ON THE BEHAVIOUR OF ATOMS IN AN
ELECTROMAGNETIC WAVE FIELD

BY

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§ 1. *Introduction.*

As well known, the properties of the atoms cannot be accounted for on the basis of the classical theory of electrons. Still they exhibit in many respects a great similarity with the properties which, on the classical theory, systems consisting of small electrically charged particles would possess. One of the main problems in the modern theory of atoms is therefore to find to what extent and in what manner the conceptions and the laws of classical electrodynamics can be used in order to establish a description of the actual properties of atoms. Now, an outstanding non-classical feature of these properties is a certain element of discontinuity which finds an appropriate expression in Bohr's postulate of the existence of discrete *stationary states* of an atom, and in the application of the ideas of Planck's *quantum-theory* to the closer description of the laws governing these states and the *transitions* between them. Thus many atomic properties may be expressed by laws which roughly spoken are a translation into a »discontinuous language« of laws which, being derived by means of classical electrodynamics, are formulated in a »continuous language«. The object of this lecture is to show in the case of a special problem of physical interest in what way such a translation can be effected, and it will be seen, how a characteristic feature of the mathematical formulation consists in the substistution of the »differentials« occurring in the formulæ of the classical theory, by finite »differences«, referring to the discrete stationary states or the transitions between them.

§ 2. *The quantum theory of periodic systems.*

Consider an atomic system consisting of one or more electrified particles, and having the property that its motion, when

calculated by means of classical mechanics, is always periodic, independent of the initial positions and velocities of the particles. Let T be the kinetic energy of the system and ω the frequency of the motion, *i.e.* the number of periods pro sec., and let the quantity J be defined by the time integral of $2T$ taken over one period:

$$J = \int_0^{1/\omega} 2\,T\,dt. \tag{1}$$

It is easily proved, *e.g.*, by means of the theorem of least action, that the energy E of the system can be considered as a function of J alone, and that the following relation holds:

$$\frac{dE}{dJ} = \omega. \tag{2}$$

The Cartesian coordinates of the particles can, considered as a function of the time be developed in Fourier series of period $\frac{1}{\omega}$. The same will therefore hold for the components of the electrical moment of the system. If ξ is one of these components we will therefore have:

$$\xi = \overset{\infty}{\underset{0}{\Sigma^\tau}}\, C_\tau \cos{(2\pi\tau\omega t + \gamma_\tau)}, \tag{3}$$

where the summation has to be extended over integer values of τ, and where the amplitudes C_τ and phase-constants γ_τ may be considered as functions of J. According to the classical electron theory of radiation, the periodically changing electrical moment (3) will give rise to the emission of a set of monochromatic electro-magnetic waves, of frequencies ω, 2ω, 3ω a.s.o. and of intensities proportional to the square of the amplitudes characterising the corresponding Fourier components of the electrical moment. Due to this radiation the energy of the system would continually decrease.

In the quantum theory of spectra, the behaviour of the periodic system under consideration is described in the following way. The system possesses a set of stationary states, which may be characterised by the integer values 0,1,2,3,..., which a »quantum number« n may take, and the energy E_n in the nth state is the same as the energy in a mechanical state of motion for which the following relation holds:

$$J = n\,h \tag{4}$$

where h is Planck's constant.

The emission of the spectrum of the atom is brought about by transitions of the atom from one state n' to another state n'' of lower energy; the waves corresponding to such a transition are monochromatic, the frequency $v_{n''}^{n'}$ being given by Bohr's frequency relation:

$$v_{n''}^{n'} = \frac{E_{n'} - E_{n''}}{h} \tag{5}$$

This relation can also be written in the following form.

$$v_{n''}^{n'} = (n' - n'') \frac{E_{n'} - E_{n''}}{hn' - hn''} = (n' - n'') \frac{\Delta E}{\Delta J} \tag{6}$$

where ΔE and ΔJ design the difference of the values of E and J in the two states involved in the transition.

When we compare the expression (6) with the expression for one of the frequencies which, on the classical theory, would be involved in the radiation from the system:

$$v = \tau \omega = \tau \frac{dE}{dJ} \tag{7}$$

where τ is an integer, we see at once that Bohr's frequency condition may be considered as the »translation« of a classical formula into a formula which takes account of the discontinuities of the quantum theory, the quotient of two differentials being replaced by the quotient of two differences, referring to a pair of stationary states.

