

The Quantum Theory of Dispersion.

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§ 1. *Introduction and Summary.*

The new quantum mechanics could at first be used to answer questions concerning radiation only through analogies with the classical theory. In Heisenberg's original matrix theory, for instance, it is assumed that the matrix elements of the polarisation of an atom determine the emission and absorption of radiation analogously to the Fourier components in the classical theory. In more recent theories* a certain expression for the electric density obtained from the quantum mechanics is used to determine the emitted radiation by the same formulæ as in the classical theory. These methods give satisfactory results in many cases, but cannot even be applied to problems where the classical analogies are obscure or non-existent, such as resonance radiation and the breadths of spectral lines.

A theory of radiation has been given by the author which rests on a more definite basis.† It appears that one can treat a field of radiation as a dynamical system, whose interaction with an ordinary atomic system may be described by a Hamiltonian function. The dynamical variables specifying the field are the energies and phases of its various harmonic components, each of which

* E. Schrödinger, 'Ann. d. Physik,' vol. 81, p. 109 (1926) ; W. Gordon, 'Z. f. Physik,' vol. 40, p. 117 (1926) ; O. Klein, 'Z. f. Physik,' vol. 41, p. 407 (1927).

† 'Roy. Soc. Proc.,' A, vol. 114, p. 243 (1927). This is referred to later by *loc. cit.*

is effectively a simple harmonic oscillator. One must, of course, in the quantum theory take these variables to be q-numbers satisfying the proper quantum conditions. One finds then that the Hamiltonian for the interaction of the field with an atom is of the same form as that for the interaction of an assembly of light-quanta with the atom. There is thus a complete formal reconciliation between the wave and light-quantum points of view.

In applying the theory to the practical working out of radiation problems one must use a perturbation method, as one cannot solve the Schrödinger equation directly. One can assume that the term (V say) in the Hamiltonian due to the interaction of the radiation and the atom is small compared with that representing their proper energy, and then use V as the perturbing energy. Physically the assumption is that the mean life time of the atom in any state is large compared with its periods of vibration. In the present paper we shall apply the theory to determine the radiation scattered by the atom, considering also the case when the frequency of the incident radiation coincides with that of a spectral line of the atom. The method used will be that in which one finds a solution of the Schrödinger equation that satisfies certain initial conditions, corresponding to a given initial state for the atom and field. In general terms it may be described as follows:—

If V_{mn} are the matrix elements of the perturbing energy V , where each suffix m or n refers to a stationary state of the whole system of atom plus field the stationary state of the atom being specified by its action variables, J say, and that of the field by a given distribution of energy among its harmonic components, or by a given distribution of light-quanta, then each V_{mn} gives rise to transitions from state n to state m^* ; more accurately, it causes the eigenfunction representing state m to grow if that representing state n is already excited, the general formula for the rate of change of the amplitude a_m of an eigenfunction being†

$$i\hbar/2\pi \cdot \dot{a}_m = \sum_n V_{mn} a_n = \sum_n v_{mn} a_n e^{2\pi i(W_m - W_n)t/\hbar}, \quad (1)$$

where v_{mn} is the constant amplitude of the matrix element V_{mn} , and W_m is the

* In *loc. cit.*, § 6, it was in error assumed that V_{mn} caused transitions from state m to state n , and consequently the information there obtained about an absorption (or emission) process in terms of the number of light-quanta existing before the process should really apply to an emission (or absorption) process in terms of the number of light-quanta in existence after the process. This change, of course, does not affect the results (namely the proof of Einstein's laws) which can depend on $|V_{mn}|^2 = |V_{nm}|^2$.

† *Loc. cit.*, equation (4). In the present paper \hbar is taken to mean just Planck's constant [instead of $(2\pi)^{-1}$ times this quantity as in *loc. cit.*] which is preferable when one has to deal much with quanta $\hbar\nu$ of radiation.

total proper energy of the state m . To solve these equations one obtains a first approximation by substituting for the a 's on the right-hand side their initial values, a second approximation by substituting for these a 's their values given by the first approximation, and so on. One or two such approximations will usually be sufficient to give a solution that is fairly accurate for times that are small compared with the life time, but may all the same be large compared with the periods of the atom. From the first approximation, namely,

$$a_m = a_{m0} + \sum_n v_{mn} a_{n0} (1 - e^{2\pi i (W_m - W_n) t / h}) / (W_m - W_n), \quad (2)$$

where a_{n0} denotes the initial value of a_n , one sees readily that when two states m and n have appreciably different proper energies, the amplitude a_m gets changed only by a small extent, varying periodically with the time, on account of transitions from state n . Only when two states, m and m' say, have the same energy does the amplitude a_m of one of them grow continually at the expense of that of the other, as is necessary for physically recognisable transitions to occur, and the rate of growth is then proportional to $v_{mm'}$.

The interaction term of the Hamiltonian function obtained in *loc. cit.* [equation (30)] does not give rise to any direct scattering processes, in which a light-quantum jumps from one state to another of the same frequency but different direction of motion (*i.e.*, the corresponding matrix element $v_{mm'} = 0$). All the same, radiation that has apparently been scattered can appear by a double process in which a third state, n say, with different proper energy from m and m' , plays a part. If initially all the a 's vanish except $a_{m'}$, then a_n gets excited on account of transitions from state m' by an amount proportional to $v_{nm'}$, and although it must itself always remain small, a calculation shows that it will cause a_m to grow continually with the time at a rate proportional to $v_{mn}v_{nm'}$. The scattered radiation thus appears as the result of the two processes $m' \rightarrow n$ and $n \rightarrow m$, one of which must be an absorption and the other an emission, in neither of which is the total proper energy even approximately conserved.

