The Effect of Electric and Magnetic Fields on Spectral Lines

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THE SEVENTH GUTHRIE LECTURE,

Entitled "The Effect of Electric and Magnetic Fields on Spectral Lines." *

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INTRODUCTION.

IN the characteristic effects on spectral lines observed when radiating substances are exposed to magnetic or electric fields we possess a valuable source of information in regard to the problem of atomic constitution. We have, indeed, in these effects a means of examining in detail the influence of controllable agencies upon intra-atomic processes. This fact has been generally realised by physicists ever since the fundamental discovery of Zeeman† 25 years ago of the characteristic effect of magnetic fields on spectral lines; and the problem was brought still more within the sphere of interest by the discovery of Stark,‡ about 10 years ago, of the analogous effect of electric fields. Owing to the development of our ideas of electro-magnetic radiation in the interval, however, the way of approach along which explanations of these effects have been sought in connection with theories of atomic constitution has undergone fundamental change. It is the main object of this lecture to expose as clearly as possible the principal features of this development.

I. THE ZEEMAN AND STARK EFFECTS AND THE CLASSICAL THEORY OF RADIATION.

According to the classical theory of electrodynamics, the constitution of the radiation emitted by a system of electrified particles should depend directly on the motion of the particles. In fact, it follows from this theory that every constituent harmonic oscillation in the electric moment of the system must give rise to the emission of a train of waves of frequency coinciding with the frequency of oscillation, and of an intensity depending on the amplitude. Notwithstanding the difficulties of accounting in a simple way for the remarkable empirical laws which govern the frequencies of the spectra of the elements, the characteristic features of Zeeman's discovery obtained, as was shown by Lorentz, an immediate interpretation on this basis. Lorentz§ assumed that each line in the spectrum of the undisturbed atom originates from the motion of an electrified particle performing a harmonic oscillation around a position of stable equilibrium within the atom, under the influence of an attraction directed towards this position and proportional to the first power of the displacement. The component of this displacement in a given direction in space may be expressed by the formula

$$\xi = C \cos 2\pi(\omega_0 t + \gamma) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where the frequency ω_0 is independent of the amplitude of oscillation C.

* In substance this report represents the contents of the Seventh Guthrie Lecture delivered before the Physical Society, March 24, 1922. Due to unavoidable circumstances the publication of this report has unfortunately been delayed until now. N.B. July, 1923.

† P. Zeeman, Phil. Mag., 5, Vol. 43, p. 226 (1897). *See* also Zeeman's collected Papers on magneto-optical phenomena, Leiden (1921).

‡ J. Stark, Berliner Sitzungsber, Nov. (1913). *See* also Elektrische Spektral-analyse, Leipzig (1914).

§ *See* H. A. Lorentz, The Theory of Electrons, Ch. 3, Leipzig (1909).

Analysing the change in the motion of the particle caused by the presence of an external magnetic field, Lorentz showed that, if the problem is treated on the basis of the ordinary theory of electrodynamics, the original purely harmonic motion is changed in such a way that it can be considered as composed of three constituent harmonic components. One of these is a linear harmonic oscillation parallel to the magnetic field, with a frequency coinciding with that of the undisturbed motion. The two others are circular harmonic rotations in opposite directions in a plane perpendicular to the field, possessing frequencies given by

$$\omega = \omega_0 \pm \omega_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where the double sign refers to the two opposite rotations. The expression for ω_H is

$$\omega_H = \frac{eH}{4\pi cm}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where H is the intensity of the magnetic field, e and m respectively the charge and mass of the oscillating particle, and c the velocity of light.

This result proved to be in most suggestive agreement with Zeeman's measurements. In fact, in a number of cases spectral lines were observed to be split up into three components, one of which was linearly polarised and appeared in the position of the original line, while the two others were placed symmetrically with regard to the original line and showed circular polarisation in opposite directions. Further, the ratio between charge and mass of the oscillating particles, calculated by means of the Lorentz expression from the displacements of these components, was found to be in close agreement with the value obtained from the deflection of cathode rays in electric and magnetic fields; and the sense of the polarisation observed for the outer components showed that the charge of these particles, like that of the cathode ray particles, possessed negative sign. This result was generally accepted as a most convincing proof of the electronic theory of matter, and it may certainly be said to have established beyond doubt the conclusion that the origin of these spectra is to be found in the motion of electrons within the atom.

For the general discussion of the Zeeman effect an electrodynamic theorem, first established by Larmor,* is of great importance. According to this theorem the motion of a system of electrons moving in a central field of force will, in the presence of a uniform magnetic field, undergo a change such that the motion of the system, to a first approximation, may be described as a possible motion of the electrons without field, on which is superposed a uniform rotation of the whole system around an axis parallel to the direction of the field, with frequency equal to ω_H, as given by formula (3).

This theorem will be seen to include Lorentz's results, since the effect of a superposed uniform rotation on a simple harmonic oscillation is to give rise to a motion of just the type described above. In fact, any elliptic harmonic oscillation may be resolved into a linear vibration in a given direction and an elliptic oscillation in a plane perpendicular to this direction; and the latter may again be considered as composed of two circular rotations with the same frequency, but opposite directions of revolution. Now a superposed rotation round a given axis will, of

* J. Larmor, Aether and Matter, p. 341, Cambridge (1900).

course, not influence a linear vibration in the direction of the axis ; it will, as regards a circular rotation in a perpendicular plane, simply augment or diminish the frequency by an amount equal to the frequency of the superposed rotation, according as the direction of this rotation is the same as or opposite to that of the original rotation.

However, although a number of spectral lines show Zeeman effects in conformity with the predictions of the theories of Lorentz and Larmor, the lines of many spectra show the so-called " anomalous " Zeeman effects. In such cases the lines are still resolved into components linearly polarised parallel to and components circularly polarised perpendicular to the field, which are arranged symmetrically with respect to the original line, and whose displacements are, at any rate for small intensities, proportional to the field. The number of components and the magnitude of their displacements may, however, differ considerably from what is the case in the " normal " effect. This variation in the character of the Zeeman effect has been found to be intimately connected with the structure of the spectra and the manner in which the lines of these spectra may be arranged in " series." Indeed, according to the rule announced by Preston,* Zeeman effects of the same type are shown not only by the lines of the same spectral series of one element, but also in respect of lines belonging to corresponding series in spectra of different elements exhibiting an analogous structure. Many efforts have been made to explain the appearance of the anomalous Zeeman effect on the basis of the classical theory of radiation. Amongst others may be mentioned the remarkable work of Voigt,† who succeeded in developing formal interpretations of a number of details of the observed phenomena. Nevertheless, great difficulties remained in the attempt to reconcile the anomalous effect with that theory; but it is hardly necessary to enter more closely into this problem here, inasmuch as new difficulties of a fundamental character arise when we try to explain the characteristic effect of electric fields on spectral lines on the basis of the classical theory, even in the case of spectra such as that of hydrogen, where the Zeeman effect is of the normal type.

As is well known, Stark discovered in 1913 that the lines of the hydrogen spectrum showed a resolution into a number of polarised components when radiating hydrogen atoms were exposed to a strong electric field. Regarded from the point of view of the classical theory of the origin of spectra, Stark's results were very surprising. Thus, if an electron performing oscillations round a position of stable equilibrium—as assumed in Lorentz's theory of the Zeeman effect—is exposed to the effect of a uniform electric field, the type of motion should not be changed at all, and the whole effect of the field should consist only in a displacement of the centre of the orbit by an amount proportional to the intensity of the field. Any possible effect on the spectral lines must therefore, on the classical theory, be due to deviations from a central attraction proportional to the displacement exhibited by the forces keeping the electron in its position in the atom. An effect of this kind—which had been considered by Voigt‡ several years before Stark's discovery—should clearly be proportional to the square or higher powers of the intensity of the external fields. In contrast to this expectation an essential feature in Stark's results was that the effect of the electric field on the hydrogen lines was, to a close approximation, directly

* Th. Preston, Nature, 59, p. 224 (1899).
† C . W. Voigt, Magneto-u id Elektrooptik, Leipzig (1908).
‡ W. Voigt, Ann. d. Phys., 43, p. 410 (1991).

proportional to the field. Viewed as a whole the Stark effect, indeed, constitutes a most complex phenomenon which not only differs greatly for different spectra and different series of lines, but which even changes essentially from line to line within one and the same spectral series.

As is well known, the difficulties here alluded to are only a few examples of the breakdown of the ideas of the classical electrodynamics when applied to atomic phenomena. Moreover, as a result of the fundamental researches of Rutherford on the phenomena of radioactivity, we may consider it as proved that the atom consists of a positively charged central nucleus surrounded by a distribution of electrons. On the theory of classical electrodynamics it is clear that such a picture of the atom does not allow of static configurations of stable equilibrium, and that we are forced to assume that the electrons within the atom rotate with high velocities. This gives rise to new difficulties, however, since on the classical theory such motions should be accompanied by a continuous emission of electromagnetic radiation, which would go on until so much energy was radiated that the electrons would fall into the nucleus. It is unnecessary to argue at length the impossibility of explaining the stability of atoms and the emission of spectra consisting of sharp lines on this atomic model, if we confine our considerations to the classical ideas of electrodynamics.