If we suppose h to converge to zero, and if at the same time we keep $(n'-n'') = \tau$ and E constant, the formula (6) will in the limit be identical with (7). But even if h remains finite the value of v expressed by (6) will still tend to coincide asymptotically with that given by (7) for $\tau = n'-n''$, if we go to the limit of very great values of n, i.e. if we consider transitions for which $n'-n''$ is small compared with the values of n' and n'' themselves. Bohr has postulated that this asymptotic coincidence of the results of the quantum theory with those of the classical theory not only is restricted to the frequencies of the spectral lines, but also to the intensities with which these lines appear and to their state of polarisation, and he considers the coincidence in question as evidence of a general law or feature, proper to the behaviour of atomic systems, which is called the

correspondence principle. In the terminology of this principle, the appearance of a spectral line originating from a transition of the n'^{th} to the n''^{th} state is said to »correspond« to the presence of the harmonic of frequency $(n'-n'')\,\omega$ in the motion, which the system would perform according to the classical electrodynamical laws.

As an example of the application of (4) of (5) and of the correspondence principle we may mention the quantum theory of the hydrogen spectrum. In the hydrogen atom the electron would, according to the classical theory, describe a closed Keplerian orbit round the nucleus as centre. The dependency between E and J is for this system expressed by:

$$E = -\frac{2\pi^2 e^4 m}{J^2} \tag{8}$$

where e and m represent the charge and mass of an electron. After the introduction of (4), the frequencies of the lines of the hydrogen spectrum are directly obtained by means of (5). The fact that lines are observed corresponding to all possible values of the difference $n'-n''$ is, according to the correspondence principle, connected with the circumstance, that in the Fourier resolution of a Keplerian motion harmonics occur corresponding to any integer value of τ.

The intensity with which a given spectral line appears is often expressed by means of a coefficient $a_{n''}^{n'}$ introduced by Einstein in 1917, which has such a value that $a_{n''}^{n'}\,dt$ denotes the probability that, in a time interval dt, an atom in the state n' shall spontaneously perform a transition to the state n''. If $\nu_{n''}^{n'}$ is the frequency of the corresponding spectral line, the mean energy emitted per second in the form of radiation of this frequency by an atom in the state n' will then be given by $a_{n''}^{n'}\,h\,\nu_{n''}^{n'}$.

At present the theory has not yet succeeded, however, in finding the exact mathematical expressions for the coefficients $a_{n''}^{n'}$; from a consideration of the behaviour of the atom according to the classical theory we can, however, derive expressions, which by the correspondence-principle allow to calculate these coefficients in the limit of high quantum numbers. If we, especially, consider a system of one degree of freedom in which

an electrical particle can perform oscillations along a straight line, the electrical moment can, on the classical theory, be represented by a formula of the type (3). According to the classical theory of radiation, the electromagnetic energy radiated pro sec. in the form of waves of frequency $\tau \omega$ will be given by $(2 \pi \tau \omega)^4 \, C_\tau^2 / 3 \, c^3$, where c is the velocity of light. The asymptotical relations for frequency and intensity holding in the limit of high quantum numbers can then be expressed by:

$$\nu_{n''}^{n'} \sim (n' - n'') \, \omega, \tag{9}$$

$$a_{n''}^{n'} \, h \, \nu_{n''}^{n'} \sim \frac{(2 \pi (n' - n'') \, \omega)^4 \, C_{n'-n''}^2}{3 \, c^3}. \tag{10}$$

It will be convenient for the following to introduce the conception of *virtual oscillator*, i. e. of an electrical dipole which harmonically oscillates with frequency $\nu_{n''}^{n'}$ and with such an amplitudee $A_{n''}^{n'}$ that the classical radiation from it would exactly correspond with the radiation of that frequency which in the mean can be ascribed to each atom in the initial state n'. These quantities $A_{n''}^{n'}$ which we will call the *characteristic amplitudes* of the transitions, will thus in the case of a linear oscillator be defined by

$$a_{n''}^{n'} \, h \, \nu_{n''}^{n'} = \frac{\left(2 \pi \, \nu_{n''}^{n'}\right)^4 \, A_{n''}^{n' \, 2}}{3 \, c^3} \tag{11}$$

