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Author: Niels Henrik David Bohr

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ON

THE QUANTUM THEORY OF LINE-SPECTRA

BY

N. BOHR

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

KØBENHAVN
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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 interpretated 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 deduced 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 $\dot{q}_1, \ldots, \dot{q}_s$ $\left(\dot{q}_k = \frac{dq_k}{dt}\right)$ 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 multiplum 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 in variance 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 p. 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. p. 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 p. 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 moving 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 corresponding to small values of n_1 and n_2. On the

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

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 motion 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

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

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

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

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 already shown in the case of purely periodic systems by means

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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 p. 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 multiplum 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.

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

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

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 $\omega_3 = \dfrac{1}{2\pi} C''_{0,0}$ 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.

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