II. Quantum-Theory of Spectra.

A short time before Stark's discovery I ventured to propose a theory of spectra which constitutes a definite break with classical electrodynamics.* This theory is based on considerations of atomic stability and emission of radiation arising from conceptions of the so-called quantum-theory, which was originated by Planck's famous theory of temperature-radiation put forward about 20 years ago, and to the development of which Einstein made fundamental contributions in its earlier stages. The application of the quantum theory to atomic problems rests upon the two following postulates :—

1. Among the conceivably possible states of motion in an atomic system there exist a number of so-called *stationary states* which, in spite of the fact that the motion of the particles in these states obeys the laws of classical mechanics to a considerable extent, possess a peculiar, mechanically inexplicable stability, of such sort that every permanent change in the motion of the system must consist in a complete transition from one stationary state to another.

2. While, in contradistinction to the classical electromagnetic theory, no radiation takes place from the atom in the stationary states themselves, a transition between two stationary states can be accompanied by the emission of electromagnetic radiation, which will have the same properties as that which would be sent out according to the classical theory from an electrified particle executing an harmonic vibration with constant frequency. This frequency ν has, however, no simple relation to the motion of the particles of the atom, but is given by the relation

$$h\nu = E' - E'' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where h is Planck's constant, and E' and E'' are the values of the energy of the atom in the two stationary states which form the initial and final states of the radiation process. Conversely, irradiation of the atom with electromagnetic waves of this

* N. Bohr, Phil. Mag., 26, pp. 1, 476, 857 (1913).

frequency can lead to an absorption process, whereby the atom is transferred back from the latter stationary state to the former.

I shall not enter here on the philosophical problem of the possibility of reaching a satisfactory description of nature by application of such formal postulates, but shall endeavour to show that they allow us to construct a theory which gives a simple and consistent interpretation of spectroscopic phenomena, for the explanation of which the classical ideas of electrodynamics have not proved themselves directly suited.

As the first application we shall consider the so-called "principle of combination of spectral lines," which was brought to light by the researches of Balmer,* Rydberg,† and Ritz‡ on series spectra, and which in recent years has proved to be of general validity in regard to spectra of very different types. According to this principle the frequency of each of the lines of a spectrum may be represented by the formula

$$\nu = T_2 - T_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where T_1 and T_2 are two among a manifold of so-called spectral terms. This law, which holds with an accuracy unrivalled in physics, has hitherto resisted any interpretation on the classical ideas, at any rate in a form suitable as a foundation for a detailed discussion of spectroscopic evidence. On our postulates, on the other hand, it is seen that the combination principle can be directly interpreted by identifying the spectral terms with the numerical values of the energy in the possible stationary states, divided by Planck's constant, and by supposing that each spectral line originates from a transition between two of these states.

At first sight this interpretation of the combination principle might be considered as being of a very formal character, since it is not only admittedly at variance with the ideas of classical electrodynamics, but also involves a radical departure from the conceptions on which physical phenomena have hitherto been based. This appears particularly in the assumption that the constitution of the radiation emitted during a process at the outset of which an atom finds itself in a certain stationary state, depends not only on this state but also on that state of the atom which appears as the result of the process. In fact, spectral lines which appear as combinations of various spectral terms with one and the same term are attributed to various possible processes of transition from a certain state of the atom to other stationary states. In the present state of the theory the mode of occurrence of these transitions is considered to be a question of probability, in the sense that an atom in a given stationary state is assumed to possess a certain probability of passing spontaneously in unit time to any of the other stationary states under consideration. This view, which exhibits a marked analogy to the theory of radioactive disintegration, conforms with the assumptions used by Einstein§ in his suggestive deduction of the law of temperature-radiation on the basis of the fundamental postulates stated above.

Notwithstanding the fundamental nature of the departure from the classical electrodynamics which is involved in the quantum theory of spectra, we shall see that it seems possible in a certain sense to regard this theory as a natural generalisa-

* Balmer, Ann. d. Physik, 25, p. 80 (1885).
† J. R. Rydberg, Handl. Akad., Stockholm, 23 (1890).
‡ W. Ritz, Physik. Zeit., 9, p. 521 (1908).
§ A. Einstein, Phys. Zeit., 18, p. 121 (1917).

tion of our ordinary ideas of radiation. Thus it is possible to correlate each of the various processes of transition giving rise to the emission of harmonic trains of waves with one of the various harmonic oscillations which occur in the electric moment of the atom, in such a way that the probability of the occurrence of a transition of a given type is to be ascribed to the presence of a corresponding harmonic oscillation in this moment. This feature of the quantum-theory of spectra, which is termed the "correspondence principle," plays an essential part in the interpretation of the spectral evidence. It may especially be emphasised that it has been possible, by means of this principle, to remove the mystery which has hitherto hung over the application of the combination principle owing to the apparent capriciousness which attends the appearance of the predicted spectral lines.

We shall also see how the correspondence principle has been of great use in developing explanations of the effects of magnetic and electric fields on spectral lines. Before entering into the detailed discussion of these problems, it is necessary to consider briefly the application of the postulates to the simple case of the interpretation of the hydrogen spectrum—which was the starting point of the theory—as well as the main features of the subsequent development of the general principles of the quantum-theory.

III. Theory of the Hydrogen Spectrum.

As is well known, the frequencies of the lines of the hydrogen spectrum may be represented to a high degree of approximation by the simple formula

$$\nu = K\left(\frac{1}{(n'')^2} - \frac{1}{(n')^2}\right). \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For $n''=1$ and $n'=2, 3, 4$ we get a series of lines in the extreme ultra-violet, first observed a few years ago by Lyman*; for $n''=2$ and $n'=3, 4, 5$ . . . the formula represents the Balmer series in the visible region; $n''=3$ and $n'=4, 5, 6$ . . . . gives the infra-red series, of which the first two members were observed by Paschen† several years ago; finally, $n''=4$ and $n'=5, 6$ . . . . correspond with a series quite recently observed in the far infra-red by Brackett.‡

Comparing (6) with formulæ (4) and (5), we may conclude, according to the general considerations of the former section, that the hydrogen spectrum is emitted by an atom which possesses a sequence of stationary states, such that the numerical value of the energy in the nth state is given by $\frac{Kh}{n^2}$. Now, according to Rutherford's theory, the hydrogen atom consists of one electron rotating round a positive nucleus of unit charge. Apart from the small effect due to the change of mass of the electron with velocity, the motion of the atom will be a very simple one, the particles describing simple periodic, elliptic orbits with the centre of gravity at the common focus. For such a motion the frequency of revolution of the particles and the dimensions

* T. Lyman, Phys. Rev., 3, p. 504 (1914).
† F. Paschen, Ann. d. Phys., 27, p. 565 (1908).
‡ F. Brackett, Nature, 109, p. 209 (1922).

of the orbits will, according to the well-known Keplerian laws, be related to the values of the total energy of the system by the simple formulæ

$$\omega=\sqrt{\frac{2W^3}{\pi^2e^4m}}\ ,\quad 2a=\frac{e^2}{W}\ . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (7)$$

where ω is the frequency of revolution and $2a$ the major axis of the orbit of the electron, while W is the work necessary to remove the particles to an infinite distance from each other. As before, e and m denote the charge and mass of the electron, while for brevity we have considered the mass of the nucleus as infinitely large. Putting now for the stationary states

$$W=\frac{Kh}{n^2}, \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (8)$$

we obtain for the frequency of revolution and the major axis in these states

$$\omega=\frac{1}{n^3}\sqrt{\frac{2K^3h^3}{\pi^2e^4m}}\ ,\quad 2a=n^2\frac{e^2}{Kh}. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (9)$$

These formulæ give a picture of the formation of the atom by means of a step-wise process in which an electron is bound with emission of radiation in a sequence of stationary orbits of rapidly increasing frequencies and decreasing dimensions, until a state is reached in which the energy of the atom is a minimum and the process of binding is brought to a final stop; this state corresponds to $n=1$ in formula (9). Introducing the empirical values for K as well as e, m and h in (9) we get values for the frequency of revolution and the major axis of the orbit in this "normal" state of the atom, which are of the same order as the values for atomic frequencies and dimensions derived from consideration of the optical and mechanical properties of gases.

On our fundamental postulates there is no question, however, of a closer direct comparison between such formulæ as (9) and formulæ derived on the classical theory of electrodynamics. In particular, we can have no direct comparison between frequencies in the stationary states and frequencies of the spectral lines, as we have assumed that each of these lines corresponds to the radiation emitted during a transition between two states, for which the frequencies of revolution may in general have quite different values. An opportunity for tracing a connection between the spectrum and the motion is offered, however, by the circumstance that the ratio between the frequencies of revolution in two successive stationary states approaches unity when the values of n gradually increase. From (6) we obtain (to a first approximation) for the frequency of the radiation emitted by a transition between two successive states corresponding to large values of n

$$\nu=\frac{2K}{n^3}.$$

Comparing with (9), we find that this expression will coincide asymptotically with the frequency of revolution in the two states if

$$K=\frac{2\pi^2e^4m}{h^3}. \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad . \qquad (10)$$

As I have shown in the Paper referred to, this condition is actually fulfilled within

the limits of experimental error, if we introduce the empirical values for K as well as h, e and m.*

The connection thus established between the hydrogen spectrum and the quantities describing the model of the hydrogen atom is evidently as close as could be expected, considering the fundamental departure from classical electrodynamics involved in our interpretation of the spectrum. This divergence becomes clear, as soon as we seek an explanation of the effects of magnetic and electric fields on the hydrogen lines; here we meet a problem quite different from that with which we are presented when regarding the matter from the point of view of the classical theory of radiation. A detailed explanation of the Stark effect could not be attained by means of such simple considerations as sufficed for the interpretation of the main features of the hydrogen spectrum; it was found possible nevertheless not only to explain the direct proportionality of the displacement of the components to the intensity of the electric force, but also to account for the absolute magnitude of the effect and the characteristic way in which it varies from line to line in the spectrum.† A closer explanation of the details of the Stark and Zeeman effects, however, demanded the development of methods for the fixation of the stationary states of the atom under the influence of external fields, as well as the formulation of further rules governing the transitions between stationary states and the polarisation of the ensuing radiation. It is of interest to point out that in the case of the Zeeman effect, for the main features of which the classical theory had offered so simple an interpretation, doubt prevailed for a time as to whether this effect could be accounted for at all on the basis of the postulates in the form stated above. In fact it is easily seen that the frequencies of the components into which the lines are split up in the field cannot be represented by a complete combination-diagram of spectral terms. As we shall presently see, a detailed theory of the Stark effect as well as of the Zeeman effect for the hydrogen lines has been established in course of the development of the quantum-theory in recent years.