The more accurate expression for the interaction energy obtained in § 3 of the present paper does give rise to direct scattering processes, whose effect is of the same order of magnitude as that of the double processes, and must be added to it. The sum of the two will be found to give just Kramers' and Heisenberg's dispersion formula* when the incident frequency does not coincide with that of an absorption or emission line of the atom. If, however, the incident frequency coincides with that of, say, an absorption line, one of the

* Kramers and Heisenberg, 'Z. f. Physik,' vol. 31, p. 681 (1925).

terms in the Kramers-Heisenberg formula becomes infinite. The present theory shows that in this case the scattered radiation consists of two parts, of which the amount of one increases proportionally to the time since the interaction commenced, and that of the other proportionally to the square of this time. The first part arises from those terms in the Kramers-Heisenberg formula that remain finite, with perhaps a contribution from the infinite term, while the second, which is much larger, is just what one would get from transitions of the atom to the upper state and down again governed by Einstein's laws of absorption and emission.

A difficulty that appears in the present treatment of radiation problems should be here pointed out. If one tries to calculate, for instance, the total probability of a light-quantum having been emitted by a given time, one obtains as result a sum or integral with respect to the frequency of the emitted light-quantum that does not converge in the high frequencies. This difficulty is not due to any fundamental mistake in the theory, but comes from the fact that the atom has, for the purpose of its interaction with the field, been counted simply as a varying electric dipole, and the field produced by a dipole, when resolved into its Fourier components, has an infinite amount of energy in the short wave-lengths, owing to the infinite field in its immediate neighbourhood. If one does not make the approximation of regarding the atom as a dipole, but uses the exact expression for the interaction energy, then the fact that the singularity in the field is of a lower order of magnitude and remains constant is sufficient to make the series or integral converge. The exact interaction energy is too complicated to be used as a basis for radiation theory at present, and we shall here use only the dipole energy, which will mean that divergent series are always liable to appear in the calculation. The best method to adopt under such circumstances is first to work out the general theory of any effect using arbitrary coefficients v_{mn} , and then to substitute for these coefficients in the final result their values given by the dipole interaction energy. If one then finds that the series all converge, one can assume that the result is a correct first approximation; if, however, any of them do not converge, one must conclude that a dipole theory is inadequate for the treatment of that particular effect. We shall find that for the phenomena of dispersion and resonance radiation dealt with in the present paper, there are no divergent series in the first approximation, so that the dipole theory is sufficient. If, however, one tries to calculate the breadth of a spectral line, one meets with a divergent series, so that a dipole theory of the atom is presumably inadequate for the correct treatment of this question.

§ 2. *Preliminary Formulæ.*

We consider the electromagnetic field to be resolved into its components of plane, plane-polarised, progressive waves, each component r having a definite frequency, direction of motion and state of polarisation, and being associated with a certain type of light-quanta. (To save writing we shall in future suppose the words "direction of motion" applied to a light-quantum or a component of the field to imply also its state of polarisation, and a sum or integral taken over all directions of motion to imply also the summation over both states of polarisation for each direction of motion. This is convenient because the two variables, direction of motion and state of polarisation, are always treated mathematically in the same way.) For an electromagnetic field of infinite extent there will be a continuous three-dimensional range of these components. As this would be inconvenient to deal with mathematically, we suppose it to be replaced by a large number of discrete components. If there are σ_r components per unit solid angle of direction of motion per unit frequency range, we can keep σ_r an arbitrary function of the frequency and direction of motion of the component r , provided it is large and reasonably continuous, and shall find that it always cancels from the final results of a calculation, which fact appears to justify our replacement of the continuous range by the discrete set.

We can express σ_r in the form $\sigma_r = (\Delta\nu_r \Delta\omega_r)^{-1}$, where $\Delta\nu_r$ can be regarded as the frequency interval between successive components in the neighbourhood of the component r , and $\Delta\omega_r$ is in the same way the solid angle of direction of motion to be associated with this component. The quantities $\Delta\nu_r$, $\Delta\omega_r$ enable one to pass directly from sums to integrals. Thus if f_r is any function of the frequency and direction of motion of the component r that varies only slightly from one component to a neighbouring one, the sum of $f_r \Delta\nu_r$ for all components having a specified direction of motion is

$$\sum_r f_r \Delta\nu_r = \int f_r d\nu_r, \quad (3)$$

and the sum of $f_r \Delta\omega_r$ for all components having a specified frequency is

$$\sum_\omega f_r \Delta\omega_r = \int f_r d\omega_r. \quad (3')$$

Also the sum of $f_r (\sigma_r)^{-1}$ for all components is

$$\sum f_r (\sigma_r)^{-1} = \sum f_r \Delta\nu_r \Delta\omega_r = \int f_r d\nu_r d\omega_r. \quad (3'')$$

If the number* N_s of quanta of energy of the component s varies only slightly from one component to a neighbouring one, one can give a meaning to the intensity of the radiation per unit frequency range. By supposing the discreteness in the number of components to arise from the radiation being confined in an enclosure (which would imply stationary waves and a special function σ_s) one obtains† for the rate of flow of energy per unit area per unit solid angle per unit frequency range

$$I_{\nu\omega} = N_s h \nu_s^3 / c^2, \quad (4)$$

a result which may be taken to hold generally for arbitrary σ_s and progressive waves.‡ If only those components with a specified direction of motion are excited, we have instead that the rate of flow of energy per unit area per unit frequency range is

$$I_\nu = N_s h \nu_s^3 / c^2 \cdot \Delta\omega_s; \quad (5)$$

while if only a single component s is excited, we have that the rate of flow of energy per unit area is

$$I = N_s h \nu_s^3 / c^2 \cdot \Delta\omega_s \Delta\nu_s = N_s h \nu_s^3 / c^2 \sigma_s. \quad (6)$$

In this last case the amplitude of the electric force has the value E given by

$$E^2 = 8\pi I / c = 8\pi N_s h \nu_s^3 / c^3 \sigma_s, \quad (7)$$

and the amplitude a of the magnetic vector potential, when chosen so that the electric potential is zero, is

$$a = cE / 2\pi\nu_s = 2(h\nu_s / 2\pi c\sigma_s)^{\frac{1}{2}} N_s^{\frac{1}{2}}. \quad (8)$$

§ 3. The Hamiltonian Function.

