that, with neglect of small quantities of the same order as the variation in the orbital constants within a single period, the secular perturbations of the shape and position of the orbit of the electron will again be given by the equations (46), if in the present case Ψ is taken equal to the sum of the mean value Ψ_E of the potential energy $-e\Phi$ of the electron relative to the external electric forces and the mean value Ψ_M of the quantity $\frac{e}{c}(\mathfrak{v}\mathfrak{A})$, both taken over an osculating orbit corresponding to some moment during the revolution and expressed as functions of $\alpha_1, \alpha_2, \alpha_3, \beta_2, \beta_3$.[1]) The latter mean value, however, is easily seen to allow of a simple interpretation. In fact, we have

$$\Psi_M = \frac{e}{c}\frac{1}{\sigma}\int_0^\sigma (\mathfrak{v}\mathfrak{A})\,dt = -\frac{e\omega}{c}B, \tag{84}$$

where ω is the frequency of revolution of the electron in the osculating orbit, and where B represents the total flux of magnetic force through this orbit, taken in

[1]) If the relativity modifications are taken into account, the orbit of the electron in the undisturbed atom is not strictly periodic, but it will be seen that the secular variations of this orbit are still obtained from the equations (46), if only, to the expression for Ψ as defined in the text, a term is added which is equal to the expression for Ψ given by formula (70) in § 3.

the same direction as that of the magnetic force which would arise from the motion of the electron according to ordinary electrodynamics.

From the considerations in § 2 it follows now in the first place that, with neglect of small quantities proportional to the square of the external forces, $\Psi = \Psi_E + \Psi_M$ will remain constant during the perturbations within a time interval, sufficiently long for the perturbing forces to produce a considerable change in the shape and position of the orbit of the electron; i. e. in a time interval of the same order as σ/λ, if λ, just as in § 2, denotes a small quantity of the same order as the ratio between the external forces acting on the electron and the attraction from the nucleus. From a consideration analogous to that given in § 2, we may further conclude that, in the stationary states of the perturbed system, the quantity $\Psi = \Psi_E + \Psi_M$ may be taken equal to the additional energy of the system due to the presence of the external fields. In fact, let us imagine that these fields are slowly established at a uniform rate within a time interval from $t = 0$ to $t = \vartheta$, where ϑ is a quantity of the same order as σ/λ. For the total alteration in the inner energy of the system during this process we get then, with neglect of small quantities proportional to λ^2,

$$\Delta_\vartheta \alpha_1 = e\int_0^\vartheta \frac{t}{\vartheta}\sum_1^3 \frac{\partial \Phi}{\partial q_k}\dot{q}_k\,dt - \frac{e}{c}\int_0^\vartheta \frac{\omega B}{\vartheta}\,dt,$$

where the first term represents the work done on the system by the slowly increasing external electric forces, while the second term represents the work performed by the induced electric forces which accompany the variation in the intensity of the magnetic field. By partial integration of the first term, we get from this equation, with the approximation under consideration,

$$\Delta_\vartheta \alpha_1 - e\Phi_\vartheta = -\frac{e}{\vartheta}\int_0^\vartheta \left(\Phi + \frac{\omega}{c}B\right)dt = \frac{1}{\vartheta}\int_0^\vartheta (\Psi_E + \Psi_M)\,dt = \frac{1}{\vartheta}\int_0^\vartheta \Psi\,dt. \tag{85}$$

Now the expression on the left side of this equation is equal to the change in the total energy of the system due to the establishment of the external field. Since the expression on the right side is seen to be a small quantity of the same order as $\lambda\alpha_1$, it follows therefore from (85) in the first place that the secular variations of α_2, α_3, β_2, β_3 during the increase of the fields will, just as in the case considered in § 2 (see page 47), be given by a set of equations of the same form as (46), where Ψ is replaced by $\frac{t}{\vartheta}\Psi$, and where again α_1 may be considered as a constant. Also in the present case it follows therefore that Ψ will remain constant during the establishment of the external fields, and we see consequently that the expression on the right side of (85) will be simply equal to Ψ; a result which, with reference to the principle of the mechanical transformability of the stationary states, leads to the conclusion mentioned above, that the value of the additional energy in the stationary states of the perturbed system is given by the value of Ψ in these states.