IV. State Relations for Periodic and Multiple-periodic Motions.

The formal basis of the application of the quantum-theory to atomic problems consists of a number of formulæ which, together with the formula (4), which has often been termed the "frequency relation," allow us to select the stationary states from among the mechanically possible motions of the particles of the atom. These latter formulæ, the so-called "state-relations," may be considered as rational generalisations of the assumption originally used by Planck regarding the possible values of the energy of a system consisting of a particle executing simple harmonic oscillations. Although it is naturally an essential object of the theory to determine the energy of the stationary states, the energy function itself is not, for more complicated systems, well suited to a general formulation of state-relations. A suitable basis for this formulation is found, however, in the so-called integral of action, which plays such an important part in analytical dynamics.

Let us first consider the simple case when the motion of the particles of the atom is simply periodic, independently of the initial conditions. In this case the

* *Cf.* also R. A. Millikan, Phil. Mag., 34, p. 1 (1917).

† N. Bohr, Phil. Mag., 27, p. 506 (1914); 30, p. 394 (1915). *Cf.* also E. Warburg, Verh. Deut. Phys. Ges., 15, p. 1259 (1913).

displacement ξ of each particle in a given direction may be expressed as a function of the time, in the well-known way, as the superposition of a number of harmonic oscillations

$$\xi=\Sigma C_\tau \cos 2\pi(\tau\omega t+\gamma_\tau) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

where ω is the frequency of the periodic motion, and the summation is over all positive integral values of τ. A similar expression holds also, of course, for the component in a given direction of the electric moment of the atom, whose variation with time determines on the classical theory the constitution of the emitted radiation. For such simply periodic systems the stationary states are fixed by a single condition which may be written

$$I=nh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (12)$$

where h is Planck's constant, and n a positive integer, the so-called *quantum-number*. The quantity I is defined by

$$I=\int_0 A\,dt \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

where the integral is the so-called integral of action taken over a complete period of the motion. If the motion is assumed to be governed by the laws of Newtonian mechanics, the integrand A is equal to twice the kinetic energy of the moving particles ($A=\Sigma mv^2$); while, if the modifications demanded by the theory of relativity are taken into account, A is given by the expression

$$A=\Sigma mv^2\left(1-\frac{v^2}{C^2}\right)^{-\frac{1}{2}}$$

For the sake of the later discussion it may be noted that this definition of I is identical with the condition

$$I\omega=\bar{A} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

where $\bar{A}$ denotes the mean value of the function A during the motion.

While the relation between I and the total energy ε for different systems may take very different forms, this relation will always obey the simple differential equation

$$\delta E=\omega\delta I \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

where δE and δI denote the difference in E and I for two mechanically possible motions of the system which differ but little from each other.

From (4) and (15) it is seen at once that, in the case of a simple harmonic with oscillator constant frequency ω_0 the motion of which is represented by (1), the equation (12) is equivalent to Planck's well-known relation

$$E=nh\omega_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

We can also easily show that in the case of the hydrogen atom (12) is equivalent to the formula (8), if in this formula the value of K given by (10) is introduced. In fact, noticing that $W=\infty$ for $I=0$, we get from (7) and (15) by simple integration

$$W=\frac{2\pi^2e^4m}{I^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

The general relations (12) and (15) allow us, further, to trace on a broader basis the formal asymptotic connection between the motion of an atomic system and the

spectrum deduced on the quantum-theory, established in the former section in the special case of the hydrogen atom.

Let us consider a transition between two states for which the values of n in formula (12) are equal to n' and n'' respectively. From the frequency relation (4) we get by means of (15)

$$\nu=\frac{1}{h}(E'-E'')=\frac{1}{h}\int_{n=n''}^{n=n'}\omega\delta I \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

If now the numbers n' and n'' are large compared with their difference and consequently the motions in the two states differ comparatively little from each other in frequency and dimensions, we may in (18) consider ω as approximately constant and thus obtain, using (12) also, the asymptotical relation

$$\nu\sim(n'-n'')\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

In the limit, for large quantum numbers, the frequency of the radiation emitted during a transition will consequently coincide asymptotically with the frequency of one of the harmonic constituents of the radiation which, on the classical theory, would be emitted from the atom owing to variation of the electric moment with time; namely, with the frequency of the trains of waves which would result from the harmonic component in the expression (11) for which $\tau=n'-n''$. Now of course there is no question of a gradual approximation of the quantum-theory in the limit of large quantum-numbers to the classical ideas of the origin of radiation. Indeed, just as in the case where these numbers are not large compared with their difference, we assume in this limit that the various harmonic components of the radiation, which would be emitted simultaneously on the classical theory, will originate in quite different processes of transition between different pairs of stationary states. It is exactly this circumstance, however, which leads us to consider the coincidence of frequencies traced in the limit as evidence of a general law which underlies the occurrence of transitions between stationary states.

This law, which has been called the "correspondence principle," states that the occurrence of each transition between two stationary states accompanied by emission of radiation is correlated to one of the constituent harmonic oscillations into which the electric moment of the atom considered as a function of the time can be resolved, to the extent that the occurrence of the transition is conditioned by the presence of the "corresponding" harmonic oscillation. This correlation demands that the probability of the occurrence of a transition shall depend on the amplitude of the corresponding harmonic oscillation of the atom, in such a way that in the limit when the quantum-number is large, the intensity of the emitted radiation in unit time in the mean shall be the same as that which would follow from the classical laws of electrodynamics. A similar connection with the classical theory will be exhibited by the polarisation of the emitted radiation. If, for instance, the corresponding harmonic oscillation in all states of the atom is a linear vibration or a circular rotation, the radiation will have the same constitution as that which on the classical theory would be emitted by an electron executing a harmonic motion of that type.

In the case above considered of a periodic system, the correspondence principle states that the appearance of a transition between two stationary states, in which the quantum-number changes from n' to n'', is conditioned by the presence in the

electric moment of the atom of an $(n'-n'')$th harmonic. This result allows us to throw light on a marked difference between the rules governing the occurrence of transitions between stationary states in the case of a Planck oscillator, on the one hand, and of the hydrogen atom on the other. In Planck's theory of temperature-radiation it is an essential assumption that, as in the classical theory, the frequency of the radiation emitted or absorbed by an oscillator shall be always equal to the characteristic frequency of oscillation. In terms of our theory of spectra this means, as seen from the comparison of (4) and (16), that the oscillator can, in a single step, only pass between two stationary states for which the quantum-number n differs by one unit. On the other hand the interpretation of the hydrogen spectrum necessarily requires that transitions between any pairs of the stationary states of the hydrogen atom shall be possible. On the correspondence principle this remarkable difference is directly accounted for by the fact that the Keplerian elliptic motion of the electron in the hydrogen atom, in contrast to the purely harmonic motion of the Planck oscillator, possesses a complete sequence of upper harmonics.

Owing to the recent development of the quantum-theory it has been possible to establish state-relations not only for simple-periodic systems, but also for systems in which the motion is of the so-called multiple-periodic type. For such systems the displacement of each particle, as well as the variation of the electric moment, may still be represented as a superposition of harmonic oscillations. In contrast to a simple-periodic system the frequencies of these oscillations are not multiples of a single fundamental frequency, but are for a multiple-periodic system of a "degree of periodicity" equal to s, built up as linear expressions of s independent fundamental frequencies in the way shown by the following formula—

$$\xi=\Sigma C_{\tau_1,\ \ldots\ \tau_s} \cos 2\pi\ [(\tau_1\omega_1+\ \ldots\ +\tau_s\omega_s)t+\gamma_{\tau_1,\ \ldots\ \tau_s}] \quad . \quad . \quad (20)$$

where ω_1 to ω_s are the fundamental frequencies, and the summation is to be extended over all negative and positive values of the integers τ_1 to τ_s.

In such a case the stationary states will be fixed by the s state relations:

$$I_1=n_1h,\ \ \ldots\ \ I_s=n_sh, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (21)$$

where n_1 to n_s are positive integers. The I's are a number of quantities expressing certain properties of the motion, which by analogy with the definition of the quantity I for a periodic system are related to the energy and fundamental frequencies of the motions through the differential equation

$$\delta E=\omega_1\delta I_1+\ \ldots\ +\omega_s\delta I_s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

expressing the energy difference for two mechanically possible motions of the system which differ very little from each other. These relations fix the quantities $I_1\ \ldots\ I_s$ save for an arbitrary constant in each, which, however, is fixed by the condition

$$I_1\omega_1+.\ \ldots\ +I_s\omega_s=\bar{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where $\bar{A}$ as in formula (14) is the mean value of the function A which appears in the integral of action.