and the asymptotical relation (10) takes the form

$$A_{n''}^{n'} \sim C_{n'-n''}. \tag{12}$$

§ 3. *The action of monochromatic light on an atomic system.*

In this paragraph we proceed to the problem which forms the proper subject of our lecture, *viz.* the problem of the reaction of an atom when exposed to an electromagnetic wave field. For the sake of simplicity we will, just as in the end of the former paragraph, consider an atomic system consisting of an electrified particle which can perform oscillations along a straight line, and moreover we will assume that the light waves falling on the atom are monochromatic and linearly polarised, the electrical vector being parallel to the direction in which the particle moves. From the analysis of *optical phenomena* we know, that

under the influence of the light, the atom will become a secondary source of radiation; in the language of the classical theory of radiation it will act as a dipole which oscillates with the same frequency as that of the incident light. The amplitude of this oscillation will be proportional to the amplitude of the electrical vector of the incident light, and its phase will directly depend on the phase of this vector, *i.e.* the secondary radiation will be *coherent* with the primary radiation. If the electrical light-vector at the position of the atom is presented by

$$\mathfrak{E} = E \cos 2\pi\nu t \tag{13}$$

the oscillating dipole»induced«in the atom can be represented by

$$\mathfrak{P} = P \cos (2\pi\nu t - \varphi). \tag{14}$$

The ratio P/E and the phase difference φ are the determining factors for the *dispersion, absorption* and *scattering* of the incident light by a gas consisting of atoms of the kind described. In fact, if N be the number of atoms per ccm., the index of refraction n will be given by

$$n^2 - 1 = 4\pi N \frac{P \cos \varphi}{E}. \tag{15}$$

The energy *absorbed* from the incident beam will be equal to $\pi\nu N P E \sin \varphi$ pro sec., corresponding to an effective absorbing cross section equal to $8\pi^2 \frac{\nu}{c} \frac{P \sin \varphi}{E}$ pro atom. The energy *scattered* by the atoms in all directions in the form of radiation of frequency ν will finally be equal to $\frac{N(2\pi\nu)^4 P^2}{3c^3}$ pro sec. If ν does not lie in the immediate neighbourhood of one of the absorption lines of the atoms, $\sin \varphi$ will be very small, and the problem of the reaction of the atom on the light will primarily consist in finding which function can represent the values of the scattering electrical moment P of the atom as a function of the frequency ν of the incident light; P being reckoned positive or negative according as the value of φ is very nearly equal to 0, or to π.

In order to establish the form of the function P, we will first investigate the influence which, on the classical theory, the light will have on the motion of the atomic system. Let the electrical

moment of the atom be ξ, and let us assume that in the undisturbed motion, ξ is represented by the series:

$$\xi_0 = R \sum_{-\infty}^{+\infty} \frac{1}{2} C_\tau e^{2\pi i \tau \omega t}. \tag{16}$$

The symbol R means, that the real part has to be taken. The summation has to be extented over positive and negative integer values of τ, zero included. The amplitudes C's are in general complex quantities, satisfying the relation

$$C_{-\tau} = \overline{C_\tau}. \tag{17}$$

These amplitudes, as well as the frequency ω, may be considered as functions of the quantity J defined by (1). Then, writing

$$\xi = \xi_0 + \xi_1 \tag{18}$$

we find, by means of the theory of perturbations, that when the atoms is exposed to the periodical field of force (13), and when second and higher powers of E are neglected, ξ_1 will be given by the double infinite series:

$$\xi_1 = R \frac{E}{4} \sum_{-\infty}^{+\infty} \sum_{-\infty}^{+\infty} \left\{ -(\tau - \tau_0) \frac{dC_\tau}{dJ} \frac{\overline{C_{\tau - \tau_0}}}{-(\tau - \tau_0)\omega + \nu} - \tau C_\tau \frac{d}{dJ} \left(\frac{\overline{C_{\tau - \tau_0}}}{-(\tau - \tau_0)\omega + \nu} \right) \right\} e^{2\pi i (\nu + \tau_0 \omega) t}. \tag{19}$$

From (19) we see that the light has induced in the atom not only a »forced vibration« of frequency ν, but also vibrations the frequencies of which are of the type $\nu + \tau_0 \omega$. Only in the case of a harmonic oscillator (all C's zero except $C_{\pm 1}$) these »compound« frequencies will not appear.