We shall now determine the Hamiltonian function that describes the interaction of the field with an atom more accurately than in *loc. cit.* We consider the atom to consist of a single electron moving in an electrostatic field of potential ϕ . According to the classical theory its relativity Hamiltonian equation when undisturbed is

$$p_x^2 + p_y^2 + p_z^2 - (W + e\phi)^2 / c^2 + m^2 c^2 = 0,$$

so that its Hamiltonian function is

$$H = W = c \{m^2 c^2 + p_x^2 + p_y^2 + p_z^2\}^{\frac{1}{2}} - e\phi. \quad (9)$$

* The rule given in *loc. cit.* that symbols representing c-number values for q-number variables should be primed need not always be observed if no confusion thus arises, as in the present case.

† *Loc. cit.*, § 6, equation (28).

‡ This is justified by the fact that one can obtain the result by an alternative method that does not require a finite enclosure, namely by using a quantum-mechanical argument similar to that of *loc. cit.* (lower part of p. 259), applied to the case of discrete momentum values.

If now there is a perturbing field of radiation, given by the magnetic vector potential $\kappa_x, \kappa_y, \kappa_z$ chosen so that the electric scalar potential is zero, the Hamiltonian equation for the perturbed system will be

$$\left(p_x + \frac{e}{c}\kappa_x\right)^2 + \left(p_y + \frac{e}{c}\kappa_y\right)^2 + \left(p_z + \frac{e}{c}\kappa_z\right)^2 - \frac{(W + e\phi)^2}{c^2} + m^2c^2 = 0,$$

which gives for the Hamiltonian function

$$\begin{aligned} H = W &= c \left\{ m^2c^2 + \left(p_x + \frac{e}{c}\kappa_x\right)^2 + \left(p_y + \frac{e}{c}\kappa_y\right)^2 + \left(p_z + \frac{e}{c}\kappa_z\right)^2 \right\}^{\frac{1}{2}} - e\phi \\ &= c \{ [m^2c^2 + p_x^2 + p_y^2 + p_z^2] + [2e/c \cdot (p_x\kappa_x + p_y\kappa_y + p_z\kappa_z) \\ &\quad + e^2/c^2 \cdot (\kappa_x^2 + \kappa_y^2 + \kappa_z^2)] \}^{\frac{1}{2}} - e\phi. \end{aligned}$$

By expanding the square root, counting the second term in square brackets [] as small, and then neglecting relativity corrections for this term, one finds approximately

$$\begin{aligned} H &= c [m^2c^2 + p_x^2 + p_y^2 + p_z^2]^{\frac{1}{2}} - e\phi + e/c \cdot (\dot{x}\kappa_x + \dot{y}\kappa_y + \dot{z}\kappa_z) \\ &\quad + e^2/2mc^2 \cdot (\kappa_x^2 + \kappa_y^2 + \kappa_z^2) \\ &= H_0 + e/c \cdot (\dot{x}\kappa_x + \dot{y}\kappa_y + \dot{z}\kappa_z) + e^2/2mc^2 \cdot (\kappa_x^2 + \kappa_y^2 + \kappa_z^2), \end{aligned} \quad (10)$$

where H_0 is the Hamiltonian for the unperturbed system given by (9). When one counts the radiation field as a dynamical system, one must add on its proper energy $\sum N_r \hbar \nu_r$ to the Hamiltonian (10).

According to the classical theory, the magnetic vector potential for any component r of the radiation is

$$\kappa_r = a_r \cos 2\pi\theta_r/\hbar = 2(\hbar\nu_r/2\pi c\sigma_r)^{\frac{1}{2}} N_r^{\frac{1}{2}} \cos 2\pi\theta_r/\hbar \quad (11)$$

from (8), where θ_r increases uniformly with the time such that $\dot{\theta}_r = \hbar\nu_r$, and is the variable that must be taken to be the canonical conjugate of N_r when the radiation field is treated as a dynamical system. The direction of this vector potential is that of the electric vector of the component of radiation. Hence the total value of the component of the vector potential in any direction, say that of the x -axis, is

$$\kappa_x = \sum_r \kappa_r \cos \alpha_{xr} = 2(\hbar/2\pi c)^{\frac{1}{2}} \sum_r \cos \alpha_{xr} (\nu_r/\sigma_r)^{\frac{1}{2}} N_r^{\frac{1}{2}} \cos 2\pi\theta_r/\hbar, \quad (12)$$

where α_{xr} is the angle between the electric vector of the component r and the x -axis. In the quantum theory, where the variables N_r, θ_r are q -numbers, the expression $2N_r^{\frac{1}{2}} \cos 2\pi\theta_r/\hbar$ must be replaced by the real q -number $N_r^{\frac{1}{2}} e^{2\pi i\theta_r/\hbar} + (N_r + 1)^{\frac{1}{2}} e^{-2\pi i\theta_r/\hbar}$. With this change one can take over the