From formula (22) we find that, for the radiation emitted during the transition of the system between two states for which the quantum-numbers in the relations (21)

are given by $n'_1 \ldots n'_s$ and $n''_1 \ldots n''_s$ respectively, the frequency, in the limit where these numbers are large compared with their differences, and where the motions in the two stationary states differ comparatively little from each other, will be given by the asymptotical relation

$$\nu = (n'_1 - n''_1)\omega_1 + \ldots + (n'_s - n''_s)\omega_s. \quad (24)$$

According to the correspondence principle we shall consequently assume that a transition between two stationary states of a multiple-periodic system will be dependent on the presence in the expression for the electric moment of the system of a constituent harmonic oscillation for which in (20) we have

$$\tau_1 = n'_1 - n''_1, \ldots \tau_s = n'_s - n''_s \quad (25)$$

The establishment of the state-relations for periodic and multiple-periodic systems depends upon the work of a great number of physicists, including Planck himself. It may be of interest to note that a general condition equivalent to (12) was used for the first time by Debye,* and that conditions of a similar type to those in (21) were proposed simultaneously by Wilson† and Sommerfeld.‡

Among the contributions to the later development of the theory we may mention the work of Ehrenfest§ on the adiabatically invariant character of the state-relations. He considers the action on the motion in the stationary states which results from a slow and uniform transformation of the field of force in which the particles of the system are moving, and points out that if the stationary states are fixed by conditions of the type (21) and (22), the effect of this transformation can be described by means of the ordinary laws of mechanics. This so-called " adiabatic principle " constitutes a natural generalisation of the application of mechanics to the description of the motion in the stationary states themselves, which is obviously not at variance with the non-mechanical character of the stability of these states. These problems are discussed in detail in a treatise by the lecturer published a few years ago, in which the correspondence principle was also developed.‖

In the application of the theory of multiple-periodic systems to spectral problems the first essential progress was made by Sommerfeld in his interpretation of the fine-structure of the hydrogen lines as revealed when these lines are observed by instruments of high dispersive power, and which is due to the fact that the motion of the electron in the hydrogen atom is no longer strictly periodic when the change of mass of the electron with the velocity is taken into consideration. This work was closely followed by the interpretation of the details of the Stark effect of the hydrogen lines carried out simultaneously by Epstein¶ and Schwarzschild,** and

* P. Debye, Wolfskehl Vortrag Göttingen (1913).

† W. Wilson, Phil. Mag., 29, 795 (1915); 31, p. 156 (1916).

‡ A. Sommerfeld, Sitz. der Münchener Akod., p. 425 and 459 (1915).

§ P. Ehrenfest, Proc. Acad. Amsterdam, 16, 591 (1914); Phil. Mag., 33, 500 (1914); *cf.* also J. M. Burgers, Phil. Mag., 33, 514 (1917).

‖ N. Bohr, On the Quantum-Theory of Line Spectra. D. Kgl. Danske Videnskabernes Selskabs Skrifter, 8, iv., 1 (1918) (quoted hereafter as Q.L.S.). For a brief survey of the present state of the theory compare also N. Bohr, Ann. d. Phys., 71, p. 277 (1923). An English translation of this Paper will appear shortly in Proc. Camb. Phil. Soc.

¶ P. Epstein, Phys. Zs., 17, p. 148 (1916); Ann. d. Phys., 50, p. 489 (1916).

** K. Schwarzschild, Berliner Sitzungsber, April (1916).

by the work of Sommerfeld* and Debye† on the interpretation of the Zeeman effect for the hydrogen lines. The theories of these effects were completed by the application of the correspondence principle, which allows us to account in detail for the limited number of components observed, as well as for their polarisation and intensities.

The method of representation of the state-relations used by these authors was based on the procedure called "separation of variables" in the integral of action. Quite apart from the more limited applicability of this procedure, the method of representing the state-relations followed here, in which the properties of periodicity of the motion are brought into the foreground, gives us in many cases a more direct insight into the physical meaning of the theoretical considerations. In the succeeding discussions of the application of the general theory we shall therefore not follow the historical order of development, but shall treat the problems in the manner which seems best suited to illustrate the main features of the theory.

V. The Effect of Magnetic and Electric Fields on the Hydrogen Lines.

On the basis of the general considerations in the preceding section we shall now consider in detail the effect of a magnetic and of an electric field on the spectral lines of hydrogen. For this purpose we shall for simplicity neglect the fine-structure of these lines; this is legitimate since the influence on the motion of the electron of variation of mass is very small compared with the effect of external magnetic and electric forces of the intensities used in experiments on the Zeeman and Stark effects. This is clearly shown by the fact that the distance between the fine-structure components of the undisturbed hydrogen lines is much smaller than the displacement of the components into which the lines are resolved in these experiments.

As in Section III., we shall therefore assume the orbit of the electron in the undisturbed atom to be a simple-periodic Keplerian ellipse, for which the frequency of revolution and the major axis are related to the energy as given by (7). Introducing the quantity I defined by (13) we get from (17)

$$E=-W=-\frac{2\pi^2e^4m}{I^2},\quad \omega=\frac{4\pi^2e^4m}{I^3},\quad 2a=\frac{I^2}{2\pi^2e^2m} \qquad \ldots\ldots \quad (26)$$

For the stationary states we obtain, therefore, introducing $I=nh$, according to the state-relation (12),

$$E_n=-\frac{1}{n^2}\frac{2\pi^2e^4m}{h^2},\quad \omega_n=\frac{1}{n^3}\frac{4\pi^2e^4m}{h^3},\quad 2a_n=n^2\cdot\frac{h^2}{2\pi^2e^2m} \qquad \ldots\ldots \quad (27)$$

which are, of course, equivalent to the formulæ (8) and (9) when the value for K is as given by (10). Finally, by the relation (4) we obtain for the frequency of the radiation emitted during a transition between two states for which n is equal to n' and n'' respectively,

$$\nu=\frac{2\pi^2e^4m}{h^3}\left(\frac{1}{(n'')^2}-\frac{1}{(n')^2}\right). \qquad \ldots\ldots\ldots \quad (28)$$

Effect of a Magnetic Field.

In considering the effect of a magnetic field we shall in the first place assume, according to Larmor's theorem, that the motion of the electron in the

* A. Sommerfeld, Phys. Zs., 17, p. 491 (1916).
† P. Debye, Phys. Zs., 17, p. 507 (1916).

hydrogen atom in the presence of the field differs from a possible motion of the atom without field, in having superposed a uniform rotation around an axis through the nucleus and parallel to the field, with a frequency ω_H given by formula (3). As a consequence of this the displacement of the electron in a given direction is no more represented by an expression of the type (11) holding for a purely periodic orbit, but its motion will contain harmonic components of three different types. One type of component will consist of linear vibrations parallel to the field with frequencies $\tau\omega$, where ω is the frequency of revolution in the periodic orbit which the electron describes in a system of reference which partakes of the superposed rotation impressed by the field. The two other types of harmonic components will be circular rotations in a plane perpendicular to the field with frequencies $\tau\omega+\omega_H$ and $\tau\omega-\omega_H$ respectively; the sense of rotation of the former being the same as, and that of the latter opposite to, the sense of the superposed rotation. Denoting the components of electric moment in directions parallel and perpendicular to the field by ξ and η respectively, we have

$$\xi=\Sigma C_\tau \cos 2\pi(\tau\omega t+\gamma_\tau)$$

and

$$\eta=\Sigma C_{\tau,\pm1} \cos 2\pi((\tau\omega\pm\omega_H)t+\gamma_{\tau,\pm1}) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (29)$$

The motion of the atom in the field is thus a typical double-periodic motion with the fundamental frequencies ω and ω_H. According to the considerations in the former section the stationary states will therefore be subject to two conditions, which may be written

$$I=nh,\ I_H=n_H h. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

Here I is equal to the quantity defined by (13) when applied to the periodic motion of the atom relative to a system of reference partaking of the superposed rotation, while I_H is equal to 2π times the component M of the angular momentum of the electron around the axis of this rotation. In fact, the change in kinetic energy of the electron due to the superposed rotation is easily seen to be equal, as a first approximation, to $2\pi\omega_H M$. Since the magnetic field does not effect the potential energy of the atom, the energy difference between two neighbouring motions will therefore be expressed by the relation

$$\delta\varepsilon=\omega\delta I+2\pi\omega_H\delta M=\omega\delta I+\omega_H\delta I_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

which corresponds to the condition (15). At the same time the condition

$$\omega I+\omega_H I_H=\bar{A}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

which corresponds to (14), is seen to be fulfilled by any motion of the atom in the field. For the total energy of the atom as a function of I and I_H we get from (3) and (26)

$$E=-\frac{2\pi^2e^4m}{I^2}+\frac{eH}{4\pi mc}I_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (33)$$

which, on inserting (30) gives for the energy in the stationary states

$$E=-\frac{2\pi^2e^4m}{h^2}\frac{1}{n^2}+\frac{heH}{4\pi mc}n_H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

It is of interest to point out that the dynamical property of the stationary states expressed by the first of the conditions (30) might have been obtained by a

direct application of Ehrenfest's adiabatic principle. In fact, as shown by Langevin* in his work on atomic magnetism, a slow and uniform establishment of an external magnetic field will, on account of the induced electric forces, affect the motion of a system of electrons revolving in a central field in such a way that the motion at any moment will differ from the original motion only by a superposed rotation possessing the Larmor frequency. On the other hand, it lies in the nature of the problem that the appearance of the second of the quantum conditions (30) can in no way be accounted for by considerations depending on ordinary mechanical and electrodynamical ideas. Indeed the appearance of this condition may be considered as a consequence of the fact that the presence of the external field impresses a new fundamental frequency on the motion of the atom, and thereby calls into play the unknown quantum mechanism governing the stability of the stationary states; the effect being that the energy differences between the various possible states corresponding to the same stationary state of the undisturbed atom will exhibit a relation to the new frequency of the same kind as that between energy and frequency in the stationary states of simple-periodic systems.† In the special case under consideration the additional periodic motion impressed on the atom by the field is of a simple-harmonic character; and it is of interest to note that the second term on the right side of equation (34), which is equal to $n_H \omega_H h$, is quite analogous to Planck's original formula (16) for the possible value of the energy of a harmonic oscillator, with the sole difference that, in accordance with the nature of the problem, n_H can take negative as well as positive values.

