ON

THE QUANTUM THEORY OF LINE-SPECTRA

BY

N. BOHR

D. Kgl. Danske Vidensk. Selsk. Skripter, naturvidensk. og mathem. Afd., 8. Række, IV.

KØBENHAVN
hovedkommissionær: ANDR. FRED. HØST & SON, kgl., hof-boghandel
bianco lunos bogtrykkeri
1918

DEDICATED TO THE MEMORY
OF MY VENERATED TEACHER

Professor C. CHRISTIANSEN

OCTOBER 9, 1843 † *NOVEMBER 28, 1917*

UDGIVET PAA CARLSBERGFONDETS BEKOSTNING

Introduction.

In an attempt to develop certain outlines of a theory of line-spectra based on a suitable application of the fundamental ideas introduced by Planck in his theory of temperature-radiation to the theory of the nucleus atom of Sir Ernest Rutherford, the writer has shown that it is possible in this way to obtain a simple interpretation of some of the main laws governing the line-spectra of the elements, and especially to obtain a deduction of the well known Balmer formula for the hydrogen spectrum[1]) The theory in the form given allowed of a detailed discussion only in the case of periodic systems, and obviously was not able to account in detail for the characteristic difference between the hydrogen spectrum and the spectra of other elements, or for the characteristic effects on the hydrogen spectrum of external electric and magnetic fields. Recently, however, a way out of this difficulty has been opened by Sommerfeld[2]) who, by introducing a suitable generalisation of the theory to a simple type of non-periodic motions and by taking the small variation of the mass of the electron with its velocity into account, obtained an explanation of the fine-structure of the hydrogen lines which was found to be in brilliant conformity with the measurements. Already in his first paper on

[1]) N. Bohr, Phil. Mag., XXVI, pp. 1, 476, 857 (1913), XXVII, p. 506 (1914), XXIX. p. 332 (1915), XXX. p. 394 (1915).

[2]) A. Sommerfeld, Ber. Akad. München, 1915, pp. 425, 459, 1916, p. 131. 1917. p. 83. Ann. de Phys., LI. p. 1 (1916).

this subject, SOMMERFELD pointed out that his theory evidently offered a clue to the interpretation of the more intricate structure of the spectra of other elements. Briefly afterwards EPSTEIN[1]) and SCHWARZSCHILD,[2]) independent of each other, by adapting SOMMERFELD's ideas to the treatment of a more extended class of non-periodic systems obtained a detailed explanation of the characteristic effect of an electric field on the hydrogen spectrum discovered by STARK. Subsequently SOMMERFELD[3]) himself and DEBYE[4]) have on the same lines indicated an interpretation of the effect of a magnetic field on the hydrogen spectrum which, although no complete explanation of the observations was obtained, undoubtedly represents an important step towards a detailed understanding of this phenomenon.

In spite of the great progress involved in these investigations many difficulties of fundamental nature remained unsolved, not only as regards the limited applicability of the methods used in calculating the frequencies of the spectrum of a given system, but especially as regards the question of the polarisation and intensity of the emitted spectral lines. These difficulties are intimately connected with the radical departure from the ordinary ideas of mechanics and electro-

[1]) P. EPSTEIN, Phys. Zeitschr. XVII, p. 148 (1916), Ann. d. Phys. L, p. 489. LI. p. 168 (1916).

[2]) K. SCHWARZSCHILD, Ber. Akad. Berlin, 1916, p. 548.

[3]) A. SOMMERFELD, Phys. Zeitschr. XVII, p. 491 (1916).

[4]) P. DEBYE, Nachr. K. Ges. d. Wiss. Göttingen, 1916, Phys. Zeitschr. XVII, p. 507 (1916).

dynamics involved in the main principles of the quantum theory, and with the fact that it has not been possible hitherto to replace these ideas by others forming an equally consistent and developed structure. Also in this respect, however, great progress has recently been obtained by the work of EINSTEIN[1]) and EHRENFEST.[2]) On this state of the theory it might therefore be of interest to make an attempt to discuss the different applications from a uniform point of view, and especially to consider the underlying assumptions in their relations to ordinary mechanics and electrodynamics. Such an attempt has been made in the present paper, and it will be shown that it seems possible to throw some light on the outstanding difficulties by trying to trace the analogy between the quantum theory and the ordinary theory of radiation as closely as possible.

The paper is divided into four parts.

Part I contains a brief discussion of the general principles of the theory and deals with the application of the general theory to periodic systems of one degree of freedom and to the class of non-periodic systems referred to above.

Part II contains a detailed discussion of the theory of the hydrogen spectrum in order to illustrate the general

[1]) A. EINSTEIN, Verh. d. D. phys. Ges. XVIII, p. 318 (1916), Phys. Zeitschr. XVIII, p. 121 (1917).

[2]) P. EHRENFEST, Proc. Acad. Amsterdam, XVI. p. 591 (1914), Phys. Zeitschr. XV. p. 657 (1914), Ann. d. Phys. LI. p. 327 (1916), Phil. Mag. XXXIII. p. 500 (1917).

considerations.

Part III contains a discussion of the questions arising in connection with the explanation of the spectra of other elements.

Part IV contains a general discussion of the theory of the constitution of atoms and molecules based on the application of the quantum theory to the nucleus atom.

Copenhagen, November 1917.

Part I.

On the general theory.

§ 1. General principles.

The quantum theory of line-spectra rests upon the following fundamental assumptions:

I. *That an atomic system can, and can only, exist permanently in a certain series of states corresponding to a discontinuous series of values for its energy, and that consequently any change of the energy of the system, including emission and absorption of electromagnetic radiation, must take place by a complete transition between two such states. These states will be denoted as the "stationary states" of the system.*

II. *That the radiation absorbed or emitted during a transition between two stationary states is "unifrequentic" and possesses a frequency ν, given by the relation*

$$E' - E'' = h\nu, \tag{1}$$

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

As pointed out by the writer in the papers referred to in the introduction, these assumptions offer an immediate interpretation of the fundamental *principle of combination of spectral lines* deduced from the measurements of the frequencies of the series spectra of the elements. According to

the laws discovered by BALMER, RYDBERG and RITZ, the frequencies of the lines of the series spectrum of an element can be expressed by a formula of the type:

$$\nu = f_{\tau''}(n'') - f_{\tau'}(n'), \tag{2}$$

where n' and n'' are whole numbers and $f_\tau(n)$ is one among a set of functions of n, characteristic for the element under consideration. On the above assumptions this formula may obviously be interpreted by assuming that the stationary states of an atom of an element form a set of series, and that the energy in the n^{th} state of the τ^{th} series, omitting an arbitrary constant, is given by

$$E_\tau(n) = -hf_\tau(n). \tag{3}$$

We thus see that the values for the energy in the stationary states of an atom may be obtained directly from the measurements of the spectrum by means of relation (1). In order, however, to obtain a theoretical connection between these values and the experimental evidence about the constitution of the atom obtained from other sources, it is necessary to introduce further assumptions about the laws which govern the stationary states of a given atomic system and the transitions between these states.

Now on the basis of a vast amount of experimental evidence, we are forced to assume that an atom or molecule consists of a number of electrified particles in motion, and, since the above fundamental assumptions imply that no emission

of radiation takes place in the stationary states, we must consequently assume that *the ordinary laws of electrodynamics cannot be applied* to these states without radical alterations. In many cases, however, the effect of that part of the electrodynamical forces which is connected with the emission of radiation will at any moment be very small in comparison with the effect of the simple electrostatic attractions or repulsions of the charged particles corresponding to COULOMB's law. Even if the theory of radiation must be completely altered, it is therefore a natural assumption that it is possible in such cases to obtain a close approximation in the description of the motion in the stationary states, by retaining only the latter forces. In the following we shall therefore, as in all the papers mentioned in the introduction, for the present *calculate the motions of the particles in the stationary states as the motions of mass-points according to ordinary mechanics* including the modifications claimed by the theory of relativity, and we shall later in the discussion of the special applications come back to the question of the degree of approximation which may be obtained in this way.

If next we consider a transition between two stationary states, it is obvious at once from the essential discontinuity, involved in the assumptions I and II, that in general it is impossible even approximately to describe this phenomenon by means of ordinary mechanics or to calculate the frequency of the radiation absorbed or emitted by such a process by means of ordinary electrodynamics. On the other hand, from the fact that it has been possible by means of ordinary mechan-

ics and electrodynamics to account for the phenomenon of temperature-radiation in the limiting region of slow vibrations, we may expect that any theory capable of describing this phenomenon in accordance with observations will form some sort of natural generalisation of the ordinary theory of radiation. Now the theory of temperature-radiation in the form originally given by PLANCK confessedly lacked internal consistency, since, in the deduction of his radiation formula, assumptions of similar character as I and II were used in connection with assumptions which were in obvious contrast to them. Quite recently, however, EINSTEIN[1]) has succeeded, on the basis of the assumptions I and II, to give a consistent and instructive deduction of PLANCK's formula by introducing certain supplementary assumptions about the *probability of transition of a system between two stationary states* and about the manner in which this probability depends on the density of radiation of the corresponding frequency in the surrounding space, suggested from analogy with the ordinary theory of radiation. EINSTEIN compares the emission or absorption of radiation of frequency ν corresponding to a transition between two stationary states with the emission or absorption to be expected on ordinary electrodynamics for a system consisting of a particle executing harmonic vibrations of this frequency. In analogy with the fact that on the latter theory such a system will without external excitation emit a radiation of frequency ν, EINSTEIN assumes in

[1]) A. EINSTEIN, loc. cit.

the first place that on the quantum theory there will be a certain probability $A^{n'}_{n''}\,dt$ that the system in the stationary state of greater energy, characterised by the letter n', in the time interval dt will start *spontaneously* to pass to the stationary state of smaller energy, characterised by the letter n''. Moreover, on ordinary electrodynamics the harmonic vibrator will, in addition to the above mentioned independent emission, in the presence of a radiation of frequency ν in the surrounding space, and dependent on the accidental phase-difference between this radiation and the vibrator, emit or absorb radiation-energy. In analogy with this, EINSTEIN assumes secondly that in the presence of a radiation in the surrounding space, the system will on the quantum theory, in addition to the above mentioned probability of spontaneous transition from the state n' to the state n'', possess a certain probability, depending on this radiation, of passing in the time dt from the state n' to the state n'', as well as from the state n'' to the state n'. These latter probabilities are assumed to be proportional to the intensity of the surrounding radiation and are denoted by $\rho_\nu B^{n'}_{n''}\,dt$ and $\rho_\nu B^{n''}_{n'}\,dt$ respectively, where $\rho_\nu\,d\nu$ denotes the amount of radiation in unit volume of the surrounding space distributed on frequencies between ν and $\nu + d\nu$, while $B^{n'}_{n''}$ and $B^{n''}_{n'}$ are constants which, like $A^{n'}_{n''}$, depend only on the stationary states under consideration. EINSTEIN does not introduce any detailed assumption as to the values of these constants, no more than to the conditions by which the different stationary states of a given system are determined or to the "a-priori probabil-

ity" of these states on which their relative occurrence in a distribution of statistical equilibrium depends. He shows, however, how it is possible from the above general assumptions, by means of BOLTZMANN's principle on the relation between entropy and probability and WIEN's well known displacement-law, to deduce a formula for the temperature radiation which apart from an undetermined constant factor coincides with PLANCK's, if we only assume that the frequency corresponding to the transition between the two states is determined by (1). It will therefore be seen that by reversing the line of argument, EINSTEIN's theory may be considered as a very direct support of the latter relation.

In the following discussion of the application of the quantum theory to determine the line-spectrum of a given system, it will, just as in the theory of temperature-radiation, not be necessary to introduce detailed assumptions as to the mechanism of transition between two stationary states. We shall show, however, that the conditions which will be used to determine the values of the energy in the stationary states are of such a type that the frequencies calculated by (1), in the limit where the motions in successive stationary states comparatively differ very little from each other, will tend to coincide with the frequencies to be expected on the ordinary theory of radiation from the motion of the system in the stationary states. In order to obtain the necessary relation to the ordinary theory of radiation in the limit of slow vibrations, we are therefore led directly to certain conclusions about the probability of transition between two stationary

states in this limit. This leads again to certain general considerations about the connection between the probability of a transition between any two stationary states and the motion of the system in these states, which will be shown to throw light on the question of the polarisation and intensity of the different lines of the spectrum of a given system.

