

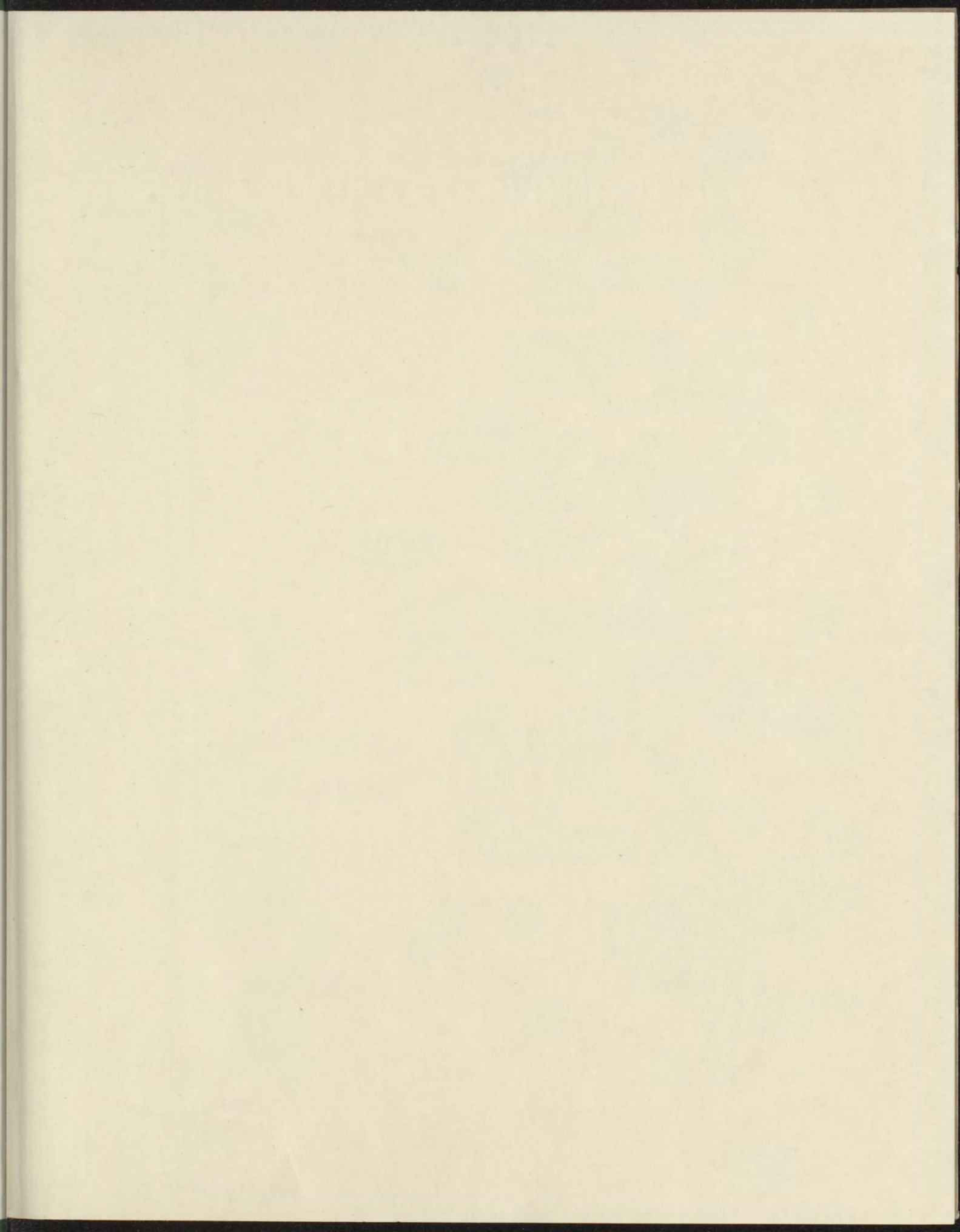
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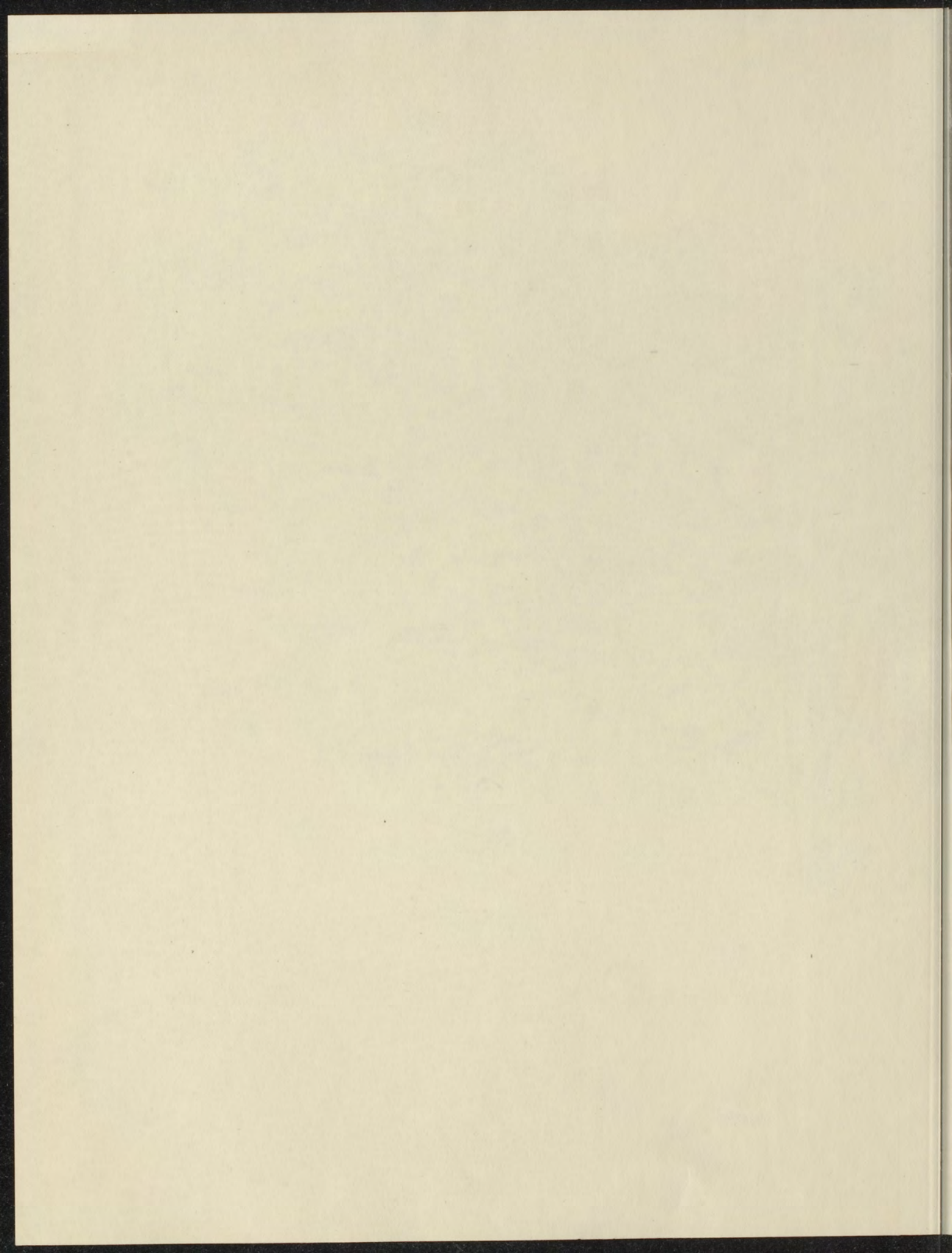


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# INTENSITIES OF SPECTRAL LINES

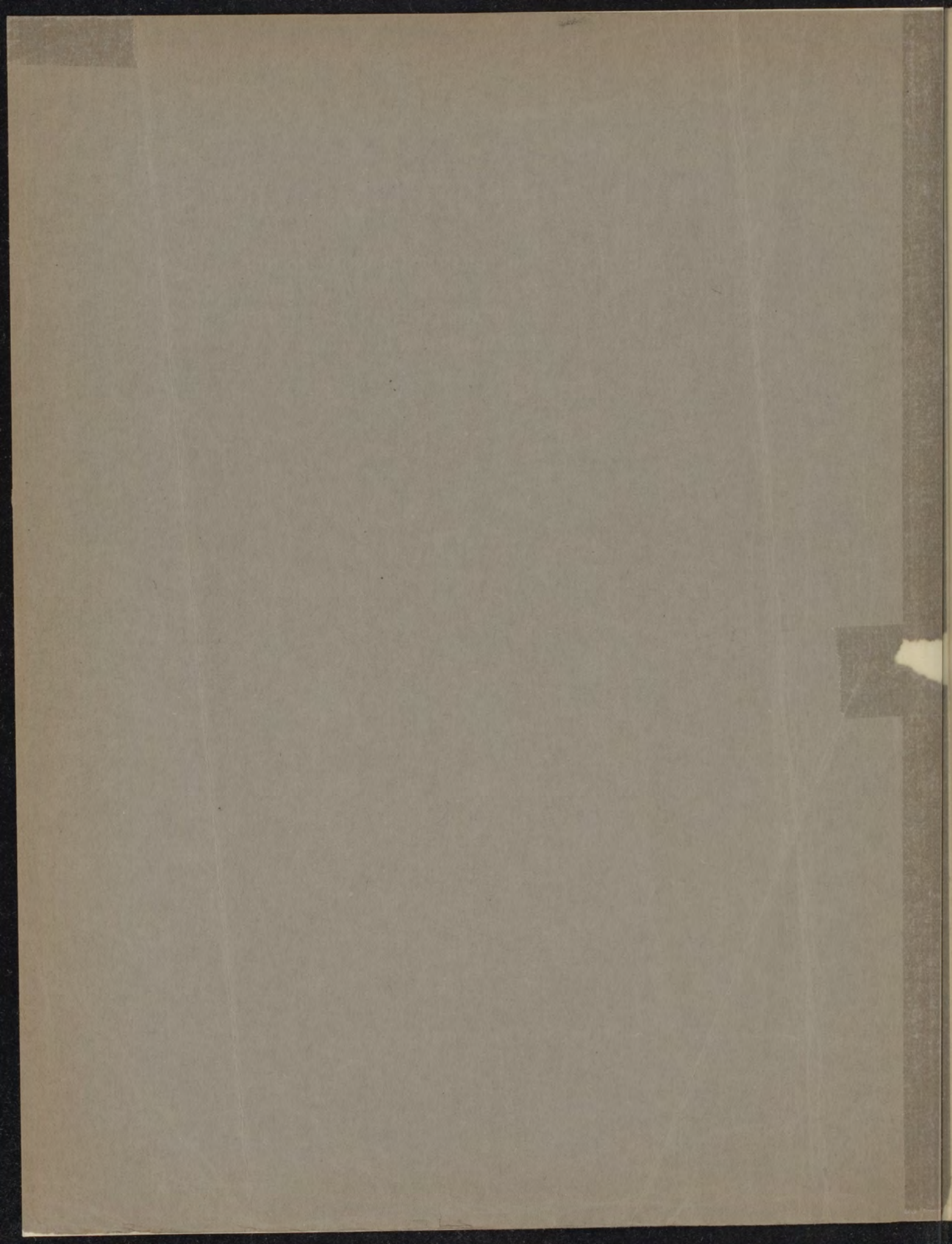
ON THE APPLICATION OF THE QUANTUM THEORY TO THE  
PROBLEM OF THE RELATIVE INTENSITIES OF THE COMPO-  
NENTS OF THE FINE STRUCTURE AND OF THE STARK EFFECT  
OF THE LINES OF THE HYDROGEN SPECTRUM

H. A. KRAMERS

KØBENHAVN — BIANCOLUNOS BOGTRYKKERI — 1919

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# INTENSITEIT VAN SPECTRAALLIJNEN.

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PROEFSCHRIFT TER VERKRIJGING VAN DEN  
GRAAD VAN DOCTOR IN DE WIS- EN NATUUR-  
KUNDE AAN DE RIJKS-UNIVERSITEIT TE  
LEIDEN, OP GEZAG VAN DEN RECTOR-MAG-  
NIFICUS, DR. P. C. T. VAN DER HOEVEN,  
HOOGLEERAAR IN DE FACULTEIT DER GE-  
NEESKUNDE, VOOR DE FACULTEIT DER WIS-  
EN NATUURKUNDE TE VERDEDIGEN OP  
DONDERDAG, 8 MEI 1919, DES NAMIDDAGS  
TE 4 UUR,



DOOR

HENDRIK ANTONIE KRAMERS,

GEBOREN TE ROTTERDAM.

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STATE OF NEW YORK

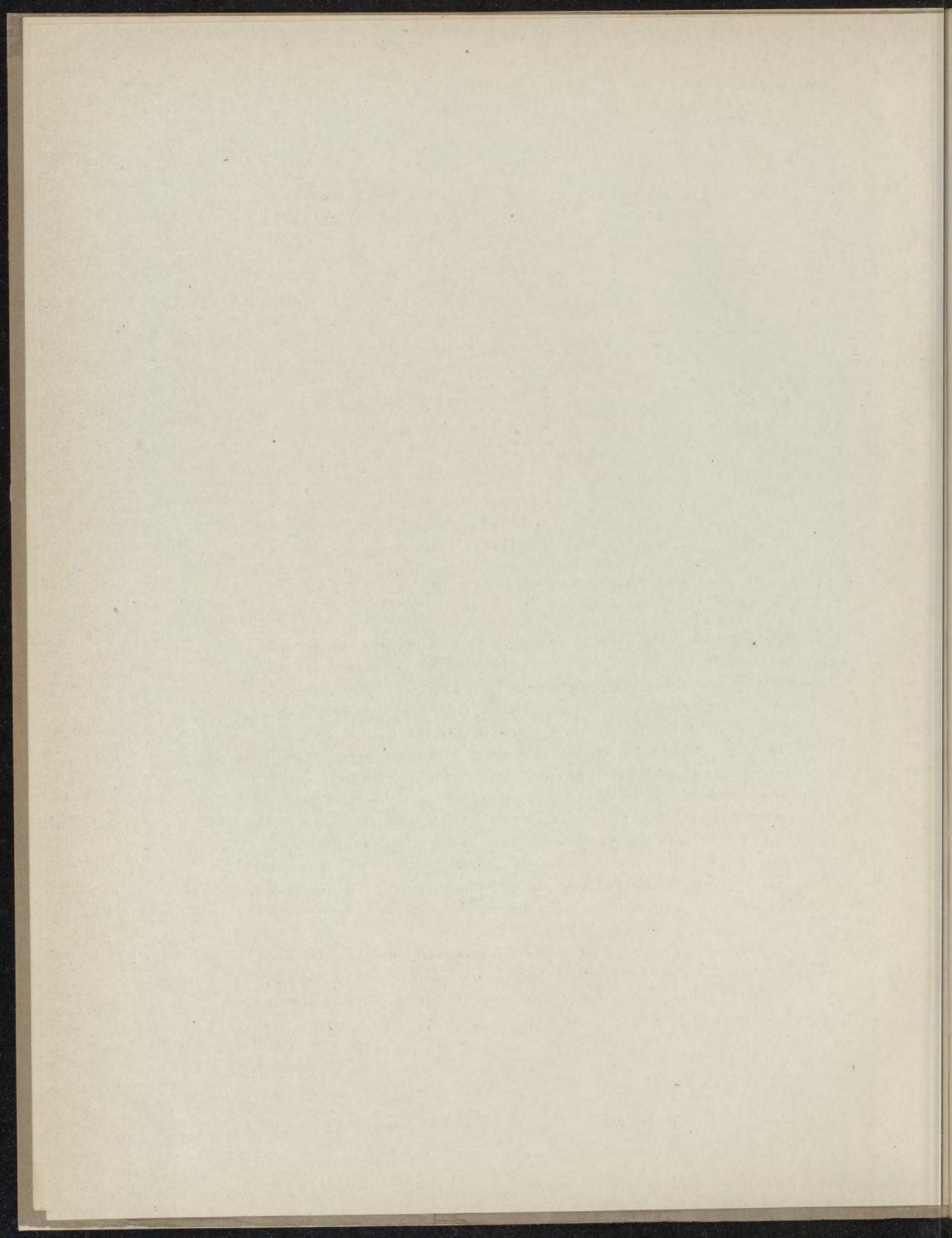
IN SENATE



*Mijn dank breng ik aan de hoogleeraren van de fakulteit der wis- en natuurkunde te Leiden voor de welwillendheid waarmede zij mij toestonden mijn verhandeling "Intensities of Spectral Lines", die verschijnt in de verhandelingen van de koninklijke Deensche akademie van wetenschappen, tegelijkertijd als proefschrift te gebruiken.*

*Persoonlijk gaat voorts in de eerste plaats mijn dank uit naar mijn promotor, professor EHRENFEST, die mij gedurende mijn Leidsche studiejaren een onwaardeerbaar leeraar en raadgever is geweest, zoowel op wetenschappelijk als op ander gebied. Maar ook mag ik niet nalaten mijn erkentelijkheid te betuigen jegens professor LORENTZ wiens colleges mij steeds een groot genot waren, professor KUENEN wiens colleges in zoo hooge mate mijn liefde voor de natuurkunde wekten, en professor KLUYVER die mij door zijn colleges op zoo suggestieve wijze in de wiskunde inleidde.*

*Ten slotte zal het den lezer van dit proefschrift duidelijk zijn hoeveel ik verschuldigd ben aan mijn onvergelykelijken vriend en leeraar, professor NIELS BOHR, onder wiens leiding ik de laatste jaren in Dene- marken heb mogen werken.*





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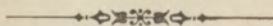
H. A. KRAMERS

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KØBENHAVN

HOVEDKOMMISSIONÆR: ANDR. FRED. HØST & SØN, KGL. HOF-BOGHANDEL

BIANCO LUNOS BOGTRYKKERI

1919

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H. J. RAMBERG

1914

Published by the University of Chicago Press

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## Introduction.

In the quantum theory of line spectra it is assumed that the laws of electrodynamics cannot be applied to atomic systems, and the assumption is made that an atomic system can exist without emitting radiation in a number of states, which are called the "stationary states" of the system, and that a process of emission or absorption of energy can only take place by a complete transition between two such states. Further it is assumed that the radiation emitted or absorbed during such a transition is unifrequent, and that its frequency is given by

$$\nu = \frac{1}{h}(E' - E''), \quad (1)$$

where  $E'$  and  $E''$  are the values of the energy in the two states, and where  $h$  is PLANCK'S constant. As well known BOHR was able, on the basis of these assumptions, to account in a convincing way for the frequencies of the lines of the series spectrum of hydrogen and for some main features of the series spectra of other elements. In the course of the last years the quantum theory of line spectra has been developed considerably, due to the work of SOMMERFELD, EPSTEIN, SCHWARZSCHILD and others, who, by extending BOHR'S original theory, were able to explain, as regards the frequencies of the components, the characteristic fine structure of the hydrogen lines and the effect which strong external electric or magnetic fields have on these lines. Now BOHR<sup>1)</sup> has shown in a recent paper, which contains a general exposure of the principles of the quantum theory of line spectra, that it is not only possible to get information as regards the frequencies of spectral lines, but that at the present state of the theory we are also able to draw some conclusions regarding the polarisation and intensities with which these lines appear, by considering the amplitudes of the harmonic vibrations in which the motion of the particles in an atomic system may be resolved. On professor BOHR'S proposal I have undertaken in the present paper to treat in detail the application of his ideas to the problem of the intensity of spectral lines in the special case of

<sup>1)</sup> N. BOHR, On the Quantum Theory of Line Spectra. D. Kgl. Danske Vidensk. Selsk. Skr. naturvidensk. og mathem. Afd., 8. Række IV, 1, 1918. This paper will in the following be referred to as: N. BOHR, loc. cit.



the fine structure and in that of the Stark effect of the hydrogen lines, and to compare the result of the calculations with the observations.

The paper is divided in two Parts.

Part I deals with the problem of the determination of the values of the amplitudes of the harmonic vibrations in which the motion of certain mechanical systems may be resolved, and is divided in four chapters.

In § 1 a short account will be given of the theory of mechanical systems for which the Hamilton-Jacobi partial differential equation may be solved by means of separation of variables, and it will be shown how it is possible to reduce the calculation of the amplitudes of the harmonic vibrations, in which the motion of these systems may be resolved, to the evaluation of simple definite integrals.

In § 2 the method exposed in § 1 will be applied to the model of a hydrogen atom which is uninfluenced by external forces, assuming that the motion is governed by the laws of relativistic mechanics.

In § 3 the same method will be applied to the model of a hydrogen atom, which is subject to the influence of an external homogeneous electric field of force, the intensity of which is so large that it is possible with a high degree of approximation to determine the motion by means of ordinary Newtonian mechanics.

In § 4 the perturbing influence is considered which a very weak homogeneous electric field of force will have on the motion of the system considered in § 2.

Part II deals with the application of the calculations given in Part I to the problem of the intensities of spectral lines, and is divided in four chapters.

§ 5 contains, besides a brief exposure of the theory of stationary states of systems which allow of separation of variables, an account of BOHR's theory of the connection between the polarisation and intensities of spectral lines emitted by an atomic system and the amplitudes of the harmonic vibrations in which the motion of such a system may be resolved.

In § 6 a discussion is given of the application of the theory to the relative intensities of the components in which the hydrogen lines are split up in case of the Stark effect, on the basis of the formulae deduced in § 3.

§ 7 contains a discussion of the relative intensities with which the components of the fine structure of the hydrogen lines appear, based on the formulae deduced in § 2 and § 4.

In § 8 a brief discussion will be given of certain questions which stand in connection with the application of the theory to the problem of the Zeeman effect of the hydrogen lines.

Finally I wish to express my best thanks to professor N. BOHR, the creator of the beautiful theory underlying the present paper, for his kind interest and encouragement during the achievement of the work.



## Part I.

### Examination of the trigonometric series representing the motion of the electron in the hydrogen atom.

#### § 1. General method applicable to conditionally periodic systems.

Consider a mechanical system of  $s$  degrees of freedom, the equations of motion of which are given by the set of canonical equations

$$\frac{dp_k}{dt} = -\frac{\partial E}{\partial q_k}, \quad \frac{dq_k}{dt} = +\frac{\partial E}{\partial p_k}, \quad (k = 1, 2, \dots, s) \quad (2)$$

where  $q_1, \dots, q_s$  is a set of generalised coordinates by means of which the positions in space of the particles of which the system consists are uniquely determined, while  $p_1, \dots, p_s$  are the canonically conjugated momenta, and where  $E$  is the energy of the system, which is assumed to be a function of the  $p$ 's and  $q$ 's only. The so called Hamilton-Jacobi partial differential equation is then obtained by writing  $p_i = \frac{\partial S}{\partial q_i}$  where  $S$  is a function of the  $q$ 's, and by putting  $E$ , considered as a function of the  $q$ 's and  $\frac{\partial S}{\partial q}$ 's, equal to a constant  $a_1$ ;

$$E\left(q_1, \dots, q_s, \frac{\partial S}{\partial q_1}, \dots, \frac{\partial S}{\partial q_s}\right) = a_1. \quad (3)$$

A complete solution of this equation will contain, besides an additional constant  $C$ ,  $s - 1$  other integration constants  $a_2, \dots, a_s$ . Now it may happen that, for a suitable choice of orthogonal generalised positional coordinates  $q_1, \dots, q_s$ , it is possible to write a complete solution of equation (3) in the form

$$S = \sum S_k(q_k; a_1, \dots, a_s) + C, \quad (4)$$

where  $S_k$  depends on the  $a$ 's and on  $q_k$  only. If this is the case it is said that the equation (3) allows of "separation of variables" for the special choice of coordinates under consideration, or briefly, that the system allows of separation of variables. For such a system  $\frac{\partial S}{\partial q_k}$ , as seen from (4), will depend on the corresponding  $q_k$  only; moreover remembering that in Newtonian, as well as in relativistic mechanics,  $E$  contains the  $p$ 's in the form of a sum of squares,  $\frac{\partial S}{\partial q_k}$  must necessarily be the square root of a one-valued function of  $q_k$ . Hence, denoting this one-valued function by  $F_k$ , we see that  $S$  may be written in the form

$$S = \sum_1^s \int^{q_k} \sqrt{F_k(q_k; a_1, \dots, a_s)} dq_k. \quad (5)$$

If the  $a$ 's satisfy the condition that every function  $F_k(q_k)$  possesses at least two successive finite real simple roots  $q_k'$  and  $q_k''$ , between which the value of the function is positive, the function  $S$  will, considered as a function of the  $q$ 's, possess  $s$  moduli of periodicity, defined by

$$I_k = \int^{q_k} \sqrt{F_k(q_k; a_1, \dots, a_s)} dq_k, \quad (k = 1, \dots, s) \quad (6)$$

where the integration is taken once up and down between  $q_k'$  and  $q_k''$ . It is clear that the quantities  $I$  thus defined are continuous functions of the  $a$ 's in the region where the  $a$ 's satisfy the just mentioned condition, and that generally the  $a$ 's may reversely be expressed as functions of the  $I$ 's. Introducing these expressions for the  $a$ 's in (5), we obtain an expression for  $S$  as a function of the  $q$ 's and of its moduli of periodicity  $I_1, \dots, I_s$ ;

$$S = \sum_1^s S_k(q_k; I_1, \dots, I_s) = \sum_1^s \int^{q_k} \sqrt{F_k(q_k; I_1, \dots, I_s)} dq_k. \quad (7)$$

Let us now define a transformation of variables

$$p_k = \frac{\partial S}{\partial q_k}, \quad w_k = \frac{\partial S}{\partial I_k}, \quad (k = 1, \dots, s) \quad (8)$$

which may be considered as transforming the variables  $q_1, \dots, q_s, p_1, \dots, p_s$ , which originally described the positions and velocities of all particles of the system at any moment, into the variables  $I_1, \dots, I_s, w_1, \dots, w_s$ . It is easily seen from the periodicity properties of  $S$  that  $w_k$ , considered as a function of the  $q$ 's and  $I$ 's, will increase by 1 if  $q_k$  continuously oscillates once up and down between its limits  $q_k'$  and  $q_k''$  and returns to its original value; while if one of the other  $q$ 's performs a similar oscillation between its limits,  $w_k$  will return to its original value. From this we see that the  $q$ 's, and also the  $p$ 's, considered as functions of the  $w$ 's and the  $I$ 's, are one-valued functions of these variables, which are periodic in every of the  $w$ 's with period 1, *i. e.* they assume their original values if the  $w$ 's increase by arbitrary integers. The  $q$ 's may therefore be expanded in an  $s$ -double Fourier series of the form

$$q_k = \sum_{\tau_1, \dots, \tau_s} C_{\tau_1, \dots, \tau_s}^{(k)} e^{2\pi i(\tau_1 w_1 + \dots + \tau_s w_s)}, \quad (9)$$

where the summation is to be extended over all positive and negative entire values of the  $\tau$ 's, and where the  $C$ 's depend on the  $I$ 's only. Similar expansions will hold for the  $p$ 's.



Now, according to a well known theorem of JACOBI, the transformation (8) leaves the canonical form of the equations of motion unaltered, *i. e.* expressing by means of (8)  $E$  as a function of the  $I$ 's and  $w$ 's, the variations of the latter quantities with the time are given by

$$\frac{dI_k}{dt} = -\frac{\partial E}{\partial w_k}, \quad \frac{dw_k}{dt} = \frac{\partial E}{\partial I_k}. \quad (k = 1, \dots, s) \quad (10)$$

Now  $E$  is, according to (3), equal to  $a_1$ , and consequently a function of the  $I$ 's only. The solution of the equations (10) is therefore immediately obtained by putting

$$I_k = \text{constant}, \quad w_k = \omega_k t + \delta_k, \quad \omega_k = \frac{\partial E}{\partial I_k}, \quad (k = 1, \dots, s) \quad (11)$$

where the  $\delta$ 's are a set of arbitrary constants, while the  $\omega$ 's obviously depend on the constants  $I$  only. We thus see that there exists for the mechanical system under consideration a family of solutions in which each of the  $q$ 's oscillates between two limiting values depending on the constants  $I_1, \dots, I_s$ . It is easily seen that  $\omega_k$  represents the mean number of oscillations which the coordinate  $q_k$  performs between its limits in unit time, taken over a time interval in which a very large number of such oscillations are performed. The variables  $w$  are called "angle variables"; the quantities  $I$ , defined as the moduli of periodicity of the function  $S$ , are canonically conjugated to the  $w$ 's. Mechanical systems for which the motion may be described by a set of angle variables  $w_1, \dots, w_s$  and canonically conjugated  $I$ 's, possessing the properties just considered, are called "conditionally periodic".

Since the  $q$ 's describe the positions of the particles in space uniquely, the displacement  $x$  of any of these particles in any direction in space will be a one-valued function of the  $q$ 's. Considered as a function of the  $I$ 's and  $w$ 's, the displacement  $x$  will therefore, just as each of the  $q$ 's, be periodic in each of the  $w$ 's with period 1, and may consequently also be expressed by a trigonometric series of the form

$$x = \sum C_{\tau_1, \dots, \tau_s} e^{2\pi i(\tau_1 w_1 + \dots + \tau_s w_s)},$$

where the coefficients  $C$  depend on the  $I$ 's only and where the summation is to be extended over all positive and negative entire values of the  $\tau$ 's. Introducing in this expression the values of the  $w$ 's given by (11), we obtain for  $x$ , considered as a function of the time, an expression of the type

$$x = \sum C_{\tau_1, \dots, \tau_s} e^{2\pi i\{(\tau_1 \omega_1 + \dots + \tau_s \omega_s)t + c_{\tau_1, \dots, \tau_s}\}}, \quad (12)$$

where the  $C$ 's and  $c$ 's are constants, showing that the motion of the particles of a conditionally periodic system may be resolved in a number of harmonic vibrations of frequencies  $|\tau_1 \omega_1 + \dots + \tau_s \omega_s|$  the amplitudes of which depend on the quantities  $I_k$  only.

For the systems under consideration the number of the quantities  $\omega$ , which may be denoted as the "fundamental frequencies" characterising the motion, is



generally equal to the number  $s$  of degrees of freedom. In special cases, however, this number may be less than  $s$ , viz. in such cases where, for all values of the  $I$ 's, there exist one or more relations of the type

$$\sum_1^s m_k \omega_k = 0, \quad (13)$$

where the  $m$ 's are a set of integers possessing no common divisor. In fact it is easily seen that by means of  $n$  relations of this kind it is possible to eliminate  $n$  of the quantities  $\omega_k$  in the expressions  $\tau_1 \omega_1 + \dots + \tau_s \omega_s$ , so that these expressions assume the form  $\tau_1 \omega_1 + \dots + \tau_{s-n} \omega_{s-n}$ . Conditionally periodic systems for which relations of the type (13) hold are called "degenerate" and play an important part in the quantum theory. In § 2 we shall meet with a typical example of a degenerate system.

We shall now proceed to derive expressions for the values of the coefficients  $C$ , which occur in the expansion in a trigonometric series

$$f(q_1, \dots, q_s) = \sum C_{\tau_1, \dots, \tau_s} e^{2\pi i(\tau_1 \omega_1 + \dots + \tau_s \omega_s)},$$

where  $f(q_1, \dots, q_s)$  is a one-valued function of the  $q$ 's. According to Fourier's theorem we have<sup>1)</sup>

$$C_{\tau_1, \dots, \tau_s} = \int_0^1 \dots \int_0^1 f(q_1, \dots, q_s) e^{-2\pi i(\tau_1 \omega_1 + \dots + \tau_s \omega_s)} dw_1 \dots dw_s, \quad (14)$$

where the  $q$ 's are regarded as functions of the  $w$ 's and the  $I$ 's. We shall transform this expression into a multiple integral taken over the  $q$ 's, instead of over the  $w$ 's, by means of the transformation formulæ (8), which by means of (7) may be written in the form

$$\omega_k = \frac{\partial S}{\partial I_k} = \sum_{i=1}^{i=s} \frac{\partial S_i}{\partial I_k} = \sum_{i=1}^{i=s} \int^{q_i} \frac{\partial V \bar{F}_i}{\partial I_k} dq_i. \quad (k = 1, \dots, s)$$

The functional determinant of this transformation is given by

$$\frac{\partial(\omega_1, \dots, \omega_s)}{\partial(q_1, \dots, q_s)} = \left| \frac{\partial^2 S}{\partial I_k \partial q_i} \right| = \left| \frac{\partial V \bar{F}_i}{\partial I_k} \right| = J,$$

and consists of the sum of a finite number of products of functions which each contain only one of the  $q$ 's. Transforming (14) we now get

$$C_{\tau_1, \dots, \tau_s} = \int \dots \int f(q_1, \dots, q_s) e^{-2\pi i \sum_k \tau_k \frac{\partial S_i}{\partial I_k}} \Delta dq_1 \dots dq_s, \quad (15)$$

<sup>1)</sup> See C. V. L. CHARLIER, Die Mechanik des Himmels. I, p. 106. It will be noted that the method followed in the present paper is a simple generalisation of the well known method by which the coordinates of a planet performing a Keplerian motion are expressed, by means of a simple Fourier series, as functions of the time.



where the integration must obviously be taken once up and down between the limits of oscillation  $q'$  and  $q''$  of every  $q$ . Let us now assume that  $f(q_1, \dots, q_s)$  can be written in the form of the sum of a finite number of products of functions, which each depend on one of the  $q$ 's only:

$$f(q_1, \dots, q_s) = \sum_r f_{1r}(q_1) f_{2r}(q_2) \dots f_{sr}(q_s). \quad (16)$$

Then it is easily seen that the value of the coefficient  $C$ , given by (15), will be equal to the sum of a finite number of products

$$C_{\tau_1, \dots, \tau_s} = \sum_r \phi_{1r} \phi_{2r} \dots \phi_{sr}, \quad (17)$$

where  $\phi_{ir}$  is a definite integral of the form

$$\phi_i = \int \varphi(q_i) e^{-2\pi i \sum_k \tau_k \frac{\partial S_i}{\partial I_k}} dq_i. \quad (18)$$

The character of these integrals may be brought out clearly by effecting the transformation

$$q_i = \frac{q_i'' + q_i'}{2} + \frac{q_i'' - q_i'}{2} \cos \psi_i. \quad (19)$$

An oscillation of  $q_i$  up and down between its limits  $q_i'$  and  $q_i''$  corresponds to an increase of  $\psi_i$  by  $2\pi$ . Further the functions  $\frac{\partial S_i}{\partial I_k}$  will be periodic in  $\psi_i$  with period  $2\pi$ , unless  $k = i$ , in which case we have obviously

$$\frac{\partial S_i}{\partial I_i} = \frac{\psi_i}{2\pi} + \text{periodic function of } \psi_i \text{ (period } 2\pi).$$

The integral (18) may therefore be written, denoting by  $P_0, P_1, \dots, P_s$  a set of periodic functions of  $\psi$  with period  $2\pi$ , in the form

$$\phi_i = \frac{1}{2\pi} \int_0^{2\pi} P_0(\psi_i) e^{-i\tau_i \psi_i} e^{-2\pi i \sum_k \tau_k P_k(\psi_i)} d\psi_i.$$

It is possible to express the coefficients  $C$  in the simple form given by (17), only if the function  $f(q_1, \dots, q_s)$  that we want to expand in a trigonometric series can be written in the form (16). Now in the quantum theory a series expansion of the rectangular Cartesian coordinates which describe the positions of the particles of the system in space is asked for, and it might be of interest to investigate whether these latter coordinates always may be expressed in terms of the coordinates  $q_1, \dots, q_s$ , in which separation of variables was obtained, by a formula of the form (16). If the set of coordinates  $q_1, \dots, q_s$  belongs to the well known class of „elliptical coordinates“, it is at once seen from the general formulæ holding for this kind



of coordinates, given by JACOBI<sup>1)</sup>, that the Cartesian coordinates are functions of the elliptical coordinates of the type (16). In the applications of the quantum theory hitherto made, separation of variables is always obtained in one or other set of elliptical coordinates<sup>2)</sup>, and, due to the special form of the expression for the kinetic energy in mechanics, it seems highly questionable if, for a mechanical system consisting of particles moving under the influence of conservative forces, it is possible to obtain separation of variables in other kinds of coordinates.

## § 2. Hydrogen atom undisturbed by external influences.

In this chapter we shall apply the above analysis to the problem of the motion of an electron of mass  $m$  and charge  $-e$  rotating round a positive nucleus of infinite mass and of charge  $Ne$ , which attracts the electron according to Coulomb's law, assuming that the motion is governed by relativistic mechanics. As well known this system represents the model of a hydrogen atom where the mass of the nucleus is regarded as infinite. If the laws of Newtonian mechanics were applied, the electron would perform a periodic Keplerian motion, but as soon as the modifications in the laws of mechanics, claimed by the theory of relativity, are taken into account the motion will no more be simply periodic. The orbit of the electron will, however, still be plane and may be described as a closed periodic orbit on which a uniform rotation round the nucleus is superposed. Moreover, assuming that the velocity  $v$  of the electron is small compared to the velocity  $c$  of light, the closed orbit in question will differ from a Keplerian orbit only by small quantities of the same order of magnitude as  $v^2/c^2$ , while also the ratio of the frequency  $\nu$  of the superposed rotation to the frequency of revolution of the electron in the closed orbit will be of the same order as  $v^2/c^2$ .

From these simple properties of the motion it would be possible, quite independently of the theory of separation of variables, at once to derive trigonometric series expressing the displacement of the electron in different directions as a function of the time with neglect of small quantities of the order  $v^2/c^2$ . In fact, the expansions in a trigonometric series for the Cartesian coordinates  $\xi$  and  $\eta$  of a point describing a closed Keplerian ellipse are well known in celestial mechanics, and from these expansions are easily obtained the expressions for the Cartesian coordinates  $x$  and  $y$  in a fixed system of coordinates, relative to which the  $\xi$ - $\eta$  system rotates uniformly with the frequency  $\nu$ . An example of a procedure of this kind will be given at the end of this chapter, where the influence of a magnetic field on the motion of the electron in the hydrogen atom will be treated. For the present, however, we will for the sake of illustration treat the problem by means of the general method

<sup>1)</sup> JACOBI, Vorl. über Dynamik, p. 202.

<sup>2)</sup> Rectangular coordinates, polar coordinates and parabolic coordinates may all be regarded as special cases of elliptical coordinates.



discussed in § 1, making use of the fact that the system under consideration allows of separation of variables in polar coordinates. This method also offers the advantage that it allows us to determine the coefficients  $C$  in the trigonometric series, which represent the displacement of the electron, to any degree of approximation desired.

Consider the motion of the electron in the plane and let the position of the electron be described by means of polar coordinates  $r$  and  $\varphi$ , where  $r$  is the length of the radius vector from the nucleus to the electron and  $\varphi$  the angle which this radius vector makes with a fixed direction. These coordinates are connected with the ordinary Cartesian coordinates  $x$  and  $y$  of the electron by means of the relation

$$x + iy = r e^{i\varphi}. \quad (20)$$

In order to find the expansion of  $x$  and  $y$  in trigonometric series it will therefore be sufficient to calculate the coefficients  $C$  in the series

$$r e^{i\varphi} = \sum C_{\tau_1, \tau_2} e^{2\pi i(\tau_1 w_1 + \tau_2 w_2)}, \quad (21)$$

where  $w_1$  and  $w_2$  are the angle variables which correspond to  $r$  and  $\varphi$  respectively in the manner described in § 1.

Introducing the notation  $\gamma = (1 - v^2/c^2)^{-1/2}$ , where  $v^2 = \left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\varphi}{dt}\right)^2$  is the square of the velocity of the electron, the momenta  $p_r$  and  $p_\varphi$  which are canonically conjugated to the coordinates  $r$  and  $\varphi$  will, according to the laws of relativistic mechanics, be given by  $p_r = m\gamma \frac{dr}{dt}$  and  $p_\varphi = m\gamma r^2 \frac{d\varphi}{dt}$ <sup>1)</sup>. The total energy of the system, which is equal to  $mc^2(\gamma - 1) - \frac{Ne^2}{r}$ , will therefore, considered as a function of  $p_r$ ,  $p_\varphi$ ,  $r$  and  $\varphi$ , be given by

$$E = mc^2 \left[ \left\{ 1 + \frac{1}{m^2 c^2} \left( p_r^2 + \frac{1}{r^2} p_\varphi^2 \right) \right\}^{1/2} - 1 \right] - \frac{Ne^2}{r}.$$

The Hamilton-Jacobi partial differential equation will consequently be of the form

$$\alpha_1 = mc^2 \left[ \left\{ 1 + \frac{1}{m^2 c^2} \left( \left( \frac{\partial S}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial S}{\partial \varphi} \right)^2 \right) \right\}^{1/2} - 1 \right] - \frac{Ne^2}{r}.$$

As this equation does not contain  $\varphi$ , a separation of variables is directly obtained by putting  $\frac{\partial S}{\partial \varphi}$  equal to the integration constant  $a_2$ , which will represent the angular momentum of the electron round the nucleus. This gives

$$\frac{\partial S}{\partial \varphi} = a_2, \quad \frac{\partial S}{\partial r} = \sqrt{m^2 c^2 \left\{ \left( \frac{a_1 + Ne^2/r}{mc^2} + 1 \right)^2 - 1 \right\} - \frac{a_2^2}{r^2}} = \sqrt{F(r)}. \quad (22)$$

Introducing now the quantities  $I$  defined by (6), we get

$$I_1 = \int \sqrt{F(r)} dr, \quad I_2 = \int_0^{2\pi} a_2 d\varphi, \quad (23)$$

<sup>1)</sup> Compare for these and the following calculations P. DEBYE, Phys. Zeitschr. XVII p. 512 (1916).

where the first integral is to be extended twice between the two roots of the integrand. Evaluating these integrals and expressing the  $a$ 's as functions of the  $I$ 's, we get, expanding after powers of  $1/c^2$  and neglecting terms containing squares and higher powers of this quantity,

$$a_1 = -\frac{2\pi^2 N^2 e^4 m}{(I_1 + I_2)^2} \left\{ 1 + \left( \frac{2\pi N e^2}{c} \right)^2 \left( -\frac{3}{4(I_1 + I_2)^2} + \frac{1}{(I_1 + I_2)I_2} \right) \right\}, \quad a_2 = \frac{I_2}{2\pi}. \quad (24)$$

In the expression for the energy  $a_1$ , the term which does not contain  $1/c^2$  gives the value of the energy for an unrelativistic motion, while the terms containing  $1/c^2$  are, as will be seen in Part II, determinative for the fine structure of the hydrogen lines. We may, however, neglect these terms in the following since, for the purpose of the present paper, it will only be necessary to calculate the values of the coefficients  $C$  in (21) to the first approximation, *i. e.* with neglect of quantities containing  $1/c^2$  and higher powers of  $1/c^2$ .

Introducing the above values for  $a_1$  and  $a_2$  in (22) we find in this way for  $S$  the expression

$$2\pi S = 2\pi \int_{\varphi}^{\varphi} \frac{\partial S}{\partial r} dr + 2\pi \int_{\varphi}^{\varphi} \frac{\partial S}{\partial \varphi} d\varphi = \int_{r}^{r} \frac{dr}{r} \sqrt{-I_2^2 + \frac{2r}{x} - \frac{r^2}{x^2 I_2^2}} + I_2 \varphi, \quad (25)$$

where we have introduced the abbreviations

$$x = \frac{1}{4\pi^2 N e^2 m}, \quad I = I_1 + I_2. \quad (26)$$

It is easily shown that  $xI^2$  will be equal to the half major axis of the orbit described by the electron.

According to (8) the angle variables  $w_1$  and  $w_2$  will be defined by

$$\left. \begin{aligned} 2\pi w_1 &= 2\pi \frac{\partial S}{\partial I_1} = \frac{1}{xI^2} \int_{r}^{r} \frac{rdr}{\sqrt{-x^2 I_2^2 I_2^2 + 2rxI^2 - r^2}}, \\ 2\pi(w_2 - w_1) &= 2\pi \left( \frac{\partial S}{\partial I_2} - \frac{\partial S}{\partial I_1} \right) = -xII_2 \int_{r}^{r} \frac{dr}{r \sqrt{-x^2 I_2^2 I_2^2 + 2rxI^2 - r^2}} + \varphi. \end{aligned} \right\} (27)$$

Introducing now the abbreviations

$$\varepsilon' = \frac{I_2}{I}, \quad \varepsilon = \sqrt{1 - \varepsilon'^2}, \quad (28)$$

where  $\varepsilon$  may be simply shown to be equal to the eccentricity of the orbit, and introducing (compare (19)) a new variable  $\psi$  by means of

$$r = xI^2(1 + \varepsilon \cos \psi), \quad (29)$$

it is easily seen that



$$\frac{dr}{\sqrt{-x^2 I^2 I_3^2 + 2rx I^2 - r^2}} = d\psi,$$

so that the equations (27) may be written in the simple form

$$\left. \begin{aligned} 2\pi w_1 &= \int_0^\psi (1 + \varepsilon \cos \phi) d\phi = \psi + \varepsilon \sin \phi + \pi, \\ 2\pi(w_2 - w_1) &= -\varepsilon' \int_0^\psi \frac{d\phi}{1 + \varepsilon \cos \phi} + \varphi = i \log \frac{\varepsilon + i\varepsilon' \sin \phi + \cos \phi}{1 + \varepsilon \cos \phi} + \varphi. \end{aligned} \right\} (30)$$

According to the definition of angle variables, an arbitrary constant may be added to the values of  $w_1$  and  $w_2$ . In the present case the additional term  $\pi$  is written on the right side of the first of the above equations in order to obtain a final formula which is as simple as possible.