Since the maximum value M_0 which the angular momentum P of the electron round the nucleus can take is obviously equal to $I/2\pi$, we see that the second of the conditions (30) is equivalent to the condition

$$M = \frac{n_H}{n} M_0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (35)$$

from which it follows at once that the numerical value of n_H can never be larger than n. We must assume that n_H can take any of the values $\pm 1, \pm 2, \ldots \pm n$, while a consideration, which would take us too long to develop here, leads us to the conclusion that no stationary state corresponds to the value $n_H = 0$. For the frequency of radiation emitted by a transition from a state for which $n = n'$ and $n_H = n'_H$ to one for which $n = n''$ and $n_H = n''_H$, we find by (4)

$$\nu = \frac{2\pi e^4 m}{h^2}\left(\frac{1}{(n'')^2} - \frac{1}{(n')^2}\right) + \frac{eH}{4\pi mc}(n'_H - n''_H) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (36)$$

According to the correspondence principle the possibility of such a transition is dependent on the presence in the electric moment of the atom of a harmonic component of frequency $(n' - n'')\omega + (n'_H - n''_H)\omega_H$. Recalling the above analysis of the motion of the electron represented by (29), we see in the first place that, as in the case of the undisturbed atom, there exist possibilities of transitions in which n changes by any number of units. Such transitions, however, will no longer give rise to the usual hydrogen lines, the frequencies of which are given by (28). Instead, as seen from (36), we obtain for each of these lines a number of components corre-

* P. Langevin, Annales de Physique et de Chimie, 5, p. 70 (1905).
† *Cf.* Q. L. S., p. 11.

sponding to the possible simultaneous changes of the quantum-number n_H. These components are of three types. In the first type, which is dependent on the linear harmonic oscillation parallel to the field, n_H remains unchanged, and the components take the same positions in the spectrum as the original lines. On the correspondence principle the radiation corresponding to these components will have the same constitution as the radiation emitted according to classical electrodynamics by an electron performing linear oscillations parallel to the field. In the two other types, which are dependent on the circular harmonic rotations perpendicular to the field, n_H decreases or increases by one unit respectively, and we get for each hydrogen line two components, which are placed symmetrically with respect to the original position of the line, and which, if observed in a direction parallel to the field, will show circular polarisation in opposite directions.

It will be seen that this interpretation of the Zeeman effect for the hydrogen lines exhibits a formal analogy with the original theory of Lorentz, discussed in Section I.; which is really remarkable, when we think of the great divergence between the ideas of classical dynamics and the postulates of the quantum-theory. In the matter, however, of the relative intensities of the components of the Zeeman effect the fundamental departure of the quantum-theory from classical electrodynamics comes to light in an interesting way. According to the classical theory the intensities of these components are determined by the condition that the total radiation of each triplet of components shall not exhibit any sensible resultant polarisation, since the orientation of the atom in the field is not subject to any limitations. On the quantum-theory, on the other hand, where the existence of such limitations is an absolutely essential feature, we should be prepared to find a resultant polarisation of the total light of each triplet, even in weak magnetic fields. Such a polarisation has actually been recorded by various investigators of the Zeeman effect, and it is especially interesting to note that Traubenberg* has, in recent experiments on the hydrogen spectrum emitted by positive rays in a magnetic field, succeeded in observing a resultant polarisation of the kind discussed.

Effect of an Electric Field.

In dealing with the influence of a uniform electric field on the hydrogen spectrum, our first problem will be to examine the effect of the field on the motion of the atom. As in the case of a magnetic field, we meet here with the question of small perturbations in a periodic orbit. In the former case Larmor's theorem allowed us at once to perceive the character of the perturbations; the problem is, however, more complicated in the case of an electric field, which not only produces alterations in the orientation of the orbit in space, but also a continuous change in the shape of the orbit. Nevertheless the problem admits of a simple solution by making use of a general theorem in the theory of perturbations.

Consider a system in which every motion is periodic, and let us imagine that the system is subject to a small external field of force. In this case the motion may be described as a periodic motion, which at any moment differs from a possible motion of the undisturbed system by small quantities proportional to the intensity of the external forces, and which at the same time undergoes slow alterations as regards shape and position of orbit at a rate which is also proportional to these forces.

* R. v. Traubenberg, Naturwissenschaften, 10, p. 791 (1922).

A study of these alterations of motion over long time intervals, which in celestial mechanics are known as "secular perturbations," allows a direct insight into the effect of the external field on the periodic properties of the motion. A fundamental law governing the course of the secular perturbation produced by a fixed field of force is now available in the general theorem referred to above, which states, that, neglecting small quantities proportional to the square of the perturbing forces, the mean value of the potential energy of the system relative to the external field, taken over an approximate period of the motion, will remain unaltered through time intervals long enough for these forces to produce a finite change in the shape and position of the orbit. If we further imagine the external field to be slowly established at a uniform rate, this mean value will, with the same approximation, represent the difference between the total energy of the perturbed system and the original value of the energy of the system before the establishment of the field.*

Reverting to the case of a hydrogen atom perturbed by a uniform electric field, we find by a simple calculation that the mean value of the potential energy of the atom relative to the field is the same as if the electron were placed on the major axis of the orbit at a point dividing the distance between the nucleus and the other focus in the ratio 3 : 1. This point may be called the "electrical centre" of the orbit, and it is an immediate consequence of the general theorem stated above that during the secular perturbation this centre will to a first approximation move in a plane perpendicular to the direction of the external electric force. Now a closer examination of the secular displacement of the electrical centre of the orbit in its plane, which is easily carried out by the simple consideration of the secular changes of angular momentum of the electron round the nucleus due to the external force, shows that the electrical centre performs a purely harmonic, in general elliptical, oscillation, symmetrically placed with regard to an axis through the nucleus parallel to the external force. Moreover the frequency of this oscillation is independent of the shape and orientation of the electron orbit and dependent only on the quantity I, defined for a periodic orbit by (13), which, neglecting small quantities proportional to the external force, will, of course, remain unaltered during the perturbations. Denoting the frequency by ω_F, we have

$$\omega_F = \frac{3I}{8\pi^2 em} F, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where F is the intensity of the electric field.†

Before proceeding to the fixation of the stationary states, we will examine what bearing these results have on the resolution of the motion of the electron into its harmonic components. For this purpose consider the motion relative to a frame of reference which performs a uniform rotation around the axis of the system in the same sense as the rotation of the electrical centre and with a frequency equal to σ. Owing to the harmonic character of the oscillation of the electrical centre this can obviously be described as motion in a periodic orbit, the shape and position of which will vary with frequency equal to $2\omega_F$. Such a motion will be double-periodic with frequencies ω_1 and ω_2, where ω_2 may be taken equal to $2\omega_F$,

* Q.L.S., p. 46.
† Q.L.S., p. 73.

while ω_1 is equal to the mean frequency of revolution of the electron in its approximately periodic orbit, calculated from perihelion to perihelion; which in the system of reference used is obviously equal to the mean frequency of revolution of the electron round the axis. The motion may therefore be considered as a superposition of elliptical harmonic vibrations of frequencies $\tau_1\omega_1+\tau_2\omega_2$, where τ_1 and τ_2 are integers. Returning now to a fixed frame of reference, the motion may be resolved into a sequence of linear harmonic vibrations parallel to the axis with frequencies $\tau_1\omega_1+\tau_2\omega_2$, and two sequences of circular harmonic rotation around this axis with frequencies $\tau_1\omega_1+\tau_2\omega_2\pm\omega_F$. Let us now introduce as fundamental frequencies for the perturbed motion the quantities ω and ω_F, where ω is the mean frequency of revolution of the electron round the axis, and therefore equal to either $\omega_1+\omega_F$ or $\omega_1-\omega_F$, according to whether the electrical centre rotates in the same direction round the axis as the electron itself or in the opposite direction. Denoting the displacement of the electron parallel to the axis by ξ, we obtain consequently

$$\xi=\Sigma C_{\tau,\tau_F}\cos 2\pi[t(\tau\omega+\tau_F\omega_F)+C_{\tau,\tau_F}], \quad . . . . . (38)$$

where $\tau+\tau_F$, being equal to $2(\tau_1+\tau_2)$ or to $2\tau_2$, is always an *even* integer. For a displacement η perpendicular to the axis we find similarly:

$$\eta=\Sigma D_{\tau\omega,\tau_F}\cos 2\pi[t(\tau\omega+\tau_F\omega_F)+d\tau,\tau_F] \quad . . . . . (39)$$

where $\tau+\tau_F$, being equal to $2(\tau_1+\tau_2)\pm1$ or $2\tau_2\pm1$, is always an *odd* integer.