In the above considerations we have by an atomic system tacitly understood a number of electrified particles which move in a field of force which, with the approximation mentioned, possesses a potential depending only on the position of the particles. This may more accurately be denoted as a system under constant external conditions, and the question next arises about the variation in the stationary states which may be expected to take place during a variation of the external conditions, e. g. when exposing the atomic system to some variable external field of force. Now, in general, we must obviously assume that this variation cannot be calculated by ordinary mechanics, no more than the transition between two different stationary states corresponding to constant external conditions. If, however, the variation of the external conditions is very slow, we may from the necessary stability of the stationary states expect that the motion of the system at any given moment during the variation will differ only very little from the motion in a stationary state corresponding to the instantaneous external conditions. If now, moreover, the variation is performed at a constant or very slowly changing rate, the forces to which the particles of the system will be exposed will not differ at any moment

from those to which they would be exposed if we imagine that the external forces arise from a number of slowly moving additional particles which together with the original system form a system in a stationary state. From this point of view it seems therefore natural to assume that, with the approximation mentioned, the motion of an atomic system in the stationary states can be calculated by direct application of ordinary mechanics, not only under constant external conditions, but in general also during a slow and uniform variation of these conditions. This assumption, which may be denoted as the principle of the "*mechanical transformability*" of the stationary states, has been introduced in the quantum theory by EHRENFEST[1]) and is, as it will be seen in the following sections, of great importance in the discussion of the conditions to be used to fix the stationary states of an atomic system among the continuous multitude of mechanically possible motions. In this connection it may be pointed out that the principle of the mechanical transformability of the stationary states allows us to overcome a fundamental difficulty which at first sight would seem to be involved in the definition of the energy difference between two stationary states

[1]) P. EHRENFEST, loc. cit. In these papers the principle in question is called the "adiabatic hypothesis" in accordance with the line of argumentation followed by EHRENFEST in which considerations of thermodynamical problems play an important part. From the point of view taken in the present paper, however, the above notation might in a more direct way indicate the content of the principle and the limits of its applicability.

which enters in relation (1). In fact we have assumed that the direct transition between two such states cannot be described by ordinary mechanics, while on the other hand we possess no means of defining an energy difference between two states if there exists no possibility for a continuous mechanical connection between them. It is clear, however, that such a connection is just afforded by EHRENFEST's principle which allows us to transform mechanically the stationary states of a given system into those of another, because for the latter system we may take one in which the forces which act on the particles are very small and where we may assume that the values of the energy in all the stationary states will tend to coincide.

As regards the problem of the statistical distribution of the different stationary states between a great number of atomic systems of the same kind in temperature equilibrium, the number of systems present in the different states may be deduced in the well known way from BOLTZMANN's fundamental relation between entropy and probability, if we know the values of the energy in these states and the *a-priori probability* to be ascribed to each state in the calculation of the probability of the whole distribution. In contrast to considerations of ordinary statistical mechanics we possess on the quantum theory no direct means of determining these a-priori probabilities, because we have no detailed information about the mechanism of transition between the different stationary states. If the a-priori probabilities are known for the states of a given atomic system, however, they may be de-

duced for any other system which can be formed from this by a continuous transformation without passing through one of the singular systems referred to below. In fact, in examining the necessary conditions for the explanation of the second law of thermodynamics EHRENFEST[1]) has deduced a certain general condition as regards the variation of the a-priori probability corresponding to a small change of the external conditions from which it follows, that the a-priori probability of a given stationary state of an atomic system must remain unaltered during a continuous transformation, except in special cases in which the values of the energy in some of the stationary states will tend to coincide during the transformation. In this result we possess, as we shall see, a rational basis for the determination of the a-priori probability of the different stationary states of a given atomic system.

§ 2. Systems of one degree of freedom.

As the simplest illustration of the principles discussed in the former section we shall begin by considering systems of a single degree of freedom, in which case it has been possible to establish a general theory of stationary states. This is due to the fact that *the motion will be simply periodic*, provided the distance between the parts of the system will

[1]) P. EHRENFEST, Phys. Zeitschr. XV p. 660 (1914). The above interpretation of this relation is not stated explicitly by EHRENFEST, but it presents itself directly if the quantum theory is taken in the form corresponding to the fundamental assumption I.

not increase infinitely with the time, a case which for obvious reasons cannot represent a stationary state in the sense defined above. On account of this, the discussion of the mechanical transformability of the stationary states can, as pointed out by EHRENFEST,[1]) for systems of one degree of freedom be based on a mechanical theorem about periodic systems due to BOLTZMANN and originally applied by this author in a discussion of the bearing of mechanics on the explanation of the laws of thermodynamics. For the sake of the considerations in the following sections it will be convenient here to give the proof in a form which differs slightly from that given by EHRENFEST, and which takes also regard to the modifications in the ordinary laws of mechanics claimed by the theory of relativity.

Consider for the sake of generality a conservative mechanical system of s degrees of freedom, the motion of which is governed by HAMILTON's equations:

$$\frac{dp_k}{dt} = -\frac{\partial E}{\partial q_k}, \quad \frac{dq_k}{dt} = \frac{\partial E}{\partial p_k}, \qquad (k = 1, \ldots, s) \qquad (4)$$

where E is the total energy considered as a function of the generalised positional coordinates $q_1, \ldots, q_s$ and the corresponding canonically conjugated momenta $p_1, \ldots, p_s$. If the velocities are so small that the variation in the mass of the particles due to their velocities can be neglected, the p's are

[1]) P. EHRENFEST, loc. cit. Proc. Acad. Amsterdam, XVI, p. 591 (1914).

defined in the usual way by

$$p_k = \frac{\partial T}{\partial q_k}, \qquad (k = 1, \ldots, s)$$

where T is the kinetic energy of the system considered as a function of the generalised velocities $\dot{q}_1, \ldots, \dot{q}_s$ $\left(\dot{q}_k = \dfrac{dq_k}{dt}\right)$ and of $q_1, \ldots, q_s$. If the relativity modifications are taken into account the p's are defined by a similar set of expressions in which the kinetic energy is replaced by

$$T' = \sum m_0 c^2 \big(1 - \sqrt{1 - v^2/c^2}\big),$$

where the summation is to be extended over all the particles of the system, and v is the velocity of one of the particles and m_0 its mass for zero velocity, while c is the velocity of light.

Let us now assume that the system performs a periodic motion with the period σ, and let us form the expression

$$I = \int_0^\sigma \sum_1^s p_k \dot{q}_k \, dt, \tag{5}$$

which is easily seen to be independent of the special choice of coordinates $q_1, \ldots, q_s$ used to describe the motion of the system. In fact, if the variation of the mass with the velocity is neglected we get

$$I = 2 \int_0^\sigma T \, dt,$$

and if the relativity modifications are included, we get a quite analogous expression in which the kinetic energy is replaced by $T'' = \sum \frac{1}{2} m_0 v^2 \sqrt{1 - v^2/c^2}$.

Consider next some new periodic motion of the system formed by a small variation of the first motion, but which may need the presence of external forces in order to be a mechanically possible motion. For the variation in I we get then

$$\delta I = \int_0^\sigma \sum_1^s (\dot{q}_k \, \delta p_k + p_k \, \delta \dot{q}_k) \, dt + \sum_1^s p_k \, \dot{q}_k \, \delta t \Big|_0^\sigma,$$

where the last term refers to the variation of the limit of the integral due to the variation in the period σ. By partial integration of the second term in the bracket under the integral we get next

$$\delta I = \int_0^\sigma \sum_1^s (\dot{q}_k \, \delta p_k - \dot{p}_k \, \delta q_k) \, dt + \sum_1^s p_k (\dot{q}_k \, \delta t + \delta q_k) \Big|_0^\sigma,$$

where the last term is seen to be zero, because the term in the bracket as well as p_k will be the same in both limits, since the varied motion as well as the original motion is assumed to be periodic. By means of equations (4) we get therefore

$$\delta I = \int_0^\sigma \sum_1^s \left(\frac{\partial E}{\partial p_k} \, \delta p_k + \frac{\partial E}{\partial q_k} \, \delta q_k \right) dt = \int_0^\sigma \delta E \, dt. \qquad (6)$$

Let us now assume that the small variation of the motion is produced by a small external field established at a uniform

rate during a time interval ϑ, long compared with σ, so that the comparative increase during a period is very small. In this case δE is at any moment equal to the total work done by the external forces on the particles of the system since the beginning of the establishment of the field. Let this moment be $t = -\vartheta$ and let the potential of the external field at $t \geq 0$ be given by Ω, expressed as a function of the q's. At any given moment $t > 0$ we have then

$$\delta E = -\int_{-\vartheta}^{0} \frac{\vartheta + t}{\vartheta} \sum_{1}^{s} \frac{\partial \Omega}{\partial q_k} \dot{q}_k \, dt - \int_{0}^{t} \sum_{1}^{s} \frac{\partial \Omega}{\partial q_k} \dot{q}_k \, dt,$$

which gives by partial integration

$$\delta E = \frac{1}{\vartheta} \int_{-\vartheta}^{0} \Omega \, dt - \Omega_t,$$

where the values for the q's to be introduced in Ω in the first term are those corresponding to the motion under the influence of the increasing external field, and the values to be introduced in the second term are those corresponding to the configuration at the time t. Neglecting small quantities of the same order as the square of the external force, however, we may in this expression for δE instead of the values for the q's corresponding to the perturbed motion take those corresponding to the original motion of the system. With this approximation the first term is equal to the mean value of the second taken over a period σ, and we have consequently

$$\int_{0}^{\sigma} \delta E \, dt = 0. \tag{7}$$

From (6) and (7) it follows that I will remain constant during the slow establishment of the small external field, if the motion corresponding to a constant value of the field is periodic. If next the external field corresponding to Ω is considered as an inherent part of the system, it will be seen in the same way that I will remain unaltered during the establishment of a new small external field, and so on. Consequently *I will be invariant for any finite transformation of the system which is sufficiently slowly performed*, provided the motion at any moment during the process is periodic and the effect of the variation is calculated on ordinary mechanics.

Before we proceed to the applications of this result we shall mention a simple consequence of (6) for systems for which every orbit is periodic independent of the initial conditions. In that case we may for the varied motion take an undisturbed motion of the system corresponding to slightly different initial conditions. This gives δE constant, and from (6) we get therefore

$$\delta E = \omega \, \delta I, \tag{8}$$

where $\omega = \dfrac{1}{\sigma}$ is the frequency of the motion. This equation forms a simple relation between the variations in E and I for periodic systems, which will be often used in the following.

Returning now to systems of one degree of freedom, we shall take our starting point from PLANCK's original theory of a *linear harmonic vibrator*. According to this theory the stationary states of a system, consisting of a particle execut-

ing linear harmonic vibrations with a constant frequency ω_0 independent of the energy, are given by the well known relation

$$E = nh\omega_0, \tag{9}$$

where n is a positive entire number, h PLANCK's constant, and E the total energy which is supposed to be zero if the particle is at rest.

From (8) it follows at once that (9) is equivalent to

$$I = \int_0^\sigma p\dot{q}\, dt = \int p\, dq = nh, \tag{10}$$

where the latter integral is to be taken over a complete oscillation of q between its limits. On the principle of the mechanical transformability of the stationary states we shall therefore assume, following EHRENFEST, that (10) holds not only for a PLANCK's vibrator but for *any periodic system of one degree of freedom* which can be formed in a continuous manner from a linear harmonic vibrator by a gradual variation of the field of force in which the particle moves. This condition is immediately seen to be fulfilled by all such systems in which the motion is of oscillating type i. e. where the moving particle during a period passes twice through any point of its orbit once in each direction. If, however, we confine ourselves to systems of one degree of freedom, it will be seen that systems in which the motion is of rotating type, i. e. where the particle during a period passes only once through every point of its orbit, cannot be formed in a

continuous manner from a linear harmonic vibrator without passing through singular states in which the period becomes infinite long and the result becomes ambiguous. We shall not here enter more closely on this difficulty which has been pointed out by EHRENFEST, because it disappears when we consider systems of several degrees of freedom, where we shall see that a simple generalisation of (10) holds for any system for which every motion is periodic.

As regards the application of (9) to statistical problems it was assumed in PLANCK's theory that the different states of the vibrator corresponding to different values of n are *a-priori equally probable*, and this assumption was strongly supported by the agreement obtained on this basis with the measurements of the specific heat of solids at low temperatures. Now it follows from the considerations of EHRENFEST, mentioned in the former section, that the a-priori probability of a given stationary state is not changed by a continuous transformation, and we shall therefore expect that for any system of one degree of freedom the different states corresponding to different entire values of n in (10) are a-priori equally probable.