Hamiltonian (10) into the quantum theory, which gives, when one includes the term $\Sigma N_r \hbar \nu_r$,

$$\begin{aligned} H = H_0 + \Sigma N_r \hbar \nu_r + e \hbar^{\frac{1}{2}} / (2\pi)^{\frac{1}{2}} c^{\frac{1}{2}} \cdot \Sigma_r \dot{x}_r (\nu_r / \sigma_r)^{\frac{1}{2}} [N_r^{\frac{1}{2}} e^{2\pi i \theta_r / \hbar} + (N_r + 1)^{\frac{1}{2}} e^{-2\pi i \theta_r / \hbar}] \\ + e^2 \hbar / 4\pi m c^3 \cdot \Sigma_{r,s} \cos \alpha_{rs} (\nu_r \nu_s / \sigma_r \sigma_s)^{\frac{1}{2}} [N_r^{\frac{1}{2}} e^{2\pi i \theta_r / \hbar} + (N_r + 1)^{\frac{1}{2}} e^{-2\pi i \theta_r / \hbar}] \\ \times [N_s^{\frac{1}{2}} e^{2\pi i \theta_s / \hbar} + (N_s + 1)^{\frac{1}{2}} e^{-2\pi i \theta_s / \hbar}] \quad (13) \end{aligned}$$

where x_r denotes the component of the vector (x, y, z) in the direction of the electric vector of the component r , *i.e.*,

$$x_r = x \cos \alpha_{xr} + y \cos \alpha_{yr} + z \cos \alpha_{zr},$$

and α_{rs} denotes the angle between the electric vectors of the components r and s , *i.e.*

$$\cos \alpha_{rs} = \cos \alpha_{xr} \cos \alpha_{xs} + \cos \alpha_{yr} \cos \alpha_{ys} + \cos \alpha_{zr} \cos \alpha_{zs}.$$

The terms in the first line of (13) are just those obtained in *loc. cit.*, equation (30), and give rise only to emission and absorption processes. The remaining terms (*i.e.*, those in the double summation) were neglected in *loc. cit.* These terms may be divided into three sets:—

(i) Those terms that are independent of the θ 's, which can be added to the proper energy $H_0 + \Sigma N_r \hbar \nu_r$. The sum of all such terms, which can arise only when $r = s$, is

$$\begin{aligned} e^2 \hbar / 4\pi m c^3 \cdot \Sigma_r \nu_r / \sigma_r \cdot [N_r^{\frac{1}{2}} e^{2\pi i \theta_r / \hbar} (N_r + 1)^{\frac{1}{2}} e^{-2\pi i \theta_r / \hbar} \\ + (N_r + 1)^{\frac{1}{2}} e^{-2\pi i \theta_r / \hbar} N_r^{\frac{1}{2}} e^{2\pi i \theta_r / \hbar}] \\ = e^2 \hbar / 4\pi m c^3 \cdot \Sigma_r \nu_r / \sigma_r \cdot (2N_r + 1). \end{aligned}$$

The terms $e^2 \hbar / 4\pi m c^3 \cdot \Sigma \nu_r / \sigma_r \cdot 2N_r$ are negligible compared with $\Sigma N_r \hbar \nu_r$, owing to the very large quantity σ_r in the denominator, while the terms $e^2 \hbar / 4\pi m c^3 \cdot \Sigma \nu_r / \sigma_r$ may be ignored since they do not involve any of the dynamical variables, in spite of the fact that the sum $\Sigma \nu_r / \sigma_r$, equal to $\int \nu_r d\nu_r d\omega_r$ from (3''), does not converge for the high frequencies.

(ii) The terms containing a factor of the form $e^{2\pi i (\theta_r - \theta_s) / \hbar}$ ($r \neq s$), whose sum is

$$\begin{aligned} e^2 \hbar / 4\pi m c^3 \Sigma_r \Sigma_{s \neq r} \cos \alpha_{rs} (\nu_r \nu_s / \sigma_r \sigma_s)^{\frac{1}{2}} [N_r^{\frac{1}{2}} (N_s + 1)^{\frac{1}{2}} e^{2\pi i (\theta_r - \theta_s) / \hbar} \\ + (N_r + 1)^{\frac{1}{2}} N_s^{\frac{1}{2}} e^{-2\pi i (\theta_r - \theta_s) / \hbar}] \\ = e^2 \hbar / 2\pi m c^3 \Sigma_r \Sigma_{s \neq r} \cos \alpha_{rs} (\nu_r \nu_s / \sigma_r \sigma_s)^{\frac{1}{2}} N_r^{\frac{1}{2}} (N_s + 1)^{\frac{1}{2}} e^{2\pi i (\theta_r - \theta_s) / \hbar}. \quad (14) \end{aligned}$$

These terms, which are the only important ones in the three sets, give rise to transitions in which a light-quantum jumps directly from a state s to a state r .

Such transitions may be called true scattering processes, to distinguish them from the double scattering processes described in § 1.

(iii) The remaining terms, each of which involves a factor of one or other of the forms $e^{\pm 4\pi i\theta_r/\hbar}$, $e^{\pm 2\pi i(\theta_r + \theta_s)/\hbar}$. These terms correspond to processes in which two light-quanta are emitted or absorbed simultaneously, and cannot arise in a light-quantum theory in which there are no forces between the light quanta. The effects of these terms will be found to be negligible, so that the disagreement with the light-quantum theory is not serious.