From the above considerations it follows that the problem of the stationary states of the hydrogen atom in the presence of external electric and magnetic forces may be treated in a manner, which is exactly analogous to that applied in § 2 in case of a periodic system exposed to a small external field of constant potential. Thus, if the secular perturbations as determined by (46) are of conditionally periodic type, we shall expect that, with neglect of small quantities proportional to λ, the cycles of shapes and positions which the orbit of the electron passes through in the stationary states of the perturbed system will be characterised by the conditions (55), and that the possible values of the additional energy of the atom in the stationary states will be fixed by these conditions with neglect of small quantities proportional to λ^2. We shall therefore conclude that, also in the presence of external magnetic forces, the lines of the hydrogen spectrum will, if only the secular perturbations are of conditionally periodic type, be split up in a number of sharp components, the frequencies of which are determined by means of the conditions (67) together with relation (1). As regards the problem of the intensities and polarisation of these components, we may further proceed in a way quite analogous to that followed in § 2. In fact, if the secular perturbations are of conditionally periodic type, the displacement of the electron in any given direction may be represented as a sum of harmonic vibrations by an expression of the same type as (65). Moreover it can be proved that the difference in the total energy of two neighbouring states of the perturbed atom will again be given by the expression (66)[1]. The general considerations in § 2 will therefore apply without alterations to the problem of the intensity and polarisation of the components into which the hydrogen lines are split up in the presence of small external forces, also if these forces are entirely or partly of magnetic origin. Similarly, it will be seen that the effect on the spectrum of a perturbed hydrogen atom, which will be due to the presence of a second external field small compared with the first, also in this case may be discussed directly by means of the considerations at the end of § 2.

We meet with a direct application of the preceding considerations, if the hydrogen atom is exposed to the simultaneous influence of an external electric and an external magnetic field, which possess axial symmetry round a common axis through the nucleus. Introducing the same set of orbital constants as described in § 2 on page 54, we get in this case that Ψ_M, as well as Ψ_E, and consequently the function $\Psi = \Psi_E + \Psi_M$ which enters in the equations (46), will, besides on α_1, depend on α_2, β_2 and α_3 but not on β_3. The general character of the secular perturbations of the orbit of the electron will therefore be the same as in the case, considered in § 2, where the atom is exposed only to an

[1]) Compare Note on page 58. Also in the presence of small magnetic forces, it will be possible to describe the motion of the perturbed system by means of a suitably chosen set of angle variables, if only the secular perturbations are of conditionally periodic type.

electric field of axial symmetry, and the conditions which fix the stationary states of the perturbed atom will again be expressed by the relations (61). As regards the question of the probability of spontaneous transition between the stationary states, we get moreover, just as in § 2, from a consideration of the harmonic vibrations into which the motion of the electron can be resolved, that only two types of transitions will be possible; in transitions of the first type n_2 remains unaltered, and the accompanying radiation is polarised parallel to the direction of the common axis of the perturbing fields; in transitions of the second type n_2 decreases or increases by one unit, and the accompanying radiation will be circularly polarised in a plane perpendicular to this axis. In this connection it may be remarked, however, that the number of components, into which a given hydrogen line is split up in the presence of a magnetic field, will in general be double as large as the number of components which appear in the presence of an external electric field of axial symmetry. In fact, in the latter case the motions of the electron in two stationary states of the perturbed atom, corresponding to the same value of n, will be symmetrical with respect to a plane through the axis, and these states will possess the same values for the additional energy, if n_1 is the same while the values of n_2 are numerically equal but have opposite signs. On the other hand, if the atom is exposed also to a magnetic field, this will not hold, because the value of the function Ψ_M, in contrast to the value of Ψ_E, will not possess the same sign for two orbits which have the same shape and position relative to the axis, but for which the direction of revolution of the electron is reversed. Considering two states of the perturbed atom for which the values of n_1 are the same and the values of n_2 are numerically equal but have opposite signs, we get therefore, if the atom is exposed only to a magnetic field of axial symmetry, that the values of the additional energy will be equal with exception of the sign; while, if the atom is exposed to a magnetic as well as to an electric field, the additional energy in two such states will in general differ also as regards its numerical value. In contrast to what in general will take place if the atom is exposed to an electric field of axial symmetry, it will thus be seen that, if the hydrogen atom is exposed only to a magnetic field possessing axial symmetry, the ensemble of components into which a given hydrogen line is resolved will be completely symmetrical with respect to the position of the original line, as regards the frequencies as well as the intensities and polarisations. Moreover it follows from the above, that if we consider a hydrogen atom exposed to an electric field of axial symmetry and imagine that an external magnetic field, which possesses symmetry round the same axis, is gradually established, each component which appears in the presence of the first field only will split up into two components, in such a way that each component polarised parallel to the axis will split up into two components of the same polarisation, while each component polarised perpendicular to the axis, and which originally showed no polarisation when viewed in a direction parallel to the axis, will split up into two components showing circular polarisations in opposite directions. If the magnetic field is small, the new components will be placed symmetrically with respect to the position of the original components and their intensities will be approximately equal, but when the perturbing influence of the magnetic forces on the motion of the electron becomes of the same order of magnitude as that of the external electric forces, the components in question will in general be placed unsymmetrically with respect to their original position, and their intensities may differ considerably.