As pointed out by PLANCK in connection with the application of (9), it is simply seen that statistical considerations, based on the assumption of equal probability for the different states given by (10), will show the necessary relation to considerations of ordinary statistical mechanics in the limit where the latter theory has been found to give results in agreement with experiments. Let the configuration

and motion of a mechanical system be characterised by s independent variables $q_1, \ldots, q_s$ and corresponding momenta $p_1, \ldots, p_s$ and let the state of the system be represented in a $2s$-dimensional phase-space by a point with coordinates $q_1, \ldots, q_s, p_1, \ldots, p_s$. Then, according to ordinary statistical mechanics, the probability for this point to lie within a small element in the phase-space is independent of the position and shape of this element and simply proportional to its volume, defined in the usual way by

$$\delta W = \int dq_1 \ldots dq_s \, dp_1 \ldots dp_s. \tag{11}$$

In the quantum theory, however, these considerations cannot be directly applied, since the point representing the state of a system cannot be displaced continuously in the $2s$-dimensional phase-space, but can lie only on certain surfaces of lower dimensions in this space. For systems of one degree of freedom the phase-space is a two-dimensional surface, and the points representing the states of some system given by (10) will be situated on closed curves on this surface. Now, in general, the motion will differ considerably for any two states corresponding to successive entire values of n in (10), and a simple general connection between the quantum theory and ordinary statistical mechanics is therefore out of question. In the limit, however, where n is large, the motions in successive states will only differ very little from each other, and it would therefore make little difference whether the points representing the systems are distributed

continuously on the phase-surface or situated only on the curves corresponding to (10), provided the number of systems which in the first case are situated between two such curves is equal to the number which in the second case lies on one of these curves. But it will be seen that this condition is just fulfilled in consequence of the above hypothesis of equal a-priori probability of the different stationary states, because the element of phase-surface limited by two successive curves corresponding to (10) is equal to

$$\delta W = \int dp\, dq = \left[\int p\, dq\right]_n - \left[\int p\, dq\right]_{n-1} \qquad (12)$$
$$= I_n - I_{n-1} = h,$$

so that on ordinary statistical mechanics the probabilities for the point to lie within any two such elements is the same. We see consequently that the hypothesis of equal probability of the different states given by (10) gives the same result as ordinary statistical mechanics in all such applications in which the states of the great majority of the systems correspond to large values of n. Considerations of this kind have led DEBYE[1]) to point out that condition (10) might have a general validity for systems of one degree of freedom, already before EHRENFEST, on the basis of his theory of the mechanical transformability of the stationary states, had shown that this condition forms the only rational generalisation of PLANCK's condition (9).

[1]) P. DEBYE, Wolfskehl-Vortrag. Göttingen 1913.

We shall now discuss the relation between the theory of *spectra of atomic systems of one degree of freedom*, based on (1) and (10), and the ordinary theory of radiation, and we shall see that this relation in several respects shows a close analogy to the relation, just considered, between the statistical applications of (10) and considerations based on ordinary statistical mechanics. Since the values for the frequency ω in two states corresponding to different values of n in (10) in general are different, we see at once that we cannot expect a simple connection between the frequency calculated by (1) of the radiation corresponding to a transition between two stationary states and the motions of the system in these states, except in the limit where n is very large, and where the ratio between the frequencies of the motion in successive stationary states differs very little from unity. Consider now a transition between the state corresponding to $n = n'$ and the state corresponding to $n = n''$, and let us assume that n' and n'' are large numbers and that $n' - n''$ is small compared with n' and n''. In that case we may in (8) for δE put $E' - E''$ and for δI put $I' - I''$, and we get therefore from (1) and (10) for the frequency of the radiation emitted or absorbed during the transition between the two states

$$\nu = \frac{1}{h}(E' - E'') = \frac{\omega}{h}(I' - I'') = (n' - n'')\omega. \qquad (13)$$

Now in a stationary state of a periodic system the displacement of the particles in any given direction may always be expressed by means of a FOURIER-series as a sum of har-

monic vibrations:

$$\xi = \sum C_\tau \cos 2\pi(\tau\omega t + c_\tau), \tag{14}$$

where the C's and c's are constants and the summation is to be extended over all positive entire values of τ. On the ordinary theory of radiation we should therefore expect the system to emit a spectrum consisting of a series of lines of frequencies equal to $\tau\omega$, but, as it is seen, this is just equal to the series of frequencies which we obtain from (13) by introducing different values for $n' - n''$. As far as the frequencies are concerned we see therefore that in the limit where n is large there exists a close relation between the ordinary theory of radiation and the theory of spectra based on (1) and (10). It may be noticed, however, that, while on the first theory radiations of the different frequencies $\tau\omega$ corresponding to different values of τ are emitted or absorbed at the same time, these frequencies will on the present theory, based on the fundamental assumption I and II, be connected with entirely different processes of emission or absorption, corresponding to the transition of the system from a given state to different neighbouring stationary states.

In order to obtain the necessary connection, mentioned in the former section, to the ordinary theory of radiation in the limit of slow vibrations, we must further claim that a relation, as that just proved for the frequencies, will, in the limit of large n, hold also for the intensities of the different lines in the spectrum. Since now on ordinary electrodynamics the intensities of the radiations corresponding to different

values of τ are directly determined from the coefficients $C_{|tau}$ in (14), we must therefore expect that for large values of n these coefficients will on the quantum theory determine the *probability of spontaneous transition* from a given stationary state for which $n = n'$ to a neighbouring state for which $n = n'' = n' - \tau$. Now this connection between the amplitudes of the different harmonic vibrations into which the motion can be resolved, characterised by different values of τ, and the probabilities of transition from a given stationary state to the different neighbouring stationary states, characterised by different values of $n' - n''$, may clearly be expected to be of a general nature. Although, of course, we cannot without a detailed theory of the mechanism of transition obtain an exact calculation of the latter probabilities, unless n is large, we may expect that also for small values of n the amplitude of the harmonic vibrations corresponding to a given value of τ will in some way give a measure for the probability of a transition between two states for which $n' - n''$ is equal to τ. Thus in general there will be a certain probability of an atomic system in a stationary state to pass spontaneously to any other state of smaller energy, but if for all motions of a given system the coefficients C in (14) are zero for certain values of τ, we are led to expect that no transition will be possible, for which $n' - n''$ is equal to one of these values.

A simple illustration of these considerations is offered by the linear harmonic vibrator mentioned above in connection with PLANCK's theory. Since in this case C_τ is equal to zero

for any τ different from 1, we shall expect that for this system only such transitions are possible in which n alters by one unit. From (1) and (9) we obtain therefore the simple result that the frequency of any radiation emitted or absorbed by a linear harmonic vibrator is equal to the constant frequency ω_0. This result seems to be supported by observations on the absorption-spectra of diatomic gases, showing that certain strong absorption-lines, which according to general evidence may be ascribed to vibrations of the two atoms in the molecule relative to each other, are not accompanied by lines of the same order of intensity and corresponding to entire multipla of the frequency, such as it should be expected from (1) if the system had any considerable tendency to pass between non-successive states. In this connection it may be noted that the fact, that in the absorption spectra of some diatomic gases faint lines occur corresponding to the double frequency of the main lines,[1]) obtains a natural explanation by assuming that for finite amplitudes the vibrations are not exactly harmonic and that therefore the molecules possess a small probability of passing also between non-successive states.

§ 3. Conditionally periodic systems.

If we consider systems of several degrees of freedom the motion will be periodic only in singular cases and the general conditions which determine the stationary states cannot

[1]) See E. C. Kemble, Phys. Rev., VIII, p. 701, 1916.

therefore be derived by means of the same simple kind of considerations as in the former section. As mentioned in the introduction, however, SOMMERFELD and others have recently succeeded, by means of a suitable generalisation of (10), to obtain conditions for an important class of systems of several degrees of freedom, which, in connection with (1), have been found to give results in convincing agreement with experimental results about line-spectra. Subsequently these conditions have been proved by EHRENFEST and especially by BURGERS[1]) to be invariant for slow mechanical transformations.

To the generalisation under consideration we are naturally led, if we first consider such systems for which the motions corresponding to the different degrees of freedom are dynamically independent of each other. This occurs if the expression for the total energy E in HAMILTON's equations (4) for a system of s degrees of freedom can be written as a sum $E_1 + \cdots + E_s$, where E_k contains q_k and p_k only. An illustration of a system of this kind is presented by a particle moving in a field of force in which the force-components normal to three mutually perpendicular fixed planes are functions of the distances from these planes respectively. Since in such a case the motion corresponding to each degree of freedom in general will be periodic, just as for a system of one degree of

[1]) J. M. BURGERS, Versl. Akad. Amsterdam, XXV, pp. 849, 918, 1055. (1917), Ann. d. Phys. LII. p. 195 (1917), Phil. Mag. XXXIII, p. 514 (1917).

freedom, we may obviously expect that the condition (10) is here replaced by a set of s conditions:

$$I_k = \int p_k \, dq_k = n_k h, \qquad (k = 1, \ldots, \ s) \tag{15}$$

where the integrals are taken over a complete period of the different q's respectively, and where $n_1, \ \ldots, \ n_s$ are entire numbers. It will be seen at once that these conditions are invariant for any slow transformation of the system for which the independency of the motions corresponding to the different coordinates is maintained.

A more general class of systems for which a similar analogy with systems of a single degree of freedom exists and where conditions of the same type as (15) present themselves is obtained in the case where, although the motions corresponding to the different degrees of freedom are not independent of each other, it is possible nevertheless by a suitable choice of coordinates to express each of the momenta p_k as a function of q_k only. A simple system of this kind consists of a particle moving in a plane orbit in a central field of force. Taking the length of the radius-vector from the centre of the field to the particle as q_1, and the angular distance of this radius-vector from a fixed line in the plane of the orbit as q_2, we get at once from (4), since E does not contain q_2, the well known result that during the motion the angular momentum p_2 is constant and that the radial motion, given by the variations of p_1 and q_1 with the time, will be exactly the same as for a system of one degree of freedom. In his funda-

mental application of the quantum theory to the spectrum of a *non-periodic system* SOMMERFELD assumed therefore that the stationary states of the above system are given by two conditions of the form:

$$I_1 = \int p_1\, dq_1 = n_1 h, \quad I_2 = \int p_2\, dq_2 = n_2 h. \tag{16}$$

While the first integral obviously must be taken over a period of the radial motion, there might at first sight seem to be a difficulty in fixing the limits of integration of q_2. This disappears, however, if we notice that an integral of the type under consideration will not be altered by a change of coordinates in which q is replaced by some function of this variable. In fact, if instead of the angular distance of the radius-vector we take for q_2 some continuous periodic function of this angle with period 2π, every point in the plane of the orbit will correspond to one set of coordinates only and the relation between p and q will be exactly of the same type as for a periodic system of one degree of freedom for which the motion is of oscillating type. It follows therefore that the integration in the second of the conditions (16) has to be taken over a complete revolution of the radius-vector, and that consequently this condition is equivalent with the simple condition that the angular momentum of the particle round the centre of the field is equal to an entire multiple of $\frac{h}{2\pi}$. As pointed out by EHRENFEST, the conditions (16) are invariant for such special transformations of the system for which the central symmetry is maintained. This follows

immediately from the fact that the angular momentum in transformations of this type remains invariant, and that the equations of motion for the radial coordinate as long as p_2 remains constant are the same as for a system of one degree of freedom. On the basis of (16), SOMMERFELD has, as mentioned in the introduction, obtained a brilliant explanation of the fine structure of the lines in the hydrogen spectrum, due to the change of the mass of the electron with its velocity.[1]) To this theory we shall come back in Part II.

As pointed out by EPSTEIN[2]) and SCHWARZSCHILD[3]) the

[1]) In this connection it may be remarked that conditions of the same type as (16) were proposed independently by W. WILSON (Phil. Mag. XXIX p. 795 (1915) and XXXI p. 156 (1916)), but by him applied only to the simple Keplerian motion described by the electron in the hydrogen atom if the relativity modifications are neglected. Due to the singular position of periodic systems in the quantum theory of systems of several degrees of freedom this application, however, involves, as it will appear from the following discussion, an ambiguity which deprives the result of an immediate physical interpretation. Conditions analogous to (16) have also been established by PLANCK in his interesting theory of the "physical structure of the phase space" of systems of several degrees of freedom (Verh. d. D. Phys. Ges. XVII p. 407 and p. 438 (1915), Ann. d. Phys. L p. 385, (1916)). This theory, which has no direct relation to the problem of line-spectra discussed in the present paper, rests upon a profound analysis of the geometrical problem of dividing the multiple-dimensional phase space corresponding to a system of several degrees of freedom into "cells" in a way analogous to the division of the phase surface of a system of one degree of freedom by the curves given by (10).

[2]) P. EPSTEIN, loc. cit.

[3]) K. SCHWARZSCHILD, loc. cit.

central systems considered by SOMMERFELD form a special case of a more general class of systems for which conditions of the same type as (15) may be applied. These are the so called *conditionally periodic systems*, to which we are led if the equations of motion are discussed by means of the HAMILTON-JACOBI partial differential equation.[1]) In the expression for the total energy E as a function of the q's and the p's, let the latter quantities be replaced by the partial differential coefficients of some function S with respect to the corresponding q's respectively, and consider the partial differential equation:

$$E\left(q_1, \ldots, \; q_s, \frac{\partial S}{\partial q_1}, \ldots, \; \frac{\partial S}{\partial q_s}\right) = \alpha_1, \tag{17}$$

obtained by putting this expression equal to an arbitrary constant α_1. If then

$$S = F(q_1, \ldots, \; q_s, \alpha_1, \ldots, \; \alpha_s) + C,$$

where $\alpha_2, \ldots, \alpha_s$, and C are arbitrary constants like α_1, is a total integral of (17), we get, as shown by HAMILTON and JACOBI, the general solution of the equations of motion (4) by putting

$$\frac{\partial S}{\partial \alpha_1} = t + \beta_1, \quad \frac{\partial S}{\partial \alpha_k} = \beta_k, \qquad (k = 2, \ldots, \; s) \tag{18}$$

[1]) See f. inst. C. V. L. CHARLIER, Die Mechanik des Himmels, Bd. I, Abt. 2.

and

$$\frac{\partial S}{\partial q_k} = p_k, \qquad (k = 1, \ldots, s) \tag{19}$$

where t is the time and $\beta_1, \ldots, \beta_s$ a new set of arbitrary constants. By means of (18) the q's are given as functions of the time t and the $2s$ constants $\alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_s$ which may be determined for instance from the values of the q's and $\ddot{q}$'s at a given moment.