§ 4. *Discussion of the Emission and True Scattering Processes.*

We shall consider now the simple emission processes, in order to discuss the divergent integral that arises in this question. Suppose a light-quantum to be emitted in state r , with a simultaneous jump of the atom from the state $J = J'$ to the state $J = J''$. If we label the final state of the whole system of atom plus field m and the initial state k , the value at time t of the amplitude a_m of the eigenfunction of the final state will be in the first approximation

$$a_m = v_{mk} (1 - e^{2\pi i(W_m - W_k)t/\hbar}) / (W_m - W_k), \quad (15)$$

obtained by putting $a_{k0} = 1$, $a_{m0} = 0$ ($n \neq k$) in equation (2). The only term in the Hamiltonian (13) that can contribute anything to the matrix element v_{mk} is the one involving $e^{2\pi i\theta_r/\hbar}$, whose $(J'', N'_1, N'_2 \dots N'_r + 1 \dots; J', N_1, N_2 \dots N_r \dots)$ matrix element is $eh^{\frac{1}{2}}/(2\pi)^{\frac{1}{2}} c^{\frac{1}{2}} \cdot \dot{x}_r(J''J') (\nu_r/\sigma_r)^{\frac{1}{2}} (N'_r + 1)^{\frac{1}{2}}$, where $\dot{x}_r(J''J')$ is the ordinary $(J''J')$ matrix element of \dot{x}_r . If there is no incident radiation we must take all the N 's zero, which gives

$$v_{mk} = eh^{\frac{1}{2}}/(2\pi)^{\frac{1}{2}} c^{\frac{1}{2}} \cdot \dot{x}_r(J''J') (\nu_r/\sigma_r)^{\frac{1}{2}},$$

and also

$$W_k = H_0(J') \quad W_m = H_0(J'') + h\nu_r.$$

Thus

$$W_m - W_k = H_0(J'') + h\nu_r - H_0(J') = h[\nu_r - \nu(J'J'')]$$

where $\nu(J'J'') = [H_0(J') - H_0(J'')]/h$ is the transition frequency between states J' and J'' , if one assumes J' to be the higher one. Hence from (15)

$$|a_m|^2 = \frac{e^2}{\pi\hbar c^3} |\dot{x}_r(J'J'')|^2 \frac{\nu_r}{\sigma_r} \frac{1 - \cos 2\pi[\nu_r - \nu(J'J'')]t}{[\nu_r - \nu(J'J'')]^2}.$$

To obtain the total probability of any light-quantum being emitted within the solid angle $\delta\omega$ about the direction of motion of a given light-quantum r with this jump of the atom, we must multiply $|a_m|^2$ by $\delta\omega/\Delta\omega_r$ and sum for all frequencies. This gives, with the help of (3)

$$\delta\omega \Sigma_\nu \frac{|a_m|^2}{\Delta\omega_r} = \delta\omega \frac{e^2}{\pi\hbar c^3} |\dot{x}_r(J'J'')|^2 \int_0^\infty \nu_r d\nu_r \frac{1 - \cos 2\pi[\nu_r - \nu(J'J'')]t}{[\nu_r - \nu(J'J'')]^2}. \quad (16)$$

The integral does not converge for the high frequencies. This is due, as mentioned in § 1, to the non-legitimacy of taking only the dipole action of the atom into account, which is what one does when one substitutes for the magnetic potential in (10) its value given by (12), which is its value at some fixed point such as the nucleus instead of its value where the electron is momentarily situated. To obtain the interaction energy exactly, one should put $\cos 2\pi [\theta_r/\hbar - \nu_r \xi_r/c]$ instead of $\cos 2\pi \theta_r/\hbar$ in (11), where ξ_r is the component of the vector (x, y, z) in the direction of motion of the component r of radiation. This will make no appreciable change for low frequencies ν_r , but will cause a new factor $\cos 2\pi \nu_r \xi_r/c$ or $\sin 2\pi \nu_r \xi_r/c$, whose matrix elements tend to zero as ν_r tends to infinity, to appear in the coefficients of (13). This will presumably cause the integral in (16) to converge when corrected, as its divergence when uncorrected is only logarithmic.

Assuming that the integrand in (16) has been suitably modified in the high frequencies, one sees that for values of t large compared with the periods of the atom (but small compared with the life time in order that the approximations may be valid) practically the whole of the integral is contributed by values of ν_r close to $\nu(J'J'')$, which means physically that only radiation close to a transition frequency can be spontaneously emitted. One finds readily for the total probability of the emission, by performing the integration,

$$\delta\omega e^2/\pi\hbar c^3 \cdot |\dot{x}_r(J'J'')|^2 \cdot 2\pi^2 t \nu(J'J''),$$

which leads to the correct value for Einstein's A coefficient per unit solid angle, namely,

$$2\pi e^2/\hbar c^3 \cdot |\dot{x}_r(J'J'')|^2 \nu(J'J'') = 8\pi^3 e^2/\hbar c^3 \cdot |x_r(J'J'')|^2 \nu^3(J'J'').$$

We shall now determine the rate at which true scattering processes occur, caused by the terms (14) in the Hamiltonian. We see at once that the frequency of occurrence of these processes is independent of the nature of the atom, and is thus the same for a bound as for a free electron. The true scattering is the only kind of scattering that can occur for a free electron, so that we should expect the terms (14) to lead to the correct formula for the scattering of radiation by a free electron, with neglect of relativity mechanics and thus of the Compton effect.