In order to obtain now the coefficients  $C_{\tau_1, \tau_2}$  in the expansion (21), we might proceed by directly applying (14), but the calculation can be made shorter by observing that the mechanical system under consideration possesses symmetry round the nucleus and that as a consequence of this all coefficients  $C_{\tau_1, \tau_2}$  in (21) will be equal to zero except those for which  $\tau_2 = 1^1$ ). This means that the expression  $re^{i\varphi} e^{-2\pi i w_2}$  will be a function of  $w_1$  only and may be expanded in a simple Fourier series. In fact from (29) and from the second of the equations (30) we have

$$\left. \begin{aligned} re^{i\varphi} e^{2\pi i(w_1 - w_2)} &= x I^2 (1 + \varepsilon \cos \phi) e^{i\varphi} \frac{\varepsilon + i\varepsilon' \sin \phi + \cos \phi}{1 + \varepsilon \cos \phi} e^{-i\varphi} \\ &= x I^2 (\varepsilon + i\varepsilon' \sin \phi + \cos \phi), \end{aligned} \right\} (31)$$

and this is, according to the first of the equations (30), a function of  $w_1$  only. Now the coefficients  $A_\tau$  in the series

$$\varepsilon + i\varepsilon' \sin \phi + \cos \phi = \sum A_\tau e^{2\pi i \tau w_1} \quad (32)$$

are easily obtained by evaluating, according to Fourier's theorem, the single definite integral

$$A_\tau = \int_0^1 (\varepsilon + i\varepsilon' \sin \phi + \cos \phi) e^{-2\pi i \tau w_1} dw_1,$$

which is simply changed into an integral over  $\phi$  because we have from the first of the equations (30)

$$dw_1 = (1 + \varepsilon \cos \phi) \frac{d\phi}{2\pi},$$

so that

$$A_\tau = \frac{(-1)^\tau}{2\pi} \int_0^{2\pi} (\varepsilon + i\varepsilon' \sin \phi + \cos \phi) (1 + \varepsilon \cos \phi) e^{-i\tau\phi - i\varepsilon\tau \sin \phi} d\phi. \quad (33)$$

<sup>1)</sup> See N. BOHR, loc. cit. Part I, p. 33.

The product of the first two factors of the integrand may be written as a sum of terms  $a_{-2}e^{-2i\varphi} + a_{-1}e^{-i\varphi} + a_0 + a_1e^{i\varphi} + a_2e^{2i\varphi}$ . Remembering that

$$\frac{1}{2\pi} \int_0^{2\pi} e^{-in\psi + i\rho \sin\psi} d\psi = J_n(\rho), \quad (n \text{ integer}) \quad (34)$$

where  $J_n(\rho)$  is the Bessel coefficient of argument  $\rho$  and order  $n$ , we see therefore that  $A_\tau$  may be written as a sum of Bessel coefficients of different orders and of argument  $\tau\varepsilon$ , each multiplied by a certain factor. Performing the necessary calculations and contracting terms by means of the well known formula

$$J_{n-1}(\rho) + J_{n+1}(\rho) = \frac{2n}{\rho} J_n(\rho), \quad (35)$$

we finally get the result

$$A_\tau = -\frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\}. \quad (36)$$

This expression becomes undetermined for  $\tau = 0$ . By introducing, however, this value for  $\tau$  directly in (33) we get  $A_0 = \frac{3}{2}\varepsilon$ . For the expansion of  $x + iy$  in a trigonometric series we therefore get from (31), (32) and (36)

$$x + iy = \frac{3}{2} \varepsilon x I^2 e^{2\pi i(-w_1 + w_2)} - x I^2 \sum \frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} e^{2\pi i(\tau-1)w_1 + w_2}, \quad (37)$$

where the summation is to be extended over all positive and negative entire values of  $\tau$  except  $\tau = 0$ , and where the factor  $xI^2$ , as mentioned, is equal to the half major axis of the orbit of the electron.

The values of the coefficients are, as mentioned above, calculated with neglect of small terms containing the square and higher powers of  $1/c$ ; it will, however, be observed that, also if these terms were taken into account, there would in the expansion for  $x + iy$  only occur terms of the form  $e^{2\pi i(\tau-1)w_1 + w_2}$ , due to the symmetry of the system.

The expressions for  $w_1$  and  $w_2$  as linear functions of the time are given by

$$w_1 = \omega_1 t + \delta_1, \quad w_2 = \omega_2 t + \delta_2, \quad (38)$$

where, according to (11),  $\omega_1 = \frac{\partial a_1}{\partial I_1}$  and  $\omega_2 = \frac{\partial a_1}{\partial I_2}$ ,  $a_1$  representing the total energy of the system as given by (24), and where  $\delta_1$  and  $\delta_2$  are constants. We thus see that the motion of the electron may be considered as a superposition of an infinite number of circular harmonic vibrations, the frequencies of which are given by the numerical values of  $\tau-1$   $\omega_1 + \omega_2$ , where  $\tau$  may assume all positive and negative entire values, and the amplitudes of which are directly given by (37).

The values of  $\omega_1$  and  $\omega_2$  differ only by small quantities of the order  $v^2/c^2$ , their difference being equal to the frequency  $\nu$  mentioned on page 10, and become equal when the relativity modifications are neglected ( $c = \infty$ ). In this case the expression (37) gives



$$x + iy = \frac{3}{2} \varepsilon x I^2 e^{2\pi i \delta} - x I^2 \Sigma \frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} e^{2\pi i(\tau\omega t + \delta)}, \quad (39)$$

where  $\omega$  is the frequency of revolution of the electron in its Keplerian orbit, and where  $\delta$  is an arbitrary constant. The last expression is easily seen to be identical with the expressions for the coordinates of a point performing a Keplerian motion, which are well known in celestial mechanics<sup>1)</sup>, and from which, as mentioned in the beginning of this section, the expression (37) could have been deduced directly.

In the preceding considerations the problem has been treated as the problem of the motion of the electron in a plane. If we, however, consider the motion of the electron in space, we have to do with a mechanical system of three degrees of freedom. This system will appear as a degenerate system, because there will occur in the trigonometric series representing the displacement of the electron in any direction in space only two fundamental frequencies, *viz.* the frequency  $\omega_1$  of the radial and the mean frequency  $\omega_2$  of the angular motion of the electron in the plane of its orbit. In the presence of a homogeneous magnetic field, however, the system will no more be degenerate, because a third fundamental frequency will occur in the motion of the electron, which no longer will remain plane. In fact, assuming that the intensity of the magnetic force is so small that we may neglect small quantities proportional to the square of this intensity, we have according to a well known theorem of LARMOR, that every possible motion in the presence of the magnetic field may be obtained by superposing on a possible motion of the system without field a slow uniform rotation round an axis through the nucleus which is parallel to the direction of the field. The frequency of this rotation will be given by

$$\nu_H = \frac{e}{4\pi mc} H, \quad (40)$$

where  $c$  is the velocity of light and  $H$  the intensity of the magnetic force. From this we see that the mean frequency of rotation of the electron round the above mentioned axis, which we will denote by  $\omega_3$ , will be equal to  $\omega_3 = \omega_2 \pm \nu_H$ , where the upper or lower sign holds according to whether the direction of the superposed rotation has the same direction as or the opposite of that of the rotation of the electron round this axis.

Let us now ask for the trigonometric series in which the displacement of the electron in different directions in space can be expanded in the presence of a magnetic field. Take the nucleus as origin of a system of rectangular Cartesian coordinates  $x, y, z$ , the  $z$ -axis of which is parallel to the direction of the magnetic field. Let the angle between the  $z$ -axis and the plane in which the electron at any moment moves be denoted by  $\vartheta$ , and let the position of the electron in this plane be described by means of rectangular coordinates  $\xi, \eta$ , the  $\eta$ -axis being perpendi-

<sup>1)</sup> See for instance CHARLIER, loc. cit. I, p. 215.



cular to the  $z$ -axis. Then the coordinates  $x, y, z$  defining the position of the electron in space will be connected with  $\xi$  and  $\eta$  by means of the formulae

$$z = \xi \cos \vartheta, \quad x + iy = (\xi \sin \vartheta + i\eta) e^{2\pi i(\omega_2 - \omega_1)t}. \quad (41)$$

Now, according to (37) and (38), the dependency on the time of the quantities  $\xi$  and  $\eta$  is expressed by

$$\xi + i\eta = \frac{3}{2} \varepsilon x I^2 e^{2\pi i(-\omega_1 + \omega_2)t} - x I^2 \sum \frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} e^{2\pi i(\overline{\tau-1}\omega_1 + \omega_2)t},$$

where the summation has to be extended over all positive and negative values of  $\tau$ , except  $\tau = 0$ , and where for simplicity we have taken the quantities  $\delta_1$  and  $\delta_2$  in (38) equal to zero, what is easily seen not to restrict the generality of the considerations. By means of this formula we get from (41), denoting  $\cos \vartheta$  by  $\mu$  and  $\sin \vartheta$  by  $\mu'$ ,

$$\left. \begin{aligned} z &= \frac{3}{2} \mu \varepsilon x I^2 e^{2\pi i(-\omega_1 + \omega_2)t} - \mu x I^2 \sum \frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} \cos 2\pi(\overline{\tau-1}\omega_1 + \omega_2)t \\ x + iy &= \frac{3}{4} (1 + \mu') \varepsilon x I^2 e^{2\pi i(-\omega_1 + \omega_2)t} - \frac{1 + \mu'}{2} x I^2 \sum \frac{1}{2\tau} \left\{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} e^{2\pi i(\overline{\tau-1}\omega_1 + \omega_2)t} \\ &- \frac{3}{4} (1 - \mu') \varepsilon x I^2 e^{2\pi i(\omega_1 - 2\omega_2 + \omega_3)t} + \frac{1 - \mu'}{2} x I^2 \sum \frac{1}{2\tau} \left\{ (1 - \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 + \varepsilon') J_{\tau+1}(\tau\varepsilon) \right\} e^{2\pi i(\overline{\tau+1}\omega_1 - 2\omega_2 + \omega_3)t}, \end{aligned} \right\} (42)$$

where again the summations are to be extended over all positive and negative entire values of  $\tau$  except  $\tau = 0$ . It is seen that the motion of the electron may be regarded as a superposition of linear harmonic vibrations parallel to the axis and of frequencies  $|\overline{\tau-1}\omega_1 + \omega_2|$ , and of circular harmonic rotations perpendicular to this axis and of frequencies  $|\overline{\tau-1}\omega_1 + \omega_3|$  and  $|\overline{\tau+1}\omega_1 - 2\omega_2 + \omega_3|$ . In the expressions, given by (42), for the amplitudes of these vibrations small quantities of the same order as  $v^2/c^2$  are neglected, just as in (37), while from the above calculation it is seen that the magnetic field, at any rate in first approximation, does not affect the values of these amplitudes.

### § 3. Hydrogen atom under the influence of a strong homogeneous electric field of force.

In this chapter we shall consider a mechanical system, consisting of an electron of charge  $-e$  and mass  $m$ , which is subject to the attraction of a nucleus of charge  $Ne$  and of infinite mass as well as to the influence of a homogeneous electric field of intensity  $F$ , assuming that the motion of the electron is governed by the laws of Newtonian mechanics. We shall assume that the force  $eF$  is small compared with the force which the nucleus exerts at any moment on the electron, and it will be our purpose to solve the equations of motion by means of trigonometric series of the type (12), in such a way that we shall neglect in the calculation of the coefficients  $C$  small quantities which are proportional to the first power



and to higher powers of  $F$ . For the system under consideration a separation of variables can be obtained if parabolic coordinates are used to describe the position of the electron in space<sup>1)</sup>. If  $x, y, z$ , are the coordinates of the electron in a system of rectangular Cartesian coordinates with the origin at the nucleus and with the  $z$ -axis parallel to the direction of the external electric force, these parabolic coordinates may be defined by

$$z = \frac{\xi - \eta}{2}, \quad x + iy = \sqrt{\xi\eta} e^{i\varphi}. \quad (43)$$

$\xi$  and  $\eta$  are two parameters defining the two paraboloids of revolution which have their common focus at the nucleus and their common axis parallel to the  $z$ -axis and which pass through the electron, while  $\varphi$  is the angular distance between the  $xz$ -plane and the plane containing the  $z$ -axis and the electron. Denoting in the usual way the differential coefficients  $\frac{dx}{dt}, \frac{d\xi}{dt}, \dots$  by  $\dot{x}, \dot{\xi}, \dots$ , the kinetic energy of the system will be given by

$$T = \frac{m}{2} (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) = \frac{m}{8} \left( \frac{\xi + \eta}{\xi} \dot{\xi}^2 + \frac{\xi + \eta}{\eta} \dot{\eta}^2 + 4\xi\eta\dot{\varphi}^2 \right),$$

so that the momenta, which are canonically conjugated to the coordinates  $\xi, \eta$  and  $\varphi$ , are given by

$$p_{\xi} = \frac{\partial T}{\partial \dot{\xi}} = \frac{m}{4} \frac{\xi + \eta}{\xi} \dot{\xi}, \quad p_{\eta} = \frac{\partial T}{\partial \dot{\eta}} = \frac{m}{4} \frac{\xi + \eta}{\eta} \dot{\eta}, \quad p_{\varphi} = \frac{\partial T}{\partial \dot{\varphi}} = m\xi\eta\dot{\varphi}.$$

Denoting the distance  $\sqrt{x^2 + y^2 + z^2}$  of the electron from the nucleus by  $r$ , the potential energy of the system will be represented by

$$P = -\frac{Ne^2}{r} + eFz = -\frac{2Ne^2}{\xi + \eta} + \frac{1}{2} e(\xi - \eta)F,$$

so that the total energy  $E$ , expressed as a function of  $p_{\xi}, p_{\eta}, p_{\varphi}, \xi, \eta, \varphi$ , which enters in the Hamiltonian equations of motions (2) of the system, will be given by

$$E = \frac{1}{2m} \left( \frac{4\xi}{\xi + \eta} p_{\xi}^2 + \frac{4\eta}{\xi + \eta} p_{\eta}^2 + \frac{1}{\xi\eta} p_{\varphi}^2 \right) - \frac{2Ne^2}{\xi + \eta} + \frac{1}{2} e(\xi - \eta)F.$$

The Hamilton-Jacobi partial differential equation will be obtained by introducing  $p_{\xi} = \frac{\partial S}{\partial \xi}, p_{\eta} = \frac{\partial S}{\partial \eta}, p_{\varphi} = \frac{\partial S}{\partial \varphi}$ , and by putting the expression for the energy thus obtained equal to a constant  $a_1$ :

$$\frac{1}{\xi + \eta} \left\{ \frac{1}{2m} \left( 4\xi \left( \frac{\partial S}{\partial \xi} \right)^2 + 4\eta \left( \frac{\partial S}{\partial \eta} \right)^2 + \left( \frac{1}{\xi} + \frac{1}{\eta} \right) \left( \frac{\partial S}{\partial \varphi} \right)^2 \right) - 2Ne^2 + \frac{1}{2} e(\xi^2 - \eta^2)F \right\} = a_1.$$

Effecting in this equation a separation of variables we find

<sup>1)</sup> P. EPSTEIN, Ann. d. Phys. L., p. 489 (1916).

$$\left. \begin{aligned} \frac{\partial S}{\partial \xi} &= \frac{1}{2\xi} \sqrt{-a_3^2 + 2(mNe^2 - a_2)\xi + 2ma_1\xi^2 - mF\xi^3}, \\ \frac{\partial S}{\partial \eta} &= \frac{1}{2\eta} \sqrt{-a_3^2 + 2(mNe^2 + a_2)\eta + 2ma_1\eta^2 + mF\eta^3}, \\ \frac{\partial S}{\partial \varphi} &= a_3, \end{aligned} \right\} \quad (44)$$

where  $a_2$  and  $a_3$  are two integration constants. According to (6) the quantities  $I_1$ ,  $I_2$  and  $I_3$  will now be given by

$$\left. \begin{aligned} I_1 &= \int \frac{d\xi}{2\xi} \sqrt{-a_3^2 + 2(mNe^2 - a_2)\xi + 2ma_1\xi^2 - mF\xi^3}, \\ I_2 &= \int \frac{d\eta}{2\eta} \sqrt{-a_3^2 + 2(mNe^2 + a_2)\eta + 2ma_1\eta^2 + mF\eta^3}, \\ I_3 &= \int_0^{2\pi} a_3' d\varphi, \end{aligned} \right\} \quad (45)$$

where in the expression for  $I_1$  and  $I_2$  the integration is to be extended twice between the roots of the integrands. Expanding after powers of  $F$ , and expressing the  $a$ 's as functions of the  $I$ 's, we find

$$\left. \begin{aligned} a_1 &= -\frac{2\pi^2 N^2 e^4 m}{(I_1 + I_2 + I_3)^2} + \frac{3F}{8\pi^2 Nem} (I_1 + I_2 + I_3)(I_1 - I_2) + \delta', \\ a_2 &= -mNe^2 \frac{I_1 - I_2}{I_1 + I_2 + I_3} + \delta'', \\ a_3 &= \frac{I_3}{2\pi}. \end{aligned} \right\} \quad (46)$$

In these formulae  $\delta'$  is a small quantity containing the second power and higher powers of  $F$ , while  $\delta''$  is a small quantity containing the first power and higher powers of  $F$ . The term in the expression for the energy  $a_1$  which is proportional to  $F$  is of large importance for the determination of the frequencies occurring in the motion of the system, but, since in the calculation of the coefficients  $C$  occurring in the trigonometric series representing the motion we shall, as mentioned, neglect small quantities proportional to  $F$  and higher powers of  $F$ , we may neglect this term, as well as the terms  $\delta'$  and  $\delta''$ . In this way we find, by introducing (46) in (44), for  $S$  expressed as a function of  $\xi$ ,  $\eta$ ,  $\varphi$ ,  $I_1$ ,  $I_2$ ,  $I_3$ ,

$$2\pi S = \frac{1}{2} \int \frac{d\xi}{\xi} \sqrt{\left(-I_3^2 + 2\frac{2I_1 + I_3}{xI} \xi - \frac{\xi^2}{x^2 I^2}\right)} + \frac{1}{2} \int \frac{d\eta}{\eta} \sqrt{\left(-I_3^2 + 2\frac{2I_2 + I_3}{xI} \eta - \frac{\eta^2}{x^2 I^2}\right)} + I_3 \varphi, \quad (47)$$

where we have introduced the abbreviations



$$z = \frac{1}{4\pi^2 N e^2 m}, \quad I = I_1 + I_2 + I_3.$$

The angle variables  $w_1$ ,  $w_2$  and  $w_3$  will now, according to (8), be defined by

$$\left. \begin{aligned} 2\pi w_1 &= 2\pi \frac{\partial S}{\partial I_1} = \frac{1}{2zI^2} \int_{\xi}^{\xi} \frac{zI(2I_2 + I_3)\xi + \xi^2}{\xi \sqrt{-z^2 I_3^2 I^2 + 2z(2I_1 + I_3)I\xi - \xi^2}} + \frac{1}{2zI^2} \int_{\eta}^{\eta} \frac{-zI(2I_2 + I_3)\eta + \eta^2}{\eta \sqrt{-z^2 I_3^2 I^2 + 2z(2I_2 + I_3)I\eta - \eta^2}}, \\ 2\pi w_2 &= 2\pi \frac{\partial S}{\partial I_2} = \frac{1}{2zI^2} \int_{\xi}^{\xi} \frac{-zI(2I_1 + I_3)\xi + \xi^2}{\xi \sqrt{-z^2 I_3^2 I^2 + 2z(2I_1 + I_3)I\xi - \xi^2}} + \frac{1}{2zI^2} \int_{\eta}^{\eta} \frac{zI(2I_1 + I_3)\eta + \eta^2}{\eta \sqrt{-z^2 I_3^2 I^2 + 2z(2I_2 + I_3)I\eta - \eta^2}}, \\ 2\pi w_3 &= 2\pi \frac{\partial S}{\partial I_3} = \frac{1}{2zI^2} \int_{\xi}^{\xi} \frac{-z^2 I_3 I^3 + zI(I_1 - I_2)\xi + \xi^2}{\xi \sqrt{-z^2 I_3^2 I^2 + 2z(2I_1 + I_3)I\xi - \xi^2}} + \frac{1}{2zI^2} \int_{\eta}^{\eta} \frac{-z^2 I_3 I^3 - zI(I_1 - I_2)\eta + \eta^2}{\eta \sqrt{-z^2 I_3^2 I^2 + 2z(2I_2 + I_3)I\eta - \eta^2}}. \end{aligned} \right\} (48)$$

Writing

$$\left. \begin{aligned} M_1 &= z(2I_1 + I_3)I, & L_1^2 &= M_1^2 - K^2 = 4z^2 I^2 I_1(I_1 + I_3), \\ K &= zI_3 I, & M_2 &= z(2I_2 + I_3)I, & L_2^2 &= M_2^2 - K^2 = 4z^2 I^2 I_2(I_2 + I_3), \end{aligned} \right\} (49)$$

and introducing (compare (19)) instead of  $\xi$  and  $\eta$  two new variables  $\phi$  and  $\chi$  by means of the formulae

$$\xi = M_1 + L_1 \cos \phi, \quad \eta = M_2 + L_2 \cos \chi, \quad (50)$$

it is easily seen that

$$\frac{d\xi}{\sqrt{-z^2 I_3^2 I^2 + 2z(2I_1 + I_3)I\xi - \xi^2}} = d\phi, \quad \frac{d\eta}{\sqrt{-z^2 I_3^2 I^2 + 2z(2I_2 + I_3)I\eta - \eta^2}} = d\chi,$$

and that the equations (48) may be written in the form

$$\left. \begin{aligned} 2\pi w_1 &= \frac{1}{2zI^2} (L_1 \sin \phi + L_2 \sin \chi) + \phi + \pi, & (a) \\ 2\pi w_2 &= \frac{1}{2zI^2} (L_1 \sin \phi + L_2 \sin \chi) + \chi + \pi, & (b) \end{aligned} \right\} (51)$$

$$2\pi w_3 = \frac{1}{2zI^2} (L_1 \sin \phi + L_2 \sin \chi) + \frac{\phi + \chi}{2} - \frac{K}{2} \left( \int_{\phi}^{\phi} \frac{d\phi}{M_1 + L_1 \cos \phi} + \int_{\chi}^{\chi} \frac{d\chi}{M_2 + L_2 \cos \chi} \right) + \varphi + \pi. \quad (c)$$

Introducing the notations

$$\sigma_1 = \frac{L_1}{2zI^2} = \frac{1}{I} \sqrt{I_1(I_1 + I_3)}, \quad \sigma_2 = \frac{L_2}{2zI^2} = \frac{1}{I} \sqrt{I_2(I_2 + I_3)},$$

the equations (51) (a) and (b) become

$$2\pi w_1 = \sigma_1 \sin \phi + \sigma_2 \sin \chi + \phi + \pi, \quad (52)$$

$$2\pi w_2 = \sigma_1 \sin \phi + \sigma_2 \sin \chi + \chi + \pi. \quad (53)$$

These equations show that  $\phi$  and  $\chi$ , and consequently  $\xi$  and  $\eta$ , are functions of  $w_1$  and  $w_2$  only. From this it follows that the displacement  $z = \frac{\xi - \eta}{2}$  of the electron in the direction of the  $z$ -axis may be expanded in a doubly infinite series of the form

$$z = \frac{\xi - \eta}{2} = \sum A_{\tau_1, \tau_2} e^{2\pi i(\tau_1 w_1 + \tau_2 w_2)}, \quad (54)$$

where the summation is to be extended over all positive and negative entire values of  $\tau_1$  and  $\tau_2$ . According to Fourier's theorem we get for  $A_{\tau_1, \tau_2}$

$$A_{\tau_1, \tau_2} = \int_0^1 \int_0^1 \frac{\xi - \eta}{2} e^{-2\pi i(\tau_1 w_1 + \tau_2 w_2)} dw_1 dw_2. \quad (55)$$

Following the procedure given in § 1 we will now transform this integral in an integral over  $\phi$  and  $\chi$ . From (52) and (53) we get for the functional determinant of this transformation

$$\frac{\partial(w_1, w_2)}{\partial(\phi, \chi)} = \frac{1}{4\pi^2} \begin{vmatrix} \sigma_1 \cos \phi + 1 & \sigma_1 \cos \phi \\ \sigma_2 \cos \chi & \sigma_2 \cos \chi + 1 \end{vmatrix} = \frac{1}{4\pi^2} (1 + \sigma_1 \cos \phi + \sigma_2 \cos \chi). \quad (56)$$

For  $z = \frac{\xi - \eta}{2}$  we get from (50)

$$\frac{\xi - \eta}{2} = \frac{M_1 - M_2}{2} + \frac{L_1 \cos \phi - L_2 \cos \chi}{2} = xI(I_1 - I_2) + xI^2(\sigma_1 \cos \phi - \sigma_2 \cos \chi).$$

Hence, if both  $\tau_1$  and  $\tau_2$  are different from zero, the integral (55) assumes the form

$$A_{\tau_1, \tau_2} = \frac{xI^2(-1)^\tau}{4\pi^2} \int_0^{2\pi} \int_0^{2\pi} (\sigma_1 \cos \phi - \sigma_2 \cos \chi)(1 + \sigma_1 \cos \phi + \sigma_2 \cos \chi) e^{-i\tau_1 \phi - i\tau_2 \chi} e^{-i\tau \sigma_1 \sin \phi - i\tau \sigma_2 \sin \chi} d\phi d\chi, \quad (57)$$

where

$$\tau = \tau_1 + \tau_2.$$

The expression (57) is equal to the sum of six terms each consisting of the product of two definite integrals of the type

$$\text{constant} \times \frac{1}{2\pi} \int_0^{2\pi} (\cos \phi)^p e^{-i\tau_1 \phi - i\tau \sigma_1 \sin \phi} d\phi, \quad (58)$$

where  $p$  is equal to 0, 1 or 2. This integral will be seen to be equal to a sum of Bessel coefficients of argument  $\tau \sigma_1$  and of different orders, each multiplied by a factor. Performing the necessary calculations, making use of (34), and contracting terms by means of (35) and of

$$\frac{1}{2}(J_{n-1}(\rho) - J_{n+1}(\rho)) = \frac{d}{d\rho} J_n(\rho) = J'_n(\rho),$$

we get the final result



$$A_{\tau_1, \tau_2} = \frac{z I^2}{\tau} (\sigma_2 J_{\tau_1}(\tau \sigma_1) J'_{\tau_2}(\tau \sigma_2) - \sigma_1 J'_{\tau_1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2)). \quad (59)$$

As regards the term  $A_{0,0}$  in the expansion (54) for  $z$ , we have obviously

$$\begin{aligned} A_{00} &= z I(I_1 - I_2) + \frac{z I^2}{4\pi^2} \int_0^{2\pi} \int_0^{2\pi} (\sigma_1 \cos \psi - \sigma_2 \cos \chi) (1 + \sigma_1 \cos \psi + \sigma_2 \cos \chi) d\psi d\chi \\ &= z I(I_1 - I_2) + z I^2 \left( \frac{\sigma_1^2}{2} - \frac{\sigma_2^2}{2} \right) = \frac{3}{2} z I(I_1 - I_2). \end{aligned}$$

The expansion for  $z$  in a trigonometric series therefore assumes the form

$$z = \frac{3}{2} z I(I_1 - I_2) + z I^2 \sum_{\tau} \frac{1}{\tau} \left\{ \sigma_2 J_{\tau_1}(\tau \sigma_1) J'_{\tau_2}(\tau \sigma_2) - \sigma_1 J'_{\tau_1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2) \right\} e^{2\pi i(\tau_1 w_1 + \tau_2 w_2)}, \quad (60)$$

where the summation is to be extended over all positive and negative entire values of  $\tau_1$  and  $\tau_2$ , with exception of the combination  $\tau_1 = 0, \tau_2 = 0$ . For the combinations for which  $\tau = \tau_1 + \tau_2 = 0$  the expression for the coefficients becomes undefined, but by introducing  $\tau = 0$  in (57) it is easily seen that the coefficients in question are equal to zero.

In order now to find the trigonometric series representing the displacement of the electron in the direction of the  $x$ -axis and of the  $y$ -axis, we might follow the procedure indicated in § 1, but the calculations may be made shorter, just as in § 2, if we observe that the  $z$ -axis is an axis of symmetry of the system, as a consequence of which the expansion for  $x + iy$  will only contain terms of the type  $Ce^{2\pi i(\tau_1 w_1 + \tau_2 w_2 + w_3)}$ . In fact, if we note that

$$\begin{aligned} K \int_0^{\psi} \frac{d\psi}{M_1 + L_1 \cos \psi} &= -i \log \frac{\left\{ (M_1 + L_1) \cos \frac{\psi}{2} + iK \sin \frac{\psi}{2} \right\}^2}{(M_1 + L_1) (M_1 + L_1 \cos \psi)} \\ K \int_0^{\chi} \frac{d\chi}{M_2 + L_2 \cos \chi} &= -i \log \frac{\left\{ (M_2 + L_2) \cos \frac{\chi}{2} + iK \sin \frac{\chi}{2} \right\}^2}{(M_2 + L_2) (M_2 + L_2 \cos \chi)}, \end{aligned}$$

the equations (51) (b) and (c) give

$$2\pi(w_2 - w_3) = -\frac{\psi}{2} + \frac{\chi}{2} - \varphi - \frac{i}{2} \log \frac{\left\{ (M_1 + L_1) \cos \frac{\psi}{2} + iK \sin \frac{\psi}{2} \right\}^2 \left\{ (M_2 + L_2) \cos \frac{\chi}{2} + iK \sin \frac{\chi}{2} \right\}^2}{(M_1 + L_1) (M_2 + L_2) (M_1 + L_1 \cos \psi) (M_2 + L_2 \cos \chi)}$$

so that, making use of (43), we have

$$\begin{aligned} (x + iy) e^{2\pi i(w_2 - w_3)} &= \sqrt{\xi \gamma} e^{i\varphi + 2\pi i(w_2 - w_3)} \\ &= e^{i\left(-\frac{\psi}{2} + \frac{\chi}{2}\right)} \frac{\left\{ (M_1 + L_1) \cos \frac{\psi}{2} + iK \sin \frac{\psi}{2} \right\} \left\{ (M_2 + L_2) \cos \frac{\chi}{2} + iK \sin \frac{\chi}{2} \right\}}{V(M_1 + L_1) (M_2 + L_2)}. \end{aligned}$$



The last expression contains only  $\psi$  and  $\chi$  and is therefore a function of  $w_1$  and  $w_2$  only, which allows of an expansion of the form

$$(x + iy)e^{2\pi i(w_2 - w_1)} = \sum B_{\tau_1, \tau_2} e^{2\pi i(\tau_1 w_1 + \overline{\tau_2 + 1} w_2)}, \quad (61)$$

where the summation is to be extended over all positive and negative entire values of  $\tau_1$  and  $\tau_2$ , and where the coefficients  $B$  according to Fourier's theorem are equal to

$$B_{\tau_1, \tau_2} = \frac{1}{\sqrt{(M_1 + L_1)(M_2 + L_2)}} \int_0^{2\pi} \int_0^{2\pi} \left\{ (M_1 + L_1) \cos \frac{\psi}{2} + iK \sin \frac{\psi}{2} \right\} \cdot \left\{ (M_2 + L_2) \cos \frac{\chi}{2} + iK \sin \frac{\chi}{2} \right\} e^{-2\pi i(\tau_1 w_1 + \overline{\tau_2 + 1} w_2)} dw_1 dw_2.$$

We will now transform this expression into an integral which is taken over  $\psi$  and  $\chi$ , making use of the expression (56) for the functional determinant of the transformation. At the same time we will introduce the abbreviations

$$t_1 = \sqrt{\frac{I_1}{I}}, \quad t_2 = \sqrt{\frac{I_2}{I}}, \quad t_{13} = \sqrt{\frac{I_1 + I_3}{I}}, \quad t_{23} = \sqrt{\frac{I_2 + I_3}{I}}, \quad t_3 = \sqrt{\frac{I_3}{I}}, \quad (62)$$

which allow us to express the quantities  $K$ ,  $M_1$ ,  $L_1$ ,  $M_2$ ,  $L_2$ ,  $\sigma_1$  and  $\sigma_2$  in the form

$$\left. \begin{aligned} K &= xI^2 t_3^2, & M_1 &= xI^2 (t_1^2 + t_{13}^2), & L_1 &= 2xI^2 t_1 t_{13}, & \sigma_1 &= t_1 t_{13}, \\ M_2 &= xI^2 (t_2^2 + t_{23}^2), & L_2 &= 2xI^2 t_2 t_{23}, & \sigma_2 &= t_2 t_{23}. \end{aligned} \right\} \quad (63)$$

In this way we get, denoting  $\tau_1 + \tau_2 + 1$  by  $\tau$ ,

$$\begin{aligned} B_{\tau_1, \tau_2} &= (-1)^\tau \frac{\sqrt{(M_1 + L_1)(M_2 + L_2)}}{4\pi^2} \int_0^{2\pi} \int_0^{2\pi} \left( \cos \frac{\psi}{2} + i \frac{K}{M_1 + L_1} \sin \frac{\psi}{2} \right) \left( \cos \frac{\chi}{2} + i \frac{K}{M_2 + L_2} \sin \frac{\chi}{2} \right) \cdot \\ &\quad \cdot (1 + \sigma_1 \cos \psi + \sigma_2 \cos \chi) e^{-i(\tau_1 + 1/2)\psi - i\tau\sigma_1 \sin \psi - i(\tau_2 + 1/2)\chi - i\tau\sigma_2 \sin \chi} d\psi d\chi \\ &= (-1)^\tau \frac{xI^2}{4\pi^2} \int_0^{2\pi} \int_0^{2\pi} (t_{13} e^{i\psi/2} + t_1 e^{-i\psi/2}) (t_{23} e^{i\chi/2} + t_2 e^{-i\chi/2}) (1 + t_1 t_{13} \cos \psi + t_2 t_{23} \cos \chi) \cdot \\ &\quad \cdot e^{-i(\tau_1 + 1/2)\psi - i\tau\sigma_1 \sin \psi - i(\tau_2 + 1/2)\chi - i\tau\sigma_2 \sin \chi} d\psi d\chi. \end{aligned} \quad (64)$$

We see that the last expression becomes equal to the sum of a number of terms each consisting of the product of two integrals of the type (58), where  $p$  is equal to 0 or 1. Making use of formula (34), we may write each of these integrals as a sum of Bessel coefficients of the same argument and of different orders. By means of elementary calculations and making use of (35), we get in this way for the  $B$ 's the final expression

$$B_{\tau_1, \tau_2} = -\frac{xI^2}{\tau} \left\{ t_{13} t_{23} J_{\tau_1}(\tau\sigma_1) J_{\tau_2}(\tau\sigma_2) - t_1 t_2 J_{\tau_1+1}(\tau\sigma_1) J_{\tau_2+1}(\tau\sigma_2) \right\}. \quad (65)$$

This expression becomes indefinite for  $\tau = 0$ , but by introducing this value of  $\tau$  directly in (64), we easily find



$$B_{-1,0} = \frac{3}{2} x I^2 \iota_1 \iota_{23}, \quad B_{0,-1} = \frac{3}{2} x I^2 \iota_2 \iota_{13}, \quad (66)$$

while for all other combinations of  $\tau_1$  and  $\tau_2$  for which  $\tau = \tau_1 + \tau_2 + 1 = 0$  the coefficients become zero. From (61), (65) and (66) we see therefore that the expansion of  $x + iy$  in a trigonometric series may be written in the form

$$\left. \begin{aligned} x + iy &= \frac{3}{2} x I^2 (\iota_1 \iota_{23} e^{2\pi i(-\omega_1 + \omega_3)} + \iota_2 \iota_{13} e^{2\pi i(-\omega_2 + \omega_3)}) \\ &- x I^2 \sum \frac{1}{\tau} \left\{ \iota_{13} \iota_{23} J_{\tau_1}(\tau\sigma_1) J_{\tau_2}(\tau\sigma_2) - \iota_1 \iota_2 J_{\tau_1+1}(\tau\sigma_1) J_{\tau_2+1}(\tau\sigma_2) \right\} e^{2\pi i(\tau_1\omega_1 + \tau_2\omega_2 + \omega_3)}, \end{aligned} \right\} (67)$$

where the summation is to be extended over all positive and negative entire values of the  $\tau$ 's, with the exception of such combinations for which  $\tau = \tau_1 + \tau_2 + 1 = 0$ .

From (60) and (67) we obtain directly the expressions for  $z$  and  $x + iy$  as functions of the time by introducing for the  $w$ 's their expressions as linear functions of the time. According to (12) we have

$$w_1 = \omega_1 t + \delta_1, \quad w_2 = \omega_2 t + \delta_2, \quad w_3 = \omega_3 t + \delta_3, \quad (68)$$

where by means of the expression (46) for  $\alpha_1$  the  $\omega$ 's are, with neglect of small quantities proportional to  $F^2$ , found to be equal to

$$\left. \begin{aligned} \omega_1 &= \omega_3 + \nu_F, & \omega_2 &= \omega_3 - \nu_F, \\ \omega_3 &= \frac{4\pi^2 N^2 e^4 m}{I^3} + \frac{3F(I_1 - I_2)}{8\pi^2 N e m}, & \nu_F &= \frac{3FI}{8\pi^2 N e m}, \end{aligned} \right\} (69)$$

while  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  are constants.

Introducing (68) in (60) and (67), and taking for simplicity  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  equal to zero, we get

$$\left. \begin{aligned} z &= \frac{3}{2} x I (I_1 - I_2) + x I^2 \sum \frac{1}{\tau} \left\{ \sigma_2 J_{\tau_1}(\tau\sigma_1) J_{\tau_2}(\tau\sigma_2) - \sigma_1 J_{\tau_1}(\tau\sigma_1) J_{\tau_2}(\tau\sigma_2) \right\} e^{2\pi i(\tau_1\omega_1 + \tau_2\omega_2)t}, \\ x + iy &= \frac{3}{2} x I^2 (\iota_1 \iota_{23} e^{2\pi i(-\omega_1 + \omega_3)t} + \iota_2 \iota_{13} e^{2\pi i(-\omega_2 + \omega_3)t}) \\ &- x I^2 \sum \frac{1}{\tau} \left\{ \iota_{13} \iota_{23} J_{\tau_1}(\tau\sigma_1) J_{\tau_2}(\tau\sigma_2) - \iota_1 \iota_2 J_{\tau_1+1}(\tau\sigma_1) J_{\tau_2+1}(\tau\sigma_2) \right\} e^{2\pi i(\tau_1\omega_1 + \tau_2\omega_2 + \omega_3)t}. \end{aligned} \right\} (70)$$

It would be easy to write the series for  $z$  as a series of cosine terms with real coefficients, but the form given above is more symmetrical. The formulae show that the motion of the electron may be regarded as a superposition of an infinite number of linear harmonic vibrations parallel to the direction of the electric force with frequencies  $|\tau_1\omega_1 + \tau_2\omega_2|$ , and of an infinite number of circular harmonic rotations perpendicular to this direction and with frequencies  $|\tau_1\omega_1 + \tau_2\omega_2 + \omega_3|$ . It may once more be remembered that, in the above expressions for the amplitudes of these frequencies, small quantities proportional to  $F$  and to higher powers of  $F$  are neglected.



From (69) we see that, if we neglect small quantities proportional to  $F^2$ , there exists a homogeneous linear relation with entire coefficients of the type (13) between the  $\omega$ 's, viz.  $\omega_1 + \omega_2 - 2\omega_3 = 0$ , so that, as far as small quantities proportional to  $F$  are concerned, the mechanical system under consideration appears as degenerate (see page 8) and the motion of the electron can be represented by trigonometric series containing only two fundamental frequencies, for instance  $\omega_3$  and  $\nu_F$ . Of these two frequencies  $\omega_3$  differs only little from the frequency of revolution of the electron in a simple Keplerian ellipse corresponding to the motion for  $F = 0$  and for which the values of the  $I$ 's are the same, while  $\nu_F$ , which is a small quantity proportional to  $F$ , may be described as a small frequency which is impressed on the motion of the electron due to the perturbing influence of the external electric field.

It may be of interest to point out how it can be seen from the formulae (69) and (70) in which manner this small frequency plays a part in the deviations of the motion of the electron from a periodic Keplerian motion. First of all it will be seen that the motion of the electron differs at any moment only by small quantities proportional to  $F$  from a Keplerian ellipse with major axis  $\propto I^2$ . Further, taking mean values, over a time interval extending from  $t'$  to  $t' + 1/\omega_3$ , on both sides of the equations (70), we get, denoting the mean values of  $x$ ,  $y$  and  $z$  in this time interval by  $\xi$ ,  $\eta$ , and  $\zeta$  respectively, and neglecting small terms proportional to  $F$ ,

$$\left. \begin{aligned} \zeta &= \frac{3}{2} x I (I_1 - I_2), \\ \xi + i\eta &= \frac{3}{2} x I^2 (\iota_1 \iota_{23} e^{-2\pi i \nu_F t} + \iota_2 \iota_{13} e^{2\pi i \nu_F t}), \end{aligned} \right\} \quad (71)$$

where  $t$  denotes some moment within the mentioned time interval. Now the quantities  $\xi$ ,  $\eta$  and  $\zeta$  have a simple meaning. In fact, since the motion which the electron performs in the time interval  $t' \rightarrow t' + 1/\omega_3$  differs from the motion in a Keplerian ellipse with major axis  $\propto I^2$  only by small quantities proportional to  $F$ , the quantities  $\xi$ ,  $\eta$  and  $\zeta$  may with this approximation be said to represent the coordinates of the mean position of the electron in the Keplerian ellipse which it at any moment may be considered to describe. From symmetry it is seen that this mean position, which may be called the "electrical centre" of the orbit, lies at a point on the major axis, and a simple calculation shows that this point lies at a distance  $\frac{2}{3} \varepsilon a$  from the nucleus if  $a$  denotes the major axis and  $\varepsilon$  the eccentricity.<sup>1)</sup> The formulae (71) therefore show that the Keplerian ellipse which the electron at any moment may be considered to describe varies, under the influence of the electric field, its shape and position in such a way that its electrical centre performs an elliptical harmonic vibration in a plane perpendicular to the  $z$ -axis round the point in which this plane cuts the  $z$ -axis. The major axis and the minor axis of the ellipse which the electrical centre describes are equal to  $3xI^2(\iota_1\iota_{23} + \iota_2\iota_{13})$  and  $3xI^2|\iota_1\iota_{23} - \iota_2\iota_{13}|$  respec-

<sup>1)</sup> This result follows at once from formula (39) on page 15. Compare also N. BOHR, loc. cit. Part II, page 70.



tively, while the frequency of revolution is proportional to the intensity of the field and equal to  $v_F$ . The variation of the plane of the orbit during this motion of the electrical centre may be found by observing that the angular momentum of the electron round the  $z$ -axis will remain constant, from which it follows that the area of the projection of the orbit on the  $x$ - $y$ -plane remains constant. It is easily seen that the plane of the orbit is perpendicular to the plane through the major axis and the  $z$ -axis every time the electrical centre passes one of the apses of the ellipse which it describes. In Part II of BOHR'S paper the appearance of the small frequency  $v_F$  has been discussed from the point of view of the theory of perturbations.