Now the class of systems, referred to, is that for which, for a suitable choice of orthogonal coordinates, it is possible to find a total integral of (17) of the form

$$S = \sum_1^s S_k(q_k, \alpha_1, \ldots, \alpha_s), \tag{20}$$

where S_k is a function of the s constants $\alpha_1, \ldots, \alpha_s$ and of q_k only. In this case, in which the equation (17) allows of what is called "separation of variables", we get from (19) that every p is a function of the α's and of the corresponding q only. If during the motion the coordinates do not become infinite in the course of time or converge to fixed limits, every q will, just as for systems of one degree of freedom, oscillate between two fixed values, different for the different q's and depending on the α's. Like in the case of a system of one degree of freedom, p_k will become zero and change its sign whenever q_k passes through one of these limits. Apart from special cases, the system will during the motion never pass twice through a configuration corresponding to the same set

of values for the q's and p's, but it will in the course of time pass within any given, however small, distance from any configuration corresponding to a given set of values $q_1, \ldots, q_s$, representing a point within a certain closed s-dimensional extension limited by s pairs of $(s-1)$-dimensional surfaces corresponding to constant values of the q's equal to the above mentioned limits of oscillation. A motion of this kind is called "conditionally periodic". It will be seen that the character of the motion will depend only on the α's and not on the β's, which latter constants serve only to fix the exact configuration of the system at a given moment, when the α's are known. For special systems it may occur that the orbit will not cover the above mentioned s-dimensional extension everywhere dense, but will, for all values of the α's, be confined to an extension of less dimensions. Such a case we will refer to in the following as a case of "degeneration".

Since for a conditionally periodic system which allows of separation in the variables $q_1, \ldots, q_s$ the p's are functions of the corresponding q's only, we may, just as in the case of independent degrees of freedom or in the case of quasi-periodic motion in a central field, form a set of expressions of the type

$$I_k = \int p_k(q_k, \alpha_1, \ldots, \alpha_s)\, dq_k, \qquad (k = 1, \ldots, s) \qquad (21)$$

where the integration is taken over a complete oscillation of q_k. As, in general, the orbit will cover everywhere dense an s-dimensional extension limited in the characteristic way

mentioned above, it follows that, except in cases of degeneration, a separation of variables will not be possible for two different sets of coordinates $q_1, \ldots, q_s$ and $q'_1, \ldots, q'_s$, unless $q_1 = f_1(q'_1), \ldots, q_s = f_s(q'_s)$, and since a change of coordinates of this type will not affect the values of the expressions (21), it will be seen that the values of the I's are completely determined for a given motion of the system. By putting

$$I_k = n_k h, \qquad (k = l, \ldots, s) \tag{22}$$

where $n_1, \ldots, n_s$ are positive entire numbers, we obtain therefore a *set of conditions which form a natural generalisation of condition* (10) holding for a system of one degree of freedom.

Since the I's, as given by (21), depend on the constants $\alpha_1, \ldots, \alpha_s$ only and not on the β's, the α's may, in general, inversely be determined from the values of the I's. The character of the motion will therefore, in general, be completely determined by the conditions (22), and especially the value for the total energy, which according to (17) is equal to α_1, will be fixed by them. In the cases of degeneration referred to above, however, the conditions (22) involve an ambiguity, since in general for such systems there will exist an infinite number of different sets of coordinates which allow of a separation of variables, and which will lead to different motions in the stationary states, when these conditions are applied. As we shall see below, this ambiguity will not influence the fixation of the total energy in the stationary states, which

is the essential factor in the theory of spectra based on (1) and in the applications of the quantum theory to statistical problems.

A well known characteristic example of a conditionally periodic system is afforded by a particle moving under the influence of the attractions from two fixed centres varying as the inverse squares of the distances apart, if the relativity modifications are neglected. As shown by JACOBI this problem can be solved by a separation of variables if so called elliptical coordinates are used, i. e. if for q_l and q_2 we take two parameters characterising respectively an ellipsoid and a hyperboloid of revolution with the centres as foci and passing through the instantaneous position of the moving particle, and for q_3 we take the angle between the plane through the particle and the centres and a fixed plane through the latter points, or, in closer conformity with the above general description, some continuous periodic function of this angle with period 2π. A limiting case of this problem is afforded by an electron rotating round a positive nucleus and subject to the effect of an additional homogeneous electric field, because this field may be considered as arising from a second nucleus at infinite distance apart from the first. The motion in this case will therefore be conditionally periodic and allow a separation of variables in parabolic coordinates, if the nucleus is taken as focus for both sets of paraboloids of revolution, and their axes are taken parallel to the direction of the electric force. By applying the conditions (22) to this motion EPSTEIN and SCHWARZSCHILD have, as mentioned

in the introduction, independent of each other, obtained an explanation of the effect of an external electric field on the lines of the hydrogen spectrum, which was found to be in convincing agreement with STARK's measurements. To the results of these calculations we shall return in Part II.

In the above way of representing the general theory we have followed the same procedure as used by EPSTEIN. By introducing the so called "angle-variables" well known from the astronomical theory of perturbations, SCHWARZSCHILD has given the theory a very elegant form in which the analogy with systems of one degree of freedom presents itself in a somewhat different manner. The connection between this treatment and that given above has been discussed in detail by EPSTEIN.[1])

As mentioned above the conditions (22), first established from analogy with systems of one degree of freedom, have subsequently been proved generally to be *mechanically invariant for any slow transformation for which the system remains conditionally periodic.* The proof of this invariance has been given quite recently by BURGERS[2]) by means of an interesting application of the theory of contact-transformations based on SCHWARZSCHILD's introduction of angle variables. We shall not enter here on these calculations but shall only consider some points in connection with the

[1]) P. EPSTEIN, Ann. d. Phys. LI, p. 168 (1916). See also Note on page 53 of the present paper.

[2]) J. M. BURGERS, loc. cit. Versl. Akad. Amsterdam, XXV, p. 1055 (1917).

problem of the mechanical transformability of the stationary states which are of importance for the logical consistency of the general theory and for the later applications. In § 2 we saw that in the proof of the mechanical invariance of relation (10) for a periodic system of one degree of freedom, it was essential that the comparative variation of the external conditions during the time of one period could be made small. This may be regarded as an immediate consequence of the nature of the fixation of the stationary states in the quantum theory. In fact the answer to the question, whether a given state of a system is stationary, will not depend only on the motion of the particles at a given moment or on the field of force in the immediate neighbourhood of their instantaneous positions, but cannot be given before the particles have passed through a complete cycle of states, and so to speak have got to know the entire field of force of influence on the motion. If thus, in the case of a periodic system of one degree of freedom, the field of force is varied by a given amount, and if its comparative variation within the time of a single period was not small, the particle would obviously have no means to get to know the nature of the variation of the field and to adjust its stationary motion to it, before the new field was already established. For exactly the same reasons it is a necessary condition for the mechanical invariance of the stationary states of a conditionally periodic system, that the alteration of the external conditions during an interval in which the system has passed approximately through all possible configurations within the above men-

tioned s-dimensional extension in the coordinate-space can be made as small as we like. This condition forms therefore also an essential point in BURGERS' proof of the invariance of the conditions (22) for mechanical transformations. Due to this we meet with a characteristic difficulty when during the transformation of the system we pass one of the cases of degeneration mentioned above, where, for every set of values for the α's, the orbit will not cover the s-dimensional extension everywhere dense, but will be confined to an extension of less dimensions. It is clear that, when by a slow transformation of a conditionally periodic system we approach a degenerate system of this kind, the time-interval which the orbit takes to pass close to any possible configuration will tend to be very long and will become infinite when the degenerate system is reached. As a consequence of this *the conditions (22) will generally not remain mechanically invariant when we pass a degenerate system*, what has intimate connection with the above mentioned ambiguity in the determination of the stationary states of such systems by means of (22).

A typical case of a degenerate system, which may serve as an illustration of this point, is formed by a system of several degrees of freedom for which every motion is *simply periodic*, independent of the initial conditions. In this case, which is of great importance in the physical applications, we have from (5) and (21), for any set of coordinates in which a separation

of variables is possible,

$$I = \int_0^\sigma (p_1\dot{q}_1 + \cdots + p_s\dot{q}_s)\, dt = \kappa_1 I_1 + \cdots + \kappa_s I_s, \qquad (23)$$

where the integration is extended over one period of the motion, and where $\kappa_1, \ldots, \kappa_s$ are a set of positive entire numbers without a common divisor. Now we shall expect that every motion, for which it is possible to find a set of coordinates in which it satisfies (22), will be stationary. For any such motion we get from (23)

$$I = (\kappa_1 n_1 + \cdots + \kappa_s n_s)h = nh, \qquad (24)$$

where n is a whole number which may take all positive values if, as in the applications mentioned below, at least one of the κ's is equal to one. Inversely, if the system under consideration allows of separation of variables in an infinite continuous multitude of sets of coordinates, we must conclude that generally every motion which satisfies (24) will be stationary, because in general it will be possible for any such motion to find a set of coordinates in which it satisfies also (22). It will thus be seen that, for a periodic system of several degrees of freedom, condition (24) forms a simple generalisation of condition (10). From relation (8), which holds for two neighbouring motions of any periodic system, it follows further that the energy of the system will be completely determined by the value of I, just as for systems of one degree of freedom.

Consider now a periodic system in some stationary state satisfying (24), and let us assume that an external field is slowly established at a continuous rate and that the motion at any moment during this process allows of a separation of variables in a certain set of coordinates. If we would assume that the effect of the field on the motion of the system at any moment could be calculated directly by means of ordinary mechanics, we would find that the values of the I's with respect to the latter coordinates would remain constant during the process, but this would involve that the values of the n's in (22) would in general not be entire numbers, but would depend entirely on the accidental motion, satisfying (24), originally possessed by the system. That mechanics, however, cannot generally be applied directly to determine the motion of a periodic system under influence of an increasing external field, is just what we should expect according to the singular position of degenerate systems as regards mechanical transformations. In fact, in the presence of a small external field, the motion of a periodic system will undergo slow variations as regards the shape and position of the orbit, and if the perturbed motion is conditionally periodic these variations will be of a periodic nature. Formally, we may therefore compare a periodic system exposed to an external field with a simple mechanical system of one degree of freedom in which the particle performs a slow oscillating motion. Now the frequency of a slow variation of the orbit will be seen to be proportional to the intensity of the external field, and it is therefore obviously impossible to establish the external

field at a rate so slow that the comparative change of its intensity during a period of this variation is small. The process which takes place during the increase of the field will thus be analogous to that which takes place if an oscillating particle is subject to the effect of external forces which change considerably during a period. Just as the latter process generally will give rise to emission or absorption of radiation and cannot be described by means of ordinary mechanics, we must expect that the motion of a periodic system of several degrees of freedom under the establishment of the external field cannot be determined by ordinary mechanics, but that the field will give rise to effects of the same kind as those which occur during a transition between two stationary states accompanied by emission or absorption of radiation. Consequently we shall expect that, during the establishment of the field, *the system will in general adjust itself in some unmechanical way* until a stationary state is reached in which the frequency (or frequencies) of the above mentioned slow variation of the orbit has a relation to the additional energy of the system due to the presence of the external field, which is of the same kind as the relation, expressed by (8) and (10), between the energy and frequency of a periodic system of one degree of freedom. As it will be shown in Part II in connection with the physical applications, this condition is just secured if the stationary states in the presence of the field are determined by the conditions (22), and it will be seen that these considerations offer a means of fixing the stationary states of a perturbed periodic system also in cases where no separation

of variables can be obtained.

In consequence of the singular position of the degenerate systems in the general theory of stationary states of conditionally periodic systems, we obtain a means of *connecting mechanically two different stationary states of a given system* through a continuous series of stationary states without passing through systems in which the forces are very small and the energies in all the stationary states tend to coincide (comp. page 14). In fact, if we consider a given conditionally periodic system which can be transformed in a continuous way into a system for which every orbit is periodic and for which every state satisfying (24) will also satisfy (22) for a suitable choice of coordinates, it is clear in the first place that it is possible to pass in a mechanical way through a continuous series of stationary states from a state corresponding to a given set of values of the n's in (22) to any other such state for which $\kappa_1 n_1 + \cdots + \kappa_s n_s$ possesses the same value. If, moreover, there exists a second periodic system of the same character to which the first periodic system can be transformed continuously, but for which the set of κ's is different, it will be possible in general by a suitable cyclic transformation to pass in a mechanical way between any two stationary states of the given conditionally periodic system satisfying (22).