Suppose that initially the atom is in the state J' and all the N 's vanish except one of them, N_s say, which has the value N_s' . We label this state for the whole system by k , and the state for which $J = J'$ and $N_s = N_s' - 1$, $N_r = 1$ with

all the other N 's zero by m . In the first approximation a_m is again given by (15), where we now have

$$v_{mk} = e^2 \hbar / 2\pi m c^3 \cdot \cos \alpha_{rs} (\nu_r \nu_s / \sigma_r \sigma_s)^{\frac{1}{2}} N_s'^{\frac{1}{2}}, \quad (17)$$

$$W_k = H_0(J') + N_s' \hbar \nu_s, \quad W_m = H_0(J') + (N_s' - 1) \hbar \nu_s + \hbar \nu_r. \quad (18)$$

Thus

$$W_m - W_k = \hbar (\nu_r - \nu_s), \quad (19)$$

and hence

$$|a_m|^2 = \frac{e^4}{2\pi^2 m^2 c^6} \cos^2 \alpha_{rs} \frac{\nu_r \nu_s}{\sigma_r \sigma_s} N_s' \frac{1 - \cos 2\pi (\nu_r - \nu_s) t}{(\nu_r - \nu_s)^2}.$$

To obtain the total probability of a scattered light-quantum being in the solid angle $\delta\omega$ we must, as before, multiply $|a_m|^2$ by $\delta\omega/\Delta\omega_r$ and sum for all frequencies ν_r , which gives*

$$\delta\omega \sum_r \frac{|a_m|^2}{\Delta\omega_r} = \delta\omega \frac{e^4}{2\pi^2 m^2 c^6} \cos^2 \alpha_{rs} \frac{\nu_s}{\sigma_s} N_s' \int \nu_r d\nu_r \frac{1 - \cos 2\pi (\nu_r - \nu_s) t}{(\nu_r - \nu_s)^2}. \quad (20)$$

We again obtain a divergent integral, of the same form as before, which we may assume becomes convergent in the more exact theory. We now have that practically the whole of the integral is contributed by values of ν_r close to ν_s and the total probability for the scattering process is

$$\delta\omega \frac{e^4}{2\pi^2 m^2 c^6} \cos^2 \alpha_{rs} \frac{\nu_s}{\sigma_s} N_s' \cdot 2\pi^2 t \nu_s = \delta\omega \frac{e^4}{\hbar m^2 c^4 \nu_s} \cos^2 \alpha_{rs} \cdot t I$$

from (6), where I is the rate of flow of incident energy per unit area. The rate of emission of scattered energy per unit solid angle is thus

$$e^4 / m^2 c^4 \cdot \cos^2 \alpha_{rs} I,$$

where α_{rs} is the angle between the electric vectors of the incident and scattered radiation, which is the correct classical formula.

* The reason why there is a small probability for the scattered frequency ν_r differing by a finite amount from the incident frequency ν_s is because we are considering the scattered radiation, after the scattering process has been acting for only a finite time t , resolved into its Fourier components. One sees from the formula (20) that as the time t gets greater, the scattered radiation gets more and more nearly monochromatic with the frequency ν_s . If one obtained a periodic solution of the Schrödinger equation corresponding to permanent physical conditions, one would then find that the scattered frequency was exactly equal to the incident frequency.

§ 5. Theory of Dispersion.

We shall now work out the second approximation to the solution of equations (1), taking the case when the system is initially in the state k , so that the first approximation, given by (2) with $a_{n0} = \delta_{nk}$, reduces to

$$a_m = \delta_{mk} + v_{mk} (1 - e^{2\pi i (W_m - W_k) t / h}) / (W_m - W_k).$$

When one substitutes these values for the a_n 's in the right-hand side of (1), one obtains

$$\begin{aligned} i\hbar/2\pi \cdot \dot{a}_m &= v_{mk} e^{2\pi i (W_m - W_k) t / h} \\ &+ \sum_n v_{mn} v_{nk} (1 - e^{2\pi i (W_n - W_k) t / h}) e^{2\pi i (W_m - W_n) t / h} / (W_n - W_k) \\ &= \left(v_{mk} - \sum_n \frac{v_{mn} v_{nk}}{W_n - W_k} \right) e^{2\pi i (W_m - W_k) t / h} + \sum_n \frac{v_{mn} v_{nk}}{W_n - W_k} e^{2\pi i (W_m - W_n) t / h}, \end{aligned}$$

and hence when $m \neq k$

$$\begin{aligned} a_m &= \left(v_{mk} - \sum_n \frac{v_{mn} v_{nk}}{W_n - W_k} \right) \frac{1 - e^{2\pi i (W_m - W_k) t / h}}{W_m - W_k} \\ &+ \sum_n \frac{v_{mn} v_{nk}}{W_n - W_k} \frac{1 - e^{2\pi i (W_m - W_n) t / h}}{W_m - W_n}. \quad (21) \end{aligned}$$

We may suppose the diagonal elements v_{nn} of the perturbing energy to be zero, since if they were not zero they could be included with the proper energy W_n . There will then be no terms in (21) with vanishing denominators, provided all the energy levels are different.

Suppose now that the proper energy of the state m is equal to that of the initial state k . Then the first term on the right-hand side of (21) ceases to be periodic in the time, and becomes

$$\{v_{mk} - \sum_n v_{mn} v_{nk} / (W_n - W_k)\} 2\pi t / i\hbar,$$

which increases linearly with the time. The rate of increase consists of a part, proportional to v_{mk} , that is due to direct transitions from state k , together with a sum of parts, each of which is proportional to a $v_{mn}v_{nk}$, and is due to transitions first from k to n and then from n to m , although the amplitude a_n of the eigenfunction of the intermediate state always remains small.