For the sake of the latter applications it will be of interest to examine the special form which the equations (70) assume when one of the quantities  $I_1$  and  $I_2$  becomes equal to zero. If for instance we assume  $I_2 = 0$ , it will be seen that the fundamental frequency  $\omega_2$  does not appear at all in the motion of the electron. In fact,  $\omega_2$  denotes the mean frequency with which the electron oscillates between two paraboloids of revolution which are characterised by the roots of the integrand in the expression for  $I_2$  given by (45). For  $I_2 = 0$  these roots coincide, so that the amplitude of these oscillations has become equal to zero, which means that the frequency  $\omega_2$  is not at all present in the motion. Introducing the value  $I_2 = 0$  in the equations (70) we have, since in this case, as seen from (62),  $\sigma_2 = \iota_2 = 0$ ,  $\iota_{13} = 1$ ,  $\iota_{23} = \iota_3$ ,  $\sigma_1 = \iota_1$  and since  $J_0(0) = 1$ ,

$$\left. \begin{aligned} z &= \frac{3}{2} \alpha I I_1 - I^2 \sum \frac{2\iota_1}{\tau} J_\tau(\tau\iota_1) \cos 2\pi\tau\omega_1 t, \\ x + iy &= \frac{3}{2} \alpha I^2 \iota_1 \iota_3 e^{2\pi i(-\omega_1 + \omega_2)t} - \alpha I^2 \sum \frac{\iota_3}{\tau} J_{\tau-1}(\tau\iota_1) e^{2\pi i(\tau-1)\omega_1 + \omega_2)t}, \end{aligned} \right\} \quad (72)$$

where the summations are to be extended over all entire values of  $\tau$  except  $\tau = 0$ . The equations (71) representing the motion of the electrical centre become

$$\zeta = \frac{3}{2} \alpha I I_1, \quad \xi + i\eta = \frac{3}{2} \alpha I^2 \iota_1 \iota_3 e^{-2\pi i v_F t},$$

showing that the electrical centre will move in a circle and that the Keplerian ellipse which the electron at any moment may be considered to describe possesses a constant eccentricity equal to  $\iota_1 = \sqrt{\frac{I_1}{I}}$ . The plane of the orbit remains perpendicular to the plane through the major axis and the  $z$ -axis, while it rotates uniformly round the latter axis with frequency  $v_F$ . The projection of the orbit on the  $x$ - $y$ -plane is at any moment a circle while the cosine of the angle between the plane of the orbit and the  $z$ -axis is equal to the eccentricity  $\iota_1$ . It will be observed that in the present simple case the equations (72) could have been obtained from the expression (39) for the motion of an electron in a Keplerian ellipse by imagining the orbit placed in a position relative to the  $z$ -axis as that just described, and by giving it a uniform rotation of frequency  $v_F$  round this axis, applying the same method of calculation as that followed on page 15.



#### § 4. Hydrogen atom under the influence of a weak homogeneous electric field of force.

In this section we shall consider the mechanical problem of the motion of an electron which is subject to the attraction of a positive nucleus of infinite mass as well as to the influence of a weak homogeneous electric field of force, and which moves according to the laws of relativistic mechanics. The general case of this problem in which the intensity of the electric force may have any value so that the deviations of the motion of the electron from a simple Keplerian motion, due to the influence of the relativity modifications in the laws of mechanics, must be considered as being of the same order of magnitude as those due to the electric field will be treated in a later paper which deals with the general problem of the effect of an electric field on the fine structure of the hydrogen lines. In this section we will only consider the special case in which the electric field is so weak that its influence on the motion of the electron is small compared with the influence which is due to the relativity modifications.

Let the nucleus be situated at the origin of a system of rectangular Cartesian coordinates  $x, y, z$ , the  $z$ -axis of which is taken parallel to the direction of the electric force. The mass and charge of the electron will again be denoted by  $m$  and  $-e$  respectively and the charge of the nucleus by  $Ne$ , while the intensity of the electric field will be denoted by  $F$ . Let further  $\lambda$  be a small quantity of the same order of magnitude as the square of the ratio between the velocity of the electron and the velocity of light, and  $f$  a small quantity of the same order of magnitude as the ratio between  $eF$  and the forces which the nucleus exerts on the electron. We shall according to the above assume that  $f$  is small compared to  $\lambda$ , and it will be our purpose to solve the equations of motion retaining only small quantities of the same order as  $\lambda$  and  $f/\lambda$ , and neglecting all quantities of higher order of magnitude such as  $f, \lambda^2$  etc. in the expressions for the coordinates  $x, y, z$  of the electron as functions of the time.

Let us introduce polar coordinates  $r, \vartheta, \varphi$ , which in the well known way are connected with  $x, y, z$  by the formulae

$$z = r \cos \vartheta, \quad x + iy = r \sin \vartheta e^{i\varphi}.$$

The velocity  $v$  of the electron will then be given by  $v^2 = (dr/dt)^2 + r^2(d\vartheta/dt)^2 + r^2 \sin^2 \vartheta (d\varphi/dt)^2$ . Introducing the notation  $\gamma = (1 - v^2/c^2)^{-1/2}$ , where  $c$  is the velocity of light, the canonically conjugated momenta of  $r, \vartheta, \varphi$  are given by

$$p_r = m\gamma \frac{dr}{dt}, \quad p_\vartheta = m\gamma r^2 \frac{d\vartheta}{dt}, \quad p_\varphi = m\gamma r^2 \sin^2 \vartheta \frac{d\varphi}{dt},$$

and the equations of motion will be of the canonical form (2) where the energy  $E$ , expressed as a function of the coordinates and momenta, will be given by<sup>1)</sup>

<sup>1)</sup> Compare for instance A. SOMMERFELD, Phys. Zeitschr. XVII, p. 506 (1916). See also § 2, page 11.



$$E = mc^2 \left[ \left\{ 1 + \frac{1}{m^2 c^2} \left( p_r^2 + \frac{1}{r^2} p_\theta^2 + \frac{1}{r^2 \sin^2 \vartheta} p_\varphi^2 \right) \right\}^{1/2} - 1 \right] - \frac{Ne^2}{r} + Fer \cos \vartheta.$$

Proceeding in the same way as in § 2 and in § 3 we get for the Hamilton Jacobi partial differential equation

$$\alpha_1 = mc^2 \left[ \left\{ 1 + \frac{1}{m^2 c^2} \left( \left( \frac{\partial S}{\partial r} \right)^2 + \frac{1}{r^2} \left( \frac{\partial S}{\partial \theta} \right)^2 + \frac{1}{r^2 \sin^2 \vartheta} \left( \frac{\partial S}{\partial \varphi} \right)^2 \right) \right\}^{1/2} - 1 \right] - \frac{Ne^2}{r} + Fer \cos \vartheta, \quad (73)$$

where  $S$  denotes a function of  $r, \vartheta, \varphi$ . This equation does not allow of separation of variables, but we will solve the equations of motion by method of approximation, by solving them first for  $F = 0$  and after that considering the perturbing influence which is due to the electric force. For  $F = 0$ , however, the problem is the same as that which we have treated in § 2 with the only difference that this time we consider the motion of the electron in space, and equation (73) is seen to allow of separation of variables. In fact, we may put

$$\frac{\partial S}{\partial r} = \sqrt{F(r)}, \quad \frac{\partial S}{\partial \vartheta} = \sqrt{a_2^2 - \frac{a_3^2}{\sin^2 \vartheta}}, \quad \frac{\partial S}{\partial \varphi} = a_3, \quad (74)$$

where  $F(r)$  has the same signification as in (22). We may now introduce the quantities  $I_1, I_2, I_3$ :

$$I_1 = \int \sqrt{F(r)} dr, \quad I_2 = \int \sqrt{a_2^2 - \frac{a_3^2}{\sin^2 \vartheta}} d\vartheta, \quad I_3 = \int_0^{2\pi} a_3 d\varphi, \quad (75)$$

where in the first and in the second integral the integration is to be extended twice between the roots of the integrand. It is easily seen that  $I_3/2\pi$  is equal to the angular momentum of the electron round the  $z$ -axis, while  $(I_2 + I_3)/2\pi$  is equal to the total angular momentum round the nucleus and plays the same part as the quantity  $I_3/2\pi$  in § 2. The plane in which the motion takes place makes an angle with the  $x$ - $y$ -plane the cosine of which is equal to  $\frac{I_3}{I_2 + I_3}$ . The energy  $\alpha_1$  of the system expressed as a function of the  $I$ 's contains  $I_2$  and  $I_3$  only in the combination  $I_2 + I_3$  and is with neglect of small quantities of the same order as  $\lambda^2$  given by the expression (24) in § 2, with the only difference that  $I_2$  is replaced by  $I_2 + I_3$ . This gives

$$\alpha_1 = -\frac{2\pi^2 N^2 e^4 m}{I^2} \left( 1 + \left( \frac{\pi Ne^2}{c} \right)^2 \left( -\frac{3}{I^2} + \frac{4}{I(I_2 + I_3)} \right) \right), \quad (76)$$

where  $I$  is written as an abbreviation for  $I_1 + I_2 + I_3$ . By means of (75) also  $\alpha_2$  and  $\alpha_3$  may be expressed as functions of the  $I$ 's, so that  $\frac{\partial S}{\partial r}$ ,  $\frac{\partial S}{\partial \vartheta}$  and  $\frac{\partial S}{\partial \varphi}$  may be expressed as functions of the  $I$ 's and of  $r, \vartheta$  and  $\varphi$  respectively. Introducing the expressions thus obtained in

$$S(r, \vartheta, \varphi; I_1, I_2, I_3) = \int_0^r \frac{\partial S}{\partial r} dr + \int_0^{\vartheta} \frac{\partial S}{\partial \vartheta} d\vartheta + \int_0^{\varphi} \frac{\partial S}{\partial \varphi} d\varphi,$$



which is a complete solution of equation (73) for  $F = 0$ , we may according to § 1 calculate the variables which are canonically conjugated to  $I_1, I_2, I_3$  by means of the formulae

$$w_1 = \frac{\partial S}{\partial I_1}, \quad w_2 = \frac{\partial S}{\partial I_2}, \quad w_3 = \frac{\partial S}{\partial I_3}.$$

The coordinates and momenta of the electron considered as functions of the  $I$ 's and  $w$ 's are periodic in each of the  $w$ 's with period 1. The rectangular coordinates  $x, y, z$  of the electron may therefore be expressed by trigonometric series of the form  $\sum C_{\tau_1, \tau_2, \tau_3} e^{2\pi i(\tau_1 w_1 + \tau_2 w_2 + \tau_3 w_3)}$ , where the coefficients  $C_{\tau_1, \tau_2, \tau_3}$  depend on the  $I$ 's only and where the summation is to be extended over all positive and negative entire values of the  $\tau$ 's. The values of the  $C$ 's may be calculated by means of the general method exposed in § 1. We will, however, not enter on these calculations because they are entirely analogous to those performed in § 2 and in § 3 and because the result may be directly deduced from formula (42). They give that the trigonometric series for  $z$  and  $x + iy$  are of the form

$$\left. \begin{aligned} z &= \sum D_{\tau} \cos 2\pi(\tau - 1)w_1 + w_2, \\ x + iy &= \sum D'_{\tau} e^{2\pi i(\tau - 1)w_1 + w_2} - \sum D''_{\tau} e^{2\pi i(\tau + 1)w_1 - 2w_2 + w_3}, \end{aligned} \right\} (77)$$

where the summations are to be extended over all positive and negative entire values of  $\tau$ , and where the coefficients  $D_{\tau}, D'_{\tau}, D''_{\tau}$  with neglect of small quantities of the same order of  $\lambda$  are given by the expressions

$$\left. \begin{aligned} D_{\tau} &= -xI^2 \frac{\mu}{2\tau} \left\{ (1 + \varepsilon')J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon')J_{\tau+1}(\tau\varepsilon) \right\}, & D_0 &= \frac{3}{2}\varepsilon\mu xI^2, \\ D'_{\tau} &= -xI^2 \frac{1 + \mu'}{4\tau} \left\{ (1 + \varepsilon')J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon')J_{\tau+1}(\tau\varepsilon) \right\}, & D'_0 &= \frac{3}{4}\varepsilon(1 + \mu')xI^2, \\ D''_{\tau} &= -xI^2 \frac{1 - \mu'}{4\tau} \left\{ (1 - \varepsilon')J_{\tau-1}(\tau\varepsilon) - (1 + \varepsilon')J_{\tau+1}(\tau\varepsilon) \right\}, & D''_0 &= \frac{3}{4}\varepsilon(1 - \mu')xI^2, \end{aligned} \right\} (78)$$

where

$$\left. \begin{aligned} \varepsilon' &= \frac{I_2 + I_3}{I}, & \varepsilon &= \sqrt{1 - \varepsilon'^2}, \\ \mu' &= \frac{I_3}{I_2 + I_3}, & \mu &= \sqrt{1 - \mu'^2}, \end{aligned} \right\} (79)$$

while  $J_p(x)$  represents the value of the Bessel coefficient of argument  $x$  and of order  $p$ . The formulae (77) and (78) are actually seen to coincide with the formulae (42), deduced in connection with the problem of the influence of a small magnetic force parallel to the  $z$ -axis, if in these formulae we replace  $\omega_1 t, \omega_2 t, \omega_3 t$  by  $w_1, w_2, w_3$  respectively. A simple consideration would show that this is just what must be expected.

As long as we assume that  $F = 0$ , *i. e.* that we have to do with the system in its undisturbed state, the motion of the electron is directly given by (77) if we consider the  $I$ 's as constants and for  $w_1, w_2, w_3$  substitute their expressions as linear functions of the time by means of the formulae



$$w_k = \omega_k t + \delta_k, \quad \omega_k = \frac{dw_k}{dt} = \frac{\partial E^0}{\partial I_k}, \quad (k = 1, 2, 3) \quad (80)$$

where we have denoted by  $E^0$  the energy of the undisturbed system expressed as a function of the  $I$ 's, which is given by the expression (76) for  $a_1$ . Since this expression contains  $I_2$  and  $I_3$  only in the combination  $I_2 + I_3$ ,  $\omega_2$  will be equal to  $\omega_3$ , which means that the system is degenerate as it was already mentioned in § 2. If we assume, however, that  $F$  is no longer equal to zero the motion of the system will be perturbed; the coordinates  $x, y, z$  of the electron may still be expressed as a function of the  $I$ 's and the  $w$ 's by means of (77), but the  $I$ 's will no more be constant during the motion and the  $w$ 's will no more be linear functions of the time. The rates of variation with the time of the  $I$ 's and  $w$ 's will according to Jacobi's fundamental theorem, mentioned in § 1, be represented by a set of canonical equations

$$\frac{dI_k}{dt} = -\frac{\partial E}{\partial w_k}, \quad \frac{dw_k}{dt} = \frac{\partial E}{\partial I_k}, \quad (k = 1, 2, 3) \quad (81)$$

where  $E$  is the total energy of the perturbed system expressed as a function of the  $I$ 's and  $w$ 's. We may write  $E$  in the form

$$E = E^0 + E^1,$$

where  $E^0$  is the energy which the system would possess if the perturbing forces vanished suddenly and which, as mentioned, depends on the  $I$ 's only, being given by the expression (76) for  $a_1$ , while  $E^1$  is the so called "perturbing potential", *i. e.* that part of the potential energy of the system which is due to the perturbing force, and which corresponds to the term  $Fez \cos \vartheta$  in (73). By means of (77) we find for  $E^1$ , expressed as a function of the  $I$ 's and  $w$ 's,

$$E^1 = Fez = Fe \Sigma D_\tau \cos 2\pi(\tau - 1w_1 + w_2), \quad (82)$$

where the quantities  $D_\tau$  with neglect of small quantities of the order  $\lambda$  are given by (78).

Owing to the fact that the trigonometric series for  $E^1$  does not contain a term which is independent of the  $w$ 's, we may simply proceed in the calculation of the perturbations in the following way<sup>1)</sup>, by putting

$$I_k = I_k^0 + I_k^1, \quad w_k = w_k^0 + w_k^1, \quad (k = 1, 2, 3) \quad (83)$$

where  $I_k^0, w_k^0$  represent the solutions of the equations (81) for  $F = 0$ , and where  $I_k^1$  and  $w_k^1$  contain only small quantities proportional to  $F$  and to higher powers of  $F$ . For  $I_k^0$  and  $w_k^0$  we have

<sup>1)</sup> It may be observed that, by applying to the quantities  $I_k$  and  $w_k$  a so called infinitesimal contact transformation, the results of the following considerations contained in the formulae (85) and (86) might have been deduced in a way which, from an analytical point of view, is more elegant. Compare J. M. BURGERS, *Het atoommodel van Rutherford-Bohr* (Haarlem, 1918), where a treatment of this kind has been used in the discussion of a number of problems concerning perturbed atomic motions.



$$I_k^0 = \text{constant}, \quad w_k^0 = \omega_k t + \delta_k, \quad \omega_k = \left( \frac{\partial E^0}{\partial I_k} \right)_0, \quad (k = 1, 2, 3) \quad (84)$$

where we have denoted by  $\left( \frac{\partial E^0}{\partial I_k} \right)_0$  the value of  $\frac{\partial E^0}{\partial I_k}$ , obtained by introducing for  $I_1, I_2, I_3$  the values  $I_1^0, I_2^0, I_3^0$  respectively. In order to find the  $I^1$ 's and  $w^1$ 's let us first consider the first three of the equations (81). As  $E^0$  does not depend on the  $w$ 's they may be written in the form

$$\frac{dI_k^1}{dt} = -\frac{\partial E^1}{\partial w_k}. \quad (k = 1, 2, 3)$$

The right sides of these equations are, as seen from (82), functions of the  $I$ 's and  $w$ 's, but if in the calculation of the  $I^1$ 's we neglect second and higher powers of  $F$  we may for the  $I$ 's and  $w$ 's introduce the values for  $I_k^0$  and  $w_k^0$  given by (84), so that the differential coefficients  $\frac{dI_k^1}{dt}$  become equal to known functions of the time. Neglecting for simplicity, here as well as in the following, the constants  $\delta_k$  appearing in (84), this gives

$$\begin{aligned} \frac{dI_1^1}{dt} &= 2\pi eF \Sigma (\tau - 1) D_\tau^0 \sin 2\pi(\tau - 1)\omega_1 + \omega_2)t, \\ \frac{dI_2^1}{dt} &= 2\pi eF \Sigma D_\tau^0 \sin 2\pi(\tau - 1)\omega_1 + \omega_2)t, \\ \frac{dI_3^1}{dt} &= 0, \end{aligned}$$

where the quantities  $D_\tau^0$  denote the expressions obtained by replacing in the quantities  $D_\tau$  the  $I$ 's by the  $I^0$ 's. These equations may be directly integrated and give, if the arbitrary constants are chosen such that in the expressions for the  $I^1$ 's no constant terms appear,

$$\left. \begin{aligned} I_1^1 &= -eF \Sigma \frac{(\tau - 1) D_\tau^0}{\tau - 1\omega_1 + \omega_2} \cos 2\pi(\tau - 1)\omega_1 + \omega_2)t, \\ I_2^1 &= -eF \Sigma \frac{D_\tau^0}{\tau - 1\omega_1 + \omega_2} \cos 2\pi(\tau - 1)\omega_1 + \omega_2)t, \\ I_3^1 &= 0. \end{aligned} \right\} \quad (85)$$

Among the terms on the right side of each of these equations the term corresponding to  $\tau = 0$  is much larger than the other terms because for  $\tau = 0$  the denominator  $(\tau - 1)\omega_1 + \omega_2$  becomes equal to  $-\omega_1 + \omega_2$ , and this quantity, which will be denoted by  $\nu$ , is a small quantity of the order  $\lambda$ . In fact, from (84) and (76) we have

$$\nu = -\omega_1 + \omega_2 = -\left( \frac{\partial E^0}{\partial I_1} \right)_0 + \left( \frac{\partial E^0}{\partial I_2} \right)_0 = \frac{2\pi^2 N^2 e^4 m}{I^0{}^2} \left( \frac{\pi N e^2}{c} \right)^2 \frac{4}{I^0(I_2^0 + I_3^0)^2}. \quad (86)$$

The term in (85) corresponding to  $\tau = 0$  becomes therefore of the order  $f/\lambda$ , and we may according to what has been said in the beginning of this section neglect



the other terms in (85) which are of the order  $f$ , so that we get

$$\left. \begin{aligned} I_1^1 &= eF \frac{D_0^0}{v} \cos 2\pi(-\omega_1 + \omega_2)t \\ I_2^1 &= -eF \frac{D_0^0}{v} \cos 2\pi(-\omega_1 + \omega_2)t \\ I_3^1 &= 0. \end{aligned} \right\} \quad (87)$$

It is seen that  $I_1^1 + I_2^1 = 0$  as far as small quantities of the order  $f/\lambda$  are concerned. As a consequence of this the value of the "inner" energy  $E^0$ , which during the perturbations will perform small oscillations, will yet remain constant as far as small quantities of this order are concerned. That this must be the case might have been seen directly from general considerations. It is further easily seen by means of (85) that the amplitudes of the oscillations which  $E^0$  performs, will be small quantities of the order  $f$ , but that the total energy  $E = E^0 + E^1$ , which is constant during the motion, will, as far as small quantities of the order  $f$  are concerned, depend on  $I_1^0$ ,  $I_2^0$  and  $I_3^0$  only, in a way which is exactly the same as that in which  $E^0$  depends on  $I_1$ ,  $I_2$ ,  $I_3$ , expressed by (76) if we take  $\alpha_1 = E^0$ .

We will now calculate expressions for the  $w$ 's by means of the last three of the equations (81). They give, if we neglect small quantities proportional to  $F^2$ ,

$$\frac{d(w_k^0 + w_k^1)}{dt} = \frac{\partial(E^0 + E^1)}{\partial I_k} = \frac{\partial E^0}{\partial I_k} + \frac{\partial E^1}{\partial I_k} = \left(\frac{\partial E^0}{\partial I_k}\right)_0 + \sum_r \frac{\partial^2 E^0}{\partial I_k \partial I_r} I_r^1 + \frac{\partial E^1}{\partial I_k},$$

where  $\left(\frac{\partial E^0}{\partial I_k}\right)_0$  has the same significations as in (84) and where the summation is to be extended over  $r = 1, 2, 3$ . As  $\frac{dw_k^0}{dt} = \omega_k = \left(\frac{\partial E^0}{\partial I_k}\right)_0$ , this equation gives

$$\frac{dw_k^1}{dt} = \sum_r \frac{\partial^2 E^0}{\partial I_k \partial I_r} I_r^1 + \frac{\partial E^1}{\partial I_k}. \quad (k = 1, 2, 3)$$

It is seen that the terms on the right side are functions of the  $I$ 's and the  $w$ 's, which may be written as trigonometric series all terms of which contain the factor  $F$ . In these series we may again replace the  $I$ 's and  $w$ 's by the  $I^0$ 's and  $w^0$ 's, given by (84) as functions of the time, and with reference to the corresponding calculation for the  $I^1$ 's it is only necessary to keep the periodic terms of frequency  $-\omega_1 + \omega_2 = 0$ . This gives, making use of the fact that  $I_1^1 + I_2^1$  as given by (87) is equal to zero,

$$\begin{aligned} \frac{dw_k^1}{dt} &= \sum_r \frac{\partial \omega_r}{\partial I_k^0} I_r^1 + eF \sum \frac{\partial D_r^0}{\partial I_k^0} \cos 2\pi(\tau - 1\omega_1 + \omega_2)t \\ &= \frac{\partial(\omega_1 - \omega_2)}{\partial I_k^0} I_1^1 + eF \frac{\partial D_0^0}{\partial I_k^0} \cos 2\pi(-\omega_1 + \omega_2)t \\ &= eF \left( -\frac{\partial v}{\partial I_k^0} \frac{D_0^0}{v} + \frac{\partial D_0^0}{\partial I_k^0} \right) \cos 2\pi(-\omega_1 + \omega_2)t = eF v \frac{\partial}{\partial I_k^0} \left( \frac{D_0^0}{v} \right) \cos 2\pi(-\omega_1 + \omega_2)t. \end{aligned}$$

Integrating and choosing the integration constants such that the  $w^1$ 's do not contain constant terms, we get



$$w_k^1 = \frac{eF}{2\pi} \frac{\partial}{\partial I_k^0} \left( \frac{D_0^0}{v} \right) \sin 2\pi(-\omega_1 + \omega_2)t. \quad (k = 1, 2, 3) \quad (88)$$

The frequency  $v$  given by (86) is easily seen to represent the frequency of the slow rotation of the Keplerian orbit which the electron at any moment may be considered to describe (compare page 10). The appearance of this small frequency  $v$  in the denominators in the expressions on the right side of (87) and (88) may physically be interpreted by observing that the deviation of the undisturbed orbit from a periodic orbit, which is characterised by this frequency, is small, so that even a small external force is sufficient to produce large changes in the character of these deviations.

In order to find now for the perturbed motion the expressions for the coordinates  $x$ ,  $y$ ,  $z$  of the electron as a function of the time, with the approximation mentioned on page 26, we shall put

$$x = x^0 + x^1, \quad y = y^0 + y^1, \quad z = z^0 + z^1, \quad (89)$$

where  $x^0$ ,  $y^0$  and  $z^0$  represent the values of these functions for  $F = 0$ , while  $x^1$ ,  $y^1$  and  $z^1$  are small quantities of the order  $f/\lambda$ . From (77) and (84) we find for  $x^0$ ,  $y^0$  and  $z^0$

$$\left. \begin{aligned} z^0 &= \Sigma D_\tau^0 \cos 2\pi(\tau - 1\omega_1 + \omega_2)t, \\ x^0 + iy^0 &= \Sigma D_\tau^0 e^{2\pi i(\tau - 1\omega_1 + \omega_2)t} + \Sigma D_\tau^{0'} e^{2\pi i(\tau + 1\omega_1 - 2\omega_2 + \omega_3)t}. \end{aligned} \right\} \quad (90)$$

The quantities  $x^1$ ,  $y^1$  and  $z^1$  will be given by

$$\left. \begin{aligned} z^1 &= \sum_k \left( \frac{\partial z}{\partial I_k} \right)_0 I_k^1 + \sum_k \left( \frac{\partial z}{\partial w_k} \right)_0 w_k^1, \\ x^1 + iy^1 &= \sum_k \left( \frac{\partial(x+iy)}{\partial I_k} \right)_0 I_k^1 + \sum_k \left( \frac{\partial(x+iy)}{\partial w_k} \right)_0 w_k^1, \end{aligned} \right\} \quad (91)$$

where the summations are to be extended over  $k = 1, 2, 3$  and where the  $I^1$ 's and  $w^1$ 's are the functions of  $t$  given by (87) and (88), while the quantities  $\left( \frac{\partial z}{\partial I_k} \right)_0$ ,  $\left( \frac{\partial z}{\partial w_k} \right)_0$ ,  $\left( \frac{\partial(x+iy)}{\partial I_k} \right)_0$ ,  $\left( \frac{\partial(x+iy)}{\partial w_k} \right)_0$  are functions of  $t$  obtained by first differentiating the expressions for  $z$  and  $x+iy$  given by (77), and by replacing in the expressions thus obtained the  $I$ 's by the constants  $I_k^0$  and the  $w$ 's by  $w_k^0 = \omega_k t$ .

It is seen from (91) that for  $z^1$  and  $x^1 + iy^1$  we obtain expressions in the form of trigonometric series. While in the series for  $z^0$  the frequencies corresponding to the single terms were of the form  $|\tau - 1\omega_1 + \omega_2|$  they will for  $z^1$  be of the form  $(\tau - 1\omega_1 + \omega_2) \pm (-\omega_1 + \omega_2)$ , so that there appear, owing to the perturbing force, new frequencies in the motion of the electron parallel to the direction of the electric force, the amplitudes of which are of the order  $f/\lambda$ , and the frequencies of which are of the form  $a\omega_1$ ,  $a - 2\omega_1 + 2\omega_2$  and  $a + 2\omega_1 - 2\omega_2$ , where  $a$  is a positive integer. As regards the motion perpendicular to the direction of the perturbing field, we see that, while  $x^0 + iy^0$  contained only terms of frequencies  $|\tau - 1\omega_1 + \omega_3|$  and  $|\tau + 1\omega_1 - 2\omega_2 + \omega_3|$ ,  $x^1 + iy^1$  contains terms of frequencies  $|\tau - 1\omega_1 + \omega_3|$



$\pm(-\omega_1 + \omega_2)$  and  $|(\tau + 1)\omega_1 - 2\omega_2 + \omega_3| \pm (-\omega_1 + \omega_2)$ , so that in this motion there appear new frequencies of the form  $\overline{a-2}\omega_1 + \omega_2 + \omega_3$ ,  $\overline{a+2}\omega_1 - \omega_2 - \omega_3$ ,  $a\omega_1 - \omega_2 + \omega_3$ ,  $a\omega_1 + \omega_2 - \omega_3$ ,  $\overline{a+2}\omega_1 - 3\omega_1 + \omega_3$  and  $\overline{a-2}\omega_1 + 3\omega_2 - \omega_3$ , where  $a$  is again a positive integer. Since the quantities  $\omega_2$  and  $\omega_3$  appearing in the calculations do not differ from each other as far as small quantities proportional to  $F$  are concerned, we see that the motion of the perturbed system under consideration with the approximation in question may still be represented as a sum of harmonic vibrations the frequencies of which are built up of only two fundamental frequencies  $\omega_1$  and  $\omega_2$ . In the undisturbed system appeared only frequencies  $\overline{a-1}\omega_1 + \omega_2$ ,  $\overline{a+1}\omega_1 - \omega_2$ ; in the perturbed system appear the new frequencies  $\overline{a-2}\omega_1 + 2\omega_2$ ,  $a\omega_1$ ,  $\overline{a+2}\omega_1 - 2\omega_2$ . The new frequencies are seen to be equal to the sum or to the difference of two of the frequencies appearing in the motion of the undisturbed system, and correspond to the sum-tones and difference-tones in acoustics. [That to the first approximation only sums and differences and not other linear combinations of the original frequencies appear, lies in the circumstance that the perturbing field is homogeneous, so that its potential is a linear function of the Cartesian coordinates of the electron.<sup>1)</sup> In fact, as a consequence of this the quantities  $I_k^1$  and  $w_k^1$  appearing in (91) contain according to (81) only frequencies which appear also in the undisturbed motion of the electron. The same is the case for the quantities  $\left(\frac{\partial z}{\partial I_k}\right)_0, \dots$  in (91), so that the new frequencies in the perturbed motion can only be sums or differences of frequencies occurring in the undisturbed motion.]

Although with the approximation mentioned  $\omega_2$  and  $\omega_3$  do not differ from each other, the fact that they are not identical will nevertheless be essential for the description of the motion over a time interval of the same order as  $\lambda/r^2$  (compare note on page 79). For sake of the applications in § 7 we shall therefore keep  $\omega_2$  and  $\omega_3$  separated in the following formulæ, what, as it will be discussed more closely in the paper mentioned on page 26, will be justified on account of the special character of the system under consideration.

Let us now proceed to the explicit calculation of the trigonometric series for  $z^1$  and for  $x^1 + iy^1$ . For  $z^1$  we get from (91), (88), (87) and (77), omitting in the calculations for the sake of simplicity, here as well as in the following, the index  $(^0)$  in  $I_1^0, I_2^0, I_3^0$  and in  $D_\tau^0$ ,

$$\begin{aligned}
 z^1 = & \frac{eF}{v} \left[ \sum \left( \frac{\partial D_\tau}{\partial I_1} - \frac{\partial D_\tau}{\partial I_2} \right) D_0 \cos 2\pi(\tau - 1)\omega_1 + \omega_2)t \cos 2\pi(-\omega_1 + \omega_2)t \right. \\
 & \left. - \sum v D_\tau \left( \tau - 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) \right) \sin 2\pi(\tau - 1)\omega_1 + \omega_2)t \sin 2\pi(-\omega_1 + \omega_2)t \right] \\
 = & \frac{eF}{2v} \sum \left[ \left( \frac{\partial D_\tau}{\partial I_1} - \frac{\partial D_\tau}{\partial I_2} \right) D_0 + v D_\tau \left( \tau - 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) \right) \right] \cos 2\pi(\tau - 2)\omega_1 + 2\omega_2)t \\
 & + \frac{eF}{2v} \sum \left[ \left( \frac{\partial D_\tau}{\partial I_1} - \frac{\partial D_\tau}{\partial I_2} \right) D_0 - v D_\tau \left( \tau - 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) \right) \right] \cos 2\pi\tau\omega_1 t,
 \end{aligned} \tag{92}$$

<sup>1)</sup> Compare BOHR, loc. cit. Part I, p. 36.



where the summations are to be extended over all positive and negative entire values of  $\tau$  including zero. Now from (78) and (86) we find by means of elementary calculations, omitting, here as well as in the following, for the sake of simplicity the argument  $\tau\varepsilon$  of the Bessel coefficients,

$$\left. \begin{aligned} \frac{\partial D_\tau}{\partial I_1} - \frac{\partial D_\tau}{\partial I_2} &= xI \frac{\mu}{2\tau\varepsilon^2} \left\{ (1 + \varepsilon')(1 - \tau\varepsilon'^2) J_{\tau-1} + (1 - \varepsilon')(1 + \tau\varepsilon'^2) J_{\tau+1} \right\} \\ &\quad + xI \frac{\mu'^2}{2\tau\mu\varepsilon'} \left\{ (1 + \varepsilon') J_{\tau-1} - (1 - \varepsilon') J_{\tau+1} \right\}, \\ \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) &= \frac{3}{2} xI \mu \frac{1 + 4\varepsilon^2}{\varepsilon}, \quad \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) = \frac{3}{2} xI \frac{-\varepsilon'^2 + \mu'^2 + 2\varepsilon^2\mu^2}{\mu\varepsilon\varepsilon'}. \end{aligned} \right\} (93)$$

Introducing these values in (92) we find after some simple reductions

$$\begin{aligned} z^1 &= \frac{3eFx^2I^3}{4v} \left[ \sum \frac{\mu^2}{2\tau\varepsilon\varepsilon'} \cdot \right. \\ &\cdot \left\{ (1 + \varepsilon')((1 + \varepsilon')(3\varepsilon' - 2) - \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau-1} + (1 - \varepsilon')((1 - \varepsilon')(3\varepsilon' + 2) + \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau+1} \right\} \\ &\cdot \cos 2\pi(\tau - 2\omega_1 + 2\omega_2)t \\ &\left. + \sum \frac{\varepsilon}{2\tau\varepsilon'} \left\{ (\varepsilon'\mu^2 + (1 + \varepsilon')(2 + 5\tau\varepsilon'\mu^2)) J_{\tau-1} + (\varepsilon'\mu^2 - (1 - \varepsilon')(2 + 5\tau\varepsilon'\mu^2)) J_{\tau+1} \right\} \cos 2\pi\tau\omega_1 t \right]. \end{aligned}$$

The expressions for the coefficients become undefined for  $\tau = 0$ , but by directly introducing  $\tau = 0$  in (92) we find that the coefficient to  $\cos 2\pi(-2\omega_1 + 2\omega_2)t$  is equal to  $\frac{3\varepsilon^2\mu^2}{\varepsilon'}$ , while the constant term in the second series becomes equal to  $\frac{3(-\varepsilon^2 + \varepsilon'^2\mu^2)}{\varepsilon'}$ .

Further it will be observed that in the second series the terms corresponding to values of  $\tau$ , which are numerically equal but of opposite sign, may be taken together, so that we finally get for  $z^1$

$$\left. \begin{aligned} z^1 &= \frac{3eFx^2I^3}{4v} \left[ \frac{3\varepsilon^2\mu^2}{\varepsilon'} \cos 2\pi(-2\omega_1 + 2\omega_2)t + \sum \frac{\mu^2}{2\tau\varepsilon\varepsilon'} \cdot \right. \\ &\cdot \left\{ (1 + \varepsilon')((1 + \varepsilon')(3\varepsilon' - 2) - \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) + (1 - \varepsilon')((1 - \varepsilon')(3\varepsilon' + 2) + \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \right\} \\ &\cdot \cos 2\pi(\tau - 2\omega_1 + 2\omega_2)t \\ &\left. + \frac{3(-\varepsilon^2 + \varepsilon'^2\mu^2)}{\varepsilon'} + \sum \frac{\varepsilon}{\tau\varepsilon'} \left\{ (2 + 5\mu^2\varepsilon'^2\tau) J_{\tau-1}(\tau\varepsilon) + (-2 + 5\mu^2\varepsilon'^2\tau) J_{\tau+1}(\tau\varepsilon) \right\} \cos 2\pi\tau\omega_1 t \right], \end{aligned} \right\} (94)$$

where

$$I^0 = I_1^0 + I_2^0 + I_3^0, \quad \varepsilon' = \frac{I_2^0 + I_3^0}{I_1^0}, \quad \varepsilon = \sqrt{1 - \varepsilon'^2}, \quad \mu' = \frac{I_3^0}{I_2^0 + I_3^0}, \quad \mu = \sqrt{1 - \mu'^2},$$

and where in the first series the summation is to be extended over all positive and negative entire values of  $\tau$  except  $\tau = 0$ , and in the second series only over all positive entire values of  $\tau$  except  $\tau = 0$ .

By a calculation quite analogous to that for  $z^1$  we may from (91), (88), (87) and (77) deduce similar expressions for  $x^1 + iy^1$ . Thus we find



$$\begin{aligned}
x^1 + iy^1 = & \frac{eF}{2v} \left[ \Sigma \left\{ \left( \frac{\partial D'_\tau}{\partial I_1} - \frac{\partial D'_\tau}{\partial I_2} \right) D_0 + v D'_\tau \left( \tau - 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_3} \left( \frac{D_0}{v} \right) \right) \right\} e^{2\pi i(\tau - 2\omega_1 + \omega_2 + \omega_3)t} \right. \\
& - \Sigma \left\{ \left( \frac{\partial D''_\tau}{\partial I_1} - \frac{\partial D''_\tau}{\partial I_2} \right) D_0 - v D''_\tau \left( \tau + 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) - 2 \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_3} \left( \frac{D_0}{v} \right) \right) \right\} e^{2\pi i(\tau + 2\omega_1 - 3\omega_2 + \omega_3)t} \\
& + \Sigma \left\{ \left( \frac{\partial(D'_\tau - D''_\tau)}{\partial I_1} - \frac{\partial(D'_\tau - D''_\tau)}{\partial I_2} \right) D_0 - v D'_\tau \left( \tau - 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_3} \left( \frac{D_0}{v} \right) \right) - \right. \\
& \left. - v D''_\tau \left( \tau + 1 \frac{\partial}{\partial I_1} \left( \frac{D_0}{v} \right) - 2 \frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_3} \left( \frac{D_0}{v} \right) \right) \right\} e^{2\pi i(\tau\omega_1 - \omega_2 + \omega_3)t} \left. \right] \quad (95)
\end{aligned}$$

From (78) we obtain

$$\begin{aligned}
\frac{\partial D'_\tau}{\partial I_1} - \frac{\partial D'_\tau}{\partial I_2} &= -xI \frac{1 + \mu'}{4\tau\varepsilon^2} \{ (1 + \varepsilon') (1 - \tau\varepsilon'^2) J_{\tau-1} + (1 - \varepsilon') (1 + \tau\varepsilon'^2) J_{\tau+1} \} - \\
&\quad - xI \frac{\mu'}{4\tau\varepsilon'} \{ (1 + \varepsilon') J_{\tau-1} - (1 - \varepsilon') J_{\tau+1} \}, \\
\frac{\partial D''_\tau}{\partial I_1} - \frac{\partial D''_\tau}{\partial I_2} &= xI \frac{1 - \mu'}{4\tau\varepsilon^2} \{ (1 + \varepsilon') (1 - \tau\varepsilon'^2) J_{\tau-1} + (1 + \varepsilon') (1 + \tau\varepsilon'^2) J_{\tau+1} \} + \\
&\quad + xI \frac{\mu'}{4\tau\varepsilon'} \{ (1 - \varepsilon') J_{\tau-1} - (1 + \varepsilon') J_{\tau+1} \}, \\
v \left( -\frac{\partial}{\partial I_2} \left( \frac{D_0}{v} \right) + \frac{\partial}{\partial I_3} \left( \frac{D_0}{v} \right) \right) &= -\frac{3}{2} xI \frac{\varepsilon\mu'}{\varepsilon'\mu}.
\end{aligned}$$

By means of these relations and of (93), (95) may be reduced to

$$\begin{aligned}
x^1 + iy^1 = & \frac{3eFx^2I^0{}^3}{4v} \left[ \frac{3(1 + \mu')\mu\varepsilon^2}{2\varepsilon'} e^{2\pi i(-2\omega_1 + \omega_2 + \omega_3)t} \right. \\
& + \Sigma \frac{\mu(1 + \mu')}{4\tau\varepsilon\varepsilon'} \{ (1 + \varepsilon') ((1 + \varepsilon')(3\varepsilon' - 2) - \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) \\
& + (1 - \varepsilon') ((1 - \varepsilon')(3\varepsilon' + 2) + \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \} e^{2\pi i(\tau - 2\omega_1 + \omega_2 + \omega_3)t} \\
& \quad - \frac{3(1 - \mu')\mu\varepsilon^2}{2\varepsilon'} e^{2\pi i(2\omega_1 - 3\omega_2 + \omega_3)t} \\
& - \Sigma \frac{\mu(1 - \mu')}{4\tau\varepsilon\varepsilon'} \{ (1 - \varepsilon') ((1 - \varepsilon')(3\varepsilon' + 2) - \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) \\
& + (1 + \varepsilon') ((1 + \varepsilon')(3\varepsilon' - 2) + \tau\varepsilon'(5 - 3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \} e^{2\pi i(\tau + 2\omega_1 - 3\omega_2 + \omega_3)t} \\
& \quad + 3\mu\mu'\varepsilon' e^{2\pi i(-\omega_2 + \omega_3)t} \\
& \left. + \Sigma \frac{\mu\varepsilon}{2\tau} \{ (3 + 5\tau(1 + \varepsilon'\mu')) J_{\tau-1}(\tau\varepsilon) + (3 - 5\tau(1 - \varepsilon'\mu')) J_{\tau+1}(\tau\varepsilon) \} e^{2\pi i(\tau\omega_1 - \omega_2 + \omega_3)t} \right] \quad (96)
\end{aligned}$$

where the summations are to be extended over all positive and negative entire values of  $\tau$  except  $\tau = 0$ , and where  $I^0$ ,  $\varepsilon$ ,  $\varepsilon'$ ,  $\mu$  and  $\mu'$  have the same signification as in (94).

In the special case where the undisturbed orbit is circular, *i. e.*  $\varepsilon' = 1$ ,  $\varepsilon = 0$ , the formulae (94) and (96) assume the simple form

$$\left. \begin{aligned} z^1 &= \frac{3eFz^2 I^0{}^3}{4v} (3\mu^2 - \mu^2 \cos 2\pi 2\omega_2 t), \\ x^1 + iy^1 &= \frac{3eFz^2 I^0{}^3}{4v} \left( 3\mu\mu' e^{2\pi i(-\omega_2 + \omega_3)t} - \frac{\mu(1 + \mu')}{2} e^{2\pi i(\omega_2 + \omega_3)t} + \frac{\mu(1 - \mu')}{2} e^{2\pi i(-3\omega_2 + \omega_3)t} \right). \end{aligned} \right\} (97)$$

From this it is seen that in this case the frequency  $\omega_1$ , which did not appear in the undisturbed motion, has also disappeared from the perturbed motion. Moreover we learn from (97) that the perturbed motion, with the approximation involved in this formula, takes place in a plane which rotates uniformly round the  $z$ -axis with a frequency  $(-\omega_2 + \omega_3)$ . In this plane the perturbed motion is periodic with period  $\omega_2$  and may be represented by

$$\xi + i\eta = -z I^0{}^2 e^{2\pi i\omega_2 t} + \frac{3eFz^2 I^0{}^3}{4w} \mu (3 - e^{2\pi i 2\omega_2 t}),$$

where the  $\eta$ -axis is perpendicular to the  $z$ -axis. The "centre of gravity" of the perturbed orbit is seen to be displaced, under the influence of the electric field, to a point on the  $\xi$ -axis situated at a distance  $\frac{3eFz^2 I^0{}^3}{4v} 3\mu$  from the nucleus, in a direction opposite to the direction of the component parallel to the  $\xi$ -axis of the force which the electric field exerts on the electron.

Another case in which the perturbed motion assumes a simple character is that for which the plane of the undisturbed orbit is perpendicular to the direction of the electric field ( $\mu' = 1$ ,  $\mu = 0$ ). In this case (94) and (96) assume the form

$$z^1 = \frac{3eFz^2 I^0{}^3}{4v} \left[ -\frac{3\varepsilon^2}{\varepsilon'} + \sum \frac{2\varepsilon}{\tau\varepsilon'} (J_{\tau-1}(\tau\varepsilon) - J_{\tau+1}(\tau\varepsilon)) \cos 2\pi\tau\omega_1 t \right], \quad x^1 + iy^1 = 0. \quad (98)$$

We see that the frequency  $\omega_2$  does not appear in the perturbed motion, and from a comparison of (98) and (90) we learn that this motion may be described as a Keplerian motion of frequency  $\omega_1$  in a plane which makes a small angle equal to  $\frac{3eFz I^0{}^2 \varepsilon}{4v \varepsilon'}$  with the  $x$ - $y$ -plane, and which rotates with a frequency  $-\omega_1 + \omega_3$  round the  $z$ -axis. The minor axis of the Keplerian ellipse is at any moment parallel to the  $x$ - $y$ -plane, and the direction in which the electrical centre is "pushed" out of the  $x$ - $y$ -plane coincides with the direction of the force which the perturbing



electric field exerts on the electron. In the paper mentioned in the beginning of this section where the general problem, in which the perturbations due to the electric force are not small compared to those due to the relativity modifications, will be treated, it will be possible to elucidate the meaning and importance of the simple character of the perturbations in the two special cases just described from a general point of view.