To obtain an example of such a cyclic transformation let us take the system consisting of an electron which moves round a fixed positive nucleus exerting an attraction varying as the inverse square of the distance. If we neglect the small relativity corrections, every orbit will be periodic independent of the ini-

tial conditions and the system will allow of separation of variables in polar coordinates as well as in any set of elliptical coordinates, of the kind mentioned on page 36, if the nucleus is taken as one of the foci. It is simply seen that any orbit which satisfies (24) for a value of $n > 1$, will also satisfy (22) for a suitable choice of elliptical coordinates. By imagining another nucleus of infinite small charge placed at the other focus, the orbit may further be transformed into another which satisfies (24) for the same value of n, but which may have any given value for the eccentricity. Consider now a state of the system satisfying (21), and let us assume that by the above means the orbit is originally so adjusted that in plane polar coordinates it will correspond to $n_1 = m$ and $n_2 = n - m$ in (16). Let then the system undergo a slow continuous transformation during which the field of force acting on the electron remains central, but by which the law of attraction is slowly varied until the force is directly proportional to the distance apart. In the final state, as well as in the original state, the orbit of the electron will be closed, but during the transformation the orbit will not be closed, and the ratio between the mean period of revolution and the period of the radial motion, which in the original motion was equal to one, will during the transformation increase continuously until in the final state it is equal to two. This means that, using polar coordinates, the values of κ_1 and κ_2 in (22) which for the first state are equal to $\kappa_1 = \kappa_2 = 1$, will be for the second state $\kappa_1 = 2$ and $\kappa_2 = 1$. Since during the transformation n_1 and n_2 will keep their values, we get therefore in the final state $I = h\big(2m + (n - m)\big) = h(n + m)$. Now in the latter state, the system allows a separation of variables not only in polar coordinates but also in any system of rectangular

Cartesian coordinates, and by suitable choice of the direction of the axes, we can obtain that any orbit, satisfying (24) for a value of $n > l$, will also satisfy (22). By an infinite small change of the force components in the directions of the axes, in such a way that the motions in these directions remain independent of each other but possess slightly different periods, it will further be possible to transform the elliptical orbit mechanically into one corresponding to any given ratio between the axes. Let us now assume that in this way the orbit of the electron is transformed into a circular one, so that, returning to plane polar coordinates, we have $n_1 = 0$ and $n_2 = n + m$, and let then by a slow transformation the law of attraction be varied until again it is that of the inverse square. It will be seen that when this state is reached the motion will again satisfy (24), but this time we will have $I = h(n + m)$ instead of $I = nh$ as in the original state. By repeating a cyclic process of this kind we may pass from any stationary state of the system in question which satisfies (24) for a value of $n > 1$ to any other such state without leaving at any moment the region of stationary states.

The theory of the mechanical transformability of the stationary states gives us a means to discuss the question of the *a-priori probability* of the different states of a conditionally periodic system, characterised by different sets of values for the n's in (22). In fact from the considerations, mentioned in § 1, it follows that, if the a-priori probability of the stationary states of a given system is known, it is possible at once to deduce the probabilities for the stationary states of any other system to which the first system can be transformed continuously without passing through a system of degener-

ation. Now from the analogy with systems of one degree of freedom it seems necessary to assume that, for a system of several degrees of freedom for which the motions corresponding to the different coordinates are dynamically independent of each other, the a-priori probability is the same for all the states corresponding to different sets of n's in (15). According to the above we shall therefore assume that the a-priori probability is the same for all states, given by (22), of any system which can be formed in a continuous way from a system of this kind without passing through systems of degeneration. It will be observed that on this assumption we obtain exactly the same relation to the ordinary theory of statistical mechanics in the limit of large n's as obtained in the case of systems of one degree of freedom. Thus, for a conditionally periodic system, the volume given by (11) of the element of phase-space, including all points $q_1, \ldots, q_s$, $p_1, \ldots, p_s$ which represent states for which the value of I_k given by (21) lies between I_k and $I_k + \delta I_k$, is seen at once to be equal to[1])

$$\delta W = \delta I_1 \, \delta I_2 \ldots \delta I_s, \tag{25}$$

if the coordinates are so chosen that the motion corresponding to every degree of freedom is of oscillating type. The volume of the phase-space limited by s pairs of surfaces, corresponding to successive values for the n's in the conditions (22), will therefore be equal to h^s and consequently be the same for every combination of the n's. In the limit

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

where the n's are large numbers and the stationary states corresponding to successive values for the n's differ only very little from each other, we thus obtain the same result on the assumption of equal a-priori probability of all the stationary states, corresponding to different sets of values of $n_1, \ldots, n_s$ in (22), as would be obtained by application of ordinary statistical mechanics.

The fact that the last considerations hold for every non-degenerate conditionally periodic system suggests the assumption that in general *the a-priori probability will be the same for all the states determined by* (22), even if it should not be possible to transform the given system into a system of independent degrees of freedom without passing through degenerate systems. This assumption will be shown to be supported by the consideration of the intensities of the different components of the STARK-effect of the hydrogen lines, mentioned in the next Part. When we consider a degenerate system, however, we cannot assume that the different stationary states are a-priori equally probable. In such a case the stationary states will be characterised by a number of conditions less than the number of degrees of freedom, and the probability of a given state must be determined from the number of different stationary states of some non-degenerate system which will coincide in the given state, if the latter system is continuously transformed into the degenerate system under consideration.

In order to illustrate this, let us take the simple case of a degenerate system formed by an electrified particle mov-

ing in a plane orbit in a central field, the stationary states of which are given by the two conditions (16). In this case the plane of the orbit is undetermined, and it follows already from a comparison with ordinary statistical mechanics, that the a-priori probability of the states characterised by different combinations of n_1 and n_2 in (16) cannot be the same. Thus the volume of the phase-space, corresponding to states for which I_1 lies between I_1 and $I_1 + \delta I_1$ and for which I_2 lies between I_2 and $I_2 + \delta I_2$, is found by a simple calculation[1]) to be equal to $\delta W = 2I_1\,\delta I_1\,\delta I_2$, if the motion is described by ordinary polar coordinates. For large values of n_1 and n_2, we must therefore expect that the a-priori probability of a stationary state corresponding to a given combination (n_1, n_2) is proportional to n_2. The question of the a-priori probability of states corresponding to small values of the n's has been discussed by SOMMERFELD in connection with the problem of the intensities of the different components in the fine structure of the hydrogen lines (see Part II). From considerations about the volume of the extensions in the phase-space, which might be considered as associated with the states characterised by different combinations (n_1, n_2), SOMMERFELD proposes several different expressions for the a-priori probability of such states. Due to the necessary arbitrariness involved in the choice of these extensions, however, we cannot in this way obtain a rational determination of the a-priori probability of states corre-

[1]) See A. SOMMERFELD, loc. cit.

sponding to small values of n_1 and n_2. On the other hand, this probability may be deduced by regarding the motion of the system under consideration as the degeneration of a motion characterised by three numbers n_1, n_2 and n_3, as in the general applications of the conditions (22) to a system of three degrees of freedom. Such a motion may be obtained for instance by imagining the system placed in a small homogeneous magnetic field. In certain respects this case falls outside the general theory of conditionally periodic systems discussed in this section, but, as we shall see in Part II, it can be simply shown that the presence of the magnetic field imposes the further condition on the motion in the stationary states that the angular momentum round the axis of the field is equal to $n' \frac{h}{2\pi}$, where n' is a positive entire number equal to or less than n_2, and which for the system considered in the spectral problems must be assumed to be different from zero. When regard is taken to the two opposite directions in which the particle may rotate round the axis of the field, we see therefore that for this system a state corresponding to a given combination of n_1 and n_2 in the presence of the field can be established in $2n_2$ different ways. The a-priori probability of the different states of the system may consequently for all combinations of n_1 and n_2 be assumed to be proportional to n_2.

The assumption just mentioned that the angular momentum round the axis of the field cannot be equal to zero is deduced from considerations of systems for which the mo-

tion corresponding to special combinations of the n's in (22) would become physically impossible due to some singularity in its character. In such cases we must assume that no stationary states exist corresponding to the combinations $(n_1, n_2, \ldots, n_s)$ under consideration, and on the above principle of the invariance of the a-priori probability for continuous transformations we shall accordingly expect that the a-priori probability of any other state, which can be transformed continuously into one of these states without passing through cases of degeneration, will also be equal to zero.

Let us now proceed to consider *the spectrum of a conditionally periodic system*, calculated from the values of the energy in the stationary states by means of relation (1). If $E(n_1, \ldots, n_s)$ is the total energy of a stationary state determined by (22) and if ν is the frequency of the line corresponding to the transition between two stationary states characterised by $n_k = n'_k$ and $n_k = n''_k$ respectively, we have

$$\nu = \frac{1}{h}\big[E(n'_1, \ldots, n'_s) - E(n''_1, \ldots, n''_s)\big]. \tag{26}$$

In general, this spectrum will be entirely different from the spectrum to be expected on the ordinary theory of electrodynamics from the motion of the system. Just as for a system of one degree of freedom we shall see, however, that in the limit where the motions in neighbouring stationary states differ very little from each other, there exists a close relation between the spectrum calculated on the quantum theory and that to be expected on ordinary electrodynamics. As in § 2

we shall further see, that this connection leads to certain general considerations about the probability of transition between any two stationary states and about the nature of the accompanying radiation, which are found to be supported by observations. In order to discuss this question we shall first deduce a general expression for the energy difference between two neighbouring states of a conditionally periodic system, which can be simply obtained by a calculation analogous to that used in § 2 in the deduction of the relation (8).

Consider some motion of a conditionally periodic system which allows of separation of variables in a certain set of coordinates $q_1, \ldots, q_s$, and let us assume that at the time $t = \vartheta$ the configuration of the system will to a close approximation be the same as at the time $t = 0$. By taking ϑ large enough we can make this approximation as close as we like. If next we consider some conditionally periodic motion, obtained by a small variation of the first motion, and which allows of separation of variables in a set of coordinates $q'_1, \ldots, q'_s$ which may differ slightly from the set $q_1, \ldots, q_s$, we get by means of HAMILTON's equations (4), using the coordinates $q'_1, \ldots, q'_s$,

$$\int_0^\vartheta \delta E \, dt = \int_0^\vartheta \sum_1^s \left(\frac{\partial E}{\partial p'_k} \delta p'_k + \frac{\partial E}{\partial q'_k} \delta q'_k \right) dt$$

$$= \int_0^\vartheta \sum_1^s (\dot{q}'_k \, \delta p'_k - \dot{p}'_k \, \delta q'_k) \, dt.$$

By partial integration of the second term in the bracket this

gives:

$$\int_0^{\vartheta} \delta E\, dt = \int_0^{\vartheta} \sum_1^s \delta(p'_k \dot{q}'_k)\, dt - \left| \sum_1^s p'_k\, \delta q'_k \right|_{t=0}^{t=\vartheta}. \qquad (27)$$

Now we have for the unvaried motion

$$\int_0^{\vartheta} \sum_1^s p'_k \dot{q}'_k\, dt = \int_0^{\vartheta} \sum_1^s p_k \dot{q}_k\, dt = \sum_1^s N_k I_k,$$

where I_k is defined by (21) and where N_k is the number of oscillations performed by q_k in the time interval ϑ. For the varied motion we have on the other hand:

$$\int_0^{\vartheta} \sum_1^s p'_k \dot{q}'_k\, dt = \int_{t=0}^{t=\vartheta} \sum_1^s p'_k dq'_k = \sum_1^s N_k I'_k + \left| \sum_1^s p'_k\, \delta q'_k \right|_{t=0}^{t=\vartheta},$$

where the I's correspond to the conditionally periodic motion in the coordinates $q'_1, \ldots, q'_s$, and the δq's which enter in the last term are the same as those in (27). Writing $I'_k - I_k = \delta I_k$, we get therefore from the latter equation

$$\int_0^{\vartheta} \delta E\, dt = \sum_1^s N_k\, \delta I_k. \qquad (28)$$

In the special case where the varied motion is an undisturbed motion belonging to the same system as the unvaried motion we get, since δE will be constant,

$$\delta E = \sum_1^s \omega_k\, \delta I_k, \qquad (29)$$

where $\omega_k = \dfrac{N_k}{\vartheta}$ is the mean frequency of oscillation of q_k between its limits, taken over a long time interval of the same order of magnitude as ϑ. This equation forms a simple generalisation of (8), and in the general case in which a separation of variables will be possible only for one system of coordinates leading to a complete definition of the I's it might have been deduced directly from the analytical theory of the periodicity properties of the motion of a conditionally periodic system, based on the introduction of angle-variables.[1]) From (29) it follows moreover that, if the system allows of a separation of variables in an infinite continuous multitude