When one applies the theory to the scattering of radiation one must consider not a single final state with exactly the same proper energy as the initial state, but a set of final states with proper energies lying close together in a range that contains the initial proper energy, corresponding to all the possible scattered light-quanta with different frequencies but the same direction of motion that

may appear. One must now determine the total probability of the system lying in any one of these final states, which is

$$\Sigma |a_m|^2 = \int (\Delta W_m)^{-1} |a_m|^2 dW_m,$$

where ΔW_m is the interval between the energy levels. The second term in the expression (21) for a_m may be neglected since it always remains small (except in the case of resonance which will be considered later) and hence

$$\Sigma |a_m|^2 = \int \left| v_{mk} - \Sigma_n \frac{v_{mn} v_{nk}}{W_n - W_k} \right|^2 \frac{2[1 - \cos 2\pi(W_m - W_k)t/\hbar]}{\Delta W_m \cdot (W_m - W_k)^2} dW_m.$$

If one assumes that the integral converges, so that for large values of t practically the whole of it is contributed by values of W_m close to W_k , one obtains

$$\Sigma |a_m|^2 = \frac{4\pi^2 t}{\hbar \Delta W_m} \left| v_{mk} - \Sigma_n \frac{v_{mn} v_{nk}}{W_n - W_k} \right|^2, \quad (22)$$

where the quantities on the right refer to that final state that has exactly the initial proper energy.

We take the states k and m to be the same as for the true scattering process considered in the preceding section, so that equations (17), (18) and (19) still hold, and $\Delta W_m = \hbar \Delta \nu_r = \hbar/\sigma_r \Delta \omega_r$. We can now take the state n to be either the state $J = J''$, $N_s = N'_s - 1$, $N_t = 0$ ($t \neq s$) for any J'' , which would make the process $k \rightarrow n$ an absorption of an s -quantum and $n \rightarrow m$ an emission of an r -quantum, or the state $J = J''$, $N_s = N'_s$, $N_r = 1$, $N_t = 0$ ($t \neq s, r$), which would make $k \rightarrow n$ the emission and $n \rightarrow m$ the absorption. In the first case we should have

$$v_{nk} = \frac{e}{c} \left(\frac{\hbar \nu_s}{2\pi c \sigma_s} \right)^{\frac{1}{2}} \dot{x}_s(J''J') N_s'^{\frac{1}{2}} \quad v_{mn} = \frac{e}{c} \left(\frac{\hbar \nu_r}{2\pi c \sigma_r} \right)^{\frac{1}{2}} \dot{x}_r(J'J''),$$

and

$$W_n = H_0(J'') + (N'_s - 1) \hbar \nu_s \quad W_n - W_k = \hbar[\nu(J''J') - \nu_s]^*,$$

and in the second

$$v_{nk} = \frac{e}{c} \left(\frac{\hbar \nu_r}{2\pi c \sigma_r} \right)^{\frac{1}{2}} \dot{x}_r(J''J') \quad v_{mn} = \frac{e}{c} \left(\frac{\hbar \nu_s}{2\pi c \sigma_s} \right)^{\frac{1}{2}} \dot{x}_s(J'J'') N_s'^{\frac{1}{2}},$$

and

$$W_n = H_0(J'') + N'_s \hbar \nu_s + \hbar \nu_r \quad W_n - W_k = \hbar[\nu(J''J') + \nu_r].$$

We shall neglect the other possible states n , namely those for which the matrix elements v_{mn} , v_{nk} come from terms in the double summation in the Hamiltonian

* The frequency $\nu(J''J')$ is not necessarily positive.

(13), as we are working only to the first order in these terms. (We are working to the second order only in the emission and absorption terms, which, as we shall find, is the same as the first order in the terms of the double summation.) We now obtain for the right-hand side of (22) in which we must take $\nu_r = \nu_s$,

$$N_s' t \Delta \omega_r \frac{e^4 \nu_s^2}{h^2 c^6 \sigma_s} \left| \frac{h}{m} \cos \alpha_{rs} - \sum_{J''} \left\{ \frac{\dot{x}_r(J'J'') \dot{x}_s(J''J')}{\nu(J''J') - \nu_s} + \frac{\dot{x}_s(J'J'') \dot{x}_r(J''J')}{\nu(J''J') + \nu_s} \right\} \right|^2 \quad (23)$$

The most convenient way of expressing this result is to find the amplitude P (a vector) of the electric moment of that vibrating dipole of frequency ν_s that would, according to the classical theory, emit the same distribution of radiation as that actually scattered by the atom. The number of light-quanta of the type r (with $\nu_r = \nu_s$) emitted by the dipole P in time t per unit solid angle is

$$2\pi^3 \nu_s^3 / hc^3 \cdot P_r^2 t,$$

where P_r is the component of P in the direction of the electric vector of the light-quanta r . Comparing this with (23) (which must first be divided by $\Delta \omega_r$ to change it to the probability of a light quantum being scattered per unit solid angle) one finds for P_r

$$\begin{aligned} P_r &= \left(\frac{8\pi N_s'}{hc^3 \nu_s \sigma_s} \right)^{\frac{1}{2}} \frac{e^2}{4\pi^2} \left| \frac{h}{m} \cos \alpha_{rs} - \sum_{J''} \left\{ \frac{\dot{x}_r(J'J'') \dot{x}_s(J''J')}{\nu(J''J') - \nu_s} + \frac{\dot{x}_s(J'J'') \dot{x}_r(J''J')}{\nu(J''J') + \nu_s} \right\} \right| \\ &= E \frac{e^2}{h \nu_s^2} \left| \frac{h}{4\pi^2 m} \cos \alpha_{rs} - \sum_{J''} [\nu(J''J')]^2 \left\{ \frac{x_r(J'J'') x_s(J''J')}{\nu(J''J') - \nu_s} \right. \right. \\ &\quad \left. \left. + \frac{x_s(J'J'') x_r(J''J')}{\nu(J''J') + \nu_s} \right\} \right|, \quad (24) \end{aligned}$$

using (7), where E is the amplitude of the electric vector of the incident radiation.