## Part II.

### Discussion of the intensities of the components of the hydrogen lines.

#### § 5. Application of the quantum theory to the problem of the intensity of spectral lines.

According to RUTHERFORD's theory of atomic structure the atom of an element consists of a number of electrons surrounding a positive nucleus, the mass of which is very large compared with that of the electrons and the charge of which is equal to  $Ne$ , where  $N$  is an integer and where  $-e$  denotes the charge of an electron. In the simple case where the atom consists of a nucleus and one electron only, *viz.* for a neutral hydrogen atom ( $N = 1$ ), a helium atom which has lost one electron ( $N = 2$ ), a lithium atom which has lost two electrons ( $N = 3$ ), etc. it has been possible to develop methods which allow us to fix the stationary states, not only when the atom is undisturbed by external influences, but also when it is exposed to the influence of constant small external forces. In special cases, where the external field is of such a character that the perturbed atom allows of separation of variables, the stationary states will, according to the theory developed by SOMMERFELD and by EPSTEIN, be given by

$$I_k = n_k h, \quad (k = 1, \dots, s) \quad (99)$$

where  $I_1, \dots, I_s$  are the quantities defined by (6), and where  $n_1, \dots, n_s$  are a set of positive integers, while  $h$  is PLANCK's constant<sup>1</sup>). For instance, in the case of a hydrogen atom (positively charged helium atom, etc.) which is exposed to a homogeneous electric field of force, the intensity of which is so large that its influence on the motion of the electron is large, compared to that which is due to the modifications in the laws of Newtonian mechanics claimed by the theory of relativity, the stationary states will be fixed by the conditions  $I_1 = n_1 h, I_2 = n_2 h, I_3 = n_3 h$ , where  $I_1, I_2, I_3$  are the quantities defined by (45) in § 3. If, however, the system is degenerate

<sup>1</sup>) Compare P. EPSTEIN, Ann. d. Phys. L., p. 489 (1916). A method which allows us to treat the problem of the stationary states of a perturbed hydrogen atom in more general cases has been developed in Part II of BOHR's often mentioned paper. This theory will, from the point of view of introduction of angle variables, be discussed in the paper mentioned in the beginning of § 4, in which it will especially be applied to the problem of the simultaneous effect of the relativity modifications and of a homogeneous electric field on the hydrogen spectrum, which problem cannot be treated by means of the method of separation of variables.



(see page 8), the number of conditions which fix the stationary states will be less than the number of degrees of freedom and equal to the number of fundamental frequencies characterising the motion, but just as in the case of a non-degenerate system these conditions will be sufficient to fix the value of the total energy of the system, which is determining for the frequencies of the spectral lines. If we, for instance, consider the undisturbed hydrogen atom in space, we have to do with a system of three degrees of freedom, the motion of which is characterised by two fundamental frequencies only. Separation of variables is possible for any set of polar coordinates with the centre at the nucleus, and three quantities  $I_1, I_2, I_3$  may be defined by the formulae (75). There will, however, only be two conditions characterising the stationary states, viz.  $I_1 = n_1 h$  and  $I_2 + I_3 = n_2 h$  (or, with the notation of § 2,  $I_1 = n_1 h, I_2 = n_2 h$ ), in intimate connection with the fact that the direction in space of the axis of the system of coordinates used for the separation is arbitrary, so that the quantities  $I_2$  and  $I_3$  themselves naturally must remain undetermined in the stationary states. A very important example of a degenerate system is further afforded by a system consisting of an electron and a nucleus, the motion of which is governed by Newtonian mechanics; this system will in the following be denoted as the model of a "simplified hydrogen atom". The motion of this system is simply periodic and its stationary states will therefore be characterised by one condition only. Separation of variables may be obtained in an infinite multitude of sets of coordinates, for instance in any set of polar coordinates and in any set of parabolic coordinates with the nucleus at the centre. In both of these cases we obtain three quantities  $I_1, I_2, I_3$ , which coincide with the analogous quantities in § 4, if we take the velocity of light  $c$  infinitely large, and with the analogous quantities in § 3, if we take the intensity of the electric force  $F$  equal to zero. The stationary states will in both cases be fixed by the single condition  $I = I_1 + I_2 + I_3 = nh$ , where  $n$  is a positive integer, in intimate connection with the fact that, due to the arbitrariness in the choice of the set of coordinates used for the separation, the values of  $I_1, I_2, I_3$  themselves must remain arbitrary in the stationary states. We therefore have directly from the formulae (24) and (46) that the energy in the stationary states of the simplified hydrogen atom is given by

$$E = -\frac{2\pi^2 N^2 e^4 m}{I^2} = -\frac{2\pi^2 N^2 e^4 m}{n^2 h^2}. \quad (100)$$

The frequency of revolution in these states will according to (11) be given by

$$\omega = \frac{\partial E}{\partial I} = \frac{4\pi^2 N^2 e^4 m}{I^3} = \frac{4\pi^2 N^2 e^4 m}{n^3 h^3}, \quad (101)$$

while the major axis of the Keplerian ellipse described by the electron may be easily shown to be equal to

$$2a = \frac{I^2}{2\pi^2 N e^2 m} = \frac{n^2 h^2}{2\pi^2 N e^2 m}. \quad (102)$$



The eccentricity of the orbit and the position of its plane in space are undetermined in the stationary states.

In the deduction of the preceding formulae, the mass of the nucleus is regarded as infinite compared with that of the electron. If we take into account that the mass of the nucleus is finite, the motion of the simplified hydrogen atom will still be periodic, the electron and the nucleus describing both a closed Keplerian orbit with their common centre of gravity at one of the foci, and separation of variables may again be obtained for any set of polar coordinates as well as for any set of parabolic coordinates with this centre of gravity at the centre. Performing the necessary calculations, it is easily found that the necessary modifications to be introduced in the above formulae on account of the finite mass of the nucleus are obtained by replacing, in the expressions for  $E$  and  $\omega$ , the quantity  $m$  by  $\frac{Mm}{M+m} = \frac{m}{1+m/M}$ , where  $M$  represents the mass of the nucleus. The expression for the major axis of the orbit of the electron remains the same, while the major axis of the orbit of the nucleus becomes equal to  $\frac{n^2 h^2}{2\pi^2 N e^2 M}$ . For the energy in the  $n^{\text{th}}$  stationary state of the simplified hydrogen atom we thus get

$$E_n = - \frac{2\pi^2 N^3 e^4 m}{n^2 h^2 (1 + m/M)}. \quad (103)$$

In the calculations in § 2, § 3 and § 4, the correction for the finite mass of the nucleus has not been taken into account, but since the motion of the electron treated in these sections shows only small deviations from the periodic Keplerian motion just considered, it is on account of the small value of  $m/M$  obviously permitted to neglect this correction in the calculation of these deviations and of their effect on the total energy in the stationary states.

From the above it is seen that the stationary states of a conditionally periodic system are fixed by a number of conditions of the type  $I_k = n_k h$ . Calling this number  $r$ , the total energy will be a function of  $n_1, \dots, n_r$ , and according to (1) the frequency  $\nu$  of the radiation emitted during a transition between two stationary states, which are characterised by  $n_1 = n'_1, \dots, n_r = n'_r$  and  $n_1 = n''_1, \dots, n_r = n''_r$ , respectively, will be given by

$$\nu = \frac{1}{h} \{ E(n'_1, \dots, n'_r) - E(n''_1, \dots, n''_r) \}. \quad (104)$$

The state of largest energy, characterised by  $n'_1, \dots, n'_r$ , will in the following be denoted as the "initial state", the state of smallest energy, characterised by  $n''_1, \dots, n''_r$ , as the "final state" of the transition in question. Formula (104) allows us to calculate all possible values for the frequencies of the spectral lines which may be emitted by the system. Thus, for the spectrum of the simplified hydrogen atom, we get from (104) for the frequency  $\nu$  of the radiation emitted during a transition from an initial state to a final state characterised by  $n'$  and  $n''$  respectively — such a transition



will in the following be indicated by the symbol  $(n' \rightarrow n'')$  —

$$\nu = KN^2 \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right), \quad K = \frac{2\pi^2 e^4 m}{h^3 (1 + m/M)}. \quad (105)$$

If we put  $N = 1$ , formula (105) represents, as shown by BOHR, to a high degree of approximation the series spectrum of hydrogen. Further, if we put  $N = 2$ , we should on the theory expect that (105) would represent the line spectrum which would be emitted by a helium atom which has lost one electron. Certain lines observed by PICKERING in stellar spectra ((7 → 4), (9 → 4), ...), and by FOWLER in a vacuum tube containing a mixture of hydrogen and helium ((4 → 3), (5 → 3), ...) were assumed by BOHR to belong to this spectrum; and the theory was subsequently supported by EVANS' observation of these lines in the spectrum of a tube filled with carefully purified helium, which did not show the ordinary lines of the Balmer series ((3 → 2), (4 → 2), ...), but which, in addition to the series observed by PICKERING and by FOWLER, showed a new series of lines lying close to the positions of the Balmer lines and which on the theory correspond to (6 → 4), (8 → 4), ...<sup>1)</sup>.

In the theories given by SOMMERFELD<sup>2)</sup> for the effect of the relativity modifications, by EPSTEIN<sup>3)</sup> and by SCHWARZSCHILD<sup>4)</sup> for the effect of a homogeneous electric field, and by SOMMERFELD<sup>5)</sup> and by DEBYE<sup>6)</sup> for the effect of a homogeneous magnetic field on the hydrogen lines, every stationary state of the simplified hydrogen atom appears, so to speak, as split up in a number of stationary states in which the values of the total energy differ only little from the values given by (103). Thus, in the case of an electric field acting on the atom, the stationary states are fixed, as mentioned above, by three entire numbers  $n_1, n_2, n_3$ , and to a stationary state of the simplified hydrogen atom characterised by a given value of  $n$  will "correspond" all stationary states of the atom, perturbed by the electric field, for which  $n_1 + n_2 + n_3$  is equal to this value. Also the three fundamental frequencies  $\omega_1, \omega_2$  and  $\omega_3$ , characterising the motion of the perturbed atom, will only differ little from the frequency of revolution  $\omega$  of the simplified hydrogen atom. The effect on the spectrum, which will be due to the influence of one of the agencies mentioned, and which may be calculated from (104), will consequently consist in the splitting up of every hydrogen line in a number of components lying very near each other. As well known, the above mentioned authors have in this way obtained results as regards the frequencies of these components, which are in convincing agreement with the experiments on the fine structure, the Stark effect and the Zeeman effect of the hydrogen lines.

<sup>1)</sup> See E. J. EVANS, *Phil. Mag.* XXIX, p. 284 (1915).

<sup>2)</sup> A. SOMMERFELD, *Ber. Akad. München*, 1915, p. 459.

<sup>3)</sup> P. EPSTEIN, *Ann. d. Phys. L.* p. 489 (1916).

<sup>4)</sup> K. SCHWARZSCHILD, *Ber. Akad. Berlin*, 1916, p. 548.

<sup>5)</sup> A. SOMMERFELD, *Phys. Zeitschr.* XVII, p. 491 (1916).

<sup>6)</sup> P. DEBYE, *Phys. Zeitschr.* XVII, p. 507 (1916).



Relation (1) allows us to determine the frequency of the radiation emitted during a transition, but gives no information as regards the intensity and polarisation of this radiation. Now the mechanism of the radiation process with which the quantum theory operates is quite unknown and must, on account of the essential discontinuity involved in relation (1), be entirely different from the radiation process in ordinary electrodynamics, which is essentially continuous. Due to this discontinuous character, it has been necessary to introduce in the quantum theory the notion of the "a-priori probability of spontaneous transition" between two stationary states of an atomic system, which was used by EINSTEIN<sup>1)</sup> in his explanation of the law of temperature radiation on the basis of the quantum theory. Imagine an atomic system in one of its stationary states, and let us for the present assume that it is uninfluenced by external radiations. Then the system must be assumed to possess a tendency within a given time interval to pass spontaneously to one of the other stationary states of the system for which the value of the total energy is smaller; in analogy with the circumstance that on ordinary electrodynamics a vibrating electron will emit radiation and loose energy independent of surrounding radiations. A measure for this a-priori probability of spontaneous transition is given by the quantity  $A'_{\nu}$ , introduced by EINSTEIN, which is defined in such a way that  $A'_{\nu} dt$  represents the probability that the atom in a stationary state characterised by one dash (') will pass spontaneously within a time interval  $dt$  to another stationary state which is characterised by two dashes (''). Besides the quantities  $A$ , EINSTEIN has introduced other quantities  $B$  which are defined in a corresponding way and which measure the probability that a transition will take place due to the presence of radiation in the surrounding space, in analogy with the circumstance that on ordinary electrodynamics a vibrating electron will emit or absorb energy due to the action of the electric and magnetic forces in the electromagnetic radiation existing in the surrounding space. These probabilities of transition due to the surrounding radiation will, however, be proportional to the density of this radiation; as a consequence of this, it is easily seen that the value of  $A'_{\nu}$  alone will be the determinative factor for a calculation of the intensity with which the corresponding spectral line will be emitted by the vacuum tube (or flame) in which the radiation is excited. In fact, in the luminescent gas (or vapour) this radiation is excited by impact of electrons, due to which one electron or several electrons are knocked out of the atom, so that the atoms in their different stationary states will not be in temperature equilibrium with the radiation present in the surrounding space; on the contrary, the density of the latter radiation will be comparatively very small, and the quantities  $B$  will not play any considerable part in the determination of the intensity of the spectrum. If  $\nu$  is the frequency of the radiation emitted during a certain transition, and  $a'$  the number of atoms present in the vacuum tube (or flame) in the initial state, the energy of the radiation of frequency  $\nu$  emitted in unit time will consequently be given by  $a' \times A'_{\nu} \times h\nu$ .

<sup>1)</sup> A. EINSTEIN, Phys. Zeitschr. XVIII, p. 121 (1917).



Although the radiation process in the quantum theory is so much unlike the radiation process in ordinary electrodynamics, it was shown by BOHR that there exists an intimate formal connection between these two theories. This connection refers in the first place to the frequencies of the radiation which on the quantum theory will be emitted by the atom and the frequencies which on the ordinary theory of electrodynamics would be emitted. Consider thus a transition between two stationary states of a non-degenerate conditionally periodic system of the type described in Part I, the initial state and final state of which are characterised by  $n_1 = n'_1, \dots, n_s = n'_s$  and  $n_1 = n''_1, \dots, n_s = n''_s$  respectively, where  $n_1, \dots, n_s$  are the integers appearing in the conditions (99), and consider the multitude of mechanically possible states of the system lying "between" the initial state and the final state, for which the quantities  $I_1, \dots, I_s$  are equal to  $I_k = \{n''_k + \lambda(n'_k - n''_k)\} h$ , ( $k = 1, \dots, s$ ), where  $\lambda$  assumes all values between 0 and 1. Then it is easily proved that the frequency  $\nu$  of the radiation emitted during the transition under consideration is equal to the mean value, taken over all states from  $\lambda = 0$  to  $\lambda = 1$ , of the frequency  $(n'_1 - n''_1)\omega_1 + \dots + (n'_s - n''_s)\omega_s$  which appears in the motion of the electron when this motion according to (12) is resolved in its constituent harmonic components. In fact, from (11) it follows that the difference in the total energy for two neighbouring mechanically possible states, characterised by  $I_1, \dots, I_s$  and  $I_1 + \delta I_1, \dots, I_s + \delta I_s$  respectively, may be expressed by the formula

$$\delta E = \omega_1 \delta I_1 + \dots + \omega_s \delta I_s, \quad (106)$$

so that we get from (1)

$$\nu = \frac{1}{h} \int_{\lambda=0}^{\lambda=1} \delta E = \frac{1}{h} \int_{\lambda=0}^{\lambda=1} (\omega_1 \delta I_1 + \dots + \omega_s \delta I_s) = \int_0^1 d\lambda \{ (n'_1 - n''_1)\omega_1 + \dots + (n'_s - n''_s)\omega_s \}. \quad (107)$$

Especially in the region of stationary states where the  $n$ 's are so large, that for small values of the numbers  $n'_k - n''_k$  the motion in the initial and in the final state differ relatively little from each other, the  $\omega$ 's may be considered as constant when  $\lambda$  varies from 0 to 1, so that the frequency  $\nu$  of the emitted radiation approaches asymptotically to the frequency  $(n'_1 - n''_1)\omega_1 + \dots + (n'_s - n''_s)\omega_s$ , present in the motion of the system.<sup>1)</sup>

From this remarkable connection in the limit of large  $n$ 's between the frequencies of the spectral lines to be expected on the quantum theory and the frequencies  $\tau_1 \omega_1 + \dots + \tau_s \omega_s$  of the harmonic vibrations in which, according to (12), the motion of a conditionally periodic system may be resolved, and which therefore according to ordinary electrodynamics would occur in the electromagnetic

<sup>1)</sup> See BOHR, loc. cit. Part I, p. 31. Compare J. M. BURGERS (Het atoommodel van Rutherford-Bohr, Haarlem, 1918), who recently has also called attention to this asymptotical relation in the region of large  $n$ 's, without entering, however, on the bearing of this relation on the problem of the intensity and polarisation of spectral lines.



radiation emitted by the atom, we may according to BOHR draw the conclusion that also the intensities and polarisations of the spectral lines emitted in the region of large  $n$ 's will asymptotically be the same as the intensities and polarisations of the corresponding lines which on ordinary electrodynamics would be emitted by the atom. This hypothesis is in agreement with the fact, that in the limit of large wave lengths PLANCK's formula for the intensity distribution in temperature radiation coincides with the formula of RAYLEIGH and JEANS, which is deduced on the basis of ordinary electrodynamics. Now the radiation energy emitted in unit time by an electron performing in a certain direction a linear harmonic motion which may be represented by  $x = C \cos 2\pi \omega t$ , where  $C$  is the amplitude and  $\omega$  the frequency of the vibration, would, according to the laws of electrodynamics, be proportional to the mean value of the square of the acceleration of the electron and would therefore be given by  $gC^2\omega^4$ , where  $g$  is a universal constant with the value of which we are not concerned here. From the above we may therefore conclude that, for a conditionally periodic system consisting of a single electron moving in a fixed field of force and the stationary states of which are determined by (99), the a-priori probability of spontaneous transition between an initial state characterised by the large integers  $n'_1, n'_2, n'_3$  and a final state characterised by  $n_1 = n'_1 - \tau_1, n_2 = n'_2 - \tau_2, n_3 = n'_3 - \tau_3$ , where  $\tau_1, \tau_2, \tau_3$  are a set of positive or negative integers which are small compared to  $n'_1, n'_2, n'_3$ , will be asymptotically given by  $gC^2\omega^4/h\omega = \frac{g}{h}C^2\omega^3$ ,

where  $\omega = \tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$  represents the frequency of the emitted radiation and  $C$  the amplitude of the harmonic vibration of this frequency occurring in the motion of the electron in the initial state or in the final state. For simplicity it has in this consideration been assumed that the vibration of frequency  $\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$  is linear, parallel to a given direction, and we may therefore further conclude that the radiation emitted during the transition in question is linearly polarised in this direction. In the cases where, on ordinary electrodynamics, the radiation of frequency  $\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$  in the states under consideration would be circular or elliptical we shall naturally conclude, that the probability of transition can be calculated in a corresponding way, and that the radiation emitted during a transition will be circularly, resp. elliptically polarised, the directions in space characterising these polarisations being the same as those characterising the corresponding harmonic vibrations in the motion of the system.

Returning now to the region of stationary states where the  $n$ 's in (99) are small numbers, we may assume, according to Bohr, that there will still exist an intimate connection between the coefficients  $C$  appearing in the trigonometric series of the type (12) by which the motion of the system may be represented and the a-priori probabilities for transitions between these states. Thus, if for the displacements of the particles in all directions in space the coefficient  $C_{\tau_1^0, \dots, \tau_s^0}$ , corresponding to the frequency  $\tau_1^0\omega_1 + \dots + \tau_s^0\omega_s$ , is



equal to zero, independent of the values of the  $I$ 's, we must expect that there will be no possibility for a transition between two stationary states for which  $n'_1 - n''_1 = \tau_1^0, \dots, n'_s - n''_s = \tau_s^0$ . If the coefficient in question is equal to zero, independent of the values of the  $I$ 's, only for the displacement of the particles in a certain given direction, we must expect that a transition for which  $n'_1 - n''_1 = \tau_1^0, \dots, n'_s - n''_s = \tau_s^0$  will give rise to a radiation polarised perpendicular to this direction. An important application of this consideration may be made to systems possessing an axis of symmetry, as for instance the systems discussed in § 3 (and in § 4). For these systems the motion of the electron may, as it is directly seen from some simple general considerations given by BOHR<sup>1</sup>), be resolved in a number of linear harmonic vibrations of frequencies  $\tau_1 \omega_1 + \tau_2 \omega_2$  parallel to the axis of symmetry, and of a number of circular harmonic rotations of frequencies  $\tau_1 \omega_1 + \tau_2 \omega_2 + \omega_3$  perpendicular to this axis. We must therefore expect that only such transitions will be possible for which  $n_3$  remains unaltered, giving rise to an emission of light polarised parallel to the axis, and such for which  $n_3$  decreases or increases by one unit, giving rise to an emission of light which is circularly polarised perpendicular to the axis. Since for the systems under consideration  $\frac{I_3}{2\pi}$  will represent the angular momentum of the electron round the axis of symmetry, we see that during transitions of the first kind this angular momentum remains unaltered, while for transitions of the second kind it decreases or increases by  $\frac{h}{2\pi}$ .<sup>2</sup>)

While these considerations in many cases allow us to draw definite conclusions as regards the polarisation with which the different lines of the spectrum of an atomic system are emitted, we meet, however, with a very difficult problem if we ask for a closer estimate of the intensity with which a spectral line, corresponding to a possible transition between two stationary states characterised by values for the  $n$ 's in (99) which are not large, is emitted. In fact, this intensity will in the first place depend on the a-priori probability  $A''$ , for the spontaneous occurrence of the transition in question. Although, of course, we must claim that the probability of spontaneous transition between two given states depends on the mechanical properties of the system and on the two sets of numbers  $n'_1, \dots, n'_s$  and  $n''_1, \dots, n''_s$  characterising these states, we cannot expect to obtain an exact expression for this probability which depends in a simple way on the amplitudes of the harmonic vibrations of frequency  $(n'_1 - n''_1)\omega_1 + \dots + (n'_s - n''_s)\omega_s$  in the motion in these states; just as it is clearly impossible to express the frequency of the emitted radiation

<sup>1</sup>) loc. cit. Part I, p. 33.

<sup>2</sup>) Compare in this connection BOHR (loc. cit. Part I, p. 34), who has pointed out that a consideration of conservation of angular momentum, which takes into account the amount of angular momentum present in the electromagnetic radiation emitted during a transition, gives a convincing support of the assumption that the angular momentum of the system round the axis cannot change by more than  $h/2\pi$ . Compare also A. RUBINOWICZ (Phys Zeitschr. XIX, p. 441, p. 465 (1918)), who by a similar consideration of conservation of angular momentum has independently arrived at some of the conclusions drawn by BOHR as regards the spectrum of atomic systems possessing an axis of symmetry.



in a simple way in terms of the values of this frequency in the two states. With reference, however, to the fact, that it is possible, as shown in the preceding, to represent the frequency  $\nu$  of the emitted radiation in a simple way as the mean value of the mentioned frequency, taken over the continuous multitude of mechanically possible states characterised by  $I_k = n_k'' + \lambda(n_k' - n_k'')$  ( $k = 1, 2 \dots s$ ) where  $\lambda$  takes all values between 0 and 1, the expectation lies at hand that it might also be possible to obtain an expression for the probability in question by comparing the emitted radiation with the intensity of the radiation emitted on ordinary electrodynamics by an electron performing a simple harmonic vibration which may be represented by

$$\xi = \bar{C} \cos 2\pi\nu t, \quad (108)$$

where  $\bar{C}$  is equal to a suitably chosen mean value of the amplitude  $C_\lambda$  of the vibration of frequency  $(n_1' - n_1'')\omega_1 + \dots + (n_s' - n_s'')\omega_s$  occurring in the motion in the different states characterised by different values for  $\lambda$ .<sup>1)</sup> The value for the probability  $A''$ , for the spontaneous occurrence of the transition in question would then be given by  $\frac{g}{h} \bar{C}^2 \nu^3$ . The exact determination of  $A''$ , however, is at present a quite unsolved problem which involves fundamental difficulties. But, even if the exact value of  $A''$  was known, a calculation of the intensities would moreover require the knowledge of the number  $a'$  of atoms which in the initial state are present in the vacuum tube; the determination of this number, which will obviously vary to a large extent with the experimental conditions (pressure, voltage, etc.), is in general a difficult problem in itself.

<sup>1)</sup> Among the possible expressions for such a mean value, an expression of the type

$$\bar{C} = e \int_0^1 \log C_\lambda d\lambda \quad (109)$$

offers itself naturally, since, with this definition of  $\bar{C}$ , the expression  $\bar{C} e^{2\pi i \nu t}$ , of which (108) forms the real part, appears directly as the logarithmic mean value of the expression

$$C_\lambda e^{2\pi i \left\{ (n_1' - n_1'')\omega_1 + \dots + (n_s' - n_s'')\omega_s \right\} t},$$

the real part of which represents the corresponding harmonic vibration which occurs in the motion of the system in the states characterised by the different values of  $\lambda$ . It follows from the well known properties of such logarithmic mean values that it makes no difference whether we take the mean values of the squares of the amplitudes or the squares of their mean values. It may moreover be remarked that in the special case where the relative intensities of the components into which a given hydrogen line is split up are asked for, — and in which, as mentioned in the text below, it is possible to obtain a direct test for a formula representing a theoretical estimate of the relative values for the a-priori probabilities of transition between the different pairs of stationary states, — the above mean value possesses the advantage that we shall obtain the same relative values for the estimate for these probabilities, whether for  $C$  we take the amplitude (or the „relative“ amplitude introduced on page 52) of the vibration itself or the „amplitude“ of the corresponding velocity, or acceleration; a point the importance of which will be understood when it is remembered how small our actual knowledge of the mechanism of radiation is. In § 8, however, it will be shown, in connection with the theory of the Zeeman effect, that mean values of the type  $\bar{C}^2$ , as defined by (109), can never represent an exact expression for the relative intensities of the components, because they do not satisfy the fundamental condition that small external forces can only produce small changes in the intensity distribution of spectral lines.



There exists, however, one case in which it seems possible on the basis of the above considerations to obtain direct information about the relative intensities with which different spectral lines are emitted, *viz.* if we consider the components in which a spectral line, emitted by an atomic system which is degenerate, is split up due to the influence of some agency on the atom. Examples are afforded by the fine structure of the hydrogen lines which is due to the influence of the relativity modifications, and by the Stark effect of the hydrogen lines which is due to the influence of an external homogeneous electric field of force on the hydrogen atom. In order to fix the ideas let us consider especially the case of the Stark effect. Under the influence of the external force a given hydrogen line ( $n' \rightarrow n''$ ) will be split up in a number of components, corresponding to transitions for which the initial states will be characterised by different combinations  $n_1 = n'_1, n_2 = n'_2, n_3 = n'_3$  ( $n'_1 + n'_2 + n'_3 = n'$ ) and the final states by corresponding combinations  $n''_1, n''_2, n''_3$  ( $n''_1 + n''_2 + n''_3 = n''$ ). Since the values of the total energy in the different initial states are approximately equal, it seems in the first place allowable to conclude that in the vacuum tube the numbers of atoms present in these states will be approximately proportional to the different a-priori probabilities of these states. In fact, this assumption presents itself naturally, in analogy with the corresponding property of a statistical distribution of a large number of atoms which is in temperature equilibrium; although of course the state of equilibrium in the luminescent vacuum tube will, as mentioned, not in general be a temperature equilibrium. As it will be seen in the following sections, the assumption in question seems to be confirmed in a general way by the observations. In the case of the Stark effect the atom forms a non-degenerate conditionally periodic system, for which the different stationary states will be a-priori equally probable (see BOHR, *loc. cit.* Part II, p. 25), and we shall consequently expect that the different initial states  $n'_1, n'_2, n'_3$  are of approximately equal occurrence in the luminous gas.

Moreover the different frequencies  $(n'_1 - n''_1)\omega_1 + \dots + (n'_3 - n''_3)\omega_3$  occurring in the motion of the electron in the different corresponding initial states, as well as in the different final states, (and also in the different states characterised by  $I_k = h\{n'_k + \lambda(n'_k - n''_k)\}$  ( $k = 1, 2, 3$ ) for a same value of  $\lambda$ ) are approximately the same, and equal to  $(n' - n'')\omega$ , so that the relative intensities with which, on ordinary electrodynamics, radiations of these frequencies would be emitted from these states are simply proportional to the squares of the amplitudes  $C$  of the harmonic vibrations of these frequencies, occurring in the motion in these states.

We are therefore led to expect that it will be possible to form an idea of the relative intensities with which the different components of the Stark effect will appear, by comparing the intensity of each component with the values of the squares of the amplitudes of the corresponding harmonic vibrations occurring in the motion of the system in the initial state and in the final state and in the mechani-



cally possible states lying "between" these states. In § 6 the values of these squares in the initial states and in the final states will be calculated on the basis of the expressions for the amplitudes deduced in § 3, and it will be shown that, simply from a consideration of these values, it is actually possible to account in main features for the intensities of the different components observed by STARK. In § 7 the same method will be applied in order to estimate the relative intensities of the fine structure components of the hydrogen lines, in which case the above consideration needs a slight modification, due to the fact that the a-priori probabilities for the different stationary states are no more equal to each other. It must, however, be emphasised already here that the method in question can only be expected to give a rather rough estimate of the relative intensities, especially when the  $n$ 's involved in the different stationary states are very small numbers. In the theory of the Stark effect we shall, for instance, meet with transitions for which the amplitudes of the corresponding frequency are equal to zero in the initial state, as well as in the final state, and where, as a matter of fact, the intensity of the corresponding component is different from zero. A closer discussion of these transitions shows, however, that the value of the amplitude of the vibration of corresponding frequency in the mechanically possible states lying "between" the initial state and the final state is different from zero for these transitions. In order to account for the finer details of the observations, we are therefore naturally induced to try to improve the estimate of the relative intensities of the components by comparing these intensities, not with the squares of the corresponding amplitudes in the initial states and final states only, but with some suitable mean value of these squares taken over the mechanical states which lie between these states, and which are characterised by the different values of  $\lambda$  between 0 and 1. Especially the logarithmic mean value of these squares, of the type defined by (109) in the note on page 46, would seem to lend itself naturally to such an attempt. A computation of these logarithmic mean values, however, would involve laborious numerical calculations and has not been given in the present paper, because we cannot expect, as mentioned in the note referred to, to obtain in this way an exact determination of the relative intensities (compare page 100) and also because, at the present state of the theory, the agreement with the observations obtained by the simpler calculations in this paper may be considered as very satisfactory.

Although we have thus met with a case where BOHR's considerations about the connection between the quantum theory and the ordinary electro-dynamical theory of radiation may be directly applied to estimate the relative intensities of spectral lines, it must be remembered that this estimate is based on the necessary continuous connection between the unknown laws governing the intensities with which spectral lines are emitted in the region where the  $n$ 's in (99) are small and the law which governs these intensities in the region of very large  $n$ 's. The estimate in question must consequently be expected to become the more uncertain the smaller the numbers  $n_1, \dots, n_s$  are which characterise the stationary states



involved in the transitions. It is therefore of great importance that, just in the case of spectral lines which are split up in components, it is possible to obtain some direct information as regards the relative intensities of these components in a way which is quite independent of the preceding considerations. In fact, a simple consideration of continuity or, as BOHR calls it, a consideration of the necessary "stability of spectral phenomena"<sup>1)</sup>, assures us at once that the intensities of the polarised components in which an unpolarised spectral line splits up under the influence of small external forces will be such, that the ensemble of all components together will show no characteristic polarisation in any direction, if small quantities proportional to the intensity of the external forces are neglected. If we consider for instance the Stark effect or the Zeeman effect of the hydrogen lines, viewed in a direction perpendicular to that of the electric or of the magnetic field, the sum of the intensities of the components polarised parallel to the field must be equal to the sum of the intensities of the components polarised perpendicular to the field. The information about the intensities given by this statement becomes more valuable the smaller the number is of the components in which the line is split up, but in general this occurs just in the cases where the  $n$ 's involved in the different transitions are small numbers and where consequently the estimate of the a-priori probabilities of spontaneous transitions, based on a consideration of the amplitudes of the harmonic vibrations in which the motion of the atom may be resolved, becomes especially uncertain.

## § 6. The Stark effect of the hydrogen lines.

In this section we will discuss in detail the estimate for the relative intensities of the components of the Stark effect of the hydrogen lines, which can be obtained from the calculations in § 3 on the basis of the considerations given in § 5, and it will be shown that it is possible to account in a convincing way for the relative intensities of the components which have been observed by STARK<sup>2)</sup> in the case of the hydrogen lines  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$ .

If the intensity of the electric field acting on the atoms is so large that the relativity modifications in the laws of mechanics governing the motion of the electron may be neglected, the hydrogen atom will form a mechanical system which allows of separation of variables in parabolic coordinates (EPSTEIN). This separation has been performed in § 3 and, as mentioned in the preceding section, the stationary states of the atom will be fixed by the three conditions

$$I_1 = n_1 h, \quad I_2 = n_2 h, \quad I_3 = n_3 h, \quad (110)$$

<sup>1)</sup> BOHR, loc. cit. Part II, p. 85.

<sup>2)</sup> J. STARK, Elektrische Spektralanalyse chemischer Atome, Leipzig, Hirzel (1914). This monograph contains a survey of STARK's investigations on the effect of an electric field on spectral lines until 1914



where  $I_1$ ,  $I_2$  and  $I_3$  are the quantities defined by (45), and where  $n_1$ ,  $n_2$  and  $n_3$  are positive integers. The different stationary states, characterised by different combinations of the  $n$ 's, will in the following be denoted by the symbol  $(n_1, n_2, n_3)$ ; they are, as mentioned, a-priori equally probable, but it must be kept in mind that, while  $n_1$  and  $n_2$  may assume the values 0, 1, 2, 3 . . . ,  $n_3$  can only assume one of the values 1, 2, 3, 4 . . . . In fact, it was pointed out by BOHR that states corresponding to  $n_3 = 0$  cannot represent possible stationary states of the atom because there is an essential singularity involved in the motion in these states<sup>1</sup>).

The value of the total energy in the stationary states will be obtained by introducing (110) in the expression (46) for the total energy of the system. The frequency  $\nu$  of the radiation emitted during a transition between an initial state  $(n'_1, n'_2, n'_3)$  and a final state  $(n''_1, n''_2, n''_3)$  — such a transition will in the following be denoted by the symbol  $(n'_1, n'_2, n'_3 \rightarrow n''_1, n''_2, n''_3)$  — will then, according to (1), be given by

$$\nu = \nu_0 + \frac{3hF}{8\pi^2 N e m} \Delta,$$

where

$$\nu_0 = \frac{2\pi^2 N^2 e^4 m}{h^3} \left( \frac{1}{n'^2} - \frac{1}{n''^2} \right), \quad \Delta = n'(n'_1 - n'_2) - n''(n''_1 - n''_2), \quad (111)$$

and where

$$n' = n'_1 + n'_2 + n'_3, \quad n'' = n''_1 + n''_2 + n''_3.$$

The expression for  $\nu_0$  coincides with formula (105) holding for the frequencies of the spectral lines emitted by the simplified hydrogen atom, when the mass of the nucleus is considered as infinite. The additional term in the expression for  $\nu$  is proportional to the intensity  $F$  of the electric force and allows us to calculate the magnitudes of the displacements from the position of the original line of the different components in which this line splits up under the influence of the electric force<sup>2</sup>). As shown by EPSTEIN and by SCHWARZSCHILD, formula (111) is in excellent agreement with the frequencies of the different components of the hydrogen lines ob-

<sup>1</sup>) BOHR, loc. cit. Part II, p. 75. In this connection it may be observed that in states for which  $n_3 = 0$  the motion of the electron would take place in a plane, and that, if the relativity modifications are neglected, the angular momentum of the electron round the nucleus would in the course of the motion become equal to zero at regular intervals and change its sign, so that in the course of time the electron would in general collide with the nucleus. On the other hand, if the relativity modifications are taken into account, the perturbing influence of these modifications would become very large and of the same order of magnitude as the influence of the electric field when the angular momentum approaches to zero. As will be shown in the paper mentioned in the beginning of § 4, the value of this angular momentum will never pass through zero and the motion of the electron would in the states in question be essentially different from that in the non-relativity case. It was pointed out by BOHR, however, that this circumstance does not, from the point of view of the quantum theory, remove the singular character of these states, which compels us to exclude them from the ensemble of possible stationary states.

<sup>2</sup>) See P. EPSTEIN, Ann. d. Phys. L., p. 489 (1916), K. SCHWARZSCHILD, Berl. Ber. p. 548 (1916). The correction for the finite mass of the nucleus in the expression for  $\nu$  will, according to what has been said in § 5 on page 40, be taken into account by simply replacing the above expression for  $\nu_0$  by that which is given in formula (105).



served by STARK. Thus the displacements of these components from the original positions of the lines are all entire multipla of the quantity  $\frac{3hF}{8\pi^2 Nem}$ , which is the same for all lines of the spectrum, and which is proportional to the intensity of the electric force. Moreover the Stark effect of the hydrogen lines was found to be symmetrical as regards the displacements as well as the intensities of the components. This agrees with the fact that to each component on one side of the position of the undisplaced line there will correspond one on the other side which is obtained by interchanging the values of  $n'_1$  and  $n'_2$ , as well as of  $n''_1$  and  $n''_2$ , and for which the value of  $\mathcal{J}$  will be numerically equal to that for the first component but of opposite sign. That two such components will also appear with the same intensity is directly explained by observing that the motion of the electron in two states of the atom for which  $I_3$  and  $I_1 + I_2$  are the same, but for which the value of  $I_1$  in the one is equal to that of  $I_2$  in the other, will be symmetrical so that the a-priori probabilities of spontaneous transition corresponding to the two components must be expected to be equal<sup>1)</sup>.

Looking apart from the symmetry of the effect, the relative intensities with which the components appear on STARK'S photographs vary in an irregular way from component to component, but are independent of the intensity of the electric force. Further, as regards the polarisation, STARK found that, when viewed in a direction perpendicular to that of the electric field, the lines show a number of components polarised parallel and a number of components polarised perpendicular to the direction of the field. When viewed in a direction parallel to the field, only the latter components appeared, with the same intensity distribution, but without showing characteristic polarisation. It was pointed out by EPSTEIN that the polarisation of the components obeys the rule, that the components which, according to (111), would correspond to transitions for which  $n'_3 - n''_3$  is an even number are polarised parallel to the direction of the field, while components, which would correspond to transitions for which  $n'_3 - n''_3$  is uneven, are polarised perpendicular to the field. On BOHR'S theory this rule receives an immediate explanation because according to this theory, as it has been discussed on page 45, only two kinds of

<sup>1)</sup> Here we have looked apart from the interesting dissymmetry in the intensities of the components of the hydrogen lines, which under certain experimental conditions appears in STARK'S observations, and which consists therein that the components on the red side of the position of the original line appear more, or less, intense than those on the blue side according as the direction of the electric field is the same as, or the opposite of, the direction of propagation of the positive rays by means of which the hydrogen lines are excited (see J. STARK, loc. cit. p. 40). This dissymmetry affords, as pointed out by BOHR (Phil. Mag. XXX, p. 404 (1915)), an interesting support for the general principles underlying the application of relation (1), because it indicates directly that the different components correspond to entirely different processes of radiation the relative occurrence of which may depend on the experimental conditions. Thus the dissymmetry in question must be ascribed to the fact that, under the mentioned conditions, the number of atoms in the vacuum tube present in a state ( $a, b, c$ ) and in a state ( $b, a, c$ ) will no more be equal to each other but will depend on the orientation of the electric field relative to the direction of the positive rays.



transitions will be possible, viz. transitions for which  $n'_3 - n''_3 = 0$  giving rise to radiation polarised parallel to the field, and transitions for which  $n'_3 - n''_3 = \pm 1$  giving rise to radiation polarised circularly in a plane perpendicular to the field.<sup>1)</sup> The components corresponding to the latter transitions will, however, appear as unpolarised when viewed parallel to the field because, due to the symmetry of the atom round the axis of the field, the numbers of the transitions, corresponding to such a component, which give rise to light polarised circularly in one direction and in the opposite direction, will in the mean be the same.

In order to discuss the intensities, we have in the following given tables for the estimate of the relative intensities of the Stark effect components of the hydrogen lines  $H_\alpha, H_\beta, H_\gamma, H_\delta$ , as it can be obtained by the method exposed in § 5.

In the *first* column the different possible transitions between two stationary states are characterised by their symbols  $(n'_1, n'_2, n'_3 \rightarrow n''_1, n''_2, n''_3)$ . On account of the symmetry of the Stark effect we have only given those transitions which give rise to components lying on one side of the undisplaced line ( $\Delta \geq 0$ ). Transitions which correspond to the same value of  $\Delta$  and which therefore contribute to the same component in the observed effect are collected by brackets. As regards the stationary states involved in these transitions we have, according to the above, assumed that no stationary states exist for which  $n_3 = 0$ . Each table is divided into two parts, the first containing the transitions for which  $n'_3 - n''_3 = 0$ , corresponding to "parallel" components, the second containing the transitions for which  $n'_3 - n''_3 = \pm 1$ , corresponding to "perpendicular" components.

The *second* column contains the value of  $\Delta = n'(n'_1 - n'_2) - n''(n''_1 - n''_2)$ , which, as seen from (111), determines the displacement of the component under consideration from the undisplaced line; the *third, fourth* and *fifth* columns contain the values of  $\tau_1 = n'_1 - n''_1, \tau_2 = n'_2 - n''_2, \tau_3 = n'_3 - n''_3$ .

The *sixth* and *seventh* columns contain the values  $R'$  and  $R''$  of the "relative amplitudes" of the harmonic vibrations of frequency  $\tau_1 \omega_1 + \tau_2 \omega_2 + \tau_3 \omega_3$ , occurring in the motion in the initial and in the final state respectively; where by relative amplitude is understood the *ratio* of the amplitude of this vibration to the half major axis of the Keplerian ellipse which the electron at any moment may be considered to describe. This half major axis remains constant during the motion and is equal to the value for  $a_n$  given by (102), i. e. equal to the quantity  $xP$  occurring in the formulae (70) and (72). The expressions for the values of the relative amplitudes of the linear vibrations parallel to the field and of the circular vibrations perpendicular to the field in a given stationary state, characterised by a certain combination of the  $n$ 's, are directly obtained by introducing (110) in the formulae (70) which represent the motion of the electron parallel and perpendicular to the direction of the field. In this way we find, denoting, as in § 2, the Bessel coefficient of order  $p$  and of argument  $\rho$  by  $J_p(\rho)$ , and its derivate with respect to  $\rho$  by  $J'_p(\rho)$ ,

<sup>1)</sup> N. BOHR, loc. cit. Part II, p. 77.



$$R(\tau_1 \omega_1 + \tau_2 \omega_2) = \frac{2}{\tau} \left\{ \begin{aligned} &\sigma_2 J_{\tau_1}(\tau \sigma_1) J'_{\tau_2}(\tau \sigma_2) - \sigma_1 J'_{\tau_1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2) \\ &= \frac{2}{\tau} \{ J_{\tau_1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2) - \sigma_2 J_{\tau_1}(\tau \sigma_1) J_{\tau_2+1}(\tau \sigma_2) - \sigma_1 J_{\tau_1-1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2) \} \end{aligned} \right\} \quad (112)$$

and

$$R(\tau_1 \omega_1 + \tau_2 \omega_2 + \omega_3) = \frac{1}{\tau} \{ \iota_{13} \iota_{23} J_{\tau_1}(\tau \sigma_1) J_{\tau_2}(\tau \sigma_2) - \iota_1 \iota_2 J_{\tau_1+1}(\tau \sigma_1) J_{\tau_2+1}(\tau \sigma_2) \} \quad (113)$$

respectively, where

$$\left. \begin{aligned} \sigma_1 &= \frac{1}{n} \sqrt{n_1(n_1 + n_3)}, & \sigma_2 &= \frac{1}{n} \sqrt{n_2(n_2 + n_3)}, & n &= n_1 + n_2 + n_3, \\ \iota_1 &= \sqrt{\frac{n_1}{n}}, & \iota_2 &= \sqrt{\frac{n_2}{n}}, & \tau &= \tau_1 + \tau_2 + \tau_3. \\ \iota_{13} &= \sqrt{\frac{n_1 + n_3}{n}}, & \iota_{23} &= \sqrt{\frac{n_2 + n_3}{n}}, & & \end{aligned} \right\} \quad (114)$$

If one of the quantities  $n_1$  and  $n_2$ , say  $n_2$ , becomes equal to zero the expressions for the amplitudes become much simpler. The character of the motion in the corresponding states of the atom has been considered in detail in § 3 on page 25, where it was seen that the motion of the electron in these states may be resolved in a number of linear vibrations of frequencies  $\tau_1 \omega_1$  parallel to the field and a number of circular harmonic rotations of frequencies  $\tau_1 \omega_1 + \omega_3$  perpendicular to the field, so that the amplitudes will be equal to zero unless  $\tau_2 = 0$ . For the expressions for the relative amplitudes of the vibrations of frequencies  $\tau_1 \omega_1$  and  $\tau_1 \omega_1 + \omega_3$ , we find from (72) and (110)

$$R(\tau_1 \omega_1) = \frac{2}{\tau} \iota_1 J'_\tau(\tau \iota_1) = \frac{\iota_1}{\tau} \{ J_{\tau-1}(\tau \iota_1) - J_{\tau+1}(\tau \iota_1) \}, \quad (115)$$

$$R(\tau_1 \omega_1 + \omega_3) = \frac{1}{\tau} \sqrt{\frac{n_3}{n}} J_{\tau_1}(\tau \iota_1), \quad (116)$$

where  $\iota_1 = \sqrt{\frac{n_1}{n}}$ ,  $\tau = \tau_1 + \tau_3$ ,  $n = n_1 + n_3$ , ( $n_2 = \tau_2 = 0$ ).