An especially simple example of a magnetic field which possesses axial symmetry is afforded by the case of a homogeneous magnetic field, discussed in the beginning of this section. In this case we have that the total magnetic flux of force through the orbit of the electron is equal to the product of the intensity H of the magnetic field and the area of the projection of the orbit on a plane perpendicular to this field. Since this area is equal to $\alpha_3/2m\omega$, we get consequently from (84)

$$\Psi_M = \frac{e\alpha_3}{2cm}H. \qquad (86)$$

From the equations (46) it follows therefore that the effect of a homogeneous magnetic field, which acts upon a hydrogen atom which at the same time is exposed to an external electric field possessing axial symmetry round an axis through the nucleus parallel to the magnetic force, will consist in a superposition of a uniform rotation of the orbit round the axis with a frequency equal to

$$o_H = \frac{1}{2\pi}\frac{\partial \Psi_M}{\partial \alpha_3} = \frac{e}{4\pi mc}H$$

on the secular perturbations which would take place in the absence of the magnetic field. This result follows also directly from Larmor's theorem, on which the simple considerations about the effect of a homogeneous magnetic field in the beginning of this section were based. Since a superposed rotation as that in question will not influence the shape of the orbit of the electron or its position relative to the axis, it follows from (61) that the value of Ψ_E in the stationary states of the atom will not be affected by the presence of the magnetic field, and that consequently the effect of this field on the additional energy of the system will simply consist in the addition of a term given by

$$\Psi_M = \frac{e}{2mc}\frac{n_2 h}{2\pi}H = n_2 o_H h. \qquad (87)$$

This result was also to be expected from a simple consideration of the mechanical effect produced on the motion by a slow and uniform establishment of the magnetic field (compare page 81). With reference to the above considerations as regards the probability of transition between stationary states, it will be seen to follow from (87), that the presence of the homogeneous magnetic field will leave the components polarised parallel to the axis unaltered, but will cause every component, which in the absence of the field was polarised perpendicular to the axis, to split up in a symmetrical doublet the members of which will show circular polarisation in opposite directions, when viewed in the direction of the axis, and will be displaced from the position of the original component by an amount corresponding to a frequency difference equal to ω_H.

A simple application of the last result is afforded by the problem of the simultaneous effect on the hydrogen lines of a homogeneous electric and a homogeneous magnetic field which have the same direction. Thus, if the intensities of the fields are so large that we may look apart from the small modifications claimed by the theory of relativity, we shall from the above expect that the effect in question will differ from the ordinary Stark effect of the hydrogen lines, only therein that every component polarised perpendicular to the field is split up in two symmetrical components corresponding to the outer members of a Lorentz triplet. This seems to agree with some observations of the effect of two such fields on the hydrogen line H_α, published by Garbasso.[1] The problem in question might also have been treated by means of the method of separation of variables, because, as may be easily shown, the perturbed system — if the relativity modifications are neglected — allows of separation of variables in parabolic coordinates, just as in the presence of the electric field only. If, on the other hand, the relativity modifications are taken into account, the method of separation of variables cannot be applied, but, with reference to the considerations at the end of the last section, it will be seen that it is possible, also in this case, to predict at once the modification in the effect of an electric field on the fine structure of the hydrogen lines, which would result from the simultaneous presence of a parallel magnetic field. Passing to the limiting case where the intensity of the electric field is equal to zero, it will thus be seen at once from the preceding, that the effect of a homogeneous magnetic field on the fine structure of the hydrogen lines will consist in the splitting up of every component in a normal Lorentz triplet. As far as the frequencies of the components are concerned, this result has been predicted by Sommerfeld and Debye, who have treated the problem under consideration by means of separation of variables in polar coordinates (compare page 84). In connection with the fixation of the stationary states in this problem, it may be remarked that we must assume that no stationary state will exist for which the angular momentum round an axis through the nucleus parallel to the magnetic field would be equal to zero. In fact, as seen in § 4, we must assume that, in case of a hydrogen atom exposed to a homogeneous electric field, no such states will be possible; and by imagining that the electric field decreases slowly to zero, while at the same time a magnetic field parallel to the electric field is slowly established, it would be possible, without passing through a degenerate system, to obtain a continuous transformation of the stationary states of the perturbed atom during which the angular momentum of the electron round the axis would remain unaltered. With