[1]) See CHARLIER, Die Mechanik des Himmels, Bd. I Abt. 2, and especially P. EPSTEIN, Ann. d. Phys. LI p. 178 (1916). By means of the well known theorem of JACOBI about the change of variables in the canonical equations of HAMILTON, the connection between the notion of angle-variables and the quantities I, discussed by EPSTEIN in the latter paper, may be briefly exposed in the following elegant manner which has been kindly pointed out to me by Mr. H. A. KRAMERS. Consider the function $S(q_1, \ldots, q_s, I_1, \ldots, I_s)$ obtained from (20) by introducing for the α's their expressions in terms of the I's given by the equations (21). This function will be a many valued function of the q's which increases by I_k if q_k describes one oscillation between its limits and comes back to its original value while the other q's remain constant. If we therefore introduce a new set of variables $w_1, \ldots, w_s$ defined by

$$w_k = \frac{\partial S}{\partial I_k}, \qquad (k = 1, \ldots, s) \qquad (1^*)$$

it will be seen that w_k increases by one unit while the other w's will come back to their original values if q_k describes one oscillation between its limits and the other q's remain constant. Inversely it will therefore

be seen that the q's, and also the p's which were given by

$$p_k = \frac{\partial S}{\partial q_k}, \qquad (k = i, \ldots, s) \tag{2*}$$

when considered as functions of the I's and w's will be periodic functions of every of the w's with period 1. According to FOURIER's theorem any of the q's may therefore be represented by an s-double trigonometric series of the form

$$q = \sum A_{\tau_1, \ldots, \tau_s} \cos 2\pi(\tau_1 w_1 + \ldots + \tau_s w_s + \alpha_{\tau_1, \ldots, \tau_s}), \tag{3*}$$

where the A's and α's are constants depending on the I's and where the summation is to be extended over all entire values of $\tau_1, \ldots, \tau_s$. On account of this property of the w's, the quantities $2\pi w_1, \ldots, 2\pi w_s$ are denoted as "angle variables". Now from (1*) and (2*) it follows according to the above mentioned theorem of JACOBI (see for instance JACOBI, Vorlesungen über Dynamik § 37) that the variations with the time of the I's and w's will be given by

$$\frac{dI_k}{dt} = -\frac{\partial E}{\partial w_k}, \quad \frac{dw_k}{dt} = \frac{\partial E}{\partial I_k}, \qquad (k = 1, \ldots, s) \tag{4*}$$

where the energy E is considered as a function of the I's and w's. Since E, however, is determined by the I's only we get from (4*), besides the evident result that the I's are constant during the motion, that the w's will vary linearly with the time and can be represented by

$$w_k = \omega_k t + \delta_k, \quad \omega_k = \frac{\partial E}{\partial I_k}, \qquad (k = 1, \ldots, s) \tag{5*}$$

where δ_k is a constant, and where ω_k is easily seen to be equal to the mean frequency of oscillation of q_k. From (5*) equation (28) follows at once, and it will further be seen that by introducing (5*) in (3*) we get the result that every of the q's, and consequently also any one-valued function of the q's, can be represented by an expression of the type (31).

of sets of coordinates, the total energy will be the same for all motions corresponding to the same values of the I's, independent of the special set of coordinates used to calculate these quantities. As mentioned above and as we have al-

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In this connection it may be mentioned that the method of SCHWARZSCHILD of fixing the stationary states of a conditionally periodic system, mentioned on page 36, consists in seeking for a given system a set of canonically conjugated variables $Q_1, \ldots, Q_s, P_1, \ldots, P_s$ in such a way that the positional coordinates of the system $q_1, \ldots, q_s$, and their conjugated momenta $p_1, \ldots, p_s$, when considered as functions of the Q's and P's, are periodic in every of the Q's with period 2π, while the energy of the system depends only on the P's. In analogy with the condition which fixes the angular momentum in SOMMERFELD's theory of central systems SCHWARZSCHILD next puts every of the P's equal to an entire multiple of $\frac{h}{2\pi}$. In contrast to the theory of stationary states of conditionally periodic systems based on the possibility of separation of variables and the fixation of the I's by (22), this method does not lead to an absolute fixation of the stationary states, because, as pointed out by SCHWARZSCHILD himself, the above definition of the P's leaves an arbitrary constant undetermined in every of these quantities. In many cases, however, these constants may be simply determined from considerations of mechanical transformability of the stationary states, and as pointed out by BURGERS (loc. cit. Versl. Akad. Amsterdam XXV p. 1055 (1917)). SCHWARZSCHILD's method possesses on the other hand the essential advantage of being applicable to certain classes of systems in which the displacements of the particles may be represented by trigonometric series of the type (31), but for which the equations of motion cannot be solved by separation of variables in any fixed set of coordinates. An interesting application of this to the spectrum of rotating molecules, given by BURGERS, will be mentioned in Part IV.

ready shown in the case of purely periodic systems by means of (8), the total energy is therefore also in cases of degeneration completely determined by the conditions (22).

Consider now a transition between two stationary states determined by (22) by putting $n_k = n'_k$ and $n_k = n''_k$ respectively, and let us assume that $n'_1, \ldots, n'_s, n''_1, \ldots, n''_s$ are large numbers, and that the differences $n'_k - n''_k$ are small compared with these numbers. Since the motions of the system in these states will differ relatively very little from each other we may calculate the difference of the energy by means of (29), and we get therefore, by means of (1), for the frequency of the radiation corresponding to the transition between the two states

$$\nu = \frac{1}{h}(E' - E'') = \frac{1}{h}\sum_1^s \omega_k (I'_k - I''_k) = \sum_1^s \omega_k (n'_k - n''_k), \quad (30)$$

which is seen to be a direct generalisation of the expression (13) in § 2.

Now, in complete analogy to what is the case for periodic systems of one degree of freedom, it is proved in the analytical theory of the motion of conditionally periodic systems mentioned above that for the latter systems the coordinates $q_1, \ldots, q_s$, and consequently also the displacements of the particles in any given direction, may be expressed as a function of the time by an s-double infinite FOURIER series of the form:

$$\xi = \sum C_{\tau_1, \ldots, \tau_s} \cos 2\pi \{(\tau_1\omega_1 + \ldots + \tau_s\omega_s)t + c_{\tau_1, \ldots, \tau_s}\}, \quad (31)$$

where the summation is to be extended over all positive and negative entire values of the τ's, and where the ω's are the above mentioned mean frequencies of oscillation for the different q's. The constants $C_{\tau_1,\ldots,\ \tau_s}$ depend only on the α's in the equations (18) or, what is the same, on the I's, while the constants $c_{\tau_1,\ldots,\ \tau_s}$ depend on the α's as well as on the β's. In general the quantities $\tau_1\omega_1 + \ldots + \tau_s\omega_s$ will be different for any two different sets of values for the τ's, and in the course of time the orbit will cover everywhere dense a certain s-dimensional extension. In a case of degeneration, however, where the orbit will be confined to an extension of less dimensions, there will exist for all values of the α's one or more relations of the type $m_1\omega_1 + \ldots + m_s\omega_s = 0$ where the m's are entire numbers and by the introduction of which the expression (31) can be reduced to a FOURIER series which is less than s-double infinite. Thus in the special case of a system of which every orbit is periodic we have $\frac{\omega_1}{\kappa_1} = \cdots = \frac{\omega_s}{\kappa_s} = \omega$, where the κ's are the numbers which enter in equation (23), and the FOURIER series for the displacements in the different directions will in this case consist only of terms of the simple form $C_\tau \cos 2\pi\{\tau\omega t + c_\tau\}$, just as for a system of one degree of freedom.

On the ordinary theory of radiation, we should expect from (31) that the spectrum emitted by the system in a given state would consist of an s-double infinite series of lines of frequencies equal to $\tau_1\omega_1 + \cdots + \tau_s\omega_s$. In general, this spectrum would be completely different from that given

by (26). This follows already from the fact that the ω's will depend on the values for the constants $\alpha_1, \ldots, \alpha_s$ and will vary in a continuous way for the continuous multitude of mechanically possible states corresponding to different sets of values for these constants. Thus in general the ω's will be quite different for two different stationary states corresponding to different sets of n's in (22), and we cannot expect any close relation between the spectrum calculated on the quantum theory and that to be expected on the ordinary theory of mechanics and electrodynamics. In the limit, however, where the n's in (22) are large numbers, the ratio between the ω's for two stationary states, corresponding to $n_k = n'_k$ and $n_k = n''_k$ respectively, will tend to unity if the differences $n'_k - n''_k$ are small compared with the n's, and as seen from (30) the spectrum calculated by (1) and (22) will in this limit just tend to coincide with that to be expected on the ordinary theory of radiation from the motion of the system.

As far as the frequencies are concerned, we thus see that for conditionally periodic systems there exists a connection between the quantum theory and the ordinary theory of radiation of exactly the same character as that shown in § 2 to exist in the simple case of periodic systems of one degree of freedom. Now on ordinary electrodynamics the coefficients $C_{\tau_1,\ldots,\tau_s}$ in the expression (31) for the displacements of the particles in the different directions would in the well known way determine the intensity and polarisation of the emitted radiation of the corresponding frequency $\tau_1\omega_1 + \ldots + \tau_s\omega_s$. As for systems of one degree of freedom we must therefore

conclude that, in the limit of large values for the n's, the probability of spontaneous transition between two stationary states of a conditionally periodic system, as well as the polarisation of the accompanying radiation, can be determined directly from the values of the coefficient $C_{\tau_1,\ldots,\tau_s}$ in (31) corresponding to a set of τ's given by $\tau_k = n'_k - n''_k$, if $n'_1, \ldots, n'_s$ and $n''_1, \ldots, n''_s$ are the numbers which characterise the two stationary states.

Without a detailed theory of the mechanism of transition between the stationary states we cannot, of course, in general obtain an exact determination of the *probability of spontaneous transition* between two such states, unless the n's are large numbers. Just as in the case of systems of one degree of freedom, however, we are naturally led from the above considerations to assume that, also for values of the n's which are not large, there must exist an intimate connection between the probability of a given transition and the values of the corresponding FOURIER coefficient in the expressions for the displacements of the particles in the two stationary states. This allows us at once to draw certain important conclusions. Thus, from the fact that in general negative as well as positive values for the τ's appear in (31), it follows that we must expect that in general not only such transitions will be possible in which all the n's decrease, but that also transitions will be possible for which some of the n's increase while others decrease. This conclusion, which is supported by observations on the fine structure of the hydrogen lines as well as on the STARK effect, is contrary to the suggestion,

put forward by SOMMERFELD with reference to the essential positive character of the I's, that every of the n's must remain constant or decrease under a transition. Another direct consequence of the above considerations is obtained if we consider a system for which, for all values of the constants $\alpha_1, \ldots, \alpha_s$, the coefficient $C_{\tau_1,\ldots,\tau_s}$ corresponding to a certain set $\tau_1^0, \ldots, \tau_s^0$ of values for the τ's is equal to zero in the expressions for the displacements of the particles in every direction. In this case we shall naturally expect that no transition will be possible for which the relation $n'_k - n''_k = \tau_k^0$ is satisfied for every k. In the case where $C_{\tau_1^0,\ldots,\tau_s^0}$ is equal to zero in the expressions for the displacement in a certain direction only, we shall expect that all transitions, for which $n'_k - n''_k = \tau_k^0$ for every k, will be accompanied by a radiation which is polarised in a plane perpendicular to this direction.

A simple illustration of the last considerations is afforded by the system mentioned in the beginning of this section, and which consists of a particle executing motions in three perpendicular directions which are independent of each other. In that case all the FOURIER coefficients in the expressions for the displacements in any direction will disappear if more than one of the τ's are different from zero. Consequently we must assume that only such transitions are possible for which only one of the n's varies at the same time, and that the radiation corresponding to such a transition will be linearly polarised in the direction of the displacement of the corresponding coordinate. In the special case where the motions in the three directions are simply harmonic, we shall

moreover conclude that none of the n's can vary by more than a single unit, in analogy with the considerations in the former section about a linear harmonic vibrator.