In the formulae (113) and (116) holding for the relative amplitudes of the circular rotations,  $\tau_3$  is considered to be equal to +1. In the case where  $\tau_3 = -1$ , however, *i. e.* for transitions during which the angular momentum of the electron round the axis of the system increases by  $h/2\pi$ , we may obviously apply the same formulae if only we reverse the sign in the values for  $\tau_1$  and  $\tau_2$ . For the relative amplitudes of the linear vibrations we have both in (112) and in (115) given two expressions, the former of which is more symmetrical, while the latter lends itself better to numerical calculations as long as no tables of the functions  $J_p(\rho)$  are at hand.

The *eighth* and *ninth* columns in the tables contain the squares of  $R'$  and  $R''$ , which quantities, according to the considerations in § 5, should be expected to afford an estimate for the relative intensities of the different components. Here it



may be remarked that the introduction of the values of the "relative amplitudes" instead of the values of these amplitudes themselves offers, with reference to the considerations just mentioned, a great advantage. Thus it will be remembered that, in the case of the estimate of the intensity of a given component, we have beforehand no direct information as regards the relative importance of the values of the corresponding amplitude in the initial state and in the final state. For this reason it is of importance that in our tables the amplitudes should be characterised by numbers which for the initial states and for the final states are of the same order of magnitude, but this is just obtained by the introduction of the relative amplitudes.

Finally the *tenth* column contains the experimental values for the intensities published by STARK in his most recent paper on the Stark effect of the hydrogen lines<sup>1)</sup>. These values refer to the relative intensities of the components of same polarisation belonging to one and the same line, and are according to STARK's statement rather uncertain on account of the well known difficulties involved in the determination of these intensities from the density of the image of the components ("Schwarzung") on the photographic plates. A reproduction of STARK's photographs of  $H_{\beta}$ ,  $H_{\gamma}$ ,  $H_{\delta}$  will be found on Plate II, Fig. 5.<sup>2)</sup> For the sake of completeness we have, for the lines  $H_{\beta}$ ,  $H_{\gamma}$  and  $H_{\delta}$ , in an *eleventh* and *twelfth* column added the values for the relative densities of the images of the components on the photographic plate, given by STARK in his above cited monograph; the densities of the components on the red side of the undisplaced line are given in the eleventh column, those on the blue side in the twelfth column.

At the head of each table we have, for the sake of orientation, indicated the magnitude in Ångström units of the displacement corresponding to  $J = 1$  for a field strength of 100.000 Volt/cm. These values are calculated by means of the following relation, which is directly found from (111),

$$\delta\lambda = \text{displ. } (J = 1; 100.000 \text{ Volt/cm}) = 10^{-8} \frac{\lambda^2}{c} \delta\nu = 10^{-8} \frac{\lambda^2}{c} \frac{3h}{8\pi^2 N e m} \frac{10^5}{300} = \frac{1}{N} 6,41 \cdot 10^{-8} \lambda^2,$$

where  $\lambda$  represents the wave length of the spectral line, expressed in Ångström units.

When considering the tables I, II, III and IV it will in the first place be observed, that for most transitions the value of  $R''$  is equal to zero. This is due to the fact that to the stationary state of the simplified hydrogen atom characterised by  $n = 2$ , which forms the final state for the transitions giving rise to the lines of the Balmer series, there corresponds, in case an electric field is applied, only three stationary states, *viz.* [002], [101] and [011], and that the motion of the electron in these

<sup>1)</sup> J. STARK, Ann. d. Phys. XLVIII, p. 193 (1915).

<sup>2)</sup> J. STARK, Elektrische Spektralanalyse chemischer Atome, Tafel III, fig. 1. The arrows on the photograph of  $H_{\beta}$  indicate the position of the unreal lines ("Geister") which, on account of the imperfection of the grating, accompany the image of a component situated at the place of the original line. The arrow on the photograph of  $H_{\gamma}$  indicates the position of the mercury line 4359 Å, which, as it is seen, appears with considerable intensity.



states is of an especially simple character. Thus in the state [002] the orbit of the electron is circular and perpendicular to the direction of the field, and the motion contains only the frequency  $\omega_3$ , while in the states [101] and [011] the motion contains only the frequencies  $\tau\omega_1$ ,  $\tau-1\omega_1 + \omega_3$  and  $\tau\omega_2$ ,  $\tau-1\omega_2 + \omega_3$  respectively. As a consequence of this there exists for each of the lines considered in the tables only one parallel component and one perpendicular component on each side of the undisplaced line for which the values of  $R'^2$  and  $R''^2$  are both different from zero, while moreover there appears in  $H_\alpha$  at the place of the undisplaced line a perpendicular component, corresponding to a transition between two circular orbits (003  $\rightarrow$  002), for which  $R'^2$  and  $R''^2$  have the maximum value 1. Just these components are seen generally to be the strongest in the observations on the Stark effect. From this we may conclude that, when estimating the intensities by the present method, the amplitudes in the final states play a part no less important than those in the initial states, in agreement with what beforehand might be expected from the principles on which this method is based. Considering further the other components for which  $R''$  is equal to zero, it will be seen from the tables that the values of  $R'^2$  give in general a good picture of the observed intensities of these components. For instance for any two components of the same polarisation of a given line the component of larger intensity corresponds generally to that for which  $R'^2$  has the larger value. In order to facilitate a comparison between the theory and the experiments we have in fig. 1, 2, 3 on Plate I and fig. 4 on Plate II represented schematically the estimate for the theoretical intensities, in such a way that the lengths of the lines representing the different components are taken proportional to the values of  $R'^2 + R''^2$ . At the same time we have in these figures reproduced the schemes, given by STARK<sup>1)</sup>, representing the result of his above mentioned recent

Table I.  
 $H_\alpha$ , 6562,8 Å (3  $\rightarrow$  2).  
 displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 2,8 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R'$	$R''$	$R'^2$	$R''^2$	int. obs.	
Par. {	111 $\rightarrow$ 011	2	1	0	0	.46	0	.21	0	1
	102 $\rightarrow$ 002	3	1	0	0	.51	0	.26	0	1,1
	201 $\rightarrow$ 101	4	1	0	0	.62	.57	.38	.33	1,2
	201 $\rightarrow$ 011	8	2	-1	0	0	0	0	0	
Perp. {	003 $\rightarrow$ 002	0	0	0	1	1.00	1.00	1.00	1.00	} 2,6
	111 $\rightarrow$ 002	0	4	1	-1	.26	0	.07	0	
	102 $\rightarrow$ 101	1	0	0	1	.75	.62	.56	.39	1
	102 $\rightarrow$ 011	5	1	-1	1	0	0	0	0	
	201 $\rightarrow$ 002	6	2	2	-1	.05	0	.00	0	

<sup>1)</sup> Ann. d. Phys. XLVIII, p. 205 (1915).



Table II.

 $H_{\beta}$ , 4861.3 Å (4 → 2).displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 1.52 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R$	$R'$	$R^2$	$R'^2$	int. obs.	Red	Blue	
Par.	112 → 002	0	1	1	0	0	0	0	1,4	0,10		
	211 → 101	2	1	1	0	.02	0	.0005	1,2	0,22	0,16	
		(4)							1	0,26	0,36	
	211 → 011	6	2	0	0	.15	0	.021	4,8	1,00	1,12	
	202 → 002	8	2	0	0	.17	0	.030	9,1	1,40	1,73	
	301 → 101	10	2	0	0	.21	.17	.045	.030	11,5	1,63	1,88
		(12)							1			
301 → 011	14	3	-1	0	0	0	0	0				
Perp.		(0)							1,4	0,62		
	112 → 011	2	1	0	1	.12	0	.014	3,3	1,08	1,08	
	103 → 002	4	1	0	1	.19	0	.036	0	} 12,6	2,03	
	211 → 002	4	2	1	-1	.06	0	.004	0			
	202 → 101	6	1	0	1	.19	.19	.037	.037	9,7	1,64	1,78
		(8)							1,3			
	202 → 011	10	2	-1	1	0	0	0	0	1,1	0,34?	0,45?
301 → 002	12	3	0	-1	.02	0	.0005	0	1	0,27?	0,25?	

Table III.

 $H_{\gamma}$ , 4340.5 Å (5 → 2).displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 1.21 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R$	$R'$	$R^2$	$R'^2$	int. obs.	Red	Blue	
Par.	221 → 011	2	2	1	0	.033	0	.0011	0	1,6	0,58	0,58
	212 → 002	5	2	1	0	.022	0	.0005	0	1,5	0,58	0,52
	311 → 101	8	2	1	0	.013	0	.0016	0	1	0,19?	0,27?
	311 → 011	12	3	0	0	.074	0	.0055	0	2,0	0,67	0,91
	302 → 002	15	3	0	0	.093	0	.0086	0	7,2	1,56	1,70
	401 → 101	18	3	0	0	.112	.080	.0125	.0063	10,8	1,76	1,78
	401 → 011	22	4	-1	0	0	0	0	0	1?		
Perp.	113 → 002	0	1	1	1	.065	0	.0041	0	} 7,2	2,18	
	221 → 002	0	2	2	-1	.031	0	.0009	0			
	212 → 101	3	1	1	1	.057	0	.0032	0	3,2	1,56	1,56
	212 → 011	7	2	0	1	.045	0	.0020	0	1,2	0,74	0,76
	203 → 002	10	2	0	1	.085	0	.0072	0	} 4,3	1,70	1,78
	311 → 002	10	3	1	-1	.025	0	.0006	0			
	302 → 101	13	2	0	1	.088	.089	.0077	.080	6,1	1,90	1,88
302 → 011	17	3	-1	1	0	0	0	0	1,1		1,51?	
401 → 002	20	4	0	-1	.014	0	.0002	0	1	0,49	1,51?	



Table IV.  
 $H_{\delta}$ , 4101,7 Å (6 → 2).  
 displ. ( $\Delta=1$ ; 100 000 Volt/cm) = 1,08 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R'$	$R''$	$R'^2$	$R''^2$	int. obs.	Red	Blue	
Par.	222 → 002	0	2	2	0	0	0	0				
	321 → 101	4	2	2	0	.008	0	.0001	0	1	0,67	0,67
	321 → 011	8	3	1	0	.027	0	.0007	0	1,2	0,85	0,81
	312 → 002	12	3	1	0	.020	0	.0004	0	1,5	0,93	1,01
	411 → 101	16	3	1	0	.016	0	.0003	0	1,2	0,71	0,92
	411 → 011	20	4	0	0	.045	0	.0020	0	1,1	0,80	0,71
	402 → 002	24	4	0	0	.060	0	.0036	0	2,8	1,42	1,37
	501 → 101	28	4	0	0	.066	.043	.0044	.0019	7,2	1,80	2,00
501 → 011	32	5	-1	0	0	0	0	0	1(?)			
Perp.	222 → 011	2	2	1	1	.028	0	.0008	0	1,3	0,92	0,89
	213 → 002	6	2	1	1	.036	0	.0013	0	} 3,2	1,52	1,52
	321 → 002	6	3	2	-1	.017	0	.0003	0			
	312 → 101	10	2	1	1	.033	0	.0011	0	2,1	1,23	1,22
	312 → 011	14	3	0	1	.023	0	.0005	0	1	0,71	0,60
	303 → 002	18	3	0	1	.049	0	.0024	0	} 2,0	1,12	1,14
	411 → 002	18	4	1	-1	.013	0	.0002	0			
	402 → 101	22	3	0	1	.051	.049	.0026	.0024	2,4	1,30	1,30
	402 → 011	26	4	-1	1	0	0	0	0	1,3	0,89(?)	0,85(?)
501 → 002	30	5	0	-1	.006	0	.00005	0	1(?)	0,73(?)	0,67(?)	

measurements on the intensities of the components. Components the appearance of which was regarded by STARK as questionable are indicated by a ? sign.

On the whole it will be seen, that it is possible on BOHR's theory to account in a convincing way for the intensities of the Stark effect components. Before discussing in detail each of the lines observed by STARK, however, it may be useful to insert some general remarks to which a closer consideration of the preceding tables naturally gives rise.

In the first place it will be observed that the agreement between theory and experiments revealed by these tables is intimately connected with the circumstance that we have disregarded stationary states for which  $n_3 = 0$ , *i. e.* for which the angular momentum of the electron round an axis through the nucleus parallel to the electric force would be equal to zero (compare page 50). In fact, if such states were taken into account (it follows from what has been said in the note on page 50 that, due to the influence of the relativity modifications, the formulae (70) and (71) would not be applicable to the states in question) we should expect the appearance of a number of additional components of rather strong intensities; the absence of such components may be considered as an experimental confirmation of the non-existence of stationary states of the type under consideration. Further



it is of interest to notice that for a transition where one of the  $\tau$ 's is negative, *i. e.* during which one of the  $n$ 's increases, the value of  $R$  is always either very small or equal to zero, and that in agreement with this the corresponding component, if observed at all, is very weak<sup>1</sup>). It is easily seen that, from a mathematical point of view, the reason for the small values of  $R$  in such cases lies in the circumstance that the coefficients  $C_{\tau_1, \dots, \tau_s}$  in a convergent trigonometric series of the type (12) not only converge to zero when the numerical value  $|\tau_1 + \dots + \tau_s|$  of the sum of the  $\tau$ 's increases, but also when the sum  $|\tau_1| + \dots + |\tau_s|$  of the numerical values of the  $\tau$ 's increases,  $|\tau_1 + \dots + \tau_s|$  remaining constant.

Special interest is afforded by transitions of the type  $(n'_1, 0, n'_3 \rightarrow 0, n''_2, n''_3)$ . For these transitions both  $R$  and  $R''$  are equal to zero, but, as mentioned in the former section, it is not allowable from this to conclude that such transitions are impossible, in intimate connection with the fact that the amplitude of the vibration of frequency  $n'_1\omega_1 - n''_2\omega_2 + (n'_3 - n''_3)\omega_3$ , although equal to zero for the motion in the initial state and in the final state, is different from zero in the mechanically possible states which lie "between" these states and which are characterised by  $I_1 = \lambda n'_1$ ,  $I_2 = (1 - \lambda)n''_2$ ,  $I_3 = n''_3 + \lambda(n'_3 - n''_3)$  ( $0 < \lambda < 1$ ). As seen from the tables weak components corresponding to transitions of the type under consideration seem actually to have been observed<sup>2</sup>).

For transitions of the type  $(a, a, c \rightarrow b, b, c)$  the amplitude of the vibration of frequency  $(a - b)\omega_1 + (a - b)\omega_2$  is equal to zero, not only in the initial state and in the final state, but also in the states characterised by  $I_1 = I_2 = b + \lambda(a - b)$ ,  $I_3 = c$ , due to the symmetry of the motion of a state for which  $I_1 = I_2$ . From this we may probably conclude that a transition of the type under consideration is impossible. In the tables we meet with two examples of such a transition, *viz.* (112  $\rightarrow$  002) in  $H_\beta$  and (222  $\rightarrow$  002) in  $H_\delta$ . In  $H_\delta$  no corresponding component has been observed, but in  $H_\beta$  a weak component has been recorded. The appearance of this component, however, (if not due to "Gittergeister") does not necessarily mean a disagreement with the theory, but is possibly due to the influence of the relativity modifications, as it will be discussed below.

When we consider the values of  $R^2$  and  $R''^2$  as affording an estimate for the intensities of the components it must be remembered that in § 3 these values are calculated with neglect of small terms proportional to the first and higher powers of the electric force. It is easily seen, however, that we may look apart from these small terms, not only on account of the preliminary and approximative character of the discussion, but also because errors of at least the same order of magnitude are

<sup>1</sup>) It will be observed that the point under consideration has an interesting connection with SOMMERFELD'S suggestion that only such transitions would be possible for which all  $n$ 's in (99) decrease or remain unaltered (hypothesis of the "Quantenungleichungen". Compare A. SOMMERFELD, Ann. d. Phys. LI p. 24 (1916). Compare also EPSTEIN'S discussion of the intensities of the Stark effect components).

<sup>2</sup>) (202  $\rightarrow$  011) in  $H_\beta$ ; (302  $\rightarrow$  011) in  $H_\gamma$ ; (402  $\rightarrow$  011) in  $H_\delta$ . Components corresponding to (401  $\rightarrow$  011) in  $H_\gamma$  and (501  $\rightarrow$  011) in  $H_\delta$  are recorded by STARR as questionable.



already involved in the assumption that the different initial states, corresponding to one and the same stationary state of the simplified hydrogen atom, are of equal occurrence in the luminous gas. Moreover the uncertainty involved in the estimate of the intensities from the density of the image of the components on the photographic plate is so large that, with intensities of the electric force of the order of magnitude used in STARK's experiments, a possible dependency of the relative intensities of the components on the intensity of the force cannot be brought to light experimentally. It may in this connection be of interest to remark that for states for which  $I_2 = 0$  the amplitudes of the vibrations of frequency  $\tau_1\omega_1 + \tau_2\omega_2 + \tau_3\omega_3$  occurring in the motion of the system will, also if the first and higher powers of the electric force are taken into account, still be equal to zero if  $\tau_2$  is different from zero (compare § 3, page 25), while in general the amplitudes of the vibrations of frequency  $\tau_1\omega_1 + \tau_2\omega_2$ , where  $\tau_1 = \tau_2$ , will be small quantities proportional to the intensity of this force in states for which  $I_1 = I_2$ .

Another point which we have disregarded in the calculations in § 3 is the influence which the modifications in the laws of mechanics, claimed by the theory of relativity, have on the motion of the electron. This influence will be treated in detail in the paper mentioned in the beginning of § 4. Here it may only be remarked that this influence will consist partly in a small effect on the frequencies of the Stark effect components, partly in a small change in the relative intensities of these components. Thus the components will, on account of the relativity modifications, be displaced from the positions determined by (111) by small quantities of the same order as  $v^2/c^2$  where  $v$  is the velocity of the electron and  $c$  the velocity of light, in such a way that the symmetry of the Stark effect will be disturbed. The intensity of the electric field applied in Stark's experiments is, however, so large that such a dissymmetry cannot be detected. Further the effect of the relativity modifications on the values of the amplitudes of the harmonic vibrations, in which the motion of the electron can be resolved, will consist in the addition of small terms of the same order as  $v^2/c^2 F$ . Especially, in a state of the atom for which  $I_1 = I_2$ , the amplitudes of the vibrations of frequencies  $\tau_1\omega_1 + \tau_2\omega_2$ , where  $\tau_1 = \tau_2$ , will no more be equal to zero but equal to a small quantity of this order<sup>1)</sup>. Components corresponding to transitions of the type ( $aac \rightarrow bbc$ ) must therefore be expected to appear with an intensity of the same order as  $(v^2/c^2 F)^2$ . This might probably explain the appearance of the component corresponding to (112  $\rightarrow$  002) in  $H\beta$ , mentioned in the above; this explanation is seen to claim that the intensity of the component under consideration decreases for increasing intensity of the electric field<sup>2)</sup>.

<sup>1)</sup> The appearance of these vibrations of new frequencies in the states under consideration is analogous to the appearance of vibrations with new frequencies and of amplitudes which are of the same order as  $Fc^2/v^2$  in the problem treated in § 4.

<sup>2)</sup> On STARK's photographs of the Stark effect of  $H\beta$  for a field of 28 500 Volt/cm the relative intensity of this component seems actually to be much stronger than on the photograph corresponding to a field of 74 000 Volt/cm.



In § 5 it has been mentioned that we possess, quite independent of the estimate which is based on the calculation of the amplitudes of the harmonic vibrations in which the motion may be resolved, another source of information about the intensities in the fact that the polarised components in which an unpolarised spectral line is split up will, when taken together, show no characteristic polarisation in any direction. This allows of an instructive application in case of the Stark effect of  $H_\alpha$ . In fact, adding the values for  $R'^2$  and  $R''^2$  belonging to the parallel components, we get 1,70 and 0,66 respectively, while adding the  $R'^2$ 's and  $R''^2$ 's for the perpendicular components, we obtain 2,19 and 1,78. From this it follows that the intensities of the perpendicular components compared with those of the parallel components must, for the hydrogen line under consideration, be expected to be considerably smaller than it would follow from a direct comparison with the values of  $R'^2$  and  $R''^2$ . Especially the component corresponding to a transition between two circular orbits perpendicular to the direction of the electric force, (003  $\rightarrow$  002), will be much less intense than the values of  $R'^2$  and  $R''^2$  would indicate. In an even more striking way a consideration of this kind applies to the ultra-violet hydrogen line (2  $\rightarrow$  1), for which the values of the  $n$ 's in the stationary states are still smaller. Thus, under the influence of an electric field, this line will split up in two parallel symmetrical components of equal intensity, (101  $\rightarrow$  001) and (011  $\rightarrow$  001) ( $R'^2 = 0,33$ ,  $R''^2 = 0$ ), and one perpendicular component (002  $\rightarrow$  001) ( $R'^2 = 1$ ,  $R''^2 = 1$ ), and since the sum of the intensities of the former must be equal to the intensity of the latter, we see that the tendency for a transition between the two circular orbits [002] and [001] is again much less than it might have been expected from a direct consideration of the values of  $R'^2$  and  $R''^2$ . In the discussion in § 7 of the fine structure and in § 8 of the Zeeman effect of the hydrogen lines we shall meet with analogous phenomena as regards the transitions between circular orbits. In the case of the Stark effect of  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$  there are so many components that it is impossible to draw any further conclusion from the fact that the sum of the intensities of the parallel and of the circular components must be the same.

The fact that the tendency for a transition between two stationary states in which the electron describes a circular orbit is less than would be expected from the corresponding values of the  $R$ 's ( $R' = R'' = 1$ ) stands probably in close connection with the fact, to be mentioned in the following (see page 61), that the tendency for other transitions to final states in which the electron describes a circular orbit (for such transitions  $R''$  is always equal to zero) is larger than would be expected from a consideration of the amplitudes of the corresponding harmonic vibration in the motion of the electron. Thus both these facts clearly indicate a tendency of the estimate of the probability of transition between two stationary states based on a consideration of the motion in these states (and in the states lying "between") — in contrast to other mechanical states of the system — to give *exaggerated* results in cases where these motions show singularities. On the whole it will be seen, from the following discussion, that the experiments on the Stark



effect not only afford a confirmation of the validity of the considerations in § 5, but also, in many respects, seem to give indications of the way in which these considerations may be extended.

Let us now discuss more closely each of the lines considered in the tables.

As regards  $H_{\alpha}$  it is seen that the intensity of the undisplaced perpendicular component has been found to be the strongest of all components observed, in agreement with what should be expected from the large values of the corresponding quantities  $R'^2$  and  $R''^2$ . Further it is seen that the increase of the intensities of the parallel components in the direction of increasing  $\Delta$  is very well illustrated by the values of the corresponding  $R^2$ 's. In addition to the components observed, the theory predicts the existence of weak parallel components at  $\Delta = \pm 8$  and of weak perpendicular components at  $\Delta = \pm 5$  and  $\Delta = \pm 6$ .

For  $H_{\beta}$  STARK records parallel as well as perpendicular components corresponding to  $\Delta = 2, 4, 6, 8, 10$  and  $12$ , but, according to STARK's own statement, it was very difficult to obtain good photographs of the Stark effect of this line, and a long exposure was necessary in order to obtain all components on the plate. These difficulties may account for the small discrepancies which seem to exist between the different observations on one hand and between these observations and the theory on the other hand, since during the long exposure any unreal component ("Geist") due to the imperfection of the grating would have special opportunity to appear. Thus according to the theory no parallel components at  $\Delta = 4$  (and  $\Delta = 12$ ) and no perpendicular components at  $\Delta = 0$  and  $\Delta = 8$  should appear, while STARK's photographs would indicate the existence of such components. (It must, however, be remarked that, as seen from the table, the perpendicular component at  $\Delta = 8$  was not recorded in STARK's publications before 1915). Further the intensity of the perpendicular component  $\Delta = 6$  would according to the theory be stronger than the perpendicular component  $\Delta = 4$ , in agreement with the photograph reproduced in fig. 5 on Plate II, but in disagreement with the values 9,7 and 12,6 for the relative intensities of these components appearing in the 10<sup>th</sup> column of Table II. The possibility for the appearance of a parallel component at  $\Delta = 0$  has been discussed on page 58 and 59. On the whole it will be seen that the agreement between the theory and the observations is satisfactory, and it seems probable that this agreement will be improved by further experiments.

In case of the Stark effect of  $H_{\gamma}$  it is seen that the agreement between the measurements and the estimate afforded by the theory is rather distinct for most components; but the perpendicular component at  $\Delta = 0$  ( $113 \rightarrow 002$ ), and also the parallel component at  $\Delta = 5$  ( $212 \rightarrow 002$ ), appear undoubtedly stronger than we would expect from the corresponding values of  $R'^2$ . This may have connection with the fact that, for the corresponding transitions, the final states correspond to a circular orbit of the electron (compare page 60).

In case of the Stark effect of  $H_{\delta}$  it is especially satisfactory that it has been possible to explain the non-appearance of a component corresponding to the trans-



Table V.  
 $H_{\beta}$ , 3971,2 Å ( $7 \rightarrow 2$ ).  
 displ. ( $\Delta = 1$ ; 100 000 V/cm) = 1,01 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R$	$R'$	$R^2$	$R'^2$	
Par.	331 $\rightarrow$ 011	2	3	2	0	.011	0	.0001	0
	322 $\rightarrow$ 002	7	3	2	0	.004	0	.0000	0
	421 $\rightarrow$ 101	12	3	2	0	.0005	0	.0000	0
	421 $\rightarrow$ 011	16	4	1	0	.020	0	.0004	0
	412 $\rightarrow$ 002	21	4	1	0	.016	0	.0003	0
	511 $\rightarrow$ 101	26	4	1	0	.014	0	.0002	0
	511 $\rightarrow$ 011	30	5	0	0	.031	0	.0010	0
	502 $\rightarrow$ 002	35	5	0	0	.046	0	.0021	0
	601 $\rightarrow$ 101	40	5	0	0	.049	.026	.0024	.0007
601 $\rightarrow$ 011	44	6	-1	0	0	0	0	0	
Perp.	223 $\rightarrow$ 002	0	2	2	1	.022	0	.0005	0
	331 $\rightarrow$ 002	0	3	3	-1	.012	0	.0001	0
	322 $\rightarrow$ 101	5	2	2	1	.019	0	.0004	0
	322 $\rightarrow$ 011	9	3	1	1	.017	0	.0003	0
	313 $\rightarrow$ 002	14	3	1	1	.023	0	.0005	0
	421 $\rightarrow$ 002	14	4	2	-1	.011	0	.0001	0
	412 $\rightarrow$ 101	19	3	1	1	.022	0	.0005	0
	512 $\rightarrow$ 011	23	4	0	1	.014	0	.0002	0
	403 $\rightarrow$ 002	28	4	0	1	.033	0	.0011	0
	511 $\rightarrow$ 002	28	5	1	-1	.008	0	.0001	0
	502 $\rightarrow$ 101	33	4	0	1	.033	.030	.0011	.0009
	502 $\rightarrow$ 011	37	5	-1	1	0	0	0	0
	601 $\rightarrow$ 002	42	6	0	-1	.007	0	.00005	0

ition (222  $\rightarrow$  002). (The relativity modifications would, as mentioned above, give rise to the appearance of this component with a small intensity inversely proportional to the square of the electric force, but it is easily seen that in the present case this effect must be expected to be much less than in the case of the analogous component in  $H_{\beta}$ .) A discrepancy between the values of  $R'^2$  and the observed intensities seems to exist in the case of the weak parallel components. Thus the component at  $\Delta = 12$  appears stronger, while the component at  $\Delta = 20$  appears perhaps weaker than it would be expected from the corresponding values of  $R'^2$ . Further the perpendicular component at  $\Delta = 6$  appears stronger than we should expect from the table. These discrepancies are more or less analogous to those observed in case of  $H_{\gamma}$ ; thus the parallel component at  $\Delta = 12$  and the perpendicular component at  $\Delta = 6$  may be considered as analogous to the components  $\Delta = 5$  and  $\Delta = 0$  in  $H_{\gamma}$ , and correspond also to transitions for which the electron in the final state [002] describes a circular orbit. As regards the problems in question it may further be observed that, especially in the case of  $H_{\gamma}$  and  $H_{\beta}$ , the value  $n = 2$  in the final



states is so small in comparison with the value of  $n$  in the initial states, that we cannot be astonished to find that a simple consideration of the values of the  $R^2$ 's in the stationary states is unable to account for the finer details of the intensity distribution. In a case like this we are naturally induced to try to improve the estimate of the relative components by taking into account the values of the  $R$ 's in the states lying "between" the initial states and the final states (compare § 5, page 48); it may, however, be shown that by means of such a consideration the estimate would not be essentially modified as regards the intensities of components corresponding to transitions for which the electron in the final state describes a circular orbit<sup>1</sup>).

In the preceding pages we have compared the theory with the observations on the Stark effect for the first four lines of the Balmer series. Owing to the agreement obtained it seems possible to predict the character of the Stark effect of other hydrogen lines which have not yet been experimentally investigated, and which correspond to other values of  $n'$  and  $n''$  in (111). In Table V we have therefore given a scheme of the values of the  $R^2$ 's referring to the Stark effect components of  $H_\epsilon$  ( $7 \rightarrow 2$ ), and in fig. 6 on Plate II a schematical picture of the theoretical estimate of the intensities of these components, obtained, just as the analogous schemes in fig. 1 . . . 4, by taking the lengths of the lines which represent the components proportional to  $R'^2 + R''^2$ . It must, however, be remarked that we may expect, in

<sup>1</sup>) This will be seen from a consideration of the following table in which, for the parallel components of  $H_\beta$ , we have, besides the values of  $R$  in the initial state and in the final state, given also the value  $R_m$  which  $R$  takes in the mechanical state lying in the middle between the initial and the final state ( $I_k = \frac{1}{2}(n'_k + n''_k)h$ , ( $k = 1, 2, 3$ )). The values of  $R_m$  give no indications of a tendency for the component  $\Delta = 12$  to appear stronger than it would be expected from the values of  $R$  only. On the other hand the ratio of  $R_m$  to  $R$  is, for the component  $\Delta = 20$ , much less than for the other components; this may be connected with the fact, mentioned in the text, that this component appears with

Transition	$\Delta$	$R$	$R_m$	$R'$
222 $\rightarrow$ (1, 1, 2) $\rightarrow$ 002	0	0	0	0
321 $\rightarrow$ (2, 1, 1) $\rightarrow$ 101	4	.008	.009	0
321 $\rightarrow$ (1.5, 1.5, 1) $\rightarrow$ 011	8	.027	.023	0
312 $\rightarrow$ (1.5, 0.5, 2) $\rightarrow$ 002	12	.020	.017	0
411 $\rightarrow$ (2.5, 0.5, 1) $\rightarrow$ 101	16	.016	.014	0
411 $\rightarrow$ (2, 1, 1) $\rightarrow$ 011	20	.045	.023	0
402 $\rightarrow$ (2, 0, 2) $\rightarrow$ 002	24	.060	.046	0
501 $\rightarrow$ (3, 0, 1) $\rightarrow$ 101	28	.066	.065	.043
501 $\rightarrow$ (2.5, 0.5, 1) $\rightarrow$ 011	32	0	.007	0

less intensity than was to be anticipated from the value of  $R$ . The value of  $R_m$  for the component  $\Delta = 32$ , for which both  $R$  and  $R'$  are equal to zero, suggests that this component will appear with an intensity of the same order of magnitude as the component  $\Delta = 4$ .



analogy with what was the case for  $H_\gamma$  and  $H_\delta$ , that this estimate will be exaggerated in the case of components corresponding to transitions for which the electron in the final states describes a circular orbit ( $\mathcal{L} = 7, \mathcal{L} = 21; \mathcal{L} = 0, \mathcal{L} = 14$ ), in such a way that these components will appear stronger than it would be expected from the values of  $R'^2$  in Table V.

The considerations in this chapter may naturally also be applied to the problem of the Stark effect of the lines of the helium spectrum which correspond to  $N = 2$  in (105). The experimental data for these lines, however, are not nearly so complete as for the hydrogen lines, only a few measurements referring to the strong visible line  $4686 \text{ \AA}$  ( $4 \rightarrow 3$ ) and to the ultra-violet lines  $3203 \text{ \AA}$  ( $5 \rightarrow 3$ ) and  $2733 \text{ \AA}$  ( $6 \rightarrow 3$ ) having been published. When a strong electric field is applied we must expect that the lines in question will show a symmetrical resolution in a number of components the frequencies of which can be obtained from (111), and an estimate of the relative intensities of which can be obtained from the preceding considerations. Table VI contains the values of  $R'^2$  and  $R''^2$  corresponding to the components of the Stark effect of  $4686 \text{ \AA}$ , while fig. 7 on Plate III contains the schematical picture of the theoretical intensities. An observation on the Stark effect of the  $4686 \text{ \AA}$  line in helium for a comparatively small electric field has been published by EVANS and CROXSON<sup>1)</sup> and is also contained in a recent paper by NYQUIST<sup>2)</sup> on the effect of an electric field on the helium spectrum. The photographs of both these authors show distinctly that the resolution of the line in question is symmetrical, but the electric field used in their experiments was not strong enough to separate the different components the existence of which is claimed by the theory. Thus EVANS and CROXSON observed only a symmetrical broadening of the line, but in NYQUIST's photographs the line in question was resolved into an undisplaced perpendicular component and two symmetrical parallel components, which are indicated in fig. 7 by arrows. The distance of each of the latter from the undisplaced line amounted to  $3,2 \text{ \AA}$  for a field of  $100.000 \text{ Volt/cm}$  (the largest intensity of the field in the experiments amounted to  $38600 \text{ Volt/cm}$ ). This would correspond to a value of  $\mathcal{L}$  equal to  $3,2/0,71 = 4,5$  which value is seen to be in excellent agreement with the position of the centre of gravity to be expected for the strong theoretical parallel components at  $\mathcal{L} = 2, 3, 4, 5$  and  $6$  (compare Table VI and fig. 7).

Measurements on the effect of an electric field on the ultra violet helium lines  $3203 \text{ \AA}$  ( $5 \rightarrow 3$ ) and  $2733 \text{ \AA}$  ( $6 \rightarrow 3$ ) have recently been published by STARK<sup>3)</sup>. Also in these experiments the intensity of the electric field, which amounted to  $28500 \text{ Volt/cm}$ , was not strong enough to obtain separately the different theoretical components. Tables VII and VIII, which are arranged in the same way as the preceding tables, contain the values of  $R'^2$  and  $R''^2$  corresponding to these components, while fig. 8 and 9 on plate III contain a schematical picture of the results obtained in

<sup>1)</sup> E. J. EVANS and C. CROXSON, Phil. Mag. XXXII, p. 327 (1916).

<sup>2)</sup> H. NYQUIST, Phys. Rev. X, p. 226 (1917).

<sup>3)</sup> J. STARK, Ann. d. Phys. LVI, p. 569 (1918).



Table VI.  
Helium, 4686 Å (4→3).  
displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 0,71 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R$	$R'$	$R^2$	$R'^2$	
Par.	121 → 021	2	1	0	0	.37	0	.14	0
	112 → 012	3	1	0	0	.42	0	.18	0
	211 → 111	4	1	0	0	.55	.46	.30	.21
	103 → 003	4	1	0	0	.45	0	.21	0
	202 → 102	5	1	0	0	.57	.50	.33	.25
	301 → 201	6	1	0	0	.63	.62	.40	.39
	211 → 021	10	2	-1	0	.01	0	.00	0
	202 → 012	11	2	-1	0	0	0	0	0
	301 → 111	12	2	-1	0	0	.01	0	.00
	301 → 021	18	3	-2	0	0	0	0	0
Perp.	004 → 003	0	0	0	1	1,00	1,00	1,00	1,00
	112 → 111	0	0	0	1	.67	.58	.45	.33
	112 → 003	0	1	1	-1	.19	0	.04	0
	103 → 102	1	0	0	1	.81	.75	.66	.56
	211 → 102	1	1	1	-1	.28	0	.08	0
	202 → 201	2	0	0	1	.62	.49	.39	.24
	112 → 021	6	1	-1	1	.04	0	.00	0
	103 → 012	7	1	-1	1	0	0	0	0
	211 → 012	7	2	0	-1	.01	0	.00	0
	202 → 111	8	1	-1	1	0	.04	0	.00
	202 → 003	8	2	0	-1	.04	0	.00	0
	301 → 102	9	2	0	-1	.04	.02	.00	.00
	202 → 021	14	2	-2	1	0	0	0	0
	301 → 012	15	3	-1	-1	0	0	0	0

these tables. In the case of the line 3203 Å STARK records two symmetrical parallel and two symmetrical perpendicular components which for a field of 100.000 Volt/cm would be displaced from the original line by an amount 3,8 Å and 1,9 Å respectively. These displacements would correspond to  $\Delta = 1,9/0,33 = 5,7$  and  $\Delta = 3,8/0,33 = 11,5$  respectively; as seen from fig. 8, in which the positions of the components observed by STARK are indicated by arrows, this is in excellent agreement with what we theoretically should expect. In the case of the line 2733 Å STARK records two symmetrical pairs of parallel components, which for a field of 100.000 Volt/cm would be displaced from the original position of the line by 1,2 Å and 5,1 Å respectively, while their relative intensities are indicated by the numbers (1) and (6) respectively; and one symmetrical pair of perpendicular components, which for a field of 100.000 Volt/cm would be displaced from the original line by 3,7 Å, and the relative intensities of which are indicated by the number (4), together with an undisplaced perpendicular component, the intensity of which is indicated by the number (7). The values of  $\Delta$



Table VII.  
Helium, 3203 Å ( $5 \rightarrow 3$ ).  
displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 0,33 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R$	$R'$	$R''$	$R'''$
Par.	221 $\rightarrow$ 111	0	1	1	0	0	0	0
	113 $\rightarrow$ 003	0	1	1	0	0	0	0
	212 $\rightarrow$ 102	2	1	1	0	.02	0	.000
	311 $\rightarrow$ 201	4	1	1	0	.03	0	.001
	221 $\rightarrow$ 021	6	2	0	0	.10	0	.010
	212 $\rightarrow$ 012	8	2	0	0	.10	0	.009
	311 $\rightarrow$ 111	10	2	0	0	.17	.10	.029
	203 $\rightarrow$ 003	10	2	0	0	.15	0	.023
	302 $\rightarrow$ 102	12	2	0	0	.19	.13	.037
	401 $\rightarrow$ 201	14	2	0	0	.22	.20	.047
	311 $\rightarrow$ 021	16	3	-1	0	.01	0	.000
	302 $\rightarrow$ 012	18	3	-1	0	0	0	0
	401 $\rightarrow$ 111	20	3	-1	0	0	.01	0
	401 $\rightarrow$ 021	26	4	-2	0	0	0	0
Perp.	122 $\rightarrow$ 021	1	1	0	1	.08	0	.006
	113 $\rightarrow$ 012	3	1	0	1	.12	0	.015
	221 $\rightarrow$ 012	3	2	1	-1	.05	0	.003
	212 $\rightarrow$ 111	5	1	0	1	.14	.10	.019
	104 $\rightarrow$ 003	5	1	0	1	.18	0	.033
	212 $\rightarrow$ 003	5	2	1	-1	.04	0	.002
	203 $\rightarrow$ 102	7	1	0	1	.20	.20	.040
	311 $\rightarrow$ 102	7	2	1	-1	.07	0	.005
	302 $\rightarrow$ 201	9	1	0	1	.18	.16	.032
	212 $\rightarrow$ 021	11	2	-1	1	.02 <sub>5</sub>	0	.001
	203 $\rightarrow$ 012	13	2	-1	1	0	0	0
	311 $\rightarrow$ 012	13	3	0	-1	.02	0	.000 <sub>5</sub>
	302 $\rightarrow$ 111	15	2	-1	1	0	.01 <sub>5</sub>	0
	302 $\rightarrow$ 003	15	3	0	-1	.02	0	.000 <sub>5</sub>
401 $\rightarrow$ 102	17	3	0	-1	.02	.01	.000 <sub>5</sub>	
302 $\rightarrow$ 021	21	3	-2	1	0	0	0	
401 $\rightarrow$ 012	23	4	-1	-1	0	0	0	

corresponding to the observed parallel components are  $1,2/0,24 = 5,0$  and  $5,1/0,24 = 21,2$  respectively, and the values of  $\Delta$  corresponding to the observed perpendicular components are  $3,7/0,24 = 15,4$  and 0 respectively; as regards the outer parallel components these values are, as seen from fig. 9, where again the positions of the components observed by STARK are indicated by arrows, in excellent agreement with the positions of the centres of gravity of the strongest components in the theoretical effect. As regards the two inner parallel components, however, we should, on the theory, rather expect the appearance of a single diffuse line in stead of two separate compo-



Table VIII.  
Helium, 2733 Å (6 → 3).  
displ. ( $\Delta = 1$ ; 100 000 Volt/cm) = 0,24 Å

Transition	$\Delta$	$\tau_1$	$\tau_2$	$\tau_3$	$R'$	$R''$	$R'^2$	$R''^2$	
Par.	231 → 021 \	0	2	1	0	.034	0	.0012	0
	321 → 201 /	0	1	2	0	.034	0	.0012	0
	222 → 012	3	2	1	0	.030	0	.0009	0
	321 → 111 \	6	2	1	0	.028	.030	.0008	.0009
	213 → 003 /	6	2	1	0	.020	0	.0004	0
	312 → 102 \	9	2	1	0	.015	0	.0002	0
	321 → 021 /	12	3	0	0	.046	0	.0022	0
	411 → 201 /	12	2	1	0	.006	0	.0000	0
	312 → 012	15	3	0	0	.064	0	.0040	0
	411 → 111 \	18	3	0	0	.086	.024	.0073	.0006
	303 → 003 /	18	3	0	0	.079	0	.0063	0
	402 → 102 \	21	3	0	0	.101	.052	.0101	.0027
	411 → 021 /	24	4	-1	0	.010	0	.0001	0
	501 → 201 /	24	3	0	0	.114	.101	.0130	.0101
	402 → 012 \	27	4	-1	0	0	0	0	0
	501 → 111 \	30	4	-1	0	0	.004	0	.0000
501 → 021	36	5	-2	0	0	0	0	0	
Perp.	222 → 111 \	0	1	1	1	.061	.067	.0037	.0037
	114 → 003 /	0	1	1	1	.062	0	.0038	0
	222 → 003 /	0	2	2	-1	.023	0	.0005	0
	213 → 102 \	3	1	1	1	.060	0	.0036	0
	321 → 102 /	3	2	2	-1	.031	0	.0009	0
	222 → 021 \	6	2	0	1	.023	0	.0005	0
	312 → 201 /	6	1	1	1	.046	0	.0021	0
	213 → 012 \	9	2	0	1	.046	0	.0021	0
	321 → 012 /	9	3	1	-1	.017	0	.0003	0
	312 → 111 \	12	2	0	1	.055	.023	.0031	.0005
	204 → 003 /	12	2	0	1	.079	0	.0062	0
	312 → 003 /	12	3	1	-1	.017	0	.0003	0
	303 → 102 \	15	2	0	1	.089	.079	.0080	.0062
	411 → 102 /	15	3	1	-1	.029	0	.0009	0
	312 → 021 \	18	3	-1	1	.013	0	.0002	0
	402 → 201 /	18	2	0	1	.084	.084	.0071	.0071
	303 → 012 \	21	3	-1	1	0	0	0	0
	411 → 012 /	21	4	0	-1	.014	0	.0002	0
402 → 111 \	24	3	-1	1	0	.007	0	.0000	
402 → 003 /	24	4	0	-1	.013	0	.0002	0	
501 → 102	27	4	0	-1	.013	.005	.0002	.0000	
402 → 021	30	4	-2	1	0	0	0	0	
501 → 012	33	5	-1	-1	0	0	0	0	



nents, because the theoretical intensities of the parallel components at  $\Delta = 6$  and the parallel component at  $\Delta = 0$  are of the same order of magnitude. It is therefore of interest to note that STARK (see loc. cit., p. 575) only has observed a single, very weak, diffuse component, and that he from analogy with the character of the Stark effect of  $H_{\delta}$  for small intensity of the electric force, has suspected this component to consist of two symmetrical components.