[1]) A. Garbasso, Phys. Zeitschr. XV, p. 123 (1914).

reference to the invariance of the a-priori probability of the stationary states during such a transformation (see Part I, page 9 and 27), we must therefore conclude that, also in the case of a hydrogen atom in the presence of a magnetic field, no stationary states exist for which the angular momentum round the axis would be equal to zero, although these states in mechanical respect do not exhibit singularities from which we might anticipate that they are physically unrealisable.[1])

In case we consider the general problem of the effect on a hydrogen atom of a small electric or magnetic field, which do not possess axial symmetry round an axis through the nucleus, or of the simultaneous effect of two such fields, which do not possess such symmetry round a common axis, we must expect that the secular perturbations of the orbit of the electron will in general not be of conditionally periodic type. In such a case we cannot obtain a complete fixation of the stationary states, and we may conclude that the presence of the external forces will not give rise to the splitting up of the hydrogen lines into a number of sharp components but to a diffusion of these lines. With a simple example, in which the secular perturbations of the atom seem not to be of conditionally periodic type, we meet if we consider the simultaneous effect on the hydrogen spectrum of an external homogeneous electric field and a homogeneous magnetic field, the directions of which make an angle with each other. If

[1]) Note added during the proof. In a dissertation which has just appeared, J. M. Burgers (Het Atoommodel van Rutherford-Bohr, Haarlem 1918) has given a very interesting general survey of the applications of the quantum theory to the problem of the constitution of atoms, and has in this connection entered upon several of the questions discussed in the present paper; for instance on the question of the relation between the spectrum of an atomic system, deduced by application of relation (1) from the values of the energy in the stationary states, and the frequencies of the harmonic vibrations into which the motion in these states can be resolved; and on the question of the determination of the relative values for the a-priori probability of the different stationary states of an atomic system by means of Ehrenfest's principle of the invariance of these values during a continuous transformation of the system. As an illustration of the latter considerations, Burgers has deduced an expression for the relative values of the a-priori probability of the different stationary states of the undisturbed hydrogen atom, by means of an enumeration of the states, determined by the conditions (22) when applied in connection with a separation of variables in polar coordinates, which correspond to a stationary state of the undisturbed atom, characterised by a given value of n in the condition $I = nh$. Excluding only such states for which the total angular momentum of the electron round the nucleus would be equal to zero, Burgers (loc. cit. p. 259) finds in this way for the value of the a-priori probability in question $(n+1)^2 - 1$. In connection with the analogous consideration, given in the Note on page 76 of the present paper, which leads to a different result, it may be of interest to remark that the necessary conformity between the relative values for the a-priori probability of the different stationary states of the undisturbed hydrogen atom, deduced from an enumeration of the stationary states of the atom which appear in the presence of a small external electric field or in the presence of a small magnetic field respectively, cannot be obtained if in both cases we would exclude only such states in which the angular momentum of the electron round the nucleus is always equal to zero. In fact, while in case of a magnetic field this would give $(n+1)^2 - 1$ different states corresponding to a given value of n, it would in case of an electric field give only $(n+1)^2 - 2$ such states. On the other hand, if the possible stationary states are selected in the manner explained in the text, the conformity in question will obviously be obtained.