The stationary states of this double-periodic motion will be fixed by two quantum conditions, which can be written in the form

$$I=nh, \quad I_F=n_Fh, \quad . . . . . (40)$$

where the quantities I and I_F are related to the total energy of the system and to the action function through the equations

$$\delta E=\omega\delta I+\omega_F\delta I_F \quad . . . . . (41)$$

and

$$\omega I+\omega_F I_F=\bar{A}, \quad . . . . . (42)$$

which correspond to the conditions (22) and (23). Consider for the moment the especially simple case where the electron moves in a circular orbit in a plane perpendicular to the axis. For such orbits the dependence of E and A on ω, so far as quantities proportional to the external force are concerned, is obviously the same as that holding for a simple Keplerian motion. It follows therefore from (41) and (42) that I_F vanishes in this case, while I coincides with the quantity defined by (13) for a simple periodic orbit. Since ω_F to a first approximation depends only on I, we deduce from this result the following general expression for the energy of the perturbed atom:

$$E=E_0(I)+\omega_F I_F, \quad . . . . . (43)$$

where $E_0(I)$ represents the energy of a simple Keplerian orbit expressed as a function of I. From (26) and (37) we find, therefore,

$$E=-\frac{2\pi^2e^4m}{I^2}+\frac{3II_F}{8\pi^2\bar{e}m}F. \quad . . . . . (44)$$

The kinematical significance of the second of the quantum conditions (40) follows simply from the general theorem of the adiabatic invariance of the quantum

conditions for multiple-periodic systems. In fact, from a consideration of a slow establishment of the external field, it follows according to the general theorem of p. 291 that the change of the energy of the atom due to the field is equal to ζeF, where ζ is equal to the distance of the electrical centre from a plane through the nucleus perpendicular to the axis. The maximum value ζ_0, in the limiting case in which the orbit degenerates into a straight line parallel to the direction of the field, is equal to $3a/2$, where $2a$ is the major axis of the Keplerian orbit, the dependence of which on I is expressed by the last of the equations (26). Comparing with the second term in (44), we get therefore the simple relation

$$\zeta=\zeta_0 \cdot \frac{I_F}{I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (45)$$

This relation imposes an obvious limit to the values which n_F can take in the stationary states corresponding to a given value of n. We conclude that n_F can take any of the values $0, \pm 1, \pm 2, \ldots \pm(n-1)$, while the limiting values $\pm n$ have to be excluded on account of the singularity of the corresponding motion.

In connection with the state-relations (40), it may still be of interest to point out that just as in the case when a magnetic field is applied, the second quantum condition ensures a relation between the additional fundamental frequency ω_F, impressed on the atom by the field, and the possible values of the energy of the atom relative to the field, which is completely analogous to formula (16) for the possible energy values of a simple Planck oscillator. This remark illustrates the physical side of the problem of the influence of the field on the stationary states of the atom. It need hardly be emphasised that neither in considering the effect of the magnetic field nor that of the electric field does it suffice to base the treatment on the application of the adiabatic principle to the problem of the slow establishment of the field; this is seen directly from the fact of the entire freedom of orientation in space of the atom in the absence of the field.

Proceeding now to the consideration of the effect of the electric field on the hydrogen lines, we obtain from (40) and (44) for the energy in the stationary states of the atom

$$E=-\frac{2\pi^2e^4m}{h^2}\frac{1}{n^2}+\frac{3h^2F}{8\pi^2em}n\,n_F. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (46)$$

By means of the general frequency-relation this gives, for the radiation emitted by a transition from a state for which $n=n'$ and $n_F=n'_F$ to a state for which $n=n''$ and $n_F=n''_F$,

$$\nu=\frac{2\pi^2e^4m}{h^3}\left(\frac{1}{(n'')^2}-\frac{1}{(n')^2}\right)+\frac{3hF}{8\pi^2em}(n'n'_F-n''n''_F). \quad . \quad . \quad . \quad . \quad . \quad . \quad (47)$$

According to the correspondence principle, the occurrence of such a transition is conditioned by the presence in the electric moment of the atom of a harmonic component of frequency $(n'-n'')\omega+(n'_F-n''_F)\omega_F$. Comparing this with our analysis of the motion in the field, we are consequently led to infer that each of the spectral components into which the hydrogen lines are split up will show a characteristic polarisation, such that all components for which $(n'-n'')+(n'_F-n''_F)$ is an even integer will show linear polarisation parallel to the field, while components for which

this expression is an odd integer will exhibit a characteristic polarisation in a direction perpendicular to the field. These results are fully confirmed by Stark's experiments; not only can the positions of the observed components for each hydrogen line be accounted for by formula (47) within the limits of experimental error, but also the polarisation of the components is found to conform to the above rules.* Moreover, by theoretical estimation, based on a calculation of the amplitudes of the corresponding harmonic oscillations of the probabilities of transitions giving rise to the various spectral components, it has even been possible to account in detail for the laws of distribution of intensities of the different components, which show great differences from line to line. The latter problem has been treated by Kramers in a Paper which contains a thorough discussion of the problem of intensities of spectral lines in relation to the correspondence principle.†

In view of these results, we may say that the Stark effect for the hydrogen lines, when properly interpreted, reveals every detail of the action of the electric field on the motion of the hydrogen atom. In contrast to the Zeeman effect, however, the image of the motion of the electron which we observe in the spectrum is so distorted that it would hardly have been possible to recognise it on the basis of our ordinary ideas of the origin of electromagnetic radiation. At the same time the fundamental departure of the quantum-theory from classical electrodynamics comes to light in a most striking way in a feature of the effect recorded by Stark.‡ While under usual conditions the components of each hydrogen line exhibit complete symmetry with respect to the position of the original line, a remarkable asymmetry is observed when the spectrum is excited under such conditions that the atom in the main receives impacts from electrons moving in the same or in the opposite direction to that of the electric force. In fact, in the latter condition the components on the long-wave side of the original line are much more intense, or less intense, respectively, than the components on the short-wave side. On the quantum-theory this observation receives immediate interpretation if we assume that under these conditions the probability of the plane in which the electric centre moves being displaced from the nucleus in the same direction as the motion of the impacting electrons, is markedly larger than the probability of this displacement being in the reverse direction. The effect under consideration has often been considered as affording a serious objection to the quantum-theory explanation of the Stark effect.§ We see, however, that, on the contrary, it must be regarded as a most direct evidence of the complete independence of the processes which give rise to the appearance of the various spectral components; and this, according to our postulates, is just an essential feature of the quantum-theory of spectra.‖

Effect of Simultaneous Electric and Magnetic Fields.

The considerations applied above allow of direct application to more complicated problems. One such problem is presented when we investigate the simultaneous effect of uniform electric and magnetic fields on the hydrogen lines.

* Q.L.S., p. 77. *Cf.* also Zs. für Phys., 2, p. 446 (1920).

† H. A. Kramers, Intensities of Spectral Lines, D. Kgl. Danske Vidensk. Selsk. Skrifter, 8, 3, 287 (1919).

‡ J. Stark, Ann. d. Physik, 56, 569 (1918).

§ *See* J. Stark, Jahrbuch d. Ra. u. El., 17, p. 161 (1921).

‖ *Cf.* N. Bohr, Phil. Mag., 30, p. 402, (1915); *see* also A. Rubinowiz, Zs. f. Phys., 5, p. 331 (1921).

In the case when the two fields are parallel the perturbations of the original periodic motion will be a simple superposition of the perturbations considered above in the case of separate fields, and the stationary states will obviously be fixed by three conditions:

$$I=nh,\ I_H=n_Hh,\ I_F=n_Fh \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

where the second condition, which determines the angular momentum of the electron round the axis of the system, as well as the third condition, which determines the position of the plane perpendicular to this axis in which the electrical centre of the orbit moves, are in every respect completely analogous to the additional quantum conditions in the formulæ (30) and (40) respectively. The energy of the atom in the stationary states will consequently be given by

$$E=-\frac{2\pi^2e^4m}{h^2}\frac{1}{n^2}+\frac{ehH}{4\pi mc}n_H+\frac{3h^2F}{8\pi^2em}n\,n_F \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

Moreover, it follows directly from the correspondence principle that the effect of the fields will consist in the resolution of every hydrogen line: partly into one set of components polarized parallel to the fields, and placed at the positions of the parallel components of the Stark effect which would appear in the absence of the magnetic field; partly into two sets of components exhibiting circular polarization in opposite directions and placed symmetrically with respect to the perpendicular components of the Stark effect, in the same way as the circularly polarized components of the usual Zeeman effect are placed with respect to the original line.* This consequence of the theory seems adequat.ly supported by the experiments.†

In many experiments on the Zeeman effect we are concerned with the disturbing effect of small electric fields which possess a component perpendicular to the direction of the magnetic force. This effect may be discussed by considering the resultant motion as a small perturbation of the motion holding in the presence of the magnetic field alone, and the problem may be treated by a method closely analogous to that applied above to the perturbations of a periodic motion. In the present case it may be shown that the electric forces will, in a first approximation, not give rise to the appearance of new fundamental frequencies in the secular changes of the periodic orbit; nor—so far as quantities proportional to the intensity of the electric field are concerned—will this field have any effect on the energy in the stationary states of the atom. The presence of this field, nevertheless, will give rise to the appearance of new harmonic oscillations with amplitudes proportional to the intensity of the field, and with frequencies equal to the sum or difference of two frequencies appearing in the atom when the magnetic field alone is present. On the correspondence principle this will, in addition to probabilities of transitions responsible for the components of the usual Zeeman effect, give rise to small probabilities of the occurrence of new types of transitions. Besides irregularities in the polarisation of the usual components, the electric field may therefore be expected to cause the appearance of new weak components, at distances from the

* Q.L.S., p. 92.