In connection with the above considerations it may be of interest to emphasize that a comparison of the observations on the Stark effect of the helium lines in question with the results to be expected on the quantum theory could not have been obtained by a direct consideration of the frequencies of the components, calculated by means of relation (1) from the values of the energy in the stationary states of the atom, but that it was of essential importance for the above comparison that we were able to obtain an estimate of the relative intensities of these components by means of a closer consideration of the motion of the electron in the atom.

### § 7. The fine structure of the hydrogen lines.

In this chapter we will give, from the point of view of BOHR's theory, a discussion of the intensities of the components of the fine structure of the hydrogen lines and of the analogous helium lines, and it will be shown that it is possible to account in a suggestive way for the observations, especially in the case of the helium lines, the fine structure of which has been carefully investigated by PASCHEN<sup>1)</sup>. Let us first consider the general expression for the frequency of the radiation which may be emitted from a hydrogen atom which is uninfluenced by external forces and in which the motion of the particles is assumed to be governed by the laws of relativistic mechanics. According to (99) the stationary states of the atom are fixed by putting the quantities  $I_1$  and  $I_2$ , defined by (23) in § 2, equal to entire multiples of PLANCK's constant  $h$  (compare page 39):

$$I_1 = n_1 h, \quad I_2 = n_2 h. \quad (117)$$

While  $n_1$  may take one of the values  $0, 1, 2 \dots$ , it must be assumed that  $n_2$  can only take one of the values  $1, 2, 3 \dots$ . In fact,  $n_2 = 0$  would correspond to a motion in which the angular momentum of the electron round the nucleus would be equal to zero, but such a motion can obviously not correspond to a stationary state of the atom because the electron would collide with the nucleus. Introducing (117) in (24) and writing  $n_1 + n_2 = n$  we get, with neglect of small quantities of the same order of magnitude as the second and higher powers of  $(v/c)^2$ , for the total energy of the atom in the stationary states

$$E = -\frac{2\pi^2 N^2 e^4 m}{h^2 n^2} \left[ 1 + \left( \frac{\pi N e^2}{hc} \right)^2 \left( -\frac{3}{n^2} + \frac{4}{n n_2} \right) \right]. \quad (118)$$

<sup>1)</sup> F. PASCHEN, Ann. d. Phys. L., p. 901 (1916).



Denoting the values of  $n_1, n_2$  and  $n$  in the initial state and in the final state of a given transition by  $n'_1, n'_2, n'$  and  $n''_1, n''_2, n''$  respectively, we get according to (1) for the frequency of the radiation emitted during this transition

$$\nu = \nu_0 + \nu_1 + \nu_2, \quad (119)$$

where

$$\nu_0 = KN^2 \left( \frac{1}{n''^2} - \frac{1}{n'^2} \right), \quad K = \frac{2\pi^2 e^4 m}{h^3} \left( \frac{M}{M+m} \right)^1) \quad (120)$$

$$\nu_1 = -\frac{3}{4} K \alpha^2 N^4 \left( \frac{1}{n''^4} - \frac{1}{n'^4} \right), \quad \alpha = \frac{2\pi e^2}{hc} \quad (121)$$

$$\nu_2 = K \alpha^2 N^4 \left( \frac{1}{n''^3 n''_2} - \frac{1}{n'^3 n'_2} \right). \quad (122)$$

The expression for  $\nu_0$  coincides with the simple formula (105) for the frequencies of the lines of the hydrogen spectrum ( $N=1$ ) and of the analogous helium lines ( $N=2$ ), which holds when the relativity modifications are neglected. The expression for  $\nu_2$  is determinative for the frequency differences of the fine structure components of a spectral line corresponding to given values of  $n'$  and  $n''$ , while  $\nu_1$ , which contains only  $n'$  and  $n''$ , has influence only on the absolute values of the frequencies of these components. In the following a hydrogen line which corresponds to a transition from an initial state  $n=n'$  to a final state  $n=n''$  will again be characterised by the symbol ( $n' \rightarrow n''$ ). In the same way a transition between an initial state  $n_1=n'_1, n_2=n'_2$  and a final state  $n_1=n''_1, n_2=n''_2$  will be denoted by ( $n'_1, n'_2 \rightarrow n''_1, n''_2$ ). The ensemble of components corresponding to all imaginable transitions between stationary states for which  $n'$  and  $n''$  have the same values will be obtained by letting  $n'_2$  assume each of the values  $1, 2, \dots, n'$  and  $n''_2$  each of the values  $1, 2, \dots, n''$ . If all transitions between stationary states were possible, the fine structure of a given line would therefore consist of a set of  $n' \times n''$  components. On account of  $n''$  being smaller than  $n'$ , this set may conveniently be described as consisting of  $n''$  congruent groups each containing  $n'$  components. Thus the line ( $3 \rightarrow 2$ ) would show two congruent triplets, the line ( $4 \rightarrow 3$ ) three congruent quartets, a. s. o. It must, however, be remarked that these groups will in general partly overlap each other (compare fig. 10, 11, 13 on Plate IV). Due to the small value of the constant  $\alpha$  appearing in (122), the frequency differences between the components of a given line are so small that it must be expected that in general they cannot be separated entirely by the instrument used for the observations. It is easily seen, however, that this will hold to a less degree for the helium lines ( $N=2$ ) than for the hydrogen lines ( $N=1$ ), because, due to the factor  $N^2$  in (120)

1) The factor  $\frac{M}{M+m}$ , which is of importance if the theory is compared with measurements of the absolute values of the frequencies of the fine structure components, does not appear in (118), because in the calculations of § 2 the mass of the nucleus was considered as infinite compared with that of the electron (compare § 5, page 40).



and the factor  $N^4$  in (122), the distances between the components will for a given helium line be much larger than for a hydrogen line in the same part of the spectrum. In conformity with this, it has for the lines of the Balmer series in hydrogen been possible only to establish the existence of narrow doublets, the members of which must be expected each to correspond to several components of the theoretical fine structure, while for some of the helium lines, especially for the lines  $(4 \rightarrow 3)$  and  $(5 \rightarrow 3)$ , PASCHEN has been able to detect a considerable number of components. For these lines PASCHEN was able to identify in detail all components found by him with components or groups of components to be expected on SOMMERFELD'S theory and the experimental value for the constant  $\alpha$ , which may be found from the observed frequency differences of the components, was in good agreement with the theoretical value ( $\alpha = \frac{2\pi e^2}{hc} = 7.30 \cdot 10^{-3}$ ). Moreover the absolute values of the frequencies gave, when the calculations were based on the complete expression (119) for  $\nu$ , values for the constant  $K$  which, within the limit of experimental errors, were the same for each of the different hydrogen lines ( $K = c. 109677.7$ ) as well as for each of the different helium lines ( $K = c. 109722.1$ ), while the ratio between these two constants was in agreement with the theoretical value  $\frac{1 + m/M_H}{1 + m/M_{He}}$ .<sup>1)</sup>

While SOMMERFELD'S theory thus afforded a convincing interpretation as regards the frequencies of the fine structure components, it was, however, in the simple form in which it was given unable to account for the intensities with which these components appeared. Especially it seemed difficult to explain the remarkable differences shown by the spectrograms of the fine structure of one and the same line which were made under different experimental conditions. Thus, in the case of the fine structure of the helium line 4686 Å, the intensity distribution for the different components on PASCHEN'S photographs showed pronounced differences if a steady voltage had been applied to the vacuum tube containing the gas ("Gleichstrombild") or if the tube had been exposed to an interrupted spark discharge ("Funkenbild"). In a recent paper SOMMERFELD<sup>2)</sup> has made an attempt to explain the intensities of the fine structure components by comparing the intensity of every component with the product of the a-priori probabilities of the initial state and of the final state of the corresponding transition, obtaining in this way what he called a "typical intensity distribution", and by discussing the possible modifications in this distribution which the experimental conditions might produce. By such considerations, however, it was not found possible to obtain a satisfactory agreement with the observations, and SOMMERFELD was led to the conclusion that the intensities cannot be explained "statistically" but claimed an explanation which takes into account the mechanism of the transition process and which therefore might be called "dynamical". From the point of view of BOHR'S theory this conclusion is evident; in the limit of large  $n$ 's, for instance, the intensities can according to this theory directly be obtained from

<sup>1)</sup> F. PASCHEN, loc. cit. p. 935.

<sup>2)</sup> A. SOMMERFELD, Ber. Akad. München, p. 83, 1917.



the properties of the motion of the electron in the atom, but can obviously not be found from an examination of the a-priori probabilities of the stationary states, although of course these quantities must be taken into account in the detailed discussion of the intensities.

*1. The relative intensities of the components of the fine structure of the lines of the spectrum of the undisturbed hydrogen atom.*

In order to discuss the interpretation of the observed intensities which can be obtained from the considerations in § 5, let us first suppose that the hydrogen atom is entirely uninfluenced by external forces. In that case the motion of the electron will take place in a plane; moreover the position of this plane would remain unaltered if the electron emitted radiation according to the laws of ordinary electrodynamics. From the formal connection with ordinary electrodynamics in the limit of large  $n$ 's we must therefore expect that also on the quantum theory the plane of the motion remains unaltered during a transition between two stationary states and that the emitted radiation is polarised in this plane. On the other hand the total radiation emitted by a large number of atoms will show no characteristic polarisation, since the position in space of the plane of the orbit in the stationary states is undetermined. Further we have seen in § 2 (compare the formulae (37) and (38)) that the motion of the electron may be considered as a superposition of a number of circular harmonic vibrations of frequencies  $|\tau_1\omega_1 + \omega_2|$ , where  $\omega_1$  and  $\omega_2$  are the frequency of the radial motion and the mean frequency of the angular motion respectively, while  $\tau_1$  is an integer which may assume all positive and negative values including zero. According to the considerations in § 5 it is therefore necessary to assume that only such transitions between stationary states will be possible for which  $n_2$  decreases or increases by 1, *i. e.* for which the angular momentum of the electron round the nucleus decreases or increases by  $h/2\pi$ , and that the emitted radiation will be circularly polarised in a direction which is the same as or the opposite of that of the direction of revolution of the electron in its orbit respectively.<sup>1)</sup> It is thus seen that a large number of the ensemble of the  $n' \times n''$  imaginable components of the fine structure of a line ( $n' \rightarrow n''$ ) will correspond to transitions which must be regarded as physically impossible, the a-priori probability for their spontaneous occurrence being equal to zero, and that we may only expect the appearance of  $2n'' - 1$  components,  $n''$  of which correspond to  $n'_2 - n''_2 = 1$  and  $n'' - 1$  of which to  $n'_2 - n''_2 = -1$ .

In order to discuss the intensities with which, according to BOHR's theory, these components may be expected to appear, it will first of all be necessary to discuss the modifications which on account of the degenerate character of the system in question must be introduced in the considerations of § 5 in order that they may be applied in the present case. As a consequence of the degeneration the

<sup>1)</sup> Compare BOHR, *loc. cit.* Part II, p. 68.



a-priori probabilities of the different stationary states are not equal to each other but they are, in the case under consideration, proportional to the values of  $n_2$ <sup>1)</sup>. Hence if we consider the ensemble of stationary states for which the value of  $n = n_1 + n_2$  is the same, the numbers of atoms in the luminescent vacuum tube present in these states may be expected to be approximately proportional to the values of  $n_2$  in these states. From this it follows that the intensities with which on ordinary electrostatics the different radiations of frequencies  $|\tau_1\omega_1 + \omega_2|$ , where  $|\tau_1 + 1|$  has a given entire value, would be emitted from the atoms in states corresponding to a given value of  $n$  are not simply proportional to the squares of the amplitudes of the vibrations of these frequencies in these states, but proportional to these squares multiplied by  $n_2$ . From the formal connection between the quantum theory and the ordinary electrostatic theory of radiation we are therefore, in analogy with the considerations in § 5, led to expect that, as a first approximation, an estimate for the relative intensities of the fine structure components ( $n'_1, n'_2 \rightarrow n''_1, n''_2$ ) of a given line may be obtained by comparing the intensity of each component with the quantities  $n'_2 R'^2$  and  $n''_2 R''^2$ , where  $R'$  and  $R''$  represent, just as in § 6, the relative amplitudes of the circular harmonic vibrations of frequency  $(n'_1 - n''_1)\omega_1 + (n'_2 - n''_2)\omega_2$  occurring in the motions in the initial and final states, *i. e.* the ratios between these amplitudes and the half major axes of the orbit.

In the tables IX and X we have given schemes for the theoretical estimate of the intensities of the fine structure components of a number of spectral lines. Tabel IX refers to the lines (3 → 2), (4 → 2) and (5 → 2), which correspond to  $H_\alpha$  (6563 Å),  $H_\beta$  (4861 Å) and  $H_\gamma$  (4340 Å) in the hydrogen spectrum; Table X refers to the lines (4 → 3), (5 → 3), (6 → 4) and (7 → 4), corresponding to 4686 Å, 3203 Å, 6560 Å and 5411 Å in the helium spectrum.

The *first* column contains the transitions giving rise to the different components, characterised by their symbol ( $n'_1, n'_2 \rightarrow n''_1, n''_2$ ).

The *second* and *third* columns contain the values of  $\tau_1 = n'_1 - n''_1$  and  $\tau_2 = n'_2 - n''_2$ . For each line the components corresponding to  $\tau_2 = +1$  and  $\tau_2 = -1$  are separated by a dotted line.

The *fourth* and *fifth* columns contain the values of  $R'$  and  $R''$  which may be found from (37) by introducing (117), and which accordingly have been calculated by means of the formula

$$R(\tau - 1 \omega_1 + \omega_2) = \frac{1}{2\tau} \{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \}, \quad (123)$$

where

$$\varepsilon' = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n}, \quad \varepsilon = \sqrt{1 - \varepsilon'^2}, \quad \tau = \tau_1 + 1.$$

In order to apply (123) in case of transitions for which  $\tau_2$  is equal to  $-1$  we must obviously introduce for  $\tau$  the negative value  $\tau = -(n' - n'')$ .

<sup>1)</sup> BOHR, loc. cit. Part I, p. 27.



Table IX.

Transition	$\tau_1$	$\tau_2$	$R$	$R'$	$n_2 R^2$	$n_2' R'^2$	Wave length	
03 → 02	0	1	1,00	1,00	3,00	2,00	6562,84 Å	$H_\alpha$
12 → 11	0	1	0,71	0,59	1,01	0,35	2,72	6563 Å
21 → 02	2	-1	0,19	0	0,04	0	2,89	(3 → 2)
13 → 02	1	1	0,228	0	0,156	0	4851,36 Å	$H_\beta$
22 → 11	1	1	0,106	0,206	0,085	0,042	1,27	4861 Å
31 → 02	3	-1	0,057	0	0,003	0	1,37	(4 → 2)
23 → 02	2	1	0,106	0	0,034	0	4340,49 Å	$H_\gamma$
32 → 11	2	1	0,101	0,108	0,020	0,012	0,42	4340 Å
41 → 02	4	-1	0,038	0	0,001	0	0,50	(5 → 2)

Table X.

Transition	$\tau_1$	$\tau_2$	$R$	$R'$	$n_2 R^2$	$n_2' R'^2$	Wave length	
04 → 03	0	1	1,00	1,00	4,00	3,00	4585,81	Helium 4686 Å (4 → 3)
13 → 12	0	1	0,775	0,71	1,80	1,01	5,71	
22 → 21	0	1	0,59	0,49	0,71	0,24	5,38	
22 → 03	2	-1	0,14	0	0,04	0	5,89	
31 → 12	2	-1	0,22	0,09	0,05	0,02	5,92	
14 → 03	1	1	0,222	0	0,198	0	3203,17	Helium 3203 Å (5 → 3)
23 → 12	1	1	0,221	0,227	0,146	0,103	3,12	
32 → 21	1	1	0,188	0,175	0,071	0,031	2,95	
32 → 03	3	-1	0,051	0	0,005	0	3,19	
41 → 12	3	-1	0,081	0,021	0,006	0,001	3,17	
15 → 04	1	1	0,215	0	0,231	0	6560,19	Helium 6560 Å (6 → 4)
24 → 13	1	1	0,227	0,228	0,206	0,156	60,15	
33 → 22	1	1	0,206	0,206	0,127	0,084	60,06	
42 → 31	1	1	0,175	0,173	0,061	0,030	59,78	
33 → 04	3	-1	0,039	0	0,005	0	60,21	
42 → 13	3	-1	0,060	0,014	0,007	0,001	60,19	
51 → 22	3	-1	0,084	0,039	0,007	0,002	60,18	
25 → 04	2	1	0,105	0	0,055	0	5411,60 Å	
34 → 13	2	1	0,104	0,100	0,043	0,030	1,57	Helium 5411 Å (7 → 4)
43 → 22	2	1	0,103	0,108	0,032	0,023	1,50	
52 → 31	2	1	0,089	0,086	0,016	0,007	1,30	
43 → 04	4	-1	0,027	0	0,002	0	1,61	
52 → 13	4	-1	0,035	0,005	0,002	0,000	1,59	
61 → 22	4	-1	0,044	0,025	0,002	0,007	1,55	







All this is in general agreement with the observations as it will be seen from a detailed discussion of the fine structures observed. Before entering on such a discussion, however, it will be necessary to consider in a certain detail the influence which small perturbing electric forces will have on the fine structure of the hydrogen lines and helium lines under consideration. That such an influence must beforehand be expected to be very considerable may for instance be seen from the circumstance that rather small electric fields will be sufficient to disturb entirely the character of the fine structure and to give rise to a regular Stark effect. Thus, in the case of  $H_{\alpha}$ , an electric field of 1000 Volt/cm would already give rise to a Stark effect for which the distance of the outer parallel components is equal to nearly two times the width of the original fine structure doublet of  $H_{\alpha}$ . From a mechanical point of view the easiness with which a fine structure is disturbed by a small external electric force is interpreted by observing that the deviation of the orbit of the electron from a purely periodic orbit due to the influence of the relativity modifications is extremely small, so that already a comparatively small electric force will produce alterations in the orbit which are of the same order of magnitude. As it will appear in the following sections a discussion of the effect of a weak electric field is of essential importance in order to obtain a theoretical understanding of the typical manner in which, on many of PASCHEN's spectrograms, the intensity distribution of the different components deviates from the simple intensity distribution to be expected from the preceding considerations in this section.

## *II. Effect of a weak electric field on the fine structure of the hydrogen lines.*

A general discussion of the effect which an electric field must be expected to have on the fine structure of a hydrogen line when its intensity increases from zero, so that the fine structure is gradually transmuted into an ordinary Stark effect in which the relativity modifications play only a secondary part, will, as mentioned in the beginning of § 4, be given in a later paper. Here we will only discuss the effect of an electric field, the intensity of which is so small that its influence is still small compared to that of the relativity modifications.

The character of the influence of a small external constant field of force on the spectrum of an atomic system has been treated by BOHR in the first and in the second Part of his often mentioned paper. As regards the frequencies of the spectral lines this effect may be directly found by means of (1) as soon as it is possible to fix the energy in the stationary states of the perturbed system. This constitutes a problem which in general may be solved if the deviations of the mechanical motion of the perturbed system from the motion in the undisturbed system are at any moment very small, and for its treatment the fundamental principle of the mechanical transformability of the stationary states, which has been introduced in the



quantum theory by EHRENFEST<sup>1)</sup>, plays an important part. From BOHR's paper it will, however, be seen that if the undisturbed system is degenerate, *i. e.* if the number of degrees of freedom is larger than the number of the conditions which fix the stationary states of the undisturbed system, complications present themselves owing to the circumstance that in such a case the stationary states of the perturbed system in general will be fixed by a larger number of conditions. In such a case a closer examination of the motion of the perturbed system, and especially a consideration of the small new frequencies, impressed on the motion of the system by the perturbing forces, is necessary in order to obtain a fixation of the stationary states. A general exposition of the methods, developed by BOHR, by means of which it is possible to fix the stationary states of a perturbed system, will be given in the later paper referred to above; in the present case, where we consider the influence of a weak homogeneous electric field on the hydrogen atom, which will not essentially disturb the character of the motion of the atom, we shall only mention the points which have direct connection with this problem, without entering more closely on a theoretical discussion.

The properties of the mechanical motion of the electron in a hydrogen atom which is exposed to a small electric field of force have been investigated in detail in § 4. From the calculations in this section it is seen that the character of this motion, with neglect of small quantities proportional to the square of the intensity of the perturbing force, may be considered as characterised by three quantities  $I_1^0$ ,  $I_2^0$  and  $I_3^0$ . If the intensity of the perturbing force is zero ( $F=0$ ),  $I_1^0$  and  $I_2^0 + I_3^0$  coincide with the quantities  $I_1$  and  $I_2$  respectively, which in the notation of § 2 characterise the motion of the electron in the undisturbed atom. The quantity  $I_3^0$  represents  $2\pi$  times the angular momentum of the electron round an axis through the nucleus parallel to the electric force. While the stationary states of the undisturbed atom, which forms a degenerate system, are fixed by the two conditions (117), the stationary states of the perturbed system will, disregarding small quantities proportional to  $F^2$ , be characterised by the following three conditions:

$$I_1^0 = n_1 h, \quad I_2^0 = (n_2 - \pi) h, \quad I_3^0 = \pi h, \quad (124)$$

where  $n_1$ ,  $n_2$  and  $\pi$  are positive integers of which  $n_2 \geq \pi$ . A state of the perturbed system satisfying these conditions for given values of  $n_1$ ,  $n_2$ ,  $\pi$  will in the following be characterised by the symbol  $(n_1, n_2; \pi)$ . Comparing with the formulae in § 4, it is seen from (124) that the motion in a stationary state of the perturbed system will, at any moment, only differ by small quantities proportional to the intensity  $F$  of the perturbing force from a stationary motion of the undisturbed system, which besides satisfying the conditions (117) satisfies the additional condition that the angular momentum of the electron round the axis is equal to an entire multiple of  $h/2\pi$ . It will be seen that the latter condition fixes the position of the plane in which the electron moves, which was naturally left undetermined

<sup>1)</sup> See BOHR, *loc. cit.* Part I, p. 8.



by the conditions (117), and that the sine of the angle which this plane makes with the axis will be equal to  $\frac{\pi}{n_2}$ .<sup>1)</sup> The different possible stationary states of the perturbed system are a-priori equally probable and are obtained by letting  $n_1$  assume the values 0, 1, 2, ...,  $n_2$  the values 1, 2, 3, ... and  $\pi$  the values 1, 2, ...,  $n_2$ . That no stationary states exist in which  $n_2$  would be equal to zero follows, as mentioned on page 68, from the fact that the motion in these states would not be physically realisable since the electron would collide with the nucleus. In states for which  $n_2$  would be different from zero, but in which  $\pi$  would be equal to zero, the mechanical motion of the electron would not show singularities, but as pointed out in BOHR's paper it is possible to conclude, from the principle of the invariance of the a-priori probability of the stationary states for continuous transformations, that these states cannot represent stationary states since it would be possible to transform them continuously into physically unrealisable states.<sup>2)</sup>

From the calculations in § 4 it follows that, with neglect of small quantities proportional to the square and higher powers of  $F$ , the total energy of the perturbed system may be expressed in terms of  $I_1^0, I_2^0, I_3^0$  by the same function as that by which in (76) the quantity  $\alpha_1$  is expressed in terms of  $I_1, I_2, I_3$  (compare page 31). Introducing (124) it will therefore be seen that the total energy of the stationary states of the perturbed system with this approximation will depend on  $n_1$  and  $n_2$  only, and will be given by the same formula as that holding for the energy in the stationary states of the undisturbed system, which was given by (118).<sup>3)</sup>

<sup>1)</sup> In BOHR's paper (Part I, page 35; Part II, page 55) it has been mentioned that quite generally we must expect that one of the conditions which fix the stationary states of an atomic system which possesses a fixed axis of symmetry will claim that the total angular momentum of the system round this axis is equal to an entire multiple of  $h/2\pi$ . Starting from this result it may directly be proved that the conditions (124) are in concordance with the principle of the mechanical transformability of the stationary states. In fact, it can be proved that during a slow increase of the intensity of the electric field the mean values of the quantities  $I_1, I_2$  and  $I_3$ , taken over the motion of the perturbed system, with neglect of small quantities proportional to  $F^2$  will remain the same. Since now, according to the calculations in § 4 (see page 30), the quantities  $I_1^0, I_2^0$  and  $I_3^0$  appearing in the conditions (124) just represent the mean values of  $I_1, I_2$  and  $I_3$ , it will therefore be seen that, if we start from a stationary motion of the undisturbed atom which satisfies the additional condition of the angular momentum, the atom will during a slow establishment of the perturbing electric field pass mechanically into a state which satisfies the conditions (124).

<sup>2)</sup> If, for instance, we imagine that the intensity of the electric force increases to values which are so large that the relativity modifications may be neglected we would obtain the system considered in § 3 and § 6, and the states in question would be continuously transformed into the corresponding states of the latter system, the motion in which, as mentioned on page 50, involves an essential singularity. Compare BOHR, loc. cit. Part II, page 56.

<sup>3)</sup> The fact that in the present case the alteration in the total energy of the system due to the presence of the external forces, *i. e.* what BOHR calls the "additional energy" of the perturbed system, is equal to zero as far as small quantities proportional to  $F$  are concerned may be directly deduced from a general theorem which states that if a conditionally periodic system is perturbed by a constant small external field of force the value of the additional energy in the stationary states of the perturbed system is, with neglect of small quantities proportional to the square of the external forces, simply equal to



With reference to the general relation which, according to BOHR, must be expected to exist between the additional energy of a degenerate system due to the presence of small external forces and the small frequency (or frequencies) impres-

the mean value of the potential energy of the system with regard to these forces, taken over a long time interval for the "corresponding" stationary motion of the undisturbed system, *i. e.* the motion in the state which would appear if the perturbing field decreased to zero infinitely slowly and at a uniform rate. This theorem follows directly from the principle of the mechanical transformability of the stationary states, since it may be shown that during such a slow change of the perturbing field the external forces will, with this approximation, not perform work on the particles of the system (compare BOHR, *loc. cit.* Part II). In order to apply the theorem in the present case we have to calculate the mean value of the potential energy of the electron with respect to a homogeneous electric field of force, taken over the motion which this electron performs in the stationary states of the undisturbed hydrogen atom, but owing to the symmetry of the latter motion round the nucleus this mean value is always equal to zero. In fact, with the notation of § 4, the perturbing potential is equal to  $Fz$ , and from (90) it is seen that the trigonometric series representing  $z$  as a function of the time for the undisturbed system does not contain a constant term, so that the mean value of  $z$  is equal to zero. (Compare also J. M. BURGERS, *Het atoommodel van Rutherford-Bohr*, Haarlem 1918, p. 128.)

In the later paper, referred to above, which deals with the transmutation of the fine structure into the Stark effect, it will be proved that, for small values of the intensity of the electric field, the additional energy in the stationary states may be represented by a series of terms of the form  $F \left[ a_1 \frac{F}{0} + a_2 \left( \frac{F}{0} \right)^2 + \dots \right]$ , if we disregard small terms the ratio of which to one of these terms is of the order  $F, F^2, \dots$  or  $0, 0^2, \dots$ . The largest term in the expression for the additional energy is thus seen to be a small quantity of the order  $\frac{F^2}{0}$ , and it is of interest that this term may be calculated already from the formulæ deduced in § 4. Thus it is seen from (94) that the mean position of the electron taken over a large time interval, which for the undisturbed orbit coincided with the nucleus, under the influence of the electric field is displaced in the direction of the positive  $z$ -axis by an amount equal to  $\frac{3eFz^2 I^0}{40} \cdot \frac{3(-\varepsilon^2 + \varepsilon'^2 \mu^2)}{\varepsilon'} = sF$ . If we now imagine that the electric force increases slowly and uniformly from zero, it will be seen that the work performed by the external force on the atom during this process will be equal to  $-\int_0^s eFd(sF) = -\frac{1}{2} seF^2$ . Since further the mean value of the potential energy of the perturbed atom with respect to the electric field is equal to  $sF \cdot eF = seF^2$ , it is seen, with reference to the principle of the mechanical transformability of the stationary states, that we may conclude that the additional energy in the stationary states of the system under consideration will be given by  $seF^2 - \frac{1}{2} seF^2 = \frac{1}{2} seF^2$ . Introducing  $I^0 = nh$ ,  $\varepsilon' = n_2/n$ ,  $\mu' = n/n_2$ ,  $0 = \frac{2\pi^2 N^2 e^4 m}{h^3} \left( \frac{2\pi Ne^2}{hc} \right)^2 \frac{1}{n^3 n_2^2}$  (compare formula (86)), and denoting the additional energy by  $\Delta E$ , we have thus

$$\Delta E = -\frac{9}{4} \left( \frac{h}{2\pi} \right)^8 \frac{c^2 F^2}{N^6 e^{10} m^3} n^5 n_2 (n^2 - 2n_2^2 + n^2).$$

This formula allows in first approximation to calculate the displacements of the components of the fine structure under the influence of an external electric field. In fact, the presence of the perturbing forces will cause that the frequency of the radiation corresponding to a transition  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$ , which gives rise to one of the components into which the fine structure component  $(n'_1, n'_2 \rightarrow n''_1, n''_2)$  is split up, will differ from the value of  $\nu$  given by (119) by an amount

$$\Delta \nu = \frac{\Delta E' - \Delta E''}{h} = -\frac{9}{4} \frac{h^7 c^2 F^2}{(2\pi)^6 N^6 e^{10} m^3} [n'^5 n'_2 (n'^2 - 2n_2'^2 + n'^2) - n''^5 n''_2 (n''^2 - 2n_2''^2 + n''^2)].$$

For the sake of orientation it may be of interest here to note that for increasing intensity of the electric field a state of the system, for which  $I_1^0 = n_1 h$ ,  $I_2^0 = (n_2 - n) h$ ,  $I_3^0 = n h$ , will be continuously



sed by the perturbing forces on the motion of the originally degenerate system, it will be seen that the circumstance, that in the present case the energy in the stationary states of the perturbed system to the first approximation does not depend on the value of the integer  $n$  appearing in the third of the conditions (124), is intimately connected with the fact that the two fundamental frequencies  $\omega_3$  and  $\omega_2$ , which together with  $\omega_1$  characterise the motion of the perturbed system, do not differ from each other as far as small quantities proportional to  $F$  are concerned (see § 4, page 33)<sup>1</sup>).

With reference to (1) it will be seen from the above that the effect of the external electric field on the spectrum of the hydrogen atom consists, as regards the frequencies, in the splitting up of every fine structure component in a number of components, because to every stationary state  $(n_1, n_2)$  of the undisturbed atom there corresponds a number of stationary states  $(n_1, n_2; n)$  of the

transformed into one among the stationary states involved in the theory of the Stark effect, for which, with the notation of § 3,  $I_3$  ( $= 2\pi \times$  angular momentum of the electron round the axis of the field) has the same value as  $I_3^0$ , but for which  $I_1 = I_2^0$  and  $I_2 = I_1^0$ .

<sup>1</sup>) From the formulæ (90) and (41) it will, with reference to the considerations on page 15 and 16, be seen that  $\omega_3 - \omega_2$  represents the frequency with which the plane of the orbit of the electron under the influence of the electric field rotates uniformly round the  $z$ -axis. As it will be proved in the paper referred to above, this frequency may, just as the additional energy, be represented by a series of the form  $F \left[ b_1 \frac{F}{0} + b_2 \left( \frac{F}{0} \right)^2 + \dots \right]$ ; the first term of this series may again be found already from the calculations in § 4, by means of a consideration of conservation of angular momentum analogous to that applied by ВОНН in his discussion of the Stark effect (loc. cit. Part II, p. 72). In fact, a rotation of the plane of the orbit will imply a change of the angular momentum of the electron round the nucleus, considered as a vector, the mean value of which, taken over a time interval large compared with  $\frac{1}{0}$  but small compared with  $\frac{1}{\omega_3 - \omega_2}$ , will have a direction perpendicular to the  $z$ -axis and, with the notation of § 4, be equal to  $\mu \frac{I_2^0 + I_3^0}{2\pi} \times 2\pi(\omega_3 - \omega_2)$ , where the first factor represents the component of the angular momentum of the electron perpendicular to the direction of the field. This mean change in angular momentum, however, is directly seen to originate from the fact that the mean position of the electron, taken over a time interval of the order mentioned, will not be placed on the  $z$ -axis but will, as seen from formula (96), be displaced from this axis by an amount  $\frac{3eFx^2I^0^3}{40} 3\mu\mu'\varepsilon'$  in a direction perpendicular to the direction of the mean change of the angular momentum. Equalizing the mean value of the change of angular momentum due to the action of the external force with the amount arising from the rotation of the plane we consequently get

$$-eF \times \frac{3eFx^2I^0^3}{40} 3\mu\mu'\varepsilon' = \mu \frac{I_2^0 + I_3^0}{2\pi} \times 2\pi(\omega_3 - \omega_2),$$

which gives

$$\omega_3 - \omega_2 = -\frac{9}{4} \frac{e^2 F^2 x^2 I^0^3}{0} \frac{\mu'\varepsilon'}{I_2^0 + I_3^0} = -\frac{9}{2} \frac{c^2 F^2}{(2\pi)^8 N^6 e^{10} m^3} I^0^5 (I_2^0 + I_3^0) I_3^0,$$

which, as it was to be expected, is seen to be a small quantity of the same order as the small frequency differences between the components into which each fine structure component is split up under the influence of the external field and which can be directly found from the formula for  $\Delta\nu$  deduced in the above note.



perturbed atom, corresponding to the different possible values of  $n$  ( $n = 1, 2, \dots, n_2$ ), but the displacements of these components from their original positions will only be small quantities proportional to the square of the electric field (the displacements being represented by small terms containing the factor  $F^2/\nu$ . Compare note 3 on page 77).

Let us now proceed to discuss the influence of the electric field on the intensities of the fine structure components. On BOHR's theory this influence may be discussed by considering the amplitudes of the harmonic vibrations in which the motion of the electron in the perturbed system may be resolved. Now for the undisturbed hydrogen atom there appear in the motion, as mentioned above, only vibrations of frequencies  $a\omega_1 \pm \omega_2$ , where  $a$  is a positive integer, and from this the conclusion was drawn that only such transitions were possible for which  $n'_2 - n''_2$  was equal to  $\pm 1$ , *i. e.* for which the angular momentum of the electron round the nucleus decreased or increased by  $h/2\pi$ . In the motion of the perturbed system, however, there appear vibrations of frequencies which did not appear in the original motion. Thus, identifying for the moment  $\omega_2$  and  $\omega_3$ , we see from the calculations in § 4 that there will occur vibrations in the motion of the perturbed system the amplitudes of which are small quantities proportional to  $F/\nu$ , and the frequencies of which are equal to  $a\omega_1$  and  $a\omega_1 \pm 2\omega_2$ , where  $a$  is an integer. On the other hand the amplitudes of the vibrations of the original frequencies which appeared already in the motion of the undisturbed atom are, as far as small quantities of this order are concerned, not influenced by the perturbing field. From these facts we may, with reference to the formal connection between the quantum theory and the ordinary theory of radiation, directly conclude that under the influence of the electric field there will appear new components in the fine structure of the hydrogen lines corresponding to transitions between an initial state  $(n'_1, n'_2)$  and a final state  $(n''_1, n''_2)$  for which  $n'_2 - n''_2 = 0$  or  $n'_2 - n''_2 = \pm 2$ , *i. e.* for which the angular momentum of the electron round the nucleus remains unchanged, or decreases or increases by  $2 \cdot h/2\pi$  (compare BOHR, *loc. cit.* Part II, p. 69). The intensities with which these new components appear will be of the same order as the square of the amplitudes of the vibrations corresponding to the new frequencies  $a\omega_1$  and  $a\omega_1 \pm 2\omega_2$ , *i. e.* they will be represented by small quantities proportional to  $(F/\nu)^2$ .

We may summarise the results of the preceding discussion by saying that the presence of a small homogeneous electric field of force in first approximation will leave the frequencies and relative intensities of the original fine structure components of the hydrogen lines unaltered, but will give rise to the appearance of new components, the frequencies of which are equal to the sum or to the difference of two of the original components. This affords a general interpretation of the fact mentioned above that the appearance and intensity of the fine structure components appearing on PASCHEN's photographs seem to depend on the experimental conditions



under which the spectrum was produced. In fact, we must naturally expect that in the vacuum tube containing the luminous gas there will always be electric fields acting on the atoms, but under different experimental conditions these fields will not be equally strong, and especially in the case where an interrupted spark discharge is applied, the intensity of such fields may become considerable.

In order to discuss in detail the intensities with which for a given value of  $F$  the new components may be expected to appear it will first of all be necessary to consider in detail the different transitions between stationary states giving rise to these components. The motion of the system in a stationary state  $(n_1, n_2; \pi)$  will be given by the formulae (83), (90), (94) and (96) in § 4, if we introduce for  $I_1^o, I_2^o, I_3^o$  and  $I^o$  in these formulae their values  $n_1, n_2 - \pi, \pi$  and  $n = n_1 + n_2$  respectively. A transition between an initial state  $(n'_1, n'_2; \pi')$  and a final state  $(n''_1, n''_2; \pi'')$  will be characterised by the symbol  $(n'_1, n'_2; \pi' \rightarrow n''_1, n''_2; \pi'')$ . If  $\omega_1, \omega_2$  and  $\omega_3$  have the same signification as in § 4 it may be shown by a closer examination of the perturbed system, as that which will be given in the later paper mentioned above, that the general relation discussed in § 5 between the frequencies which an atomic system will emit during a transition between two stationary states, and the frequencies occurring in the motion of the system, will in the present case exist therein that the frequency of the radiation emitted during a transition  $(n'_1, n'_2; \pi' \rightarrow n''_1, n''_2; \pi'')$  will be equal to the mean value of the frequency  $(n'_1 - n''_1)\omega_1 + (n'_2 - \pi' - n''_2 - \pi'')\omega_2 + (\pi' - \pi'')\omega_3$  occurring in the motion in the states corresponding to  $I_1^o = n'_1 + \lambda(n'_1 - n''_1), I_2^o + I_3^o = n''_2 + \lambda(n'_2 - n''_2), I_3^o = \pi'' + \lambda(\pi' - \pi'')$ , where  $\lambda$  takes all possible values between 0 and 1. Now the motion of the perturbed system may be resolved in a number of linear harmonic vibrations parallel to the electric force, the frequencies of which are of the type  $|\tau_1\omega_1 + \tau_2\omega_2|$ , and in a number of circular harmonic rotations perpendicular to the electric force and of frequencies  $|\tau_1\omega_1 + \tau_2\omega_2 + \omega_3|$ , as it is seen from (94) and (96). We shall therefore expect that, just as in the theory of the Stark effect, two kinds of transitions will be possible, *viz.* transitions for which  $\pi' - \pi'' = 0$  and which give rise to radiations polarised parallel to the electric force, and transitions for which  $\pi' - \pi'' = \pm 1$  and which give rise to radiations of circular polarisation perpendicular to the electric force.<sup>1)</sup> Further from (83), (90) and (94) it is seen that the motion of the electron parallel to the electric force consists partly of vibrations of frequencies  $|\tau_1\omega_1 + \omega_2|$  which also occurred in the undisturbed motion, and the amplitudes of which in first approximation are not affected by the electric force, partly of vibrations of frequencies  $|\tau_1\omega_1|$  and  $|\tau_1\omega_1 + 2\omega_2|$  the amplitudes of which are proportional to  $F/v$ . From this we may conclude that two types

<sup>1)</sup> This conclusion will be seen to be supported by a consideration of conservation of angular momentum round the axis of the field during the transitions, as that mentioned in note 2 on page 45. In this connection it may be of interest to observe that the effect of the external electric field in producing new components has intimate relation to the possibility for these forces to change the total angular momentum of the electron round the nucleus during a transition between two stationary states (compare RUBINOWICZ, l. c.).



of transitions will be possible for which  $n$  remains unaltered, *viz.* transitions for which  $n_2 - n$  and therefore also  $n_2$  changes by one unit, and which give rise to radiations corresponding to the original components of the fine structure; and transitions for which  $n_2 - n$  and therefore also  $n_2$  remains unaltered or changes by two units, giving rise to radiations which correspond to the new components. In the same way it is easily seen from (83), (90) and (96) that also the transitions for which  $n$  changes by one unit may be divided into transitions for which  $n_2$  changes by one unit and which contribute to the original components, and transitions for which  $n_2$  remains unchanged or changes by two units and which contribute to the new components. According to the considerations in § 5 we shall further expect that it will be possible, from the numerical values of the amplitudes of the corresponding harmonic vibrations occurring in the initial states and in the final states, to obtain an estimate for the relative intensities with which for a given hydrogen line ( $n' \rightarrow n''$ ) all these components will appear. Let us consider the estimate which in this way may be obtained from (94) and (96) for the intensities of the new components assuming that the direction of the perturbing electric field is perpendicular to the direction in which the spectrum is viewed. The radiations giving rise to a new component characterised by  $(n'_1, n'_2 \rightarrow n''_1, n''_2)$  will originate from different transitions  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  where  $n'_1, n'_2, n''_1, n''_2$  have the same values, but where  $n'$  and  $n''$  may assume different pairs of values. For  $n' - n'' = 0$  these transitions give rise to radiations polarised parallel to the electric force; for  $n' - n'' = \pm 1$  they will give rise to radiations polarised perpendicular to this direction. The new components might therefore in general be expected to show characteristic polarisation if the direction of the electric force was the same at all points in the luminescent vacuum tube which contribute to the formation of the spectroscopical image. In order to obtain an estimate for the intensities of the radiations corresponding to these transitions we shall, in analogy with the procedure followed in § 6, for each transition  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  calculate the square of the relative amplitude of the harmonic vibration of frequency  $(n'_1 - n''_1)\omega_1 + (n'_2 - n''_2)\omega_2 + (n'_3 - n''_3)\omega_3$  occurring in the motion in the initial state and in the final state, where just as in the preceding sections under relative amplitudes are understood the actual amplitudes divided by the length of the half major axis of the Keplerian orbit which the electron at any moment may be considered to describe. Now this half major axis is equal to  $zI^{0.2}$  so that from (94) and (96) the values of the relative amplitudes may directly be found. The expressions obtained in this way are all seen to contain the factor  $\frac{3eFxI^0}{4v}$ , which by means of (124) and (86) may be written in the form

$$\frac{3eFxI^0}{4v} = \frac{3}{2} F \left( \frac{h}{2\pi} \right)^6 \frac{c^2}{e^3 m^3} \cdot \frac{n^4 n_2^2}{N^5} = k F \frac{n^4 n_2^2}{N^5},$$

where  $k$  is a constant the value of which may be simply calculated from the experimental data, owing to the fact that we, with reference to formula (105), can write  $k$  in the form



$$k = \frac{3}{32\pi^2} \frac{c^2}{K^2 e},$$

where  $K/c$  is RYDBERG'S constant. Taking  $K/c = 1,097 \cdot 10^5$  and using MILLIKAN'S value for  $e$  ( $e = 4,77 \cdot 10^{-10}$ ), we find

$$k = 0,00165. \quad (125)$$

The expressions for the relative amplitudes may now be written in the form

$$\begin{aligned} R(\tau\omega_1) &= \frac{kFn^4n_2^2}{N^5} \frac{\varepsilon}{\tau\varepsilon'} \left\{ (2 + 5\mu^2\varepsilon'^2\tau) J_{\tau-1}(\tau\varepsilon) + (-2 + 5\mu^2\varepsilon'^2\tau) J_{\tau+1}(\tau\varepsilon) \right\}, \\ R(\overline{\tau-2\omega_1+2\omega_2}) &= \frac{kFn^4n_2^2}{N^5} \frac{\mu^2}{2\tau\varepsilon\varepsilon'} \left\{ (1+\varepsilon')((1+\varepsilon')(3\varepsilon'-2) - \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) + (1-\varepsilon')((1-\varepsilon')(3\varepsilon'+2) + \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \right\}, \\ R(\tau\omega_1 - \omega_2 + \omega_3) &= \frac{kFn^4n_2^2}{N^5} \frac{\mu\varepsilon}{2\tau} \left\{ (3 + 5\tau(1 + \varepsilon'\mu')) J_{\tau-1}(\tau\varepsilon) + (3 - 5\tau(1 - \varepsilon'\mu')) J_{\tau+1}(\tau\varepsilon) \right\}, \\ R(\overline{\tau-2\omega_1+\omega_2+\omega_3}) &= \frac{kFn^4n_2^2}{N^5} \frac{\mu(1+\mu')}{4\tau\varepsilon\varepsilon'} \left\{ (1+\varepsilon')((1+\varepsilon')(3\varepsilon'-2) - \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) + (1-\varepsilon')((1-\varepsilon')(3\varepsilon'+2) + \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \right\}, \\ R(\overline{\tau+2\omega_1-3\omega_2+\omega_3}) &= \frac{kFn^4n_2^2}{N^5} \frac{\mu(1-\mu')}{4\tau\varepsilon\varepsilon'} \left\{ (1-\varepsilon')((1-\varepsilon')(3\varepsilon'+2) - \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau-1}(\tau\varepsilon) + (1+\varepsilon')((1+\varepsilon')(3\varepsilon'-2) + \tau\varepsilon'(5-3\varepsilon'^2)) J_{\tau+1}(\tau\varepsilon) \right\}, \end{aligned} \quad (126)$$

where the quantities  $\varepsilon'$ ,  $\varepsilon$ ,  $\mu'$  and  $\mu$  are functions of the  $n$ 's which according to (94) and (124) are expressed by means of the formulae

$$\varepsilon' = \frac{n_2}{n}, \quad \varepsilon = \frac{1}{n} \sqrt{n^2 - n_2^2}, \quad \mu' = \frac{n}{n_2}, \quad \mu = \frac{1}{n} \sqrt{n_2^2 - n}, \quad (n = n_1 + n_2).$$

In case of circular orbits ( $\varepsilon' = 1$ ,  $\varepsilon = 0$ ,  $n_1 = 0$ ) the formulae (126) according to (97) assume the simple form

$$\left. \begin{aligned} R(2\omega_2) &= \frac{kFn^6}{N^5} \mu^2, \\ R(\omega_2 + \omega_3) &= \frac{kFn^6}{N^5} \frac{\mu(1+\mu')}{2}, \\ R(-3\omega_2 + \omega_3) &= \frac{kFn^6}{N^5} \frac{\mu(1+\mu')}{2}. \end{aligned} \right\} \quad (127)$$

The appearance of the factor  $n^4n_2^2$  in the formulae indicates that the intensities of the perturbed components will, for the same intensity of the electric field, increase very fast if the quantity  $n'$  characterising the initial state increases, so that for instance in the Balmer series the higher members will be much more influenced by an electric field than the first members. Further the appearance of  $N^5$  in the denominator indicates that for a hydrogen line ( $N=1$ ) the influence of an electric field will again be much stronger than for one of the analogous helium lines ( $N=2$ ) in the same part of the spectrum, in agreement with what might be directly expected from the fact that for the latter lines the frequency differences of the fine structure components are much smaller than for the former lines, while the frequency differences for the components of the Stark effect are larger.