the effects of the two fields on the motion of the electron are of the same order of magnitude we may in this case expect that the hydrogen lines will not be resolved into sharp components but will become diffuse. From the considerations on page 60 of the effect on the spectrum of a perturbed periodic system due to a second external field, the perturbing effect of which is small compared with that of the first, we may conclude, however, that, if the effect of one of the fields on the motion of the electron is large compared with that of the other, the hydrogen lines will still show a resolution in a number of components, the spectral widths of which are small compared with the displacements which they have undergone due to the presence of the weaker of the external fields. In the discussion of this problem we shall for simplicity neglect the influence of the relativity modifications, assuming that the effect on the spectrum produced by each external field separately is large compared with the inherent fine structure of the hydrogen lines. Denoting, as in § 2, by μ a small constant of the same order as the ratio between the forces on the electron due to the weaker of the external fields and those due to the stronger of these fields, and by λ a small constant of the same order as the ratio between the latter forces and the attraction from the nucleus, we have, as shown on page 61, that, with neglect of small quantities of the same order of magnitude as $\lambda\mu^2$,[1]) the change in the additional energy of the atom due to the presence of the weaker field is, in general, directly obtained by taking the mean value of the function Ψ, corresponding to the weaker field, over the cycle of shapes and positions which the orbit of the electron passes through in the stationary states of the atom in the presence of the stronger field only. In the special case under consideration, however, the perturbed system, formed by the atom in the presence of the stronger field only, is degenerate, the secular perturbations of the orbit of the electron being of a simple periodic character. The mean value in question will therefore not be completely determined, but will be different for the different periodic cycles of shapes and positions of the orbit, which represent the continuous multitude of stationary motions which the electron may perform in each of the stationary states of the atom in the presence of the stronger field only. In order to fix the stationary states in the presence of both fields and the change in the additional energy of the atom due to the presence of the weaker field, it will thus, as mentioned on page 62, be necessary to examine the relation between the mean value in question and the frequency of the slow periodic "secular" variations which the cycles under consideration will undergo under the influence of the weaker of the external fields. Now, in the special case under consideration this problem may be treated very simply, if we imagine the weaker field as composed of two homogeneous fields of which the one is parallel and the other perpendicular to the stronger field, and if we consider separately the secular effect due to each of these fields. In fact, due to the symmetry

[1]) Rigorously this result holds with neglect of small quantities of the same order of magnitude as the largest of the quantities λ^2 and $\lambda\mu^2$, but for the sake of simplicity it is here and in the following assumed that μ is not smaller than $\sqrt{\lambda}$ (compare page 61).

with respect to the axis of the stronger field, exhibited by the periodic cycle of shapes and positions which the orbit of the electron would pass through if the atom were exposed to this field only, it is easily seen that the contribution, which the perpendicular component of the weaker field gives to the mean value of Ψ corresponding to the latter field, will vanish. From this it follows that the secular effect of the weaker field, with neglect of small quantities proportional to μ^2, will be the same as if only the parallel component of this field was acting on the atom; and we see consequently that, in the stationary states of the atom in the presence of both fields, the possible cycles of shapes and positions of the orbit of the electron will be characterised in the same way as if the weaker field was parallel to the stronger. The problem, however, of the fixation of the stationary states of a hydrogen atom in the presence of a homogeneous electric field and a homogeneous magnetic field, which are parallel to each other, is very simple. In fact, as it appears from the considerations on page 91, the stationary states will in this case be fixed completely by two conditions, of which the one, in the same way as in the simple theory of the Stark effect, defines the position of the plane in which the electrical centre of he orbit of the electron moves, while the other defines the value of the angular momentum of the electron round the axis of the fields in the same way as in the simple theory of the Zeeman effect. In connection with the problem under consideration here, it may be useful for the sake of illustration to note, that, if the perturbing effect of the electric field is large compared with that of the magnetic, the second of these conditions may be said to be imposed on the system by the slow and uniform rotation, which the magnetic field produces on the periodic cycle of shapes and positions of the orbit of the electron, which would appear if the atom was exposed to the electric field only. If, on the other hand, the effect of the magnetic field is large compared with that of the electric field, the first condition may be said to be imposed on the system by the slow periodic oscillation in the shape and position relative to the axis, which the electric field produces on the uniformly rotating orbit which the electron would describe if the atom was exposed to the magnetic field only.

If we consider a hydrogen atom which is exposed to the simultaneous influence of a homogeneous electric field of intensity F and a homogeneous magnetic field of intensity H, the direction of which makes an angle φ with the direction of the electric field, it follows from the above that, if the perturbing influence of the electric field is large compared with that of the magnetic field, the main effect produced by the latter field on the spectrum may be described as the splitting up of each Stark effect component, polarised perpendicular to the axis of the electric field, into two circularly polarised components, corresponding to the outer members of a Lorentz triplet which would be produced by a magnetic field of intensity $H \cos \varphi$. On the other hand, if the perturbing effect of the magnetic field is large compared with that of the electric, it follows that the main effect, produced by the latter field on the spectrum, may be described as the resolution of the middle component and of each of the outer components of the normal ZEEMAN effect into a number of components, corresponding to the parallel and perpendicular components respectively of a STARK effect produced by an electric field of intensity $F \cos \varphi$.