† Garbasso, Phys. Zs., 15, p. 729 (1914).

original lines twice that of the outer components in the normal effect. Such effects have actually been observed.*

Before concluding our consideration of the effect of external fields on the hydrogen spectrum, it may be of interest to characterise, in a few words, the difference between the treatment given here and the method applied in their original investigations on the Stark and Zeeman effects for the hydrogen lines by the authors mentioned in Section IV. These methods were based mainly on the so-called procedure of separation of variables, which in every case inevitably leads to a number of quantum conditions equal to the number of degrees of freedom of the system. As we have seen, however, a treatment of the effect of magnetic and electric fields on the hydrogen lines, adapted to illustrate the physical side of the problem, can be given by using a smaller number of quantum conditions, equal to the degree of periodicity of the motion. The principal objection to the use of a higher number of quantum conditions is that by their use the inherent stability of the spectral phenomena under consideration does not come to light. In fact, these conditions imply the formal fixation of certain properties of the motion of the atom which, in contrast to those fixed by our treatment, are unstable in the presence of external forces which are yet so small that they cannot essentially influence the spectrum. Apart from this, the method of separation of variables has a more limited applicability. This is seen, for instance, on taking into consideration the influence of variability of mass of the electron, which for simplicity has been neglected in the foregoing analysis. The problem of the fine structure of the hydrogen lines can be treated by separation of variables, and so also can the effect of magnetic fields on this fine structure, as was shown by Sommerfeld.† But this is no longer true when we approach the problem of the effect of electric fields on the fine-structure. In this case the motion is of such a complex nature that no set of generalised co-ordinates can be found which allows of a separation of variables. On the other hand, as shown by Kramers,‡ the problem can be successfully treated by considering the motion as a perturbed periodic motion, and examining the periodic properties of the secular perturbations. In this way it is possible to follow theoretically the details in the transformation of the fine-structure of the hydrogen lines which accompanies a gradual increase in the electric field from very small intensities to intensities of the order of magnitude usually applied in experiments on the Stark effect, in which the effect of variability of mass of the electron plays only a very small part. Experiments allowing of a test of these theoretical predictions would be of great interest.

VI. The Effect of External Fields on the Spectra Emitted by Atoms containing Several Electrons.

Notwithstanding their greater complexity the so-called series spectra of many elements show a marked analogy with the hydrogen spectrum. On the quantum-theory of spectra this is accounted for by the assumption that in the stationary states concerned in the emission of these spectra one of the electrons in the atom

* Q.L.S., p. 98.
† A. Sommerfeld, Phys. Zeitschr., 17, p. 497 (1916).
‡ H. A. Kramers, Zeitschr. f. Phys., 3, p. 199 (1920).

moves, at any rate during the greater part of its path, at a distance from the nucleus large compared with the distances of the other electrons. According to this view the spectral lines are emitted by transition processes in which the motion of this electron alone undergoes essential changes, while the orbits of the other electrons coincide quite closely with their orbits in the normal state of the atom. Just as the hydrogen spectrum may be regarded as evidencing a process by which the neutral atom is formed by the binding of the electron by the nucleus, so a series spectrum of this type for another element may be considered as evidencing the last stage of a process in which the atom is formed by the successive capture and binding of electrons in the field of the nucleus. Time will not allow me to enter here into the details of the results it has been possible to attain regarding the general features of atomic constitution by an elaboration of this point of view.* I shall confine myself to showing how these ideas on the origin of series spectra allow us to account for certain main features of the structure of these spectra as well as of the effect of electric and magnetic fields on their lines.

In so far as it remains at distances from the nucleus large compared with the dimensions of the orbits of the inner electrons the force exerted by the rest of the atom on the outer electron will coincide very nearly with the force due to a nucleus of unit charge. In the case in which the outer electron remains always outside the region in which the inner electrons move, its motion may therefore be considered as a Keplerian motion undergoing slow secular perturbations, and of much the same type as the motion in the hydrogen atom under the influence of an external field. In the case when the outer electron penetrates at intervals during its revolution into the inner region, its motion will be composed of a sequence of outer loops, each coinciding closely with part of a Keplerian ellipse and connected with the next by an inner orbital loop in which the motion may differ essentially from a Keplerian motion.

The inherent stability of atomic structure—brought to light so strikingly by experiments on the impact of atoms and free electrons—suggests in the first place that this penetration into the inner region will involve no interchange of energy between the outer electron and the rest of the atom, in the sense that for one and the same electron orbit the various outer loops will coincide closely with parts of ellipses corresponding to the same value of the energy of the hydrogen atom. Moreover, the general central symmetry of the electronic arrangement in the nuclear atom suggests that consecutive loops will as a first approximation have the same shape and be spaced at equal angles to each other in the orbital plane. This means that the motion may be considered as a plane periodic motion on which is superposed a uniform rotation in its plane, a description which may be assumed to hold in a first approximation for the outer orbit, whether it penetrates into the inner region or not. On this motion may be superposed again a slow precession of the orbital plane around the invariant axis of angular momentum of the atom.

The resolution of a motion of this type into its harmonic components may be simply effected in the following way. In a system of reference partaking of the

* *Cf.* The Theory of Spectra and Atomic Constitution, Camb. Univ. Press (1922), containing three essays of which the first two deal in a general way with the problems considered in the former sections of this lecture, while the third gives a detailed discussion of the theory of the constitution of atoms. *See also* my Paper Linienspectren und Atombau (Ann. d. Physik, 71, p. 229, 1923) which contains a more detailed account of the interpretation of spectra with complete reference to the literature.

rotation of the orbit in its plane and the precession of the orbital plane, the motion of the electron will be composed of a sequence of elliptic harmonic oscillations of frequencies $\tau\omega$, where τ is an integer and ω the frequency of revolution. It is seen that each of these oscillations, as a consequence of the uniform rotation of the orbit in its plane, will be resolved into two circular harmonic rotations in opposite directions, with frequencies $\tau\omega \pm \omega_R$, where ω_R is the frequency of the orbital rotation. As in the consideration of the Zeeman effect, each of these will, on account of the precession of the orbital plane, be resolved into a linear harmonic vibration parallel to the fixed axis with unaltered frequency, and two circular harmonic rotations in opposite directions with frequencies increased or diminished by the frequency of precession. Denoting this frequency by ω_P we find consequently for the displacement of the outer electron in directions parallel and perpendicular to the invariant axis respectively,

$$\xi = \Sigma C_{\tau,\pm 1} \cos 2\pi[(\tau\omega \pm \omega_R)t + \gamma_{\tau,\pm 1}], \quad \eta = \Sigma D_{\tau,\pm 1,\pm 1} \cos 2\pi [(\tau\omega \pm \omega_R \pm \omega_P)t + \delta_{\tau,\pm 1,\pm 1}]. \quad . \quad . \quad . \quad . \quad (50)$$

By analogy with the general theory of the state-relations for periodic and multiple-periodic systems we shall assume that the motion of the outer electron in the stationary states is determined by a set of conditions which may be written

$$I = nh, \; I_R = n_\cdot h, \; I_P = n_{\cdot\cdot} h \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (51)$$

where the quantities I, I_R and I_P are correlated with the fundamental frequencies in the triple-periodic motion of the outer electron by the relation

$$\delta E = \omega\delta I + \omega_R \delta I_R + \omega_P \delta I_P, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (52)$$

which refers to two states of the atom for which the orbits of the inner electrons retain their shape and relative configuration while the shape of the orbit of the outer electron as well as its orientation relative to the inner orbits differ slightly.

Since the perturbations of the outer orbit from a Keplerian ellipse occur almost entirely in the region close to perihelion, where the electron remains only a small fraction of the period required to traverse an orbital loop, this period will to a high degree of approximation be equal to that required for the description of the Keplerian ellipse of which the outer loop forms a part. With this approximation we have therefore

$$\delta E = \omega\delta I_0, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

where I_0 is the quantity defined by (13) as applied to this ellipse. Comparing (52) with (53) we may therefore write

$$I_0 = I + \Phi(I_R, I_P), \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

where Φ is a function of I_R and I_P subject to the relation

$$\omega\delta\Phi = \omega_R \delta I_R + \omega_P \delta I_P. \quad , \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (55)$$

from which it follows that the ratios ω_R/ω and ω_P/ω, with the approximation under consideration, are independent of I. For the dependence of the work W required to remove the outer electron from the atom we obtain now in accordance with (26)

$$W=\frac{2\pi^2e^4m}{I_0}=\frac{2\pi^2e^4m}{(I+\Phi)^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

Writing for simplicity $E=-W$ we get with reference to (51) for the energy in the stationary states

$$E=-\frac{2\pi^2e^4m}{h^2}\cdot\frac{1}{[n+\alpha(n_R, n_P)]^2}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (57)$$

where α stands for Φ/h. This formula accounts at once for the series structure of the spectra under consideration. In fact, the empirical expressions for the spectral terms within each series have in a first approximation just the same form as (57), if α is taken as a constant characteristic of each series, and n is given a sequence of consecutive integral values. In other words, each series of spectral terms may be correlated to the stationary states corresponding to a sequence of integral values of the "principal" quantum number n and constant values of the "subordinate" quantum integers n_R and n_P.