III. Comparison of the theory with the observations on the fine structure.

We shall now proceed to compare the estimate of the relative intensities, obtainable from the preceding considerations, with PASCHEN'S observations. As mentioned at the end of the first section of this chapter it is necessary, in order to account for these observations, to pay attention to the disturbances which the fine structure undergoes as a consequence of the presence of external forces, and we shall therefore in the following discussion from the beginning take the intensities of the "new" components, discussed in the second section, into account. The first problem with which we meet will therefore be to compare these intensities for a given value of the intensity  $F$  of the external electric field with the intensities of the original components. Now the latter intensities were already estimated in the preceding section on the basis of the formulae (123), the numerical results being given in tables IX and X. It is, however, not possible to compare the numbers in these tables directly with the numbers obtained from (126) and (127) because in the formulae (123) are given the relative values of the amplitudes of the circular harmonic rotations which the electron in the undisturbed hydrogen atom performs in the plane of its motion. On the other hand, in order to take into account that the electron moves in space and that the position in space of the plane of its motion is arbitrary, it will obviously be sufficient to multiply the numbers  $n'_2 R'^2$  and  $n''_2 R''^2$  in tables IX and X by the factor  $2/3$ , the numbers thus obtained representing an estimate of the relative intensities of that part of the original components which may be considered as polarised parallel to the direction of the electric force, or that part which is polarised perpendicular to this direction, which two parts are equal on account of the original components being unpolarised. It must, however, be observed that we could also have obtained an estimate for the intensities of the original components by considering the different transitions ( $n'_1, n'_2; n''_1, n''_2; n''$ ) between stationary states of the perturbed system which contribute to these components, but this would complicate our tables without necessity, and moreover we shall have the opportunity to come back to this other method of estimating the intensities of the original components in § 8, where the influence of a magnetic field on the fine structure of the hydrogen lines will be discussed.

In the tables XI, XII and XIII we have given a scheme of the estimate which according to the preceding considerations can be obtained for the intensities of the new and of the original components in case of the fine structure of the helium lines  $4686 \text{ \AA}$  ( $4 \rightarrow 3$ ) and  $3203 \text{ \AA}$  ( $5 \rightarrow 3$ ) ( $N = 2$ ) and of the hydrogen line  $H_\alpha$ ,  $6563 \text{ \AA}$ , ( $3 \rightarrow 2$ ) ( $N = 1$ ). In the calculation of the tables we have taken  $F = 1$  *i. e.* the intensities of the new components refer to an intensity of the perturbing electric field of 300 Volt/cm.

The *first* column contains the symbols ( $n'_1, n'_2 \rightarrow n''_1, n''_2$ ) characterising the transitions between two stationary states of the hydrogen atom to which the new and the original components correspond.



The *second* column contains the symbols  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  characterising the transitions between two stationary states of the perturbed system which contribute to the new components. For each component the transitions which give rise to radiation polarised parallel to the direction of the electric force and those giving rise to radiation polarised perpendicular to this direction are collected in brackets and indicated by Par. and Perp. respectively. According to what has been said on page 77, only such states are taken into account for which  $n$  is different from zero.

The *third* and *fourth* columns contain the values of the squares of the relative amplitudes of the vibrations of frequencies  $(n'_1 - n'_1)\omega_1 + (n'_2 - n' - n''_2 - n'')\omega_2 + (n' - n'')\omega_3$  in the initial states and final states respectively, calculated by means of (125), (126) and (127). For the original components these columns contain the values of the squares of the quantities  $R'$  and  $R''$  appearing in tables IX and X.

The *fifth* and *sixth* columns contain the sums of these squares corresponding to each of the new components respectively, the quantities corresponding to radiation polarised parallel and to radiation polarised perpendicular to the axis being taken together respectively. For the original components these columns contain the values of  $\frac{2}{3}n'_2R'^2$  and  $\frac{2}{3}n''_2R''^2$ .

The *seventh* column contains the values of the wave lengths for the different components. These values may be calculated from the expression (119) for the frequencies of these components and are taken from PASCHEN's often mentioned paper.

We will now proceed to discuss the observations on the fine structure of the hydrogen lines ( $N = 1$ ) and of the analogous helium lines ( $N = 2$ ) in detail, and we shall first consider the latter lines for which we may compare with the detailed results of PASCHEN's observations. Especially in case of two of these lines, *viz.* 4686 Å ( $4 \rightarrow 3$ ) and 3203 Å ( $5 \rightarrow 3$ ), PASCHEN has been able to obtain in detail a confirmation of SOMMERFELD's theory regarding the frequencies of the fine structure components, and just for these lines a theoretical interpretation of the observed intensities seems only possible if the effect of a perturbing electric field is taken into account.

Let us first consider the helium line 4686 Å ( $4 \rightarrow 3$ ) for which the observed fine structure exhibits the richest details and therefore offers the best opportunity for a comparison with the theory. In fig. 10 on Plate IV a scheme is given of the theoretical and of the empirical results regarding the fine structure of this line. In the theoretical scheme the original components are indicated by drawn lines and the new components by dotted lines. The lengths of the latter lines are for each component taken proportional to the sum of the corresponding quantities  $s(R'^2)$  and  $s(R''^2)$  appearing in Table XI, while those of the former lines are taken proportional to twice the sum of the quantities  $\frac{2}{3}n'_2R'^2$  and  $\frac{2}{3}n''_2R''^2$  appearing in this table. The intensities of the new components, as given in the figure, would correspond to an intensity of 600 Volt/cm. In this connection it may be noted,



however, that owing to the fact that the relative amplitudes corresponding to the new components are of widely different order of magnitude in the initial and in the final state, we cannot expect that the sums of  $s(R'^2)$  and  $s(R''^2)$  will give more than an estimate of the order of magnitude of the intensities with which the new components must be expected to appear in comparison with the original components. The schemes representing the results of the measurements are taken from PASCHEN's paper. The one corresponds to what PASCHEN calls the "continuous discharge image" ("Gleichstrombild") of the fine structure, which appears when a

Table XI.  
Helium, 4686 Å ( $4 \rightarrow 3$ ).

New components (Perturbing field 300 Volt/cm)

Component	Transition	$R^2$	$R'^2$	$s(R'^2)$	$s(R''^2)$	Wave length	
04 → 12	Par. {	04; 2 → 12; 2	0	0		4685,684 Å	
		04; 1 → 12; 1	0	.0019	0		
	Perp. {	04; 3 → 12; 2	0	0			
		04; 2 → 12; 1	0	.0014	0		
		04; 1 → 12; 2	0	0			
13 → 21	Par. 13; 1 → 21; 1	.113	0	.11	0	5,331	
	Perp. 13; 2 → 21; 1	.056	0	.06	0		
13 → 03	Par. {	13; 3 → 03; 3	.031	0		5,837	
		13; 2 → 03; 2	.110	0	.32		0
		13; 1 → 03; 1	.176	0			
	Perp. {	13; 3 → 03; 2	0	0			
		13; 2 → 03; 1	.075	0			
		13; 2 → 03; 3	.019	0	.14		0
	13; 1 → 03; 2	.048	0				
22 → 12	Par. {	22; 2 → 12; 2	.018	.0009	.06	.004	5,764
		22; 1 → 12; 1	.046	.0035			
	Perp. {	22; 2 → 12; 1	0	.0020	.01	.002	
		22; 1 → 12; 2	.011	0			
31 → 21	Par. 31; 1 → 21; 1	.005	.0003	.005	.000	5,544	
31 → 03	Par. 31; 1 → 03; 1	0	0	0	0	6,050	
	Perp. 31; 1 → 03; 2	0	0	0	0		
Original components		$R^2$	$R'^2$	${}^2/3n_2R'^2$	${}^2/3n_2'R'^2$	Wave length	
04 → 03		1,00	1,00	2,66	2,00	4685,810 Å	
13 → 12		0,60	0,50	1,20	0,68	5,710	
22 → 21		0,35	0,24	0,46	0,16	5,384	
22 → 03		0,02	0	0,03	0	5,890	
31 → 12		0,05	0,01	0,03	0,01	5,924	



Table XII.  
Helium, 3203 Å (5 → 3).

New components (Perturbing field 300 Volt/cm)

Component	Transition	$R^2$	$R'^2$	$s(R^2)$	$s(R'^2)$	Wave length	
05 → 03	Par. {	05; 3 → 03; 3	.26	0	1,32	.0015	3203,167 Å
		05; 2 → 03; 2	.46	.00043			
		05; 1 → 03; 1	.60	.00111			
	Perp. {	05; 4 → 03; 3	.19	0	0,86	.0012	
		05; 3 → 03; 2	.26	.00055			
		05; 2 → 03; 1	.26	.00055			
		05; 2 → 03; 3	.05	0			
		05; 1 → 03; 2	.10	.00009			
14 → 12	Par. {	14; 2 → 12; 2	.47	0	1,20	.0008	3,111
		14; 1 → 12; 1	.73	.00077			
	Perp. {	14; 3 → 12; 2	.28	0	0,93	.0006	
		14; 2 → 12; 1	.35	.00058			
		14; 1 → 12; 2	.30	0			
23 → 21	Par. 23; 1 → 21; 1	.36	0	0,36	0	2,941	
	Perp. 23; 2 → 21; 1	.18	0	0,18	0		
23 → 03	Par. {	23; 3 → 03; 3	.04	0	0,54	0	3,177
		23; 2 → 03; 2	.19	0			
		23; 1 → 03; 1	.31	0			
	Perp. {	33; 3 → 03; 2	0	0	0,30	0	
		23; 2 → 03; 1	.17	0			
		23; 2 → 03; 3	.04	0			
		23; 1 → 03; 2	.10	0			
32 → 12	Par. {	32; 2 → 12; 2	.02	.00009	0,09	.0009	3,131
		32; 1 → 12; 1	.07	.00080			
	Perp. {	32; 2 → 11; 1	0	.00054	0,01	.0005	
		32; 1 → 12; 2	.01	0			
41 → 21	Par. 41; 1 → 21; 1	.005	.00003	0,005	.0000	2,992	
41 → 03	Par. 41; 1 → 03; 1	0	0	0	0	3,228	
	Perp. 41; 1 → 03; 2	0	0	0	0		
Original components		$R^2$	$R'^2$	${}^{2/3}n_2R^2$	${}^{2/3}n_2R'^2$	Wave length	
14 → 03		.049	0	.132	0	3203,171 Å	
23 → 12		.049	.052	.097	.069	3,118	
32 → 21		.036	.031	.047	.021	2,953	
32 → 03		.002	0	.003	0	3,190	
41 → 12		.006	.000	.004	.001	3,169	



Table XIII.  
Hydrogen,  $H_{\alpha}$ , 6562 Å (3 → 2).

New components (Perturbing field 300 Volt/cm)

Component	Transitions	$R'^2$	$R''^2$	$s(R'^2)$	$s(R''^2)$	Wave length
03 → 11	Par. 03; 1 → 11; 1	0	0	0	0	6562,70 Å
	Perp. 03; 2 → 11; 1	0	0	0	0	
12 → 02	Par. { 12; 2 → 02; 2 12; 1 → 02; 1	0,91	0	4,4	0	2,86
		3,54	0			
	Perp. { 12; 2 → 02; 1 12; 1 → 02; 2	0	0	0,8	0	
		0,82	0			
21 → 11	Par. 21; 1 → 11; 1	0,27	.0045	0,3	.005	2,75
Original components		$R'^2$	$R''^2$	$^{2/3}n_2 R'^2$	$^{2/3}n_2 R''^2$	Wave length
03 → 02		1,00	1,00	2,00	1,33	6562,84 Å
12 → 11		0,50	0,35	0,67	0,23	2,72
21 → 02		0,04	0	0,03	0	2,89

steady voltage is applied to the vacuum tube; the other to the "spark discharge image" ("Funkenbild"), which appears when the tube is exposed to an interrupted spark discharge. The heights and breadths of the hatched extensions representing the components are chosen so as to represent approximately the observed intensity and degree of diffusion. For the sake of the following discussion the observed components are, as shown in the figure, characterised by the ciphers I, II, . . . , VII.

When comparing the observations with the theory it will in the first place be seen that, although the spectrogram corresponding to the continuous discharge undoubtedly approaches more than the spectrogram obtained by the application of an interrupted discharge to the aspect of the theoretical fine structure of the spectral line of the undisturbed atom, both images given by PASCHEN differ essentially from it, because the components corresponding to (31 → 21) and (31 → 03) are present on both of them.<sup>1)</sup>

The strongest three components I, II and III in PASCHEN's continuous discharge image correspond, in agreement with the theory, to the three transitions (04 → 03),

<sup>1)</sup> Since at the time of PASCHEN's experiments a spectrogram of the fine structure would rather be considered as showing the normal effect when the maximum number of components appeared, no special attention seems to have been paid to an examination of the experimental conditions under which the smallest number of components appeared. In order to test the predictions of BOHR's theory the latter point has been examined by Dr. H. M. HANSEN at the Copenhagen physical laboratory. Although this investigation has not yet been completed, some preliminary photographs of the line 4686 Å, taken by application of a low voltage to the vacuum tube, indicate that the components (31 → 21) and (31 → 03), if present at all, were at any rate less intense compared with the main components I, II and III than in the spectrograms published by PASCHEN.



(13 → 12), (22 → 21) in which the angular momentum of the electron round the nucleus decreases by  $h/2\pi$ . From table XI the first of these components would be expected to be stronger than the second and the second again stronger than the third. PASCHEN, however, characterises their intensities by the numbers 7, 7,5, 3 respectively *i. e.* he finds the component (04 → 03) a little weaker than (13 → 12). This seems to indicate again that the a-priori probability of spontaneous transition between two circular orbits in the region of small  $n$ 's is less than it would be expected from the numbers obtained by the method of estimating intensities by means of the values of the amplitudes of the harmonic vibrations occurring in the motion of the atom, these values giving, in a singular case as this, an exaggerated picture of the intensities (compare page 60). In PASCHEN's spark discharge image the three components in question also appear, but they have become more diffuse, and I has become stronger than II, the relative intensities being now characterised by 7, 6, 0,5 respectively. This might obtain an explanation if we assume that, in the case of a spark discharge, perturbing electric fields have been acting on the atoms of such intensity that the new components (22 → 12) and (13 → 03) have appeared with considerable intensity. In fact, these components lie so near to (04 → 03) that they may be assumed together with the latter component to contribute to the intensity of the component I observed by PASCHEN, while on the other hand the new component (04 → 12) which lies very near to (13 → 12) will, as seen from the table, only possess a very small intensity in comparison with (22 → 12) and (13 → 03), and cannot therefore be expected to contribute essentially to the intensity of component II. In this connection it must, however, be remarked that the amplitudes of the harmonic vibrations of frequencies which correspond to the original components, in general, owing to the influence of the perturbing field, will have changed by small amounts proportional to  $F^2/\omega^2$ , and that as a consequence of this we may be prepared to find that the intensities of these components themselves have varied by amounts which are of the same order of magnitude as the intensities of the new components.

The weak original components (22 → 03) and (31 → 12) which correspond to transitions for which the angular momentum increases by  $h/2\pi$ , and the theoretical distance between which would be equal to 0,034 Å, are in the continuous discharge spectrogram, as well as in the spark discharge spectrogram, recorded by PASCHEN as a single line, which in figure 10 is indicated by IV.

Moreover PASCHEN has observed separately the new components (31 → 03), (31 → 21) and (13 → 21), indicated in the figure by V, VI and VII respectively. In table XI the values of  $s(R'^2)$  and  $s(R''^2)$  corresponding to (31 → 03) are equal to zero but, as pointed out in the analogous case in the Stark effect (see page 58, compare also page 99), it is not permissible from this to draw the conclusion that the a-priori probability for this transition is zero. Also the component (31 → 21) appears both on PASCHEN's continuous discharge image and spark discharge image and is stronger than (31 → 03), in agreement with the table. Finally, as regards (13 → 21), no corresponding component is observed in the continuous discharge image, but on the



other hand a very strong component has been observed in the spark discharge image, which lies in the middle between the theoretical positions of (13 → 21) and (04 → 21). On the present theory it seems necessary to assume that the component VII corresponds to (13 → 21) only. In fact, the intensity of the component (04 → 21) should be expected to be connected with the value of the amplitude of the vibration of frequency  $(-2\omega_1 + 3\omega_2)$  in the motion of the electron, but under the influence of a perturbing homogeneous electric field such frequencies do not in first approximation appear in the motion of the electron in the atom. The component in question is much stronger than the other two separate new components (31 → 21) and (31 → 03), in agreement with the table according to which (13 → 21) is the strongest new component after (13 → 03). On the other hand it remains a remarkable fact that the new component IV appears so much stronger than the original component III which lies quite near to it, while it does not appear at all in the continuous discharge spectrogram. Apart from this difficulty, which perhaps will disappear when further experimental data become available, the observations on the fine structure of 4686 Å seem to allow of a complete theoretical interpretation if the effect of the presence of electric fields in the vacuum tube is taken into account in the way described in the preceding. As regards the intensities of the perturbing electric forces in question it is seen from the table, which gives the values of the relative amplitudes for a force of 300 Volt/cm, that forces of 500 à 1000 Volt/cm would be sufficient to give rise to new components of considerable intensities which are of the same order of magnitude as those of the new components in the spark discharge image, while in case of the continuous discharge image these forces may have been of the order 100 à 300 Volt/cm.<sup>1)</sup>

Let us next proceed to the helium line 3203 Å (5 → 3), where the discussion of the observed fine structure is quite analogous to that for 4686 Å. In fig. 11 we have given a scheme of the theoretical fine structure and of the components observed by PASCHEN in the continuous discharge spectrogram. The original components are again represented by drawn lines, the new components by dotted lines. The lengths of the lines representing the original and the new components are taken proportional to the sums of the quantities appearing in the 5th and 6th columns of table XII, which is arranged in the same way as table XI. The lengths of the new components in the figure correspond to a perturbing field of 90 Volt/cm. Owing to the factor  $n^4 n_0^2$  in formula (126), the values for the relative amplitudes in the initial states, corresponding to the new components, are, for same values of  $F$ , several times larger than for the new components in 4686 Å. This seems to offer an explanation of the fact, mentioned by PASCHEN, that in the spark discharge spectrogram of the fine structure under consideration no sharp components could be

<sup>1)</sup> In the case of one of the photographs published by PASCHEN, which is taken under such conditions that the electric current had to pass a long sparking length, the electric forces have obviously been very large since the two strongest components could not be observed separately but appeared as a broad diffuse line.



observed, but that only two broad diffuse lines were visible (with their centres of gravity lying at 3203,140 Å and 3202,964 Å), because if the electric forces present in the luminous gas are of the same order of magnitude as in the case of the spark discharge image of 4686 Å, these forces must be expected to be strong enough to destroy the details of the fine structure to a large degree. In the continuous discharge spectrogram the strongest three components I, II, III correspond to the original components (14 → 03), (23 → 12) and (32 → 21), and their intensities may according to PASCHEN be characterised by the numbers 7, 8, 4 respectively, in general agreement with the values of  $n'_0 R'^2$  and  $n''_0 R''^2$  for these components given in table X. It must be expected, however, that component I contains not only the light of the original component (14 → 03) but also that of the original component (41 → 12) (and perhaps (32 → 03)) and of the new components (05 → 03) and (23 → 03); that II represents, besides (23 → 12), also (14 → 12) and perhaps (32 → 12), and finally that III represents, besides (32 → 21), also the new component (23 → 21). The two other weak components which PASCHEN observes in the continuous discharge image correspond to the two only new components which could be expected to appear separately, *viz.* (41 → 03) and (41 → 21).

The helium lines (6 → 3), (7 → 3), (8 → 3) and (9 → 3) have also been examined by PASCHEN. For the first three of these it was found possible to detect three components I, II, III which must be assumed to correspond to transitions to the final states (03), (12) and (21) respectively and the positions of which coincide to a high degree of approximation with those of the original components ( $n'-4, 4 \rightarrow 0,3$ ), ( $n'-3, 3 \rightarrow 1, 2$ ) and ( $n'-2, 2 \rightarrow 2, 1$ ). In agreement with the present theory, the intensity of I was smaller than that of II but a deal larger than that of III. The energy differences between the different initial states were so small that separate new components could not be observed, but the perturbing influence of electric fields in the vacuum tube is no doubt considerable for these lines.

PASCHEN has further examined the helium lines (6 → 4), (7 → 4), ... (12 → 4). The first of these lines, 6560 Å, appeared only very weak in the spectrograms and a fine structure could not be observed. An estimate for the intensities of the original components of this line has been given in table X. All the other lines showed two diffuse components the strongest of which in some spectrograms again showed a resolution in two components. Fig. 12 contains a scheme of the theoretical and of the observed fine structure of the line 5411,2 Å (7 → 4). For simplicity only the original components are drawn, their intensities as estimated from table X being indicated by the lengths of the lines. The arrows indicate the centres of gravity of the components observed by PASCHEN. The two small arrows on the right indicate the positions of the centres of gravity of the two components in which, in one of PASCHEN'S spectrograms, the stronger component was resolved. It will be seen that the observations are in agreement with the theory. The existence of separate new components, on account of the small frequency differences between the different possible initial states, could not be observed. As it may be seen from PASCHEN'S



paper the theory agrees with the observations also in the case of the fine structure of the other lines ( $8 \rightarrow 4$ ), ( $9 \rightarrow 4$ ), ... of the series in question; the stronger of the observed components may be ascribed to transitions to the final states (04), (13), (22), the weaker to transitions to the final state (31). It need hardly be remarked that it must be expected for all the lines in question that the details of the theoretical fine structure are influenced and disturbed to a high degree by the presence of electric fields in the vacuum tube. In fact, as seen from the observations on 4686 Å, the intensity of these fields seems, in case a continuous voltage was applied to the vacuum tube, to have been of the order of magnitude of 100 à 300 Volt/cm, but fields of this intensity will, as may be seen for instance from the formulae (126), be large enough to change the character of the stationary states corresponding to  $n = 6, 7, 8, \dots$  almost completely. That it has been possible to observe a fine structure at all is, just as in case of the fine structure of the lines ( $6 \rightarrow 3$ ), ( $7 \rightarrow 3$ ), ..., due to the fact that the final states involved in the transitions ( $n'' = 3$ ,  $n'' = 4$ ) are yet stable against the perturbing influence of electric fields of this order of magnitude.

Before leaving the comparison with the observations on the fine structure of the helium lines it may be of interest to emphasize that a further test of the theory may be obtained by an examination of a possible characteristic polarisation of these components with respect to the direction of the electric field in the discharge. Thus from the tables XI, XII and XIII it will be seen that, if the phenomenon is viewed in a direction perpendicular to the external electric force, we must expect that all the new components will contain a greater percentage of light polarised parallel to the electric force than of light polarised perpendicular to this direction, and especially that the component ( $31 \rightarrow 21$ ) of the line 4686 Å and the component ( $41 \rightarrow 21$ ) of the line 3203 Å should be completely polarised in the direction of the electric field. The question of the polarisation of the fine structure components seems not to have been examined by PASCHEN, and it also appears doubtful whether such a polarisation would have been detectable at all with the experimental arrangement used by this investigator, since the electric field may have quite different directions at the different points in the luminous gas which contribute to the formation of the spectroscopical image.

We shall now briefly consider the hydrogen lines ( $N = 1$ ) the fine structure of which has also been discussed in PASCHEN'S paper. For this element we must expect that, owing to the circumstance that the denominator  $N^5$  appearing in formula (126) is only equal to 1, the effect of small electric fields in the vacuum tube is yet much larger than for the helium lines discussed in the preceding. This is in agreement with the well known experimental fact that in the case of the Balmer series it is very difficult to obtain spectrograms which show a distinct fine structure. In table XIII we have, as mentioned, given an estimate for the intensities of the original and of the new components in case of  $H_\alpha$  ( $3 \rightarrow 2$ ), corresponding to an intensity of the electric field of 300 Volt/cm. The values for  $s(R^2)$  in this table are so large that, already for a field of 150 Volt/cm, the influence of the field on the



initial state ( $n' = 3$ ) can hardly any more be considered as a perturbation of the fine structure, but may rather be described as an effect of the same order of magnitude as the influence of the relativity modifications. On the other hand, as seen from the value of  $R'^2$  corresponding to the transition (21;  $1 \rightarrow 11$ ; 1), the motion in the final states is yet rather stable against perturbing forces of the order of magnitude in question. Owing to this, as well as to the smallness of the frequency differences involved in the theoretical fine structure, it has therefore only been possible to observe a doublet consisting of two diffuse components. In fig. 13 the theoretical fine structure has been schematically represented in the same way as in the figures 10 and 11. The lengths of the new components correspond to a perturbing field of 100 Volt/cm. The arrows indicate the position of the centres of gravity of the components observed by PASCHEN. The theoretical distance between the two strong original components ( $03 \rightarrow 02$ ) and ( $12 \rightarrow 11$ ) is 0,142 Å, while the width of the observed doublet was about 0,12 Å.<sup>1)</sup> The reason for this discrepancy must mainly be sought in the appearance of the new component ( $21 \rightarrow 11$ ), as well as in the splitting up of the components ( $03 \rightarrow 02$ ) and ( $12 \rightarrow 11$ ) into several components under the influence of the perturbing forces.<sup>2)</sup> This point will be discussed more closely in the later paper on the transmutation of the fine structure into the Stark effect, referred to above, but it has been mentioned here in order to draw attention to the difficulties which are involved in an exact determination of the constant  $K$  for hydrogen, appearing in formula (120), from measurements on the wave length of the hydrogen lines. As regards the measurements of the relative intensities of the components of the  $H_\alpha$  doublet, MEISSNER finds that the relative intensities of the component of larger and of that of shorter wave length may be represented by the numbers 7 and 5 respectively.<sup>3)</sup> This seems again to indicate that the a-priori probability for a transition between two circular orbits ( $03 \rightarrow 02$ ) is less than would be expected from the estimate afforded by table IX, which is based on the method discussed in § 5. As regards the other lines in the Balmer series of hydrogen,  $H_\beta, H_\gamma, \dots$ , doublets the width of which is of the right order of magnitude have been observed, but these lines are disturbed to a yet higher degree by small electric fields in the vacuum tube than  $H_\alpha$ . In general it will be seen that, when different investigators have found different values for the width of the doublet of one and the same hydrogen line, this may be due to the presence of perturbing fields of different intensities in the luminous gas. Especially, when certain authors find that the doublets of the higher members of the Balmer series are smaller than should be expected from SOMMERFELD's theory of the fine structure of the spectral lines emitted by the undisturbed hydrogen

<sup>1)</sup> See PASCHEN, loc. cit. p. 933, compare also SOMMERFELD, Ann. d. Phys. LI, p. 68 (1916).

<sup>2)</sup> From the formula for  $\Delta\nu$  given in note 3 on page 77 it is simply seen that in first approximation all components in which ( $03 \rightarrow 02$ ) will split up under the influence of an electric field are displaced in the direction of shorter wave length, while those of ( $12 \rightarrow 11$ ) are displaced in the direction of longer wave length.

<sup>3)</sup> See F. PASCHEN, loc. cit. p. 933.



atom<sup>1)</sup>, this does not constitute a difficulty for the theory but it just what should be expected according to the above considerations of the effect of perturbing fields on the fine structure.

### § 8. The effect of a magnetic field on the fine structure of the hydrogen lines.

In this chapter we shall briefly consider certain points which present themselves in connection with the application of the quantum theory to the problem of the effect of a magnetic field on the fine structure of the hydrogen lines, and from which it is possible to draw conclusions which are of interest in connection with the problems discussed in the preceding chapters.

The problem of the influence of a homogeneous magnetic field on the hydrogen atom may be treated in a similar way as the influence of an electric field on the simplified hydrogen atom, since the equations of motion of the electron also in the presence of the magnetic field may be written in the canonical form and since, if we look apart from small quantities proportional to the square of the intensity of the magnetic force, a solution of these equations may be obtained by separation of variables in the HAMILTON-JACOBI partial differential equation if polar coordinates are introduced.<sup>2)</sup> The motion in the stationary states will then be fixed by three conditions of the type (99). The results obtained in this way may be very simply interpreted. In fact, as mentioned in § 2, the mechanical motion of the electron in the hydrogen atom in the presence of a homogeneous magnetic field differs from a mechanical motion in the absence of this field only by a slow and uniform superposed rotation round an axis through the nucleus parallel to the magnetic force, the frequency  $\nu_H$  of which is given by (40), and it is simply shown that the stationary states of the system in the presence of the field are obtained by superposing a rotation of this kind on a stationary motion of the atom without field which, besides satisfying the conditions (117) characterising the stationary states of the undisturbed atom, satisfies the further condition that the value of the angular momentum of the electron round the axis is equal to an entire multiple of  $h/2\pi$ <sup>3)</sup>. Denoting this value by  $n h/2\pi$ , the stationary states may, in analogy with the notation used in the preceding chapter, be characterised by the symbol  $(n_1, n_2; n)$ . Further the different possible stationary states corresponding to different combinations of  $n_1, n_2, n$  ( $n_2 \geq n$ ) will again be a-priori equally probable, but just as in the case of the perturbed system treated in the preceding chapter, we must assume that neither  $n_2$  nor  $n$  can assume the value zero.

<sup>1)</sup> See T. R. MERTON and J. W. NICHOLSON, *Trans. Roy. Soc. A* 555 (1918).

<sup>2)</sup> Compare A. SOMMERFELD, *Phys. Zeitschr.* XVII, p. 491 (1916), and especially P. DEBYE, *ibid.* p. 507.

<sup>3)</sup> Compare BOHR, *loc. cit.* Part. II, p. 82.



Proceeding to discuss the effect of the magnetic field on the spectrum we see in the first place that the energy in a given stationary state will differ from the energy in the corresponding stationary state of the undisturbed atom, which was given by (118), only by a small term proportional to the intensity  $H$  of the magnetic field, which represents the effect of the superposed rotation on the kinetic energy of the system. This term is simply shown to be equal to  $\pm n h \nu_H = \pm n h \frac{eH}{4\pi m c}$ , where the upper or the lower sign holds according to whether the direction of the superposed rotation is the same as or the opposite of that of the revolution of the electron round the axis respectively. Considering a transition  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  between the initial state  $(n'_1, n'_2; n')$  and the final state  $(n''_1, n''_2; n'')$  we see therefore that the frequency of the emitted radiation will be given by

$$\nu = \nu_0 + \nu_1 + \nu_2 + \nu_3, \quad (128)$$

where  $\nu_0$ ,  $\nu_1$  and  $\nu_2$  have the same signification as in (120), (121) and (122), while  $\nu_3$  is given by

$$\nu_3 = \pm \frac{eH}{4\pi m c} (n' - n''). \quad (129)$$

As shown by SOMMERFELD and DEBYE the formulæ (128) and (129) offer an interpretation, as regards the frequencies, of the effect of a magnetic field on the hydrogen lines, since, putting  $n' - n'' = 0$  and  $n' - n'' = \pm 1$ , and disregarding the terms  $\nu_1$  and  $\nu_2$ , which refer to the fine structure, we obtain the frequencies of the three components in which the hydrogen lines are split up, these lines showing a normal Zeeman effect. Further BOHR showed that it is possible, on the basis of the formal connection between the quantum theory of line spectra and the ordinary theory of radiation, to obtain a natural interpretation of the characteristic polarisation of the observed three components, as well as of the fact that no further components appear; the theory of the Zeeman effect thereby obtaining a remarkable formal analogy with the theory originally devised by LORENTZ on the basis of the classical theory of electrodynamics.

From the considerations in § 2 it is seen that in the presence of a homogeneous magnetic field the motion of the electron in the hydrogen atom may be resolved in a number of linear harmonic vibrations of frequencies  $|\tau_1 \omega_1 + \omega_2|$  parallel to the direction of the field, and in a number of circular harmonic rotations of frequencies  $|\tau_1 \omega_1 + \omega_2 \pm \nu_H|$  perpendicular to this direction. Now it is easily shown that the frequency emitted during a transition  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  will be equal to the mean value of the frequency  $(n'_1 - n''_1) \omega_1 + (n'_2 - n''_2) \omega_2 \pm (n' - n'') \nu_H$ , taken over the multitude of mechanically possible states, lying between the initial state and the final state, which are characterized by  $n_k = n''_k + \lambda(n'_k - n''_k)$ , ( $k=1, 2$ ) and  $n = n'' + \lambda(n' - n'')$ ,  $\lambda$  assuming all values between 0 and 1. With reference to the formal connection between the quantum theory and the ordinary theory of radiation we may therefore conclude that only such transitions will be possible for which  $n$  remains unchanged, the emitted radiation being polarised parallel to



the axis, and transitions for which  $n$  decreases or increases by one unit, the emitted radiation being circularly polarised perpendicular to the axis, and that for both types of transitions  $n_2$  must either decrease or increase by one unit. From this it follows directly with reference to (128) and (129) that, as mentioned in BOHR'S paper, the effect of the magnetic field on the fine structure of the hydrogen lines will consist in the splitting up of every fine structure component into one undisplaced component polarised parallel to the direction of the field and two symmetrical components at a distance  $\frac{eH}{4\pi mc}$  from the undisplaced component, which appear as circularly polarised in opposite directions when viewed in the direction of the field and as linearly polarised perpendicular to the field when viewed in a direction perpendicular to the field.

As regards the intensities of these components we may in the first place obviously conclude that the latter two components are of equal intensity, since, if the effect is viewed in the direction of the field, they must not show characteristic polarisation when taken together. Further when viewed in a direction perpendicular to the field the intensity of each of the perpendicular components must be equal to half the intensity of the parallel undisplaced component, since we must equally assume that, when viewed in this direction, the ensemble of components into which the unpolarised fine structure component is split up does not exhibit characteristic polarisation. The theoretical effect of a magnetic field on the fine structure of the hydrogen lines may therefore be described as the splitting up of every fine structure component into a LORENTZ triplet.

We have thus met with an illustrative application of the considerations on page 49 at the end of § 5, and it is seen that the problem of the Zeeman effect of the fine structure of the hydrogen lines does not involve a new intensity problem if the intensity distribution in the undisturbed fine structure is known. It will therefore be of special interest in this case to compare the relative intensities of the Zeeman effect components with the amplitudes of the harmonic vibrations occurring in the states of the perturbed motion, since, owing to the circumstance that we have beforehand some information about these intensities, such a comparison will give us valuable information about the way in which the estimate of the relative intensities of spectral components, based on the values of these amplitudes, may be expected to fail if the numbers characterising the stationary states are small. For this purpose we have in the case of two special lines, *viz.* the helium line 4686 Å ( $4 \rightarrow 3$ ) and the hydrogen line  $H_\alpha$  (6562 Å), ( $3 \rightarrow 2$ ), calculated the squares of the relative amplitudes of the corresponding harmonic vibrations which occur in the initial states and in the final states involved in the different transitions giving rise to the different components of the Zeeman effect of the fine structure. The result of these calculations will be found in tables XIV and XV.

The *first* column contains the symbols ( $n'_1, n'_2 \rightarrow n''_1, n''_2$ ) characterising the transitions corresponding to the fine structure components of the undisturbed hydrogen atom.



The *second* column contains the symbols  $(n'_1, n'_2; n' \rightarrow n''_1, n''_2; n'')$  characterising the transitions which may take place between two stationary states of the atom perturbed by the magnetic field. The transitions corresponding to the same fine structure component which give rise to radiation of similar polarisation are collected in brackets, the character of the polarisation being indicated by Par. or Perp.

The *third* and *fourth* columns contain the squares of the relative amplitudes, given by (42), of the vibrations of frequency  $(n'_1 - n''_1)\omega_1 + (n'_2 - n''_2)\omega_2 \pm (n' - n'')\omega_H = (n'_1 - n''_1)\omega_1 + (n'_2 - n' - n''_2 - n'')\omega_2 + (n' - n'')\omega_3$  occurring in the initial state and in the final state of the transition under consideration respectively. These relative amplitudes are calculated by means of the expressions

$$\left. \begin{aligned} R(\tau-1 \omega_1 + \omega_2) &= \frac{\mu}{2\tau} \{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \}, \\ R(\tau-1 \omega_1 + \omega_3) &= \frac{1 + \mu'}{4\tau} \{ (1 + \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 - \varepsilon') J_{\tau+1}(\tau\varepsilon) \}, \\ R(\tau+1 \omega_1 - 2\omega_2 + \omega_3) &= \frac{1 - \mu'}{4\tau} \{ (1 - \varepsilon') J_{\tau-1}(\tau\varepsilon) - (1 + \varepsilon') J_{\tau+1}(\tau\varepsilon) \}. \end{aligned} \right\} \quad (130)$$

where  $\varepsilon' = \frac{n_2}{n}$ ,  $\varepsilon = \sqrt{1 - \varepsilon'^2}$ ,  $n = n_1 + n_2$ ,  $\mu' = \frac{n}{n_2}$ ,  $\mu = \sqrt{1 - \mu'^2}$ .

The *fifth* and *sixth* columns contain the sums  $s(R'^2)$  and  $s(R''^2)$  of the squares of the relative amplitudes belonging to the transitions corresponding to a same fine structure component which give rise to radiations of similar polarisation.

The *seventh* and *eighth* columns contain the values of  $n'_2 R'^2$  and  $n''_2 R''^2$ , appearing in tables IX and X, multiplied by the factor  $2/3$ . These numbers, as mentioned on page 84, afford an estimate for the relative intensities of the fine structure components which is directly comparable with the estimate afforded by the numbers in the fifth and sixth columns.

When considering these tables it will in the first place be observed that for a given fine structure component the quantities  $s(R^2)$  Par. and  $s(R^2)$  Perp., which correspond to the intensity of the undisplaced parallel component and to twice the intensity of one of the outer components of the LORENTZ triplet respectively, are not equal to each other, although, as mentioned in the above, these two intensities are the same. Moreover the quantities  $s(R^2)$  Par. and  $s(R^2)$  Perp. differ both from the value of the quantity  $2/3 n_2 R^2$  appearing in the seventh and eighth columns, which corresponds to the same intensity. From the connection with ordinary electrodynamics in the region of large  $n$ 's we know that for a fine structure component  $(n'_1 n'_2 \rightarrow n''_1 n''_2)$  for which the  $n$ 's are large numbers these three quantities would tend to coincide, but in the case of the lines considered in the tables they show considerable differences. If we especially would consider the hydrogen line  $(2 \rightarrow 1)$ , which corresponds to the smallest possible values for  $n'$  and  $n''$ , these differences become still more marked. This line will not show a fine structure because in the undisturbed atom only the



Table XIV.  
Helium, 4686 Å (4 → 3).

Component	Transition	$R^2$	$R'^2$	$s(R^2)$	$s(R'^2)$	$(\frac{2}{3}n_g R^2)$	$(\frac{2}{3}n_g' R'^2)$	
04 → 03	Par. {	04; 3 → 03; 3	0,44	0	2,13	1,45	2,66	2,00
		04; 2 → 03; 2	0,75	0,56				
		04; 1 → 03; 1	0,94	0,89				
	Perp. {	04; 4 → 03; 3	1,00	1,00	2,53	2,16		
		04; 3 → 03; 2	0,77	0,69				
		04; 2 → 03; 1	0,56	0,44				
		04; 2 → 03; 3	0,06	0				
		04; 1 → 03; 2	0,14	0,03				
13 → 12*	Par. {	13; 2 → 12; 2	0,33	0	0,88	0,38	1,20	0,68
		13; 1 → 12; 1	0,53	0,38				
	Perp. {	13; 3 → 12; 2	0,60	0,50	1,09	0,78		
		13; 2 → 12; 1	0,42	0,28				
		13; 1 → 12; 2	0,07	0				
22 → 21	Par. 22; 1 → 21; 1	0,27	0	0,27	0	0,47	0,16	
	Perp. 22; 2 → 21; 1	0,35	0,24	0,35	0,24			
22 → 03	Par. {	22; 2 → 03; 2	0	0	0,015	0	0,026	0
		22; 1 → 03; 1	0,015	0				
	Perp. {	22; 2 → 03; 1	0	0	0,030	0		
		22; 2 → 03; 3	0,019	0				
		22; 1 → 03; 2	0,011	0				
31 → 12	Par. 31; 1 → 12; 1	0	0,006	0	0,006	0,034	0,010	
	Perp. 31; 1 → 12; 2	0,051	0,008	0,051	0,008			

Table XV.  
Hydrogen, 6562 Å,  $H_\alpha$  (3 → 2).

Component	Transition	$R^2$	$R'^2$	$s(R^2)$	$s(R'^2)$	$(\frac{2}{3}n_g R^2)$	$(\frac{2}{3}n_g' R'^2)$	
03 → 02	Par. {	03; 2 → 02; 2	0,56	0	1,46	0,75	2,00	1,33
		03; 1 → 02; 1	0,90	0,75				
	Perp. {	03; 3 → 02; 2	1,00	1,00	1,80	1,56		
		03; 2 → 02; 1	0,69	0,56				
		03; 1 → 02; 2	0,11	0				
12 → 11	Par. 12; 1 → 11; 1	0,38	0	0,38	0	0,67	0,23	
	Perp. 12; 2 → 11; 1	0,50	0,35	0,50	0,35			
21 → 02	Par. 21; 1 → 02; 1	0	0	0	0	0,026	0	
	Perp. 21; 1 → 02; 2	0,038	0	0,038	0			



transition ( $02 \rightarrow 01$ ) will be possible. In the presence of a magnetic field it will split up into a normal LORENTZ triplet, where the undisplaced parallel component corresponds to the transition ( $02; 1 \rightarrow 01; 1$ ) and each of the outer components to the transition ( $02; 2 \rightarrow 01; 1$ ). The values of  $R'^2$  and  $R''^2$  corresponding to the former transition are easily seen to be equal to  $3/4$  and 0 respectively, while those corresponding to the latter transition are both equal to 1.