The effects just described, however, which are the same as would take place if only the parallel component of the weaker field was acting on the atom, will not be the only effects of the presence of the weaker field on the spectrum. In fact, although the perpendicular component of the weaker field, apart from small quantities proportional to μ^2, will not have any secular effect on the cycle of shapes and positions which the orbit of the electron would pass through if the atom was exposed to the stronger field only, it will obviously produce alterations in the motion of the electron within this cycle which are proportional to μ. Thus, if the weaker field was parallel to the stronger, the motion of the electron in the perturbed atom would be composed of a number of linear harmonic vibrations parallel to the direction of the fields, the frequencies of which are of the type $|\tau\omega_P + \mathfrak{t}_1 \mathfrak{o}_1|$, and of a number of circular harmonic rotations perpendicular to this direction, the frequencies of which are of the type $|\tau\omega_P + \mathfrak{t}_1 \mathfrak{o}_1 + \mathfrak{o}_2|$ (compare page 59). In the general case, however, where the weaker field is not parallel to the stronger, there will, in the expression for the displacement of the electron in any given direction, in addition appear a number of harmonic vibrations the amplitudes of which are proportional to μ and the frequencies of which, as a closer consideration of the perturbations learns, are equal to the sum or difference of the frequency of one of the harmonic vibrations, in which the motion in this direction could be resolved if the external fields were parallel to each other, and one of the small frequencies of type $|\mathfrak{t}_1 \mathfrak{o}_1 + \mathfrak{o}_2|$, which appear in the expression for the secular perturbations of the electron in this case. A part of these additional vibrations will again possess frequencies of the types $|\tau\omega_P + \mathfrak{t}_1 \mathfrak{o}_1|$ and $|\tau\omega_P + \mathfrak{t}_1 \mathfrak{o}_1 + \mathfrak{o}_2|$, and will cause that the motion, instead of consisting of vibrations which are exactly linear and exactly circular as in the case where the external fields are parallel to each other, will be composed of elliptical harmonic vibrations which partly are nearly linear and parallel to the direction of the stronger field and partly nearly circular and perpendicular to this direction. On account of this we shall expect that, due to the presence of the perpendicular component of the weaker field, the different components mentioned above will not be sharply polarised. Further there will, in the motion of the perturbed atom, also appear a number of circular harmonic rotations perpendicular to the stronger field, the amplitudes of which are small quantities proportional to μ, and the frequencies of which are of the type $|\tau\omega_P + \mathfrak{t}_1 \mathfrak{o}_1 + 2\mathfrak{o}_2|$. From this we shall expect the appearance in the spectrum of a number of new weak components, corresponding to a type of transition between stationary states which would not be possible if the two external fields were parallel to eachother. When considering more closely the frequencies of these new components, it must be remembered, however, that, as mentioned above, the present method of treating the problem of the perturbations assures us of the conditionally periodic character of the motion of the electron within a time interval of the same order of magnitude as σ/λ, only if we look apart from small quantities of the same order as μ^2; and we must therefore be prepared to find that the frequencies of the vibrations of small amplitudes will not be defined with the same degree of approximation as the frequencies of the vibrations of large amplitudes. Thus, while the frequencies of the latter vibrations are defined with neglect of small quantities proportional to $\lambda\mu^2$, the frequencies of the small vibrations under consideration are obviously defined only with neglect of small quantities proportional to $\lambda\mu$. In intimate connection with the general want of definition of the energy in the stationary states for perturbed systems of the type in question, we must accordingly be prepared to find that, in contrast to the strong components, for which we may expect that by far the larger part of the intensity is contained within a spectral interval of a width proportional to $\lambda\mu^2$, the new components will be diffused over spectral intervals of a width proportional to $\lambda\mu$.[1]) Thus, in case the effect of the external electric field is large compared with that of the magnetic field, we might expect at first sight that, on each side of every of the STARK effect components polarised parallel to the electric force, there would appear a weak component which would be circularly polarised and be displaced from this component by an amount twice that of the displacement of the strong components into which the perpendicularly polarised STARK effect components are split up as a consequence of the small magnetic field. We must be prepared, however, to find that these weak components will be so diffuse, that they are not separated from the weak perpendicular component which has the same frequency as the strong parallel components on each side of which the weak components under consideration would lie, and which appears as a consequence of the above mentioned want of sharpness as regards the polarisation of the strong components. On the other hand, if the effect of the magnetic field is large compared with that of the electric field, any weak component of the type under consideration, which corresponds to transitions in which the