Another example which has more direct physical importance, since it includes all the special applications of the quantum theory to spectral problems mentioned in the introduction, is formed by a conditionally periodic system possessing an axis of symmetry. In all these applications a separation of variables is obtained in a set of three coordinates q_1, q_2 and q_3, of which the first two serve to fix the position of the particle in a plane through the axis of the system, while the last is equal to the angular distance between this plane and a fixed plane through the same axis. Due to the symmetry, the expression for the total energy in HAMILTON's equations will not contain the angular distance q_3 but only the angular momentum p_3 round the axis. The latter quantity will consequently remain constant during the motion, and the variations of q_1 and q_2 will be exactly the same as in a conditionally periodic system of two degrees of freedom only. If the position of the particle is described in a set of cylindrical coordinates z, ρ, ϑ, where z is the displacement in the direction of the axis, ρ the distance of the particle from this axis and ϑ is equal to the angular distance q_3, we have therefore

$$\begin{aligned} z &= \sum C_{\tau_1,\tau_2} \cos 2\pi\big\{(\tau_1\omega_1 + \tau_2\omega_2)t + c_{\tau_1,\tau_2}\big\} \\ \text{and} \quad \rho &= \sum C'_{\tau_1,\tau_2} \cos 2\pi\big\{(\tau_1\omega_1 + \tau_2\omega_2)t + c'_{\tau_1,\tau_2}\big\}, \end{aligned} \tag{32}$$

where the summation is to be extended over all positive and negative entire values of τ_1 and τ_2, and where ω_1 and ω_2 are the mean frequencies of oscillation of the coordinates q_1 and q_2. For the rate of variation of ϑ with the time we have further

$$\frac{d\vartheta}{dt} = \dot{q}_3 = \frac{\partial E}{\partial p_3} = f(q_1, q_2, p_1, p_2, p_3)$$
$$= \pm \sum C''_{\tau_1,\tau_2} \cos 2\pi \big\{(\tau_1\omega_1 + \tau_2\omega_2)t + c''_{\tau_1,\tau_2}\big\},$$

where the two signs correspond to a rotation of the particle in the direction of increasing and decreasing q_3 respectively, and are introduced to separate the two types of symmetrical motions corresponding to these directions. This gives

$$\pm\vartheta = 2\pi\omega_3 t + \sum C'''_{\tau_1,\tau_2} \cos 2\pi \big\{(\tau_1\omega_1 + \tau_2\omega_2)t + c'''_{\tau_1,\tau_2}\big\}, \quad (33)$$

where the positive constant $\omega_3 = \frac{1}{2\pi} C''_{0,0}$ is the mean frequency of rotation round the axis of symmetry of the system. Considering now the displacement of the particle in rectangular coordinates x, y and z, and taking as above the axis of symmetry as z-axis, we get from (32) and (33) after a simple contraction of terms

$$\begin{aligned} x &= \rho\cos\vartheta \\ &= \sum D_{\tau_1,\tau_2} \cos 2\pi \big\{(\tau_1\omega_1 + \tau_2\omega_2 + \omega_3)t + d_{\tau_1,\tau_2}\big\} \\ \text{and } y &= \rho\sin\vartheta \\ &= \pm \sum D_{\tau_1,\tau_2} \sin 2\pi \big\{(\tau_1\omega_1 + \tau_2\omega_2 + \omega_3)t + d_{\tau_1,\tau_2}\big\}, \end{aligned} \quad (34)$$

where the D's and d's are new constants, and the summation is again to be extended over all positive and negative values of τ_1 and τ_2.

From (32) and (34) we see that the motion in the present case may be considered as composed of a number of linear harmonic vibrations parallel to the axis of symmetry and of frequencies equal to the absolute values of $(\tau_1\omega_1 + \tau_2\omega_2)$, together with a number of circular harmonic motions round this axis of frequencies equal to the absolute values of $(\tau_1\omega_1 + \tau_2\omega_2 + \omega_3)$, and possessing the same direction of rotation as that of the moving particle or the opposite if the latter expression is positive or negative respectively. According to ordinary electrodynamics the radiation from the system would therefore consist of a number of components of frequency $\tau_1\omega_1 + \tau_2\omega_2$ polarised parallel to the axis of symmetry, and a number of components of frequencies $\tau_1\omega_1 + \tau_2\omega_2 + \omega_3$ and of circular polarisation round this axis (when viewed in the direction of the axis). On the present theory we shall consequently expect that in this case only two kinds of transitions between the stationary states given by (22) will be possible. In both of these n_1 and n_2 may vary by an arbitrary number of units, but in the first kind of transition, which will give rise to a radiation polarised parallel to the axis of the system, n_3 will remain unchanged, while in the second kind of transition n_3 will decrease or increase by one unit and the emitted radiation will be circularly polarised round the axis in the same direction as or the opposite of that of the rotation of the particle respectively.

In the next Part we shall see that these conclusions are supported in an instructive manner by the experiments on the effects of electric and magnetic fields on the hydrogen spectrum. In connection with the discussion of the general theory, however, it may be of interest to show that the formal analogy between the ordinary theory of radiation and the theory based on (1) and (22), in case of systems possessing an axis of symmetry, can be traced not only with respect to frequency relations but also by considerations of *conservation of angular momentum*. For a conditionally periodic system possessing an axis of symmetry the angular momentum round this axis is, with the above choice of coordinates, according to (22) equal to $\frac{I_3}{2\pi} = n_3 \frac{h}{2\pi}$. If therefore, as assumed above for a transition corresponding to an emission of linearly polarised light, n_3 is unaltered, it means that the angular momentum of the system remains unchanged, while if n_3 alters by one unit, as assumed for a transition corresponding to an emission of circularly polarised light, the angular momentum will be altered by $\frac{h}{2\pi}$. Now it is easily seen that the ratio between this amount of angular momentum and the amount of energy $h\nu$ emitted during the transition is just equal to the ratio between the amount of angular momentum and energy possessed by the radiation which according to ordinary electrodynamics would be emitted by an electron rotating in a circular orbit in a central field of force. In fact, if a is the radius of the orbit, ν the frequency of revolu-

tion and F the force of reaction due to the electromagnetic field of the radiation, the amount of energy and of angular momentum round an axis through the centre of the field perpendicular to the plane of the orbit, lost by the electron in unit of time as a consequence of the radiation, would be equal to $2\pi\nu aF$ and aF respectively. Due to the principles of conservation of energy and of angular momentum holding in ordinary electrodynamics, we should therefore expect that the ratio between the energy and the angular momentum of the emitted radiation would be $2\pi\nu$,[1]) but this is seen to be equal to the ratio between the energy $h\nu$ and the angular momentum $\frac{h}{2\pi}$ lost by the system considered above during a transition for which we have assumed that the radiation is circularly polarised. This agreement would seem not only to support the validity of the above considerations but also to offer a direct support, independent of the equations (22), of the assumption that, *for an atomic system possessing an axis of symmetry, the total angular momentum round this axis is equal to an entire multiple of* $\frac{h}{2\pi}$.

A further illustration of the above considerations of the relation between the quantum theory and the ordinary theory of radiation is obtained if we consider a conditionally periodic system subject to the *influence of a small perturbing field of force*. Let us assume that the original system allows of separation of variables in a certain set of coordi-

[1]) Comp. K. Schaposchnikow, Phys. Zeitschr. XV, p. 454 (1914).

nates $q_1, \ldots, q_s$, so that the stationary states are determined by (22). From the necessary stability of the stationary states we must conclude that the perturbed system will possess a set of stationary states which only differ slightly from those of the original system. In general, however, it will not be possible for the perturbed system to obtain a separation of variables in any set of coordinates, but if the perturbing force is sufficiently small the perturbed motion will again be of conditionally periodic type and may be regarded as a superposition of a number of harmonic vibrations just as the original motion. The displacements of the particles in the stationary states of the perturbed system will therefore be given by an expression of the same type as (31) where the fundamental frequencies ω_k and the amplitudes $C_{\tau_1,\ldots,\tau_s}$ may differ from those corresponding to the stationary states of the original system by small quantities proportional to the intensity of the perturbing forces. If now for the original motion the coefficients $C_{\tau_1,\ldots,\tau_s}$ corresponding to certain combinations of the τ's are equal to zero for all values of the constants $\alpha_1, \ldots, \alpha_s$, these coefficients will therefore for the perturbed motion, in general, possess small values proportional to the perturbing forces. From the above considerations we shall therefore expect that, in addition to the main probabilities of such transitions between stationary states which are possible for the original system, there will for the perturbed system exist small probabilities of new transitions corresponding to the above mentioned combinations of the τ's. Consequently we shall expect that the effect of the perturbing field on the

spectrum of the system will consist partly in a small displacement of the original lines, partly in the appearance of new lines of small intensity.

A simple example of this is afforded by a system consisting of a particle moving in a plane and executing harmonic vibrations in two perpendicular directions with frequencies ω_1 and ω_2. If the system is undisturbed all coefficients C_{τ_1,τ_2} will be zero, except $C_{1,0}$ and $C_{0,1}$. When, however, the system is perturbed, for instance by an arbitrary small central force, there will in the FOURIER expressions for the displacements of the particle, in addition to the main terms corresponding to the fundamental frequencies ω_1 and ω_2, appear a number of small terms corresponding to frequencies given by $\tau_1\omega_1 + \tau_2\omega_2$ where τ_1 and τ_2 are entire numbers which may be positive as well as negative. On the present theory we shall therefore expect that in the presence of the perturbing force there will appear small probabilities for new transitions which will give rise to radiations analogous to the so called harmonics and combination tones in acoustics, just as it should be expected on the ordinary theory of radiation where a direct connection between the emitted radiation and the motion of the system is assumed. Another example of more direct physical application is afforded by the effect of an external homogeneous electric field in producing new spectral lines. In this case the potential of the perturbing force is a linear function of the coordinates of the particles and, whatever is the nature of the original system, it follows directly from the general theory of perturbations that

the frequency of any additional term in the expression for the perturbed motion, which is of the same order of magnitude as the external force, must correspond to the sum or difference of two frequencies of the harmonic vibrations into which the original motion can be resolved. With applications of these considerations we will meet in Part II in connection with the discussion of SOMMERFELD's theory of the fine structure of the hydrogen lines and in Part III in connection with the problem of the appearance of new series in the spectra of other elements under the influence of intense external electric fields.

As mentioned we cannot without a more detailed theory of the mechanism of transition between stationary states obtain quantitative information as regards the general question of the intensities of the different lines of the spectrum of a conditionally periodic system given by (26), except in the limit where the n's are large numbers, or in such special cases where for all values of the constants $\alpha_1, \ldots, \alpha_s$ certain coefficients $C_{\tau_1,\ldots,\tau_s}$ in (31) are equal to zero. From considerations of analogy, however, we must expect that it will be possible also in the general case to obtain an *estimate of the intensities* of the different lines in the spectrum by comparing the intensity of a given line, corresponding to a transition between two stationary states characterised by the numbers $n'_1, \ldots, n'_s$ and $n''_1, \ldots, n''_s$ respectively, with the intensities of the radiations of frequencies $\omega_1(n'_1 - n''_1) + \cdots + \omega_s(n'_s - n''_s)$ to be expected on ordinary electrodynamics from the motions in these states; although of course this estimate becomes

more uncertain the smaller the values for the n's are. As it will be seen from the applications mentioned in the following Parts this is supported in a general way by comparison with the observations.

Færdig fra Trykkeriet d. 27, April 1918.

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 2α of the relative orbit of the particles, quite independent of the degree of eccentricity of this orbit, are given by

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

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

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

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])

[1]) For the literature on this subject the reader is referred to the

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

$$\begin{aligned} W_n &= \frac{1}{n^2}\,\frac{2\pi^2 N^2 e^4 M m}{h^2(M+m)}, \\ \omega_n = \frac{1}{n^3}\,\frac{4\pi^2 N^2 e^4 M m}{h^3(M+m)}, &\quad 2\alpha_n = n^2\,\frac{h^2(M+m)}{2\pi^2 N e^2 M m}. \end{aligned} \tag{41}$$

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,

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

papers cited in the introduction.

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, 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, accord-

ing 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.

§ 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, page 41). 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 $\kappa_1 I_1 + \cdots + \kappa_s I_s$, where $I_1, \ldots, I_s$ are defined by (21) and calculated with respect to the set of coordinates just mentioned, and where the κ's are a set of entire positive numbers without a common divisor. For simplicity let us assume that at least one of the κ's, say κ_s, is equal to one, and that consequently, as mentioned on page 40, 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

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

Since for the undisturbed system $\omega_k = \kappa_k \omega_s$, the differences $\omega_k - \kappa_k \omega_s$ 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 $\mathfrak{v}_k$. Consider now the multitude of states of the perturbed system for which $\sum_1^s \kappa_k I_k$ 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)

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

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 $\mathfrak{v}_k$, 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, $\kappa_1 = 2$ and $\kappa_2 = 1$, while in the second case we have $\kappa_1 = \kappa_2 = 1$. 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 $\mathfrak{v} = \omega_1 - \kappa_1\omega_2$ 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])

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

[1]) In this connection it may be of interest to note that the possibility of a rational interpretation of 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 31, 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.