Consider first that part of (19), which corresponds to a dipole of frequency ν, and for which consequently $\tau_0 = 0$. Representing it by $\mathfrak{P}$, we can write it in the form

$$\mathfrak{P} = R \frac{E}{2} \sum_{1}^{\infty} \tau \frac{d}{dJ} \left(\frac{|C|^2 \tau \omega}{(\tau \omega)^2 - \nu^2} \right) e^{2\pi i \nu t}. \tag{20}$$

Now this expression can be transformed so as to refer to the actual properties of the atom, by replacing the differential coefficients in an adequate way by quotients of differentials. In the case of the formulæ (7) and (6) such a transformation was brought about by letting the differences on the right hand term refer to two stationary states, while the left hand term referred

to a transition between these two states. Such a thing is not possible here, however, since the expression for the scattering electrical momentum of the atom, which appears on the left hand side of (20), necessarily must represent a property of a given stationary state of the atom. In agreement with this, the differences appearing when transforming the right hand side will refer to two transitions; the stationary state in question being the final state for the one and the initial state for the other. In fact, the asymptotical relations (9) and (12) suggest directly that we must transform (20) in the following way:

$$\mathfrak{P}_n = \frac{E}{2h} \sum_{1}^{\infty} \tau \left[\frac{\left(A_n^{n+\tau}\right)^2 \nu_n^{n+\tau}}{\left(\nu_n^{n+\tau}\right)^2 - \nu^2} - \frac{\left(A_{n-\tau}^n\right)^2 \nu_{n-\tau}^n}{\left(\nu_{n-\tau}^n\right)^2 - \nu^2} \right] \cos 2\pi\nu t \quad (21)$$

where the left member refers to the scattering momentum in the nth stationary state. There has been no question of a rigid deduction of (21) from (20), but there are several reasons which make it possible for us to believe that formula (21) is right. First of all, it is easily proved, that in agreement with the correspondence principle, the formulæ (21) and (20) become assymptotically identical in the limit of high quantum numbers. Further the formula (21) contains only quantities which are directly measurable by experiment, viz. the frequencies of the light which the atoms may radiate and the quantities A which govern the intensity of these radiations.

A peculiar consequence follows from the circumstance that there do not exist stationary states corresponding to all positive and negative values of n. If, for instance, only such states exist for which $n=0,1,2\ldots$, a great number of terms appearing in (21) have to be left out. Denoting by the index *abs* any quantity referring to transitions which the atom in a given state may perform by absorption of light to a state of greater energy, and by the index *em* a quantity referring to a transition to a state of less energy, (21) may also be given the form:

$$\mathfrak{P} = \frac{E}{2h} \left\{ \sum_{abs} \frac{A_{abs}^2 \, \nu_{abs}}{\nu_{abs}^2 - \nu^2} - \sum_{em} \frac{A_{em}^2 \, \nu_{em}}{\nu_{em}^2 - \nu^2} \right\} \cos 2\pi\nu t \quad (22)$$

where the summations have to be extented to all the absorption and all the emission lines of the atom in the state under consideration.

In the special case where the atom is in its normal state, *viz.* the state of smallest energy, no emission of radiation is possible, and no terms exist belonging to the second summation inside the brackets. In other words the subtrahends appearing in the »differences« by which the classical differentials were replaced, disappear; a feature which illustrates very clearly the profound difference between the quantum theory of atoms and the classical theory of electrons. Formally, the formula thus obtained for the scattering momentum in the normal state of an atom, coincides with the classical formula for the scattering from an atomic system in which the particles can perform harmonic oscillations of frequencies ν_{abs} round their positions of equilibrium. It leads immediately to a dispersion formula of the Helmholtz-Ketteler type, which has been confirmed by experiments on dispersion in gases and vapours, not only in frequency regions far from the frequencies of the absorption lines which form singular points for the function $\mathfrak{P}$, but also in the neighbourhood of these lines, where $\mathfrak{P}$ assumes very large values giving rise to the so-called anomalous dispersion. In the immediate neighbourhood of an absorption line, formula (22) must be expected to fail. This is connected with the fact, that even the classical formula (19) only holds if ν is different from any of the natural frequencies $\tau\omega$ of the system, since in case of coincidence the change of the motion of the electron due to the external wave field would, due to resonance, no longer be small. The problem of the corrections to be applied to (22) in order to represent the scattering also inside the absorption lines has not yet found a satisfactory solution.