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[1]) Compare Note on page 61. With reference to the general validity of relation (1), it will be seen that the assumption, that the weak components possess this degree of diffusion, implies the assumption, that the corresponding transitions (the probability of occurrence of which is very small compared with the probability of the transitions responsible for the strong components) will generally take place between two states of the perturbed atom, which do not both belong to the well defined ensemble of stationary states in which at any moment the great majority among a large number of atoms will be present. Thus, in case the effect of the external electric field is large compared with that of the magnetic field, we may expect that, in both states involved in the transitions in question, the positions of the plane in which the electrical centre moves will coincide with positions of this plane in states belonging to the ensemble just mentioned, while the angular momentum of the electron round the axis of the electric field will generally change by an amount which will not be equal to an entire multiple of $h/2\pi$. On the other hand, if the effect of the magnetic field is the larger, the angular momentum of the electron round the axis of this field will, in the transitions in question, change by two times $h/2\pi$, while we may expect that the plane in which the electrical centre moves will generally, in at least one of the states involved in these transitions, differ from the positions of this plane in the ensemble of stationary states referred to.

angular momentum of the electron round the axis of the magnetic field changes by two times $h/2\pi$, will lie at a distance from the original hydrogen line, which is approximately twice as large as that of the outer components of the normal ZEEMAN effect, and will therefore be distinctly separated from the strong components into which each of the components of the normal ZEEMAN effect is split up in the presence of the small electric field. We must be prepared, however, to find that the weak components will not, as it might be expected at first sight, form two sets of distinctly separated lines, but that they will only appear as two diffuse lines of circular polarisation in opposite directions and of a spectral width proportional to $\lambda\mu$.[1])

§ 6. The continuous hydrogen spectrum.

We shall conclude the considerations of this Part by a brief discussion of the characteristic continuous spectrum of hydrogen in the ultra violet region, which is intimately connected with the series spectrum given by (35). This spectrum consists of a radiation, the frequencies of which are continuously distributed over a spectral interval extending from the head of the Balmer series in the direction of higher frequencies.[2]) The existence of a continuous spectrum of this type is just what should be expected from a natural generalisation of the principles underlying the quantum theory of series spectra.[3]) Thus the spectrum under consideration may be directly explained by application of relation (1), if we assume that the complete spectrum, emitted by a system consisting of a nucleus and of an electron, originates not only from radiations, emitted during transitions between two states belonging to the multitude of stationary states in which the electron describes a closed orbit, characterised by the condition $I = nh$, but also from radiations emitted during

[1]) No experiments, which allow to test the preceding results in detail, seem to have been recorded, but it would appear that the above considerations afford an explanation of the general character of the remarkable deviations from a normal ZEEMAN effect, observed by F. PASCHEN and E. BACK (Ann. d. Phys. XXXIX, p. 897 (1912)) in experiments in which the hydrogen lines were excited by passing a powerful condensed discharge through a capillary tube placed at right angles with the direction of the magnetic field. Besides the characteristic want of sharpness of the polarisation of the middle component, exhibited by all the spectrograms published by PASCHEN and BACK, especially one of their photographs (Tafel VIII, Bild 4) seems to suggest the presence of a weak, perpendicularly polarised, diffuse line on each side of the original line and at a distance from it twice that of the outer components of the normal effect.

[2]) This spectrum has been observed as an emission spectrum in spectra of solar protuberances and planetary nebulæ (See J. EVERSHED, Phil. Trans. Roy. Soc. 197 A, p. 399 (1901) and W. H. WRIGHT, Lick Observatory Bulletin, No. 291 (1917)) as well as in direct laboratory experiments on spectra excited by positive rays (See J. STARK, Ann. d. Phys. LII, p. 255 (1917)). Further it has been observed as an absorption spectrum in the spectra of several stars (see W. HUGGINS, An Atlas of Representative Stellar Spectra, p. 85 (1899) and J. HARTMANN, Phys. Zeitschr. XVIII p. 429 (1917)).