So far the considerations have been independent of our special assumptions as regards the deviations of the orbit of the outer electron from a Keplerian orbit and of the dynamical significance of the symbols I_R and I_P. Applying a relation analogous to (32) it is simply shown, however, that with the assumptions used as to the character of the perturbations, $2\pi I_R$ will be the angular momentum of the outer electron around the nucleus, while $2\pi I_P$ will be the resultant angular momentum of the whole atom around the invariant axis. On the basis of this result a detailed classification of the manifold of terms has been obtained correlating each series of "terms" in extended sense with a given value of n_R, while the complex structure of these terms (doublets, triplets, &c.) is accounted for by correlating each term "component" to a given value of n_P. This classification, which is due principally to Sommerfeld, has received most convincing support from the application of the correspondence principle. According to this principle the appearance of a transition from a stationary state characterised by n', n'_R, n'_P to another state characterised by n'', n''_R, n''_P, is conditioned by the presence in the motion of a constituent harmonic vibration of frequency $(n'-n'')\omega+(n'_R-n''_R)\omega_R+(n'_P-n''_P)\omega_P$. In view of the analysis of the motion expressed by (50) we conclude therefore that while for a given transition n can change by an arbitrary number of units, n_R can only increase or decrease by a single unit, and n_P remains unchanged or changes by one unit. The classification of the empirical manifold of spectral terms has indeed been effected in such a way that these theoretical rules of combination are obeyed.

Proceeding now to the effect of electric and magnetic fields on series spectra, we find that the application of the same principles which have guided us in examining these effects in the case of the hydrogen spectrum leads us to a number of theoretical predictions which have been found to be fulfilled to a large extent.

In the case of the electric field we meet at once with a typical difference from the conditions encountered in hydrogen. Owing to the periodic character of the electronic orbit in hydrogen, the external field produces a finite change in the shape and position of the orbit, due to an accumulation of the effects of the secular perturbations. In the motion involved in the series spectra of other elements, on the

other hand, we have in the undisturbed atom to do with an electronic orbit which is continuously undergoing regular changes as regards its position in space, of a type that limits a cumulative effect of the perturbations to time intervals of the same order of magnitude as the periods characteristic of these changes of position. As long as these periods are short compared with the period of the changes which the same field would produce in a purely Keplerian orbit of the same dimensions, the character of the motion will undergo only small periodic changes, and notably there will appear no secular perturbations chacterised by a new frequency proportional to the first power of the external forces. In the case of the series spectra of elements other than hydrogen there will, therefore, be no question of a splitting up of the spectral lines into components with a displacement proportional to the field, at any rate so far as the spectral terms involved differ from the hydrogen terms with the same principal quantum number by an amount which is large compared with the effect of the same field on the hydrogen terms. In this case any resolution or displacement of the spectral lines will be proportional to the second power of the electric forces, and the effect will be the smaller, the more the spectral terms involved deviate from the hydrogen terms, which deviations, according to (55) and (56), indeed give a measure of the frequencies of the changes of position of the orbit in space.

These theoretical expectations are completely confirmed by the experiments of Stark and other investigators, which have shown that an effect of the electric field on the lines, of the same order of magnitude as exists in hydrogen, occurs only for lines for which at least one of the two spectral terms involved coincides closely with the hydrogen term of the same quantum number; while for lines where both terms deviate considerably from hydrogen terms, the effect is very small, if measureable at all.

The problem of the influence of electric fields on the spectral lines can be followed in great detail, both as regards the theoretical predictions as well as their confirmation by experiment. It will, however, carry us too far here to enter more closely into these questions. I shall, however, mention one very important feature brought out by Stark's experiments, namely, the production of new combination lines under the influence of the field. This phenomenon receives an immediate explanation on the theory. In fact, although, as mentioned, the electric field does not change the type of the motion of the electron in a first approximation, there will nevertheless, on account of the perturbations, appear new constituent harmonic oscillations in the motion, with amplitudes proportional to the electric forces, and with frequencies equal to the sums or differences of frequencies belonging to harmonic constituents present in the undisturbed motion. Owing to these new oscillations, which are analogous to the "combination tones" well known in acoustics, the atom will acquire, apart from the transitions giving rise to the usual spectral lines in the presence of the field, possibilities of new transitions giving rise to new spectral lines, the frequencies of which will be equal to the sum or difference of the frequencies of lines which appeared in the undisturbed spectrum.* As far as experimental evidence is available, these expectations are fulfilled both as regards the position of the new lines, and as regards their intensities estimated on the correspondence principle. The observation of such "true" combination lines has been

* *Cf.* Q.L.S., pp. 36 and 108.

generally considered among the strongest supports of the combination principle, although at the same time the apparent capriciousness of their appearance threw a veil of mystery over the application of this principle. To-day it is seen, however, that the quantum-theory has not only afforded a formal interpretation of the combination principle, but that it has also contributed materially to the clearing up of the mystery surrounding its applications.

Considering next the effect of a uniform magnetic field we find that the application of the laws of electrodynamics, together with the correspondence principle, leads to very simple deductions. In fact, quite independently of the character of the motion of the electrons in the absence of the field, we should expect from Larmor's theorem that the effect of the field would consist simply in the superposition of a uniform rotation of the whole atom around an axis parallel to the field. Just as in the case of hydrogen, the superposed rotation will give rise to the appearance of a new quantum condition, to the effect that only those orientations of the atom relative to the field are possible in which the component of the total angular momentum of the atom parallel to the field is equal to an integral multiple of $h/2\pi$. Moreover, on the correspondence principle, the effect of the superposed rotation on each of the harmonic constituents in the motion of the atom, in the absence of the field, would involve the resolution of each line into a normal Lorentz triplet.

These theoretical expectations are, however, as already mentioned at the beginning of this lecture, only partly fulfilled. While all spectra consisting of single lines, indeed, show the normal effect, the series spectra of more complicated types exhibit, as is well known, the so-called anomalous Zeeman effect. On the correspondence principle this may be considered as proving that, in contrast to the laws of classical electrodynamics, the magnetic field will, for spectra of such types, not only affect the motion of the atom as a whole, but will also directly influence the interplay between the various electrons in the atom. This is especially clearly shown by the way in which the anomalous Zeeman effects, as first observed by Paschen and Back, are gradually transformed by increasing field intensity; as well as by the appearance observed by the same authors of new components in the complex structure of the series lines in the presence of the magnetic field.* The latter phenomenon may be considered as the complete analogue of the appearance of new series lines in the presence of external electric fields. At the same time these effects show clearly that the magnetic field does not directly influence those properties of the motion which are fixed by the principal quantum number n as well as by the subordinate quantum-number n_R. This is also satisfactory, since not only the approximately Keplerian character of the orbital loops but also the rotation of these loops in their plane, depends only on the simple assumption that the effects on the motion of the outer electron exerted by the rest of the atom conform approximately to that of a central field of force. On the other hand the properties of the motion fixed by the quantum number n_p involve directly the dynamic character of the configuration of inner electron orbits, and may be considered as representing primarily the finer interplay of the outer electron and the atomic residue. In view of the above considerations the anomalous Zeeman effect suggests that these features of the interplay cannot even in a first approximation be described by the

* F. Paschen und E. Back, Ann. d. Phys., 39, p. 897 (1912), and Physica, 1, p. 261 (1921).

laws of classical electrodynamics. Indeed, only on this view does the breaking down of Larmor's theorem in these cases seem intelligible; and it is therefore most satisfactory that the other features in regard to the complex structure of series spectra also point definitely to this conclusion.*

A most suggestive clue to the examination of this problem may be considered as afforded by Preston's rule, which was referred to at the beginning of this lecture, as well as by the rules first established by Runge concerning the simple numerical relations between the displacements of the components of the anomalous effects and those of the normal Zeeman effect. In this respect a step of great significance has recently been made by Landé, who has succeeded from the empirical rules in deriving general laws governing the way in which a given spectral term, under the influence of a magnetic field, is split up into a number of term-components, as well as the manner in which these components combine with each other to give rise to the observed resolution of the spectral lines.† It is to be hoped that these beautiful results will help to clear up the still unsolved secrets of electron interplay in the atom. Ingenious and suggestive attempts have already been made in this direction, but a satisfactory solution is hardly yet in sight. As indicated above, such a solution will presumably demand a still greater departure from the classical conceptions, even though it may be expected to conform with the general ideas regarding the stability of atoms and the radiation emitted by them, the illustration of which forms the principal purpose of this lecture.

* *Cf.* N. Bohr, Ann. d. Phys., 71, p. 277 (1923).

† A. Landé, Zeitschr. f. Phys., 5, p. 231 (1921), and 15, p. 189 (1923).