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 $q_1, q_2, \ldots, q_s$ 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 $\alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_s$. 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 $\alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_s$, 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])

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

where Ω is considered as a function of $\alpha_1, \ldots, \alpha_s, \beta_1, \ldots, \beta_s$ and t, obtained by introducing for the q's their expressions as

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

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 with the so called "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 32, 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

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

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^2, 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 $N_k = \kappa_k$, where $\kappa_1, \ldots, \kappa_s$ 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,

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

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 $I = \sum \kappa_k I_k$. 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 $\dfrac{t}{\vartheta}\psi$. 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

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

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 80 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 transforma-

bility 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 82, 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 $\mathfrak{s}$ 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

$$\delta\psi = \mathfrak{v}\,\delta\mathfrak{I}, \tag{49}$$

where $\mathfrak{v} = \dfrac{1}{\mathfrak{s}}$ is the frequency of the secular perturbations, and where the quantity $\mathfrak{I}$ is defined by

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

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 $\mathfrak{I} = 0$ must beforehand be expected to be a stationary state. In fact, for this value of $\mathfrak{I}$, 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

$$\mathfrak{J} = \mathfrak{n}h, \tag{51}$$

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 $\mathfrak{v}$ 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 com-

plex. 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 β'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,

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

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

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

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

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

where the $\mathfrak{C}$'s and $\mathfrak{c}$'s are constants, the former of which, besides on I, depend on the $\mathfrak{I}$'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

$$\mathfrak{I}_k = \mathfrak{n}_k h, \qquad (k = 1, \ldots,\ s-l) \tag{55}$$

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 $\mathfrak{I}_k$, 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 *degener-*

ate, 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

$$\delta\psi = \mathfrak{v}\,\delta\mathfrak{J}, \tag{56}$$

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

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

where $\mathfrak{s} = 1/\mathfrak{v}$ 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 100, 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,

$$\delta\psi = \mathfrak{v}_1\,\delta\mathfrak{I}_1 + \mathfrak{v}_2\,\delta I_2, \tag{59}$$

where $\mathfrak{v}_1$ is the frequency with which the shape of the or-

bit 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 $\mathfrak{v}_2$ 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

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

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])

$$\mathfrak{J}_1 = \mathfrak{n}_1 h, \quad \mathfrak{J}_2 = \mathfrak{n}_2 h, \tag{61}$$

[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,

where $\mathfrak{n}_1$ and $\mathfrak{n}_2$ 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 frequencies 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 sys-

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 64, this condition would also seem to obtain an independent support from considerations of conservation of angular momentum during a transition between two stationary states.

tem during continuous transformations of the external conditions (see Part I, page 14 and page 49), 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 134).

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 in 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)

$$\mathfrak{v} = \frac{1}{2\pi}\frac{D\beta_2}{Dt} = \frac{1}{2\pi}\frac{\delta\psi}{\delta\alpha_2}, \tag{62}$$

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,

$$\delta\psi = 2\pi\mathfrak{v}\,\delta\alpha_2. \tag{63}$$

This relation, which corresponds to (56), is seen to coincide with (59), since in the present case $\mathfrak{v}_2 = 0$ and $\mathfrak{J}_1 = 2\pi\alpha_2$. 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 loses 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 of 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 $2\alpha_n$ 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:

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

where the summation is to be extended over all positive and negative entire values of τ, $\mathfrak{t}_1$, …, $\mathfrak{t}_{s-1}$, 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 $\mathfrak{I}_1$, …, $\mathfrak{I}_{s-1}$ 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 $\mathfrak{v}_1$, …, $\mathfrak{v}_{s-1}$ 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, $\mathfrak{I}_1$, …, I_{s-1} differ by δI, $\delta\mathfrak{I}_1$, …, $\delta\mathfrak{I}_{s-1}$ respectively, is given by the relation[1])

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

which coincides with (52) if $\delta\mathfrak{J} = 0$, and which will be seen to

[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 $\mathfrak{J}_1, \ldots, \mathfrak{J}_{s-1}$. 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 53 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 $I, \mathfrak{J}_1, \ldots, \mathfrak{J}_{s-1}$, and the corresponding angle variables may

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

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

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

conveniently be denoted by w, $\mathfrak{w}_1$, ..., $\mathfrak{w}_{s-1}$ respectively. Introducing the new variables, the total energy of the perturbed system will be a function of I, $\mathfrak{J}_1$, ..., $\mathfrak{J}_{s-1}$ 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, $\mathfrak{w}_1$, ..., $\mathfrak{w}_{s-1}$ 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, $\mathfrak{w}_1$, ..., $\mathfrak{w}_{s-1}$ by ω, $\mathfrak{v}_1$, ..., $\mathfrak{v}_{s-1}$ respectively, the formulæ (65) and (66) are therefore directly obtained, just as the corresponding formulæ (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.

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 61, it follows from the discussion of the general character of the secular perturbations on page 104 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 $\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1$ and in a number of circular harmonic rotations perpendicular to the axis with frequencies $\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1 + \mathfrak{v}_2$. 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 $\mathfrak{n}_2 \frac{h}{2\pi}$, 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 64).[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

[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.

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 64, 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 external 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

[1]) In analogy with the considerations on page 97 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 $\mu\lambda$.

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 17 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 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 peculiarity of the motion, some of the coefficients $C_{\tau,\mathfrak{t}_1,\ldots,\,\mathfrak{t}_{s-1}}$ in the expressions (65) for the displacements of the particles as a sum of harmonic vibrations, corresponding to certain combinations of the numbers τ, $\mathfrak{t}_1$, $\ldots$, $\mathfrak{t}_{s-1}$, 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 64).[1]) In the preceding con-

[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

siderations 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 stationary 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 wall 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 effect on the spectrum of the perturbed

of the example in § 5 on page 192.

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 31, 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])

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

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)

[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.

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 so called *fine structure* of the hydrogen lines. Moreover the theory was supported in the most striking way by PASCHEN's[1]) 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 view of perturbed periodic systems. Thus, by a simple application of relativistic mechanics, it is found that, if the equation of a Keplerian el-

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

lipse 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 $\mathfrak{v}_R$, 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,

$$\mathfrak{v}_R = \omega(1 - \gamma) = \frac{1}{2}\omega\left(\frac{Ne^2}{pc}\right)^2. \qquad (69)$$

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

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

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 $C = -\dfrac{N^2 e^4}{2c^2 m}$.

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 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

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

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 α_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 $n_2 = \mathfrak{n}$, 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

[1]) Compare Part I, page 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

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 *num-*

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.

ber 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,[1]) 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, page 47). 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 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 con-

[1]) A. SOMMERFELD, Ber. Akad. München, 1917, p. 83.

siderations 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 59

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

and

$$\begin{aligned} x &= \sum C_\tau \cos 2\pi\big\{(\tau\omega_1 + \omega_2)t + c_\tau\big\}, \\ \pm y &= \sum C_\tau \sin 2\pi\big\{(\tau\omega_1 + \omega_2)t + c_\tau\big\}, \end{aligned} \tag{73}$$

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 64 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])

[1]) *Note added during the proof.* As remarked in Part I, this con-

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 explicit 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

sideration 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)).

on the hydrogen spectrum, discovered by 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

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

where 2α is the major axis, ε the eccentricity and u the so called eccentric anomaly, this gives

$$\begin{aligned}\psi &= eF\cos\varphi\,\frac{1}{2\pi}\int_0^{2\pi}\alpha(\cos u + \varepsilon)(1 + \varepsilon\cos u)\,du \\ &= \frac{3}{2}\varepsilon\alpha eF\cos\varphi.\end{aligned} \tag{74}$$

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 $\cos\varphi$ 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 α_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 $z = 1$ 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

[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.

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 107. 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[1]) 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

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

according to formula (74)

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

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

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

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 α and ω remain constant during the perturbations,

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

where

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

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

$$P_x \frac{DP_x}{Dt} + P_y \frac{DP_y}{Dt} = 0,$$

which together with (5*) gives

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

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

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

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

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

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 α and ω the values of α_n and ω_n given by (41),

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

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 $\mathfrak{v}_F$, 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 $\mathfrak{v}_F$. 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

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

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 $\frac{3}{2}\alpha_n$.

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 36). 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

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

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 $n_1 - n_2 = \mathfrak{n}$. 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 $n + \mathfrak{n}$ 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

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

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

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

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 motion of the election 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 128, 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_2 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 page 49). 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])

[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 state 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 82), 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 47, afford a rational means of determining the a-priori probability of the stationary states of an atomic system.

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_2 is changed by an uneven number of units, 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 64). 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 experimen-

[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

tal 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_2 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 136 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*

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.

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 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 modifications 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 107. 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 145). 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 fines 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 mo-

[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 112).

tion 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 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 36, 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

$$\mathfrak{v}_H = \frac{e}{4\pi m e} H, \tag{79}$$

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 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.[2]) Moreover, as regards the effect of the magnetic field on the total energy of the system,[3]) it will be observed

[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.

[2]) 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.

[3]) 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, it 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 8) 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 so called "normal" state of an atomic system (i. e. the stationary state of the system which possesses

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 $2\pi P\mathfrak{v}_H$, 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

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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.

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 $\mathfrak{v}_H$ 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

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

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 143). 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])

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2(n_1+n_2+n_3)^2} \pm \frac{ehn_3}{4\pi mc}H, \qquad (81)$$

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 $\mathfrak{n} = n_3$. 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

[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 $\mathfrak{v}_H$; 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.

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 110). 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 perturbations 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 $\mathfrak{v}_H$, 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 $\mathfrak{v}_H$. 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 empirical rule of EPSTEIN concerning the observed polarisations of the components of the STARK effect of the hydrogen lines (see page 149). 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 $\tau\omega + \mathfrak{v}_H$ or $\tau\omega - \mathfrak{v}_H$, 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

$$\delta E = \delta E_0 + \delta \mathfrak{E} = \omega\, \delta I + \mathfrak{v}_H\, \delta \mathfrak{I}, \tag{82}$$

where E_n 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 $\mathfrak{I}$ 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 $\mathfrak{I} = \mathfrak{n}h$, we are therefore from a consideration, quite analogous to that given in § 2 on page 114, 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 64.

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 charac-

teristic 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 $\operatorname{div}\mathfrak{A} = 0$ and $\operatorname{curl}\mathfrak{A} = \mathfrak{H}$, 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_1, q_2, q_3 of the electron in space

are defined by the equations[1])

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

where the p's are the momenta defined in the usual way (compare page 15), 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 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,

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

$$= \frac{e}{c}\sum_1^3 \dot{q}_k \frac{\partial(\mathfrak{v}\mathfrak{A})}{\partial \dot{q}_k} = \frac{e}{c}(\mathfrak{v}\mathfrak{A}).$$

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

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 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 α'_1, α'_2, α'_3, β'_1, β'_2, β'_3, which are related to the q's and p''s and the time in the same way as the orbital constants α_1, α_2, α_3, β_1, β_2, β_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 α'_1, α'_2, α'_3, β'_1, β'_2, β'_3 differ from the corresponding orbital constants α_1, α_2, α_3, β_1, β_2, β_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

α_1, α_2, α_3, β_1, β_2, β_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 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

[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.

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,

$$\begin{aligned} \Delta_\vartheta \alpha_1 - e\Phi_\vartheta &= -\frac{e}{\vartheta} \int_0^\vartheta \left(\Phi + \frac{\omega}{c} B \right) dt \\ &= \frac{1}{\vartheta} \int_0^\vartheta (\psi_E + \psi_M) \, dt = \frac{1}{\vartheta} \int_0^\vartheta \psi \, dt. \end{aligned} \tag{85}$$

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 91), 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

[1]) Compare Note on page 112. 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.

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 104, 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 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 $\mathfrak{n}_2$ 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 $\mathfrak{n}_2$ 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 $\mathfrak{n}_1$ is the same while the values of $\mathfrak{n}_2$ 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 $\mathfrak{n}_1$ are the same and the values of $\mathfrak{n}_2$ 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)

$$\psi_M = \frac{e\alpha_3}{2cm} H. \tag{86}$$

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

$$\mathfrak{v}_H = \frac{1}{2\pi} \frac{\partial \psi_M}{\partial \alpha_3} = \frac{e}{4\pi mc} H$$

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

$$\psi_M = \frac{e}{2mc}\frac{\mathfrak{n}_2 h}{2\pi}H = \mathfrak{n}_2\mathfrak{v}_H h. \tag{87}$$

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 159). 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 $\mathfrak{v}_H$.

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 165). In connection with

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

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 reference to the invariance of the a-priori probability of the stationary states during such a transformation (see Part I, page 14 and page 49), 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 slates in mechanical respect do not exhibit singularities from which we might anticipate that they are physically unrealisable.[1])

[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 149 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.

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 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 117 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 119, 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

[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 119).

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 121, 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 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 179, 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 the 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 $|\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1|$, and of a number of circular harmonic rotations perpendicular to this direction, the frequencies of which are of the type $|\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1 + \mathfrak{v}_2|$ (compare page 114). 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 $|\mathfrak{t}_1\mathfrak{v}_1 + \mathfrak{v}_2|$, 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 $|\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1|$ and $|\tau\omega_P + \mathfrak{t}_1\mathfrak{v}_1 + \mathfrak{v}_2|$, 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 $|\tau\omega_P + \mathfrak{k}_1\mathfrak{v}_1 + 2\mathfrak{v}_2|$. 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 each other. 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 exter-

[1]) Compare Note on page 119. 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

nal 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 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 ZEE-

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.

MAN 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

[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.

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.[1]) 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.[2]) 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 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

[1]) This spectrum has been observed as an emission spectrum in spectra of solar protuberances and planetary nebulae (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)).

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

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 hyper-

[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.

bolic 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, 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 so called 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.

Færdig fra Trykkeriet d. 30, December 1918.

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