[3]) Compare N. BOHR, Phil. Mag. XXVI, p. 17 (1913); and also P. DEBYE, Phys. Zeitschr. XVIII, p. 428 (1917).

transitions between two states, one (or both) of which belong to the multitude of states in which the electron possesses sufficient energy to remove to infinite distance from the nucleus. While the electron in the states of the type first mentioned may be said to be "bound" by the nucleus to form an atom, it may in the states of the last mentioned type be described as "free". In order to account for the appearance of the continuous spectrum, it is necessary to assume that the motions in the latter states are not restricted by extra-mechanical conditions of the type holding for the former states, but that all motions, which are consistent with the application of ordinary mechanics, will represent physically possible states. This assumption would also seem to present itself naturally from the point of view on the principles of the quantum theory, taken in the present paper.[1]) Thus it will in the first place be observed that any attempt to discriminate between the different states of the type in question, by means of considerations of the mechanical stability of stationary states for slow transformations of the external conditions, would fail on account of the essentially non-periodic character of the motion, which is irreconcilable with the idea of invariance of extra-mechanical conditions for such transformations. Next, with reference to the formal analogy between the quantum theory and the ordinary theory of radiation, it will be seen that the fact, that the motion of a free electron in its hyperbolic orbit cannot be resolved in a sum of harmonic vibrations of discontinuously varying frequencies but can only be represented by a Fourier integral extended over a continuous range of frequencies, suggests beforehand that the free electron may pass, under emission or absorption of radiation, to any one among a continuous multitude of other states corresponding to a continuous multitude of values for the energy of the system. From the preceding considerations we may infer, by application of (1), that the complete spectrum emitted by the hydrogen atom will, besides the series spectrum and the continuous ultra-violet spectrum mentioned above, which corresponds to transitions from a state in which the electron is free to a stationary state characterised by $n = 2$ in (41), contain a set of continuous spectra, corresponding to transitions from free states to other stationary states, and each extending in the direction of larger frequencies from one of the values of the frequency, given by (35) if we put $n' = \infty$. Moreover, we may expect the presence of a weak continuous spectrum, extending as a continuous back ground over the whole region of frequencies, which will correspond to transitions between two different states in both of which the electron is free. The relative intensities of these different continuous spectra, and the laws according to which the intensity is distributed within each of them, may be expected to vary to a large extent according to the different conditions under which the radiation is excited. Thus,

[1]) A view contrary to this has been taken by EPSTEIN, who in a recent paper (Ann. d. Phys. L, p. 815 (1916)) has made an attempt to obtain an explanation of certain observations on the photoelectric effect of hydrogen occluded in metals, by applying conditions of the same type as (22) to states of the hydrogen atom in which the electron describes a hyperbolic orbit, and has tried in a similar way to develop a theory of the characteristic β-ray spectra of radioactive substances.

while the continuous spectrum of hydrogen, when observed as emission spectrum in stars, shows a abrupt beginning at the head of the Balmer series, the continuous spectrum, observed by Stark in his experiments referred to above, was not sharply limited but showed a pronounced maximum in the spectral region which corresponds to transitions between two states, in the first of which the velocity of the free electron relative to the nucleus, before the "collision" with the latter, was of the same order of magnitude as the velocity of the positive rays by means of which the spectrum was excited.

Besides the series spectrum and the connected continuous spectrum just considered, there exists, as well known, another hydrogen spectrum, the socalled many-line spectrum, which on account of its complex structure and its resemblance with the band spectra, emitted by other elements and combinations of elements, is generally ascribed to the hydrogen molecule and not to the atom. This assumption would also seem to present itself directly from the point of view of the quantum theory, according to which the simple structure of the series spectrum is directly connected with the simple periodic character of the motion of the particles in the atom, while a spectrum of a complexity of the order exhibited by the many-line spectrum must be assumed to originate from a system the motion of which does not show such simple periodicity properties. The problem of the constitution of the hydrogen molecule, to be expected on the quantum theory, and the possible motions of the particles of this system will be treated in Part IV. In this connection we shall also consider the problem of dispersion of light in hydrogen gas and the problem of the voltage necessary to produce the lines of the series spectrum of hydrogen by an electric discharge in this gas.

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Det Kgl. Danske Videnskabernes Selskabs Skrifter.

Naturvidenskabelig og mathematisk Afdeling,

8de Række.

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