In this connection it may be of interest to notice that, for all the fine structure components considered, the value of  $s(R^2)$  Perp. is larger than that of  $s(R^2)$  Par., and that in the case of the components ( $04 \rightarrow 03$ ), ( $03 \rightarrow 02$ ) and especially ( $02 \rightarrow 01$ ) this seems to be due mainly to the large values of  $R'^2$  and  $R''^2$  ( $R'^2 = R''^2 = 1$ ) corresponding to transitions between two stationary states in both of which the orbit of the electron is circular. This is in agreement with the analogous facts mentioned in the discussion of the theory of the Stark effect and of the fine structure, which seemed to indicate the general result that the estimate of the intensities of spectral lines by means of the values of the amplitudes of the corresponding harmonic vibrations in the states implied in the transitions assumes, in the region of small  $n$ 's, an exaggerate character as soon as, owing to the singular character of the motion in these states, the values of these amplitudes become either especially large (*e. g.* transition from circular orbit to circular orbit) or especially small (*e. g.* transition from non-circular orbit to circular orbit).

An interesting remark may further be made in connection with the Zeeman effect of the component ( $21 \rightarrow 02$ ) in  $H_\alpha$ . This component will, under the influence of the magnetic field, be split up into an undisplaced parallel component corresponding to ( $21; 1 \rightarrow 02; 1$ ) and two perpendicular components corresponding to ( $21; 1 \rightarrow 02; 2$ ) the intensity of each of which is equal to half the intensity of the undisplaced component. The values of  $R'^2$  and  $R''^2$  corresponding to ( $21; 1 \rightarrow 02; 1$ ) are, however, both equal to zero, so that we are able to conclude by purely theoretical argument that the a-priori probability for a transition, for which the amplitudes of the harmonic vibrations of corresponding frequency occurring in the motion in the initial state and in the final state are both equal to zero, will not necessarily be equal to zero. In the discussion of the Stark effect and of the influence on the fine structure due to a small electric field we have already met with analogous transitions, and just as in those cases, we have in the present case that the amplitude of the corresponding harmonic vibration is different from zero in the mechanically possible states lying between the initial state and final state, and which here are characterised by ( $2\lambda, 2 - \lambda; 1$ ), where  $0 < \lambda < 1$ .

Especially when considering transitions of the type just discussed the question arises whether the estimate of the intensities of the components in which a spectral line is split up would not be essentially improved by comparing these intensities with some kind of mean value of the square of the corresponding amplitude taken



over the states lying between the initial state and the final state. Although, as mentioned in § 5 (compare page 63), such a calculation may perhaps permit of accounting in more detail for the observed intensities, a consideration of the Zeeman effect of the hydrogen lines can, however, be used to show that no simple type of mean value will be able to give an exact measure for the relative intensities. Let us thus especially consider the hydrogen line ( $2 \rightarrow 1$ ), which in a magnetic field will show the components  $(02; 1 \rightarrow 01; 1)$  and  $(02; 2 \rightarrow 01; 1)$ . In the states characterised by  $(0, 1 + \lambda; 1)$  the square of the relative amplitude of the harmonic vibration of frequency  $\omega_2$  is, as seen from (130), given by  $1 - \frac{1}{(1 + \lambda)^2}$ , while in the states characterised by  $(0, 1 + \lambda; 1 + \lambda)$  the square of the relative amplitude of the harmonic vibration of frequency  $\omega_3$  is equal to 1. Now it is beforehand clear that any simple type of mean value of  $1 - \frac{1}{(1 + \lambda)^2}$ , taken over all values of  $\lambda$  between 0 and 1, never can be equal to 1, which number obviously represents any such mean value corresponding to the second transition. Since nevertheless the corresponding intensities are the same, we are therefore directly led to the above conclusion. If, for instance, we would use the logarithmic mean value defined by (109) which, as mentioned on page 46, for several reasons offers itself naturally for an estimate of the intensities, we would for the first transition, as it may be shown by a simple calculation, get the value  $\frac{3\sqrt{3}}{16}$ , while for the second transition we would get 1. Even if we may be justified in expecting that in general it will be possible by means of the mean value in question to obtain a closer estimate of the relative intensities of spectral lines, we see from this example that, in case the  $n$ 's are small, the errors involved in such an estimate may become considerable in especially chosen unfavourable cases.

In concluding this paper it may be useful once more to emphasize the incomplete and preliminary character of the underlying considerations. Nevertheless the results obtained as regards the applications to the Stark effect and to the fine structure of the hydrogen lines must be considered as affording a general support of BOHR's fundamental hypothesis of the connection between the intensity of spectral lines and the amplitudes of the harmonic vibrations into which the motion of the electron in the atom may be resolved, the more so because it seemed possible to obtain a natural understanding of certain marked deviations of the observed intensities from the preliminary theoretical estimate of the intensity distribution obtained on the basis of this hypothesis. It seems therefore justifiable to conclude that BOHR's considerations offer a sound basis for a further development of the theory of intensities of spectral lines.



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## DESCRIPTION OF PLATES

Plate I and Plate II. Stark effect of hydrogen lines. Fig. 1, 2, 3 and 4. Comparison for  $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$  of theoretical estimate of relative intensities of components with STARK's observations (see page 55).

Fig. 5. Reproduction of STARK's photographs of effect of electric field on  $H_\beta$ ,  $H_\gamma$  and  $H_\delta$  (see page 54).

Fig. 6. Theoretical estimate of effect of electric field on hydrogen line  $H_\epsilon$  (see page 63).

Plate III. Stark effect of helium lines. Fig. 7, 8, 9. Theoretical aspect of electric resolution of 4686 Å, 3203 Å, 2733 Å, compared with the rough analysis of this resolution observed by NYQUIST and by STARK, the observed components being indicated by arrows (see page 64).

In all figures of theoretical estimate of intensities of Stark effect components, components represented by dots mean that the theoretical estimate for the intensity of these components is too small to be conveniently represented on the same scale as other components.

Plate IV. Fine structure of hydrogen and helium lines. Fig. 10, 11, 13. Theoretical fine structure of helium lines 4686 Å and 3203 Å, and of hydrogen line  $H_\alpha$ , compared with PASCHEN's observations. Lengths of drawn components proportional to estimate of intensities of components of fine structure for undisturbed atom. For the sake of convenience, however, component (04 → 03) in fig. 10 and component (03 → 02) in fig. 13 are represented by lines 2.5 times shorter than that corresponding to scale of other components. Dotted lines represent estimates of intensities of new components corresponding to electric field of 600 Volt/cm in fig. 10, of 90 Volt/cm in fig. 11 and of 100 Volt/cm in fig. 13 (see pages 85, 90 and 93).

Fig. 12. Theoretical estimate of intensities of original components of fine structure of helium line 5411 Å, compared with PASCHEN's observations (see page 91).

Components represented by small squares in the case of original components and by one dot in the case of new components have generally theoretical intensities which are far too small to be conveniently represented on the scale used.

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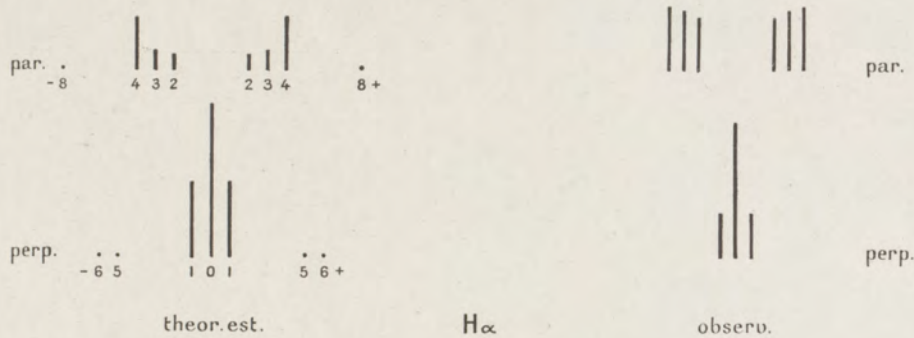


Fig.1

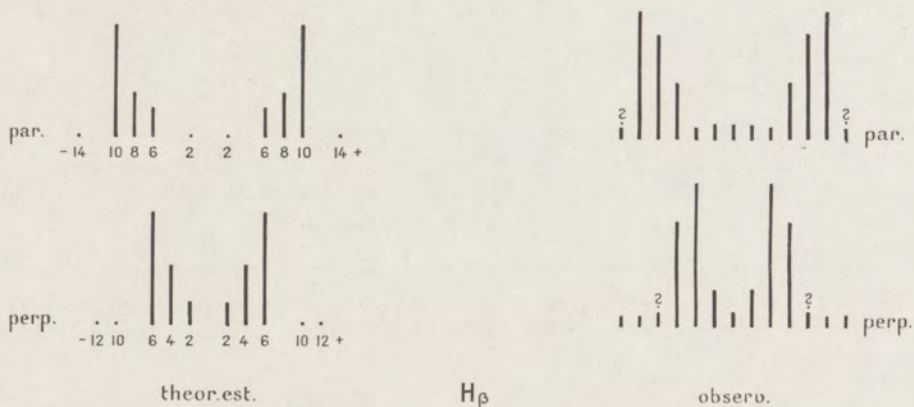


Fig.2

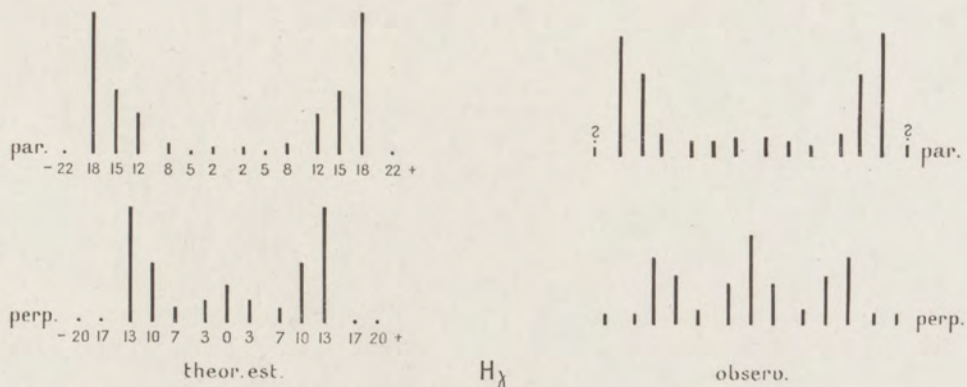
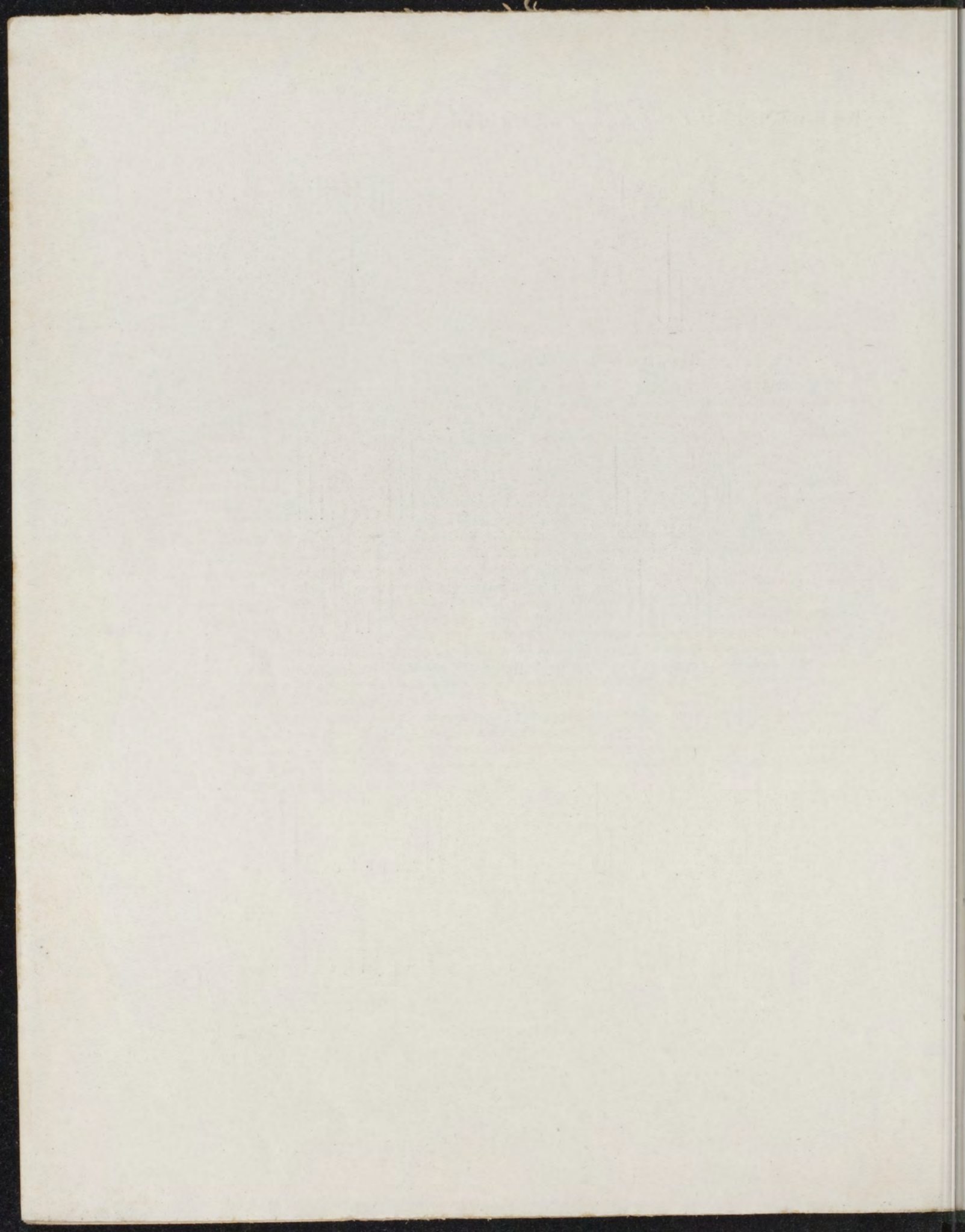


Fig.3







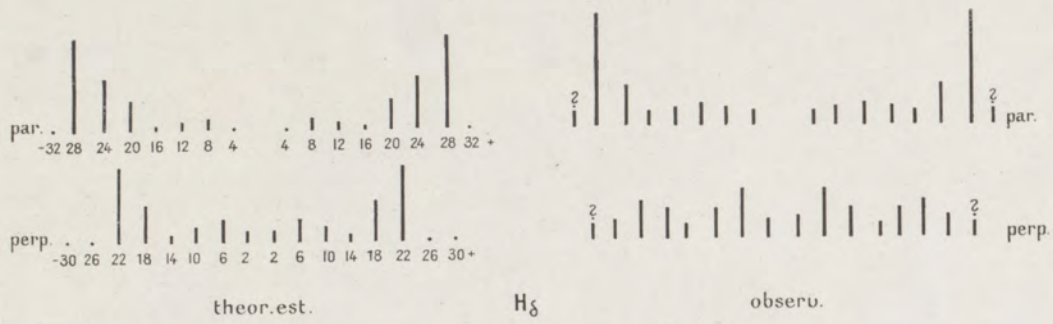


Fig.4

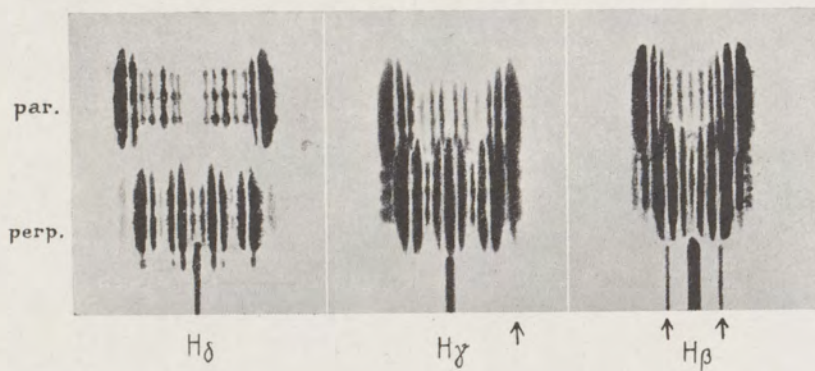


Fig.5

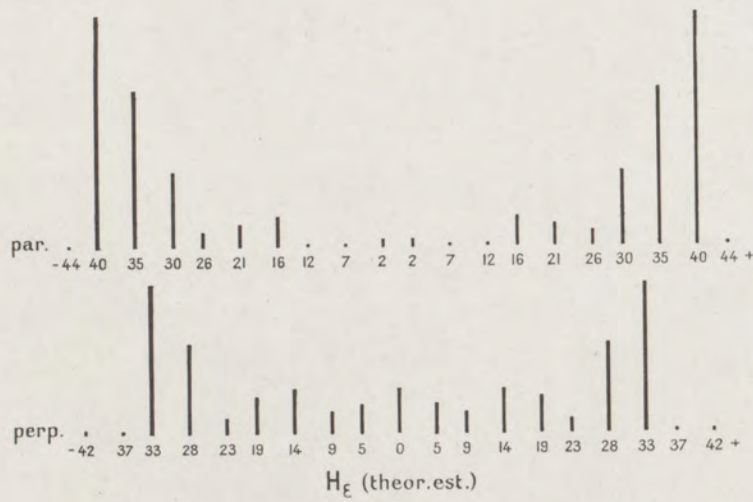
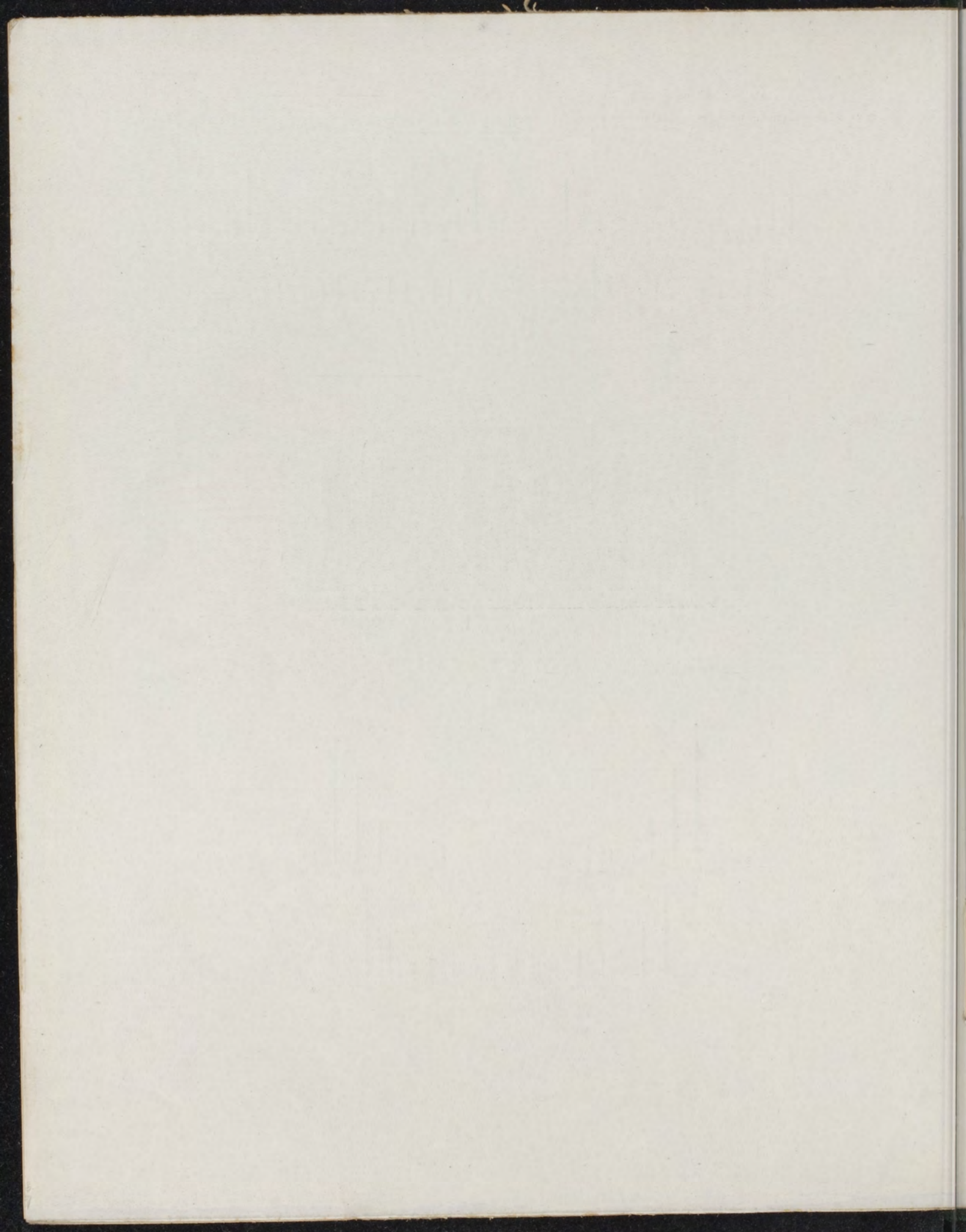


Fig.6







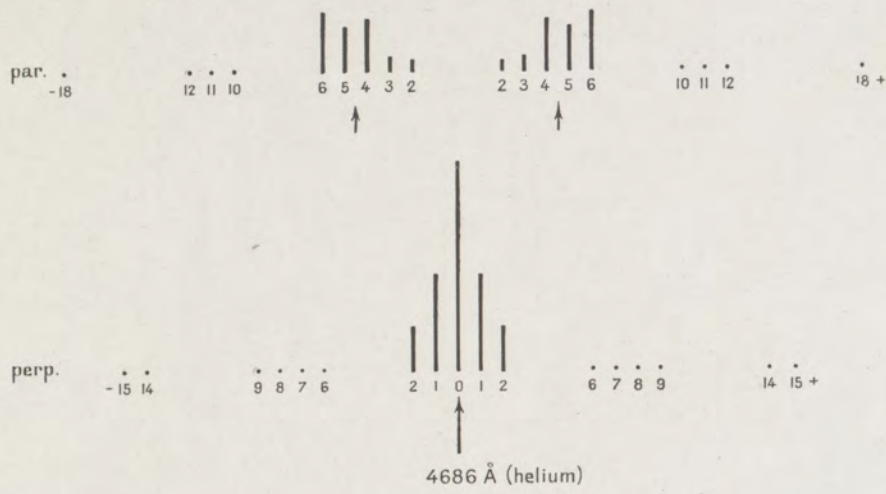


Fig.7

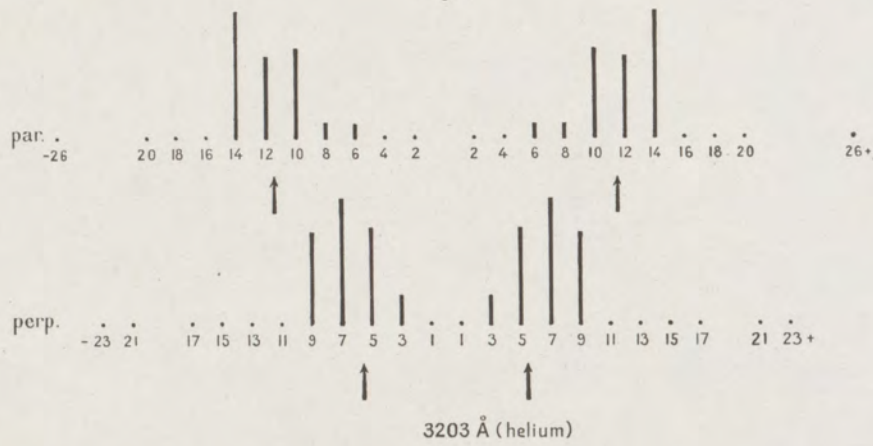
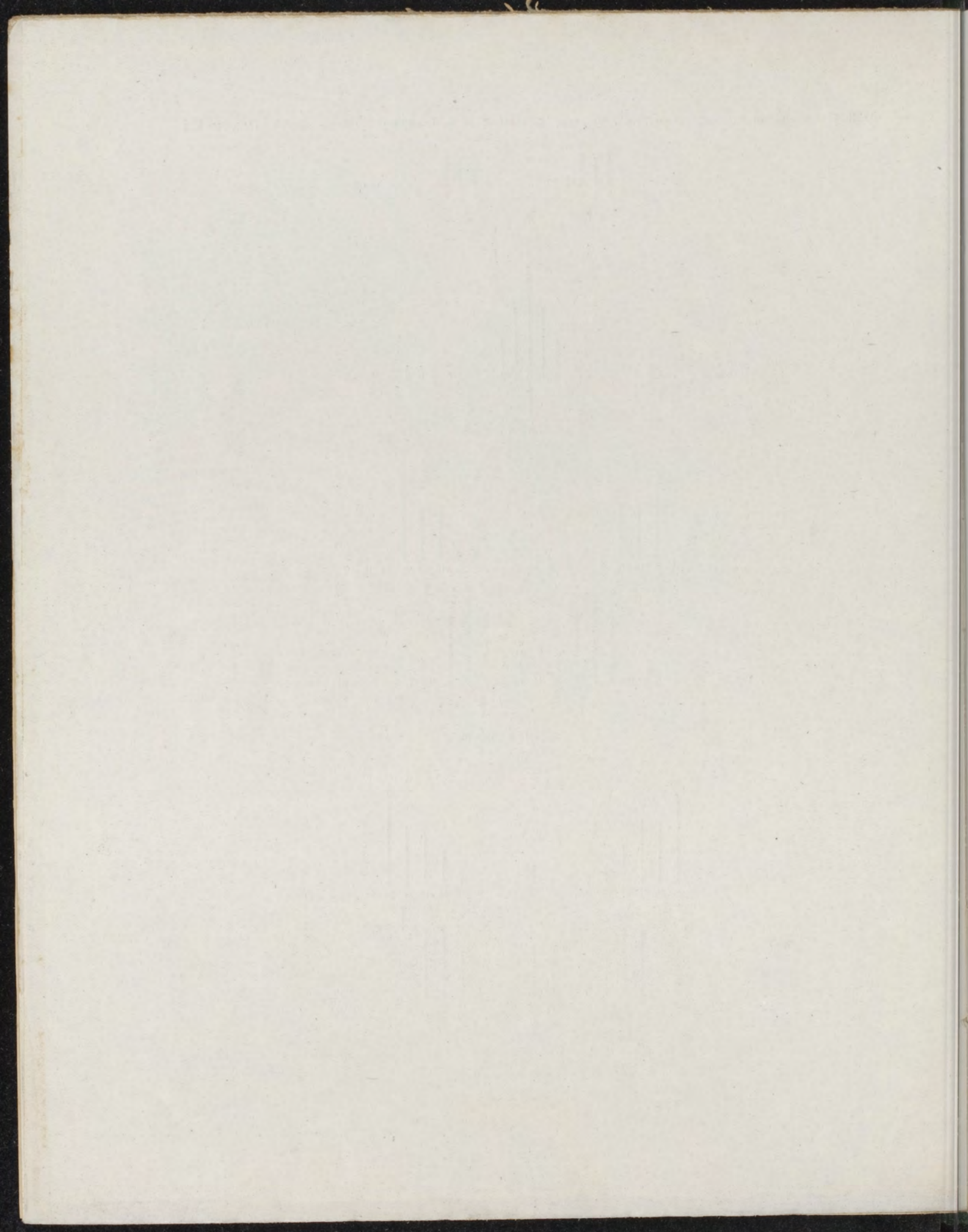


Fig.8



Fig.9







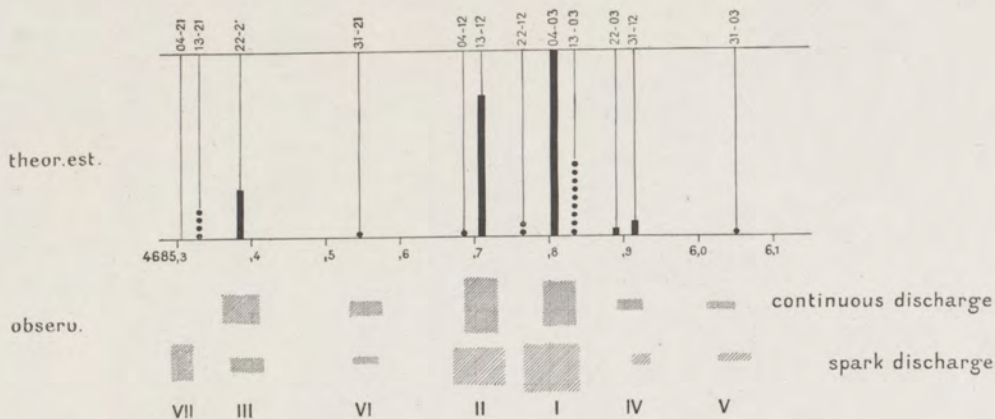


Fig.10 4686 Å (helium), (4→3).

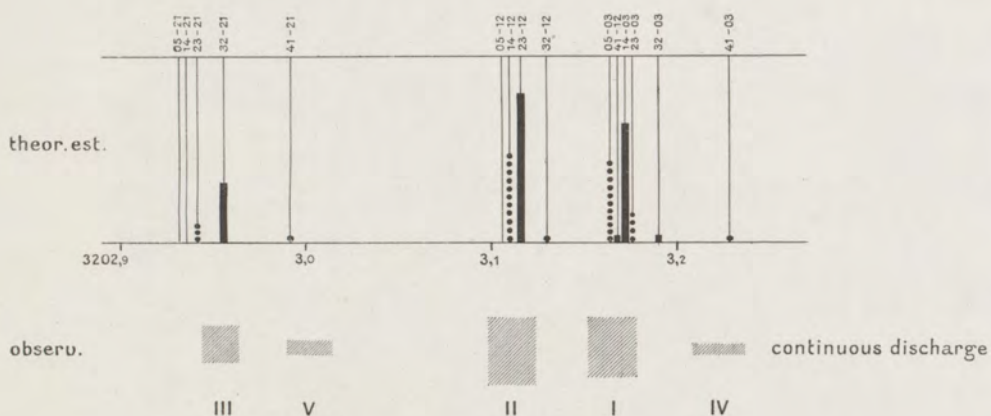


Fig.11 3203 Å (helium), (5→3).

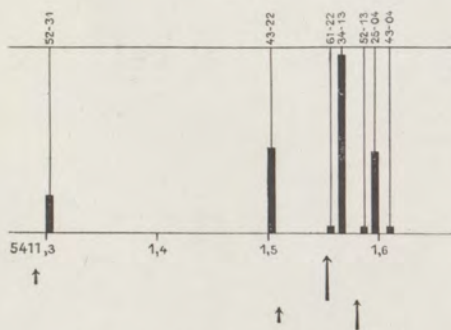


Fig.12 5411 Å (helium), (7→4).

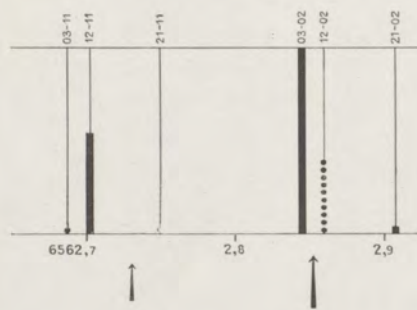
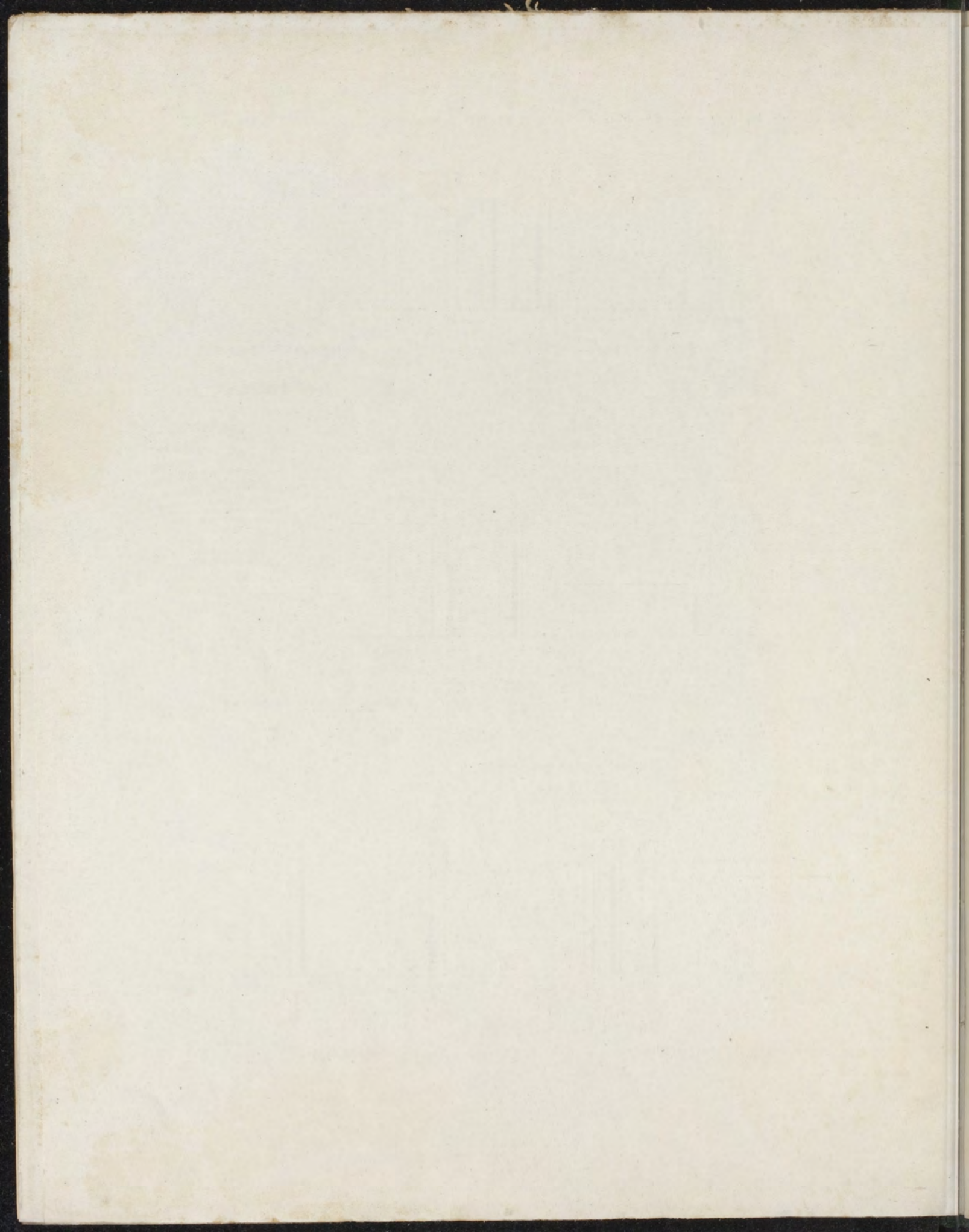


Fig.13 6562 Å (hydrogen, H<sub>α</sub>), (3→2).

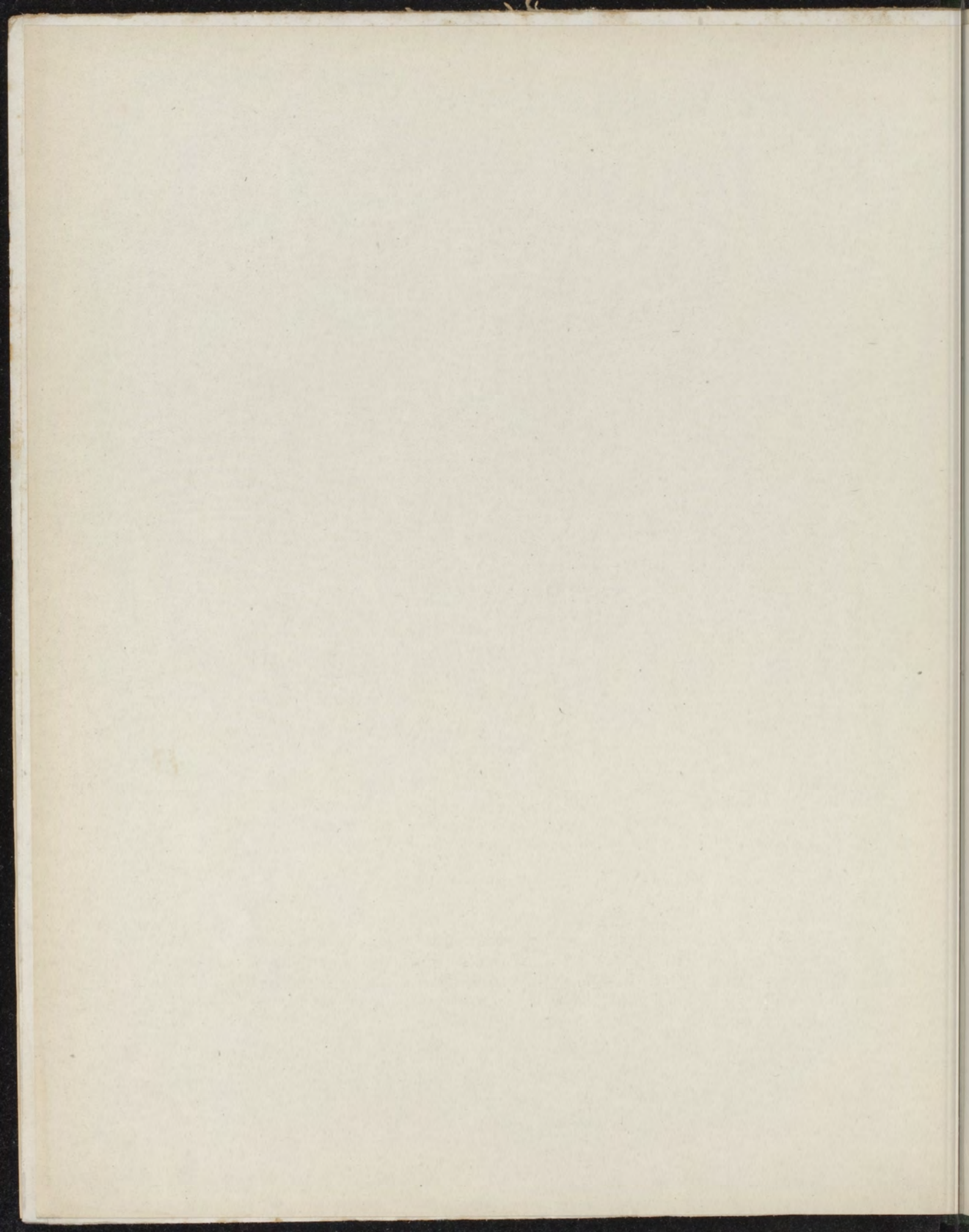






STELLINGEN.







## STELLINGEN.

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### I.

De moeilijkheden die zich in de quantentheorie voordoen wanneer men te maken heeft met een zoogenaamd „ontaard” systeem kan men niet ontgaan met behulp van EPSTEIN's hypothese dat werkelijk ontaarde systemen niet voorkomen in de natuur; een juist begrip van dezelve moet gezocht worden in een natuurlijke begrenzing van de toepassing der mechanica op het gebied der quantentheorie.

### II.

De veronderstellingen op welke PLANCK's zoogenaamde tweede stralings-theorie berust leiden bij een consequente doorvoering tot resultaten die onvereinigbaar schijnen te zijn met de fundamenteele principes van de warmtetheorie.

### III.

Een poging om quantenvoorwaarden in te voeren voor de hyperbolische banen welke het electron in het waterstofatoom kan beschrijven rondom den kern schijnt met het wezen der stationnaire toestanden in strijd te zijn.

### IV.

Wanneer men de vastlegging der stationnaire toestanden beschouwt vanuit het gezichtspunt van samenhang tusschen energie en frequentie laat zich het vraagstuk van de quantenvoorwaarden voor de vrije beweging van een willekeurig vast lichaam om zijn zwaartepunt op eenvoudige wijze overzien.



## V.

Om het optreden van een karakteristieke Röntgenstraling, die harder is dan de K-straling, te verklaren is het niet noodig de fundamenteele veronderstelling te verlaten dat voor een electron dat zich in een cirkelvormige baan beweegt het hoekmoment rondom het middelpunt gelijk is aan een geheel veelvoud van  $h/2\pi$ .

## VI.

Het schijnt dat voor een mechanisch systeem, bestaande uit een massapunt dat zich in een konstant krachtveld beweegt, separatie van variabelen in de partieele differentiaal-vergelijking van HAMILTON-JACOBI alleen bereikt kan worden voor elliptische coördinaten.

## VII.

Voor een verdere ontwikkeling van de quantentheorie zou het ten zeerste gewenscht zijn nauwkeurige metingen te kunnen uitvoeren van de relatieve intensiteit van spektraallijnen, ook als deze zich bevinden op plaatsen in 't spectrum die ver van elkaar liggen.

## VIII.

Teneinde trigonometrische reeksen te vinden, die formeel voldoen aan de bewegings-vergelijkingen voor twee planeten die zich in eenzelfde vlak rondom de zon bewegen, is het niet noodig te veronderstellen dat de coëfficiënten in deze reeksen naar machten van de excentriciteiten ontwikkeld zijn, doch is het voldoende aan te nemen dat deze coëfficiënten voorgesteld kunnen worden door reeksen die voortschrijden naar opklimmende machten van de verhouding tusschen de massa der planeten en de massa van de zon.

## IX.

Wanneer men rekening houdt met de elektrische krachten die de ionen van een elektrolyt op elkaar uitoefenen is het mogelijk de eigenschappen der sterke elektrolyten te verklaren, uitgaande van de eenvoudige veronderstelling dat zoodanige elektrolyten in niet al te groote concentraties totaal gedissocieerd zijn. (Vgl. N. BJERRUM, Zeitschr. f. Elektrochem. 24, pag. 321 (1918))



## X.

HJELMSLEV's onderzoeken over „werkelijkheidsmeetkunde”, in welke o. a. aangetoond wordt hoe een meetkunde opgebouwd kan worden zonder dat men eischt dat twee rechte lijnen slechts een punt gemeen hebben, leveren een essentieele bijdrage tot de behandeling van het probleem van de toepassing van de resultaten der abstracte geometrie op de natuur.

## XI.

De merkwaardige wetmatigheden die CHRISTIANSEN gevonden heeft bij zijn ballo-electrische onderzoeken openen de mogelijkheid voor een dieper inzicht in de samenhang tusschen de constitutie der materie en de schijnbaar zoo willekeurige verschijnselen der wrijvings-electriciteit.

## XII.

Het nauwkeurige onderzoek over de invloed van de botsingen der molekulen op de magnetische eigenschappen van een gas wijst er op dat een verklaring van de para- en diamagnetische eigenschappen der lichamen niet kan worden gegeven zonder een ingrijpende verandering in de gewoonlijk aangenomen wetten der mechanica en elektrodynamica.

## XIII.

Beschouw een gravitatieveld volgens EINSTEIN's theorie met het lijnelement  $ds^2 = \Sigma g_{\mu\nu} dx_\mu dx_\nu$ , waar  $x_1, x_2$  en  $x_3$  ruimtecoördinaten en  $x_4$  tijdcoördinaat zijn, en waar de gravitatiepotentialen  $g_{\mu\nu}$  niet van  $x_4$  afhangen. De meest algemeene transformatie der coördinaten voor welke de getransformeerde gravitatiepotentialen wederom onafhankelijk van den tijd zijn, en waarbij een punt dat in rust was in rust blijft, is gegeven door

$$x'_k = \Phi_k(x_1, x_2, x_3), \quad (k = 1, 2, 3)$$

$$x'_4 = a x_4 + \psi(x_1, x_2, x_3),$$

waar  $\Phi_k$  en  $\psi$  willekeurige functies zijn, terwijl  $a$  een konstante is. Met betrekking tot deze groep van transformaties bezitten de grootheden

$$R_{kl} = \frac{1}{2} \sqrt{g_{44}} \left[ \frac{\partial}{\partial x_k} \left( \frac{g_{l4}}{g_{44}} \right) - \frac{\partial}{\partial x_l} \left( \frac{g_{k4}}{g_{44}} \right) \right] \quad (k, l = 1, 2, 3)$$

en

$$G_{kl} = g_{kl} - \frac{g_{k4} g_{l4}}{g_{44}} \quad (k, l = 1, 2, 3)$$



het karakter van een tensor; de  $R$ 's bepalen een antisymmetrische tensor, de  $G$ 's een symmetrische. Deze tensoren kunnen beschouwd worden als uitdrukking te geven aan de „rotatorische” eigenschappen van het beschouwde stationnaire zwaarteveld, samenhangende met de Corioliskracht die in elk punt op een in beweging zijnde massa werkt. De absolute waarde van de hoeksnelheid die op elk punt aan de rotatie beantwoordt is gegeven door de scalaire grootheid  $\Omega$ , die bepaald is door

$$2\Omega^2 = \sum (k, l, a, b = 1, 2, 3) G^{ka} G^{lb} R_{kl} R_{ab},$$

waar de grootheden  $G^{kl}$  op de gewone wijze gedefinieerd zijn als de algebraïsche complementen van de grootheden  $G_{kl}$ .