If the atom is in one of its higher states, also terms belonging to the second sum inside the brackets of (22) appear. In the neighbourhood of the frequency ν_{em} of an emission line, the atom will then give rise to an anomalous dispersion of similar kind as in the case of an absorption line, with the difference that the sign of $\mathfrak{P}$ is reversed. This socalled »negative dispersion« is closely connected with the prediction made by Einstein, that the atom for such a frequency will exhibit a »negative absorption«, *i.e.* light waves of this frequency, passing through a great number of atoms in the state under consideration, will increase in intensity.

Until now we have only considered those terms in the ex-

pression (19) which correspond to $\tau_0 = 0$, i.e. we have investigated that part of the classical scattering which has the same frequency as the incident light and is coherent with it, and we have established the analogon of those terms in the quantum theory. To the other terms in (19), there correspond, however, also well defined mathematical expressions in the quantum theory; these expressions mean that the atom, under the influence of the light, will not only scatter radiation of the same frequency, but also radiation of other frequencies, the intensity of which, however, is again proportional to the intensity of the incident light. The classical frequencies of these radiations being of the form $|\nu + \tau_0 \omega|$, we are, from the correspondence principle, naturally led to expect that in the nth state of the atom these frequencies will be of the form $\left| \nu + \nu_{n-\tau_0}^n \right|$ or $\left| \nu + \nu_n^{n+\tau_0} \right|$, where ν_b^a should be put equal to $- \nu_a^b$ if b should be larger than a. It would lead us too far to give in detail the transformation of (19) which in these cases leads to an expression of the amplitudes of the scattering momentum of the atom, and the reader is referred to the second paper cited in the literature reference. We will only add a few remarks regarding the finite results.

If τ_0 is positive the scattered frequencies are of the type $\nu + \nu_{n-\tau_0}^n$ and their amplitudes will contain terms of the type

$$\frac{E}{4h} A_{n-\tau}^{n+\tau} A_n^{n+\tau} \left(\frac{1}{\nu_n^{n+\tau} - \nu} + \frac{1}{\nu_{n-\tau_0}^{n+\tau} + \nu} \right) \tag{23}$$

where τ represents some whole number. Besides these terms also other terms of similar structure appear. In order to obtain these expressions, it is necessary not only to replace the differential coefficients in (19) by the quotients of differences, but also to replace the factors which contain the amplitudes C in a non differentiated form by half the sum of two quantities referring to two definite transitions. It is interesting in this connection to remember that also in the mathematical theory of difference equations, one is lead from the very beginning not only to consider differences of the type $\frac{1}{\omega} [f(x + \omega) - f(x)]$, but also sums of the type $\frac{1}{2} [f(x + \omega) + f(x)]$ (Comp. N. E. Nørlund, Differenzenrechnung).

If τ_0 is negative, the scattered frequencies are partly of the type $\nu + \nu^n_{n-\tau_0} = \nu - \nu^{n-\tau_0}_n$, corresponding to values of τ_0 for which this expression is positive, partly of the type $\left| \nu + \nu^{n+\tau_0}_n \right| = \nu^n_{n+\tau_0} - \nu$, again corresponding to values of τ_0 for which the last expression is positive. In both cases the amplitudes are again expressed by sums of terms, the structure of each of which is similar to that of the expression (23).

The generalization of our considerations to systems of more degrees of freedom, the motion of which is not of a simply periodic, but of a so-called multiple periodic type, and the stationary states of which are determined by more than one quantum number, does not involve any difficulty, and no new features are brought to light by its results. An exception is formed, however, by systems for which the number of quantum numbers determining the stationary states is less than that of degrees of freedom. In the case of such systems, which often are called »degenerate«, and of which the undisturbed hydrogen atom forms an important example, it has not yet been possible to solve the problem of the amplitudes of the scattered radiation in a satisfactory way, the difficulty being mainly that of determining the character of the polarisation of the scattered rays.

The results of which I have tried to give you some idea in this lecture suggest the possibility of a theoretical treatment of atomic properties, in which from the outset all formula referring directly to the classical theory of electrons are banished, and in which only formulæ having a direct meaning in the sense of the quantum theory are allowed. Although it is uncertain on what lines such a program can be worked out and carried through, interesting and promising results have already been obtained in the papers (3) and (4) mentioned in the literature list, which contain an audacious attempt of developing a new »*quantum mechanics*«.

LITERATURE

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