We can put this result in a different form by using the following relations, which follow from the quantum conditions,

$$\sum_{J''} [x_r(J'J'') x_s(J''J') - x_s(J'J'') x_r(J''J')] = [x_r x_s - x_s x_r](J'J') = 0 \quad (25)$$

and

$$\begin{aligned} \sum_{J''} [x_r(J'J'') \dot{x}_s(J''J') - \dot{x}_s(J'J'') x_r(J''J')] &= [x_r \dot{x}_s - \dot{x}_s x_r](J'J') \\ &= i\hbar / 2\pi m \cdot \cos \alpha_{rs}, \quad (26) \end{aligned}$$

which gives

$$\begin{aligned} \sum_{J''} [x_r(J'J'') x_s(J''J') \nu(J''J') + x_s(J'J'') x_r(J''J') \nu(J''J')] \\ = \hbar / 4\pi^2 m \cdot \cos \alpha_{rs}. \quad (27) \end{aligned}$$

Multiplying (25) by ν_s and adding to (27), we obtain

$$\Sigma_{J''} [x_r (J' J'') x_s (J'' J') \{ \nu (J'' J') + \nu_s \} + x_s (J' J'') x_r (J'' J') \{ \nu (J'' J') - \nu_s \}] \\ = \hbar / 4\pi^2 m \cdot \cos \alpha_{rs}. \quad (28)$$

With the help of this equation, (24) reduces to

$$P_r = E \frac{e^2}{\hbar} \left| \Sigma_{J''} \left\{ \frac{x_r (J' J'') x_s (J'' J')}{\nu (J'' J') - \nu_s} + \frac{x_s (J' J'') x_r (J'' J')}{\nu (J'' J') + \nu_s} \right\} \right|,$$

so that the vector P is equal to

$$P = E \frac{e^2}{\hbar} \left| \Sigma_{J''} \left\{ \frac{x (J' J'') x_s (J'' J')}{\nu (J'' J') - \nu_s} + \frac{x_s (J' J'') x (J'' J')}{\nu (J'' J') + \nu_s} \right\} \right|, \quad (29)$$

where x without a suffix means the vector (x, y, z) . This is identical with Kramers' and Heisenberg's result.*

In applying the formula (22), instead of taking the final state m of the system to be one for which the atom is again in its initial state $J = J'$, we can take a new final state for the atom, $J = J'''$ say. The frequency ν_r for the scattered radiation that gives no change of total proper energy is now

$$\nu_r = \nu_s - \nu (J''' J') = \nu_s + \nu (J'' J''') - \nu (J'' J'), \quad (30)$$

which differs from the incident frequency ν_s , so that we obtain in this way the non-coherent scattered radiation. (We assume that this ν_r is positive as otherwise there would be no non-coherent scattered radiation associated with the final state $J = J'''$ of the atom.) In the present case we have $v_{mk} = 0$, corresponding to the fact that the true scattering process does not contribute to the non-coherent radiation. We now obtain for P_r , after a similar and almost identical calculation to that leading to equation (24),

$$P_r = E \frac{e^2}{\hbar} \frac{1}{\nu_r \nu_s} \left| \Sigma_{J''} \nu (J'' J') \nu (J'' J''') \left\{ \frac{x_r (J''' J'') x_s (J'' J')}{\nu (J'' J') - \nu_s} + \frac{x_s (J''' J'') x_r (J'' J')}{\nu (J'' J') + \nu_r} \right\} \right| \quad (31)$$

This result can be put in the form corresponding to (29) with the help of equations analogous to (25) and (26) referring to the non-diagonal $(J''' J')$ matrix elements of $[x_r x_s - x_s x_r]$ and $[x_r \dot{x}_s - \dot{x}_s x_r]$. These equations give, corresponding to (28),

$$\Sigma_{J''} [x_r (J''' J'') x_s (J'' J') \{ \nu (J'' J') + \nu_r \} + x_s (J''' J'') x_r (J'' J') \{ \nu (J'' J''') - \nu_r \}] = 0.$$

* Kramers and Heisenberg, *loc. cit.*, equation (18). For previous quantum-theoretical deductions of the dispersion formula see Born, Heisenberg and Jordan, 'Z. f. Physik,' vol. 35, p. 557, Kap. 1, equation (40) (1926); Schrödinger, *loc. cit.*, § 2, equation (23); and Klein, *loc. cit.*, § 5, equation (82).

When the left-hand side of this equation is subtracted from the summation in (31) one obtains, on account of the relations

$$\begin{aligned} \nu(J''J') \nu(J''J''') &= \nu(J''J') [\nu(J''J') + \nu_r - \nu_s] \\ &= [\nu(J''J') - \nu_s] [\nu(J''J') + \nu_r] + \nu_r \nu_s, \end{aligned}$$

and

$$\nu(J''J') \nu(J''J''') = [\nu(J''J''') - \nu_r] [\nu(J''J') + \nu_r] + \nu_r \nu_s$$

which follow from (30), the result

$$P_r = E \frac{e^2}{h} \left| \sum_{J''} \left\{ \frac{x_r(J''J''') x_s(J''J')}{\nu(J''J') - \nu_s} + \frac{x_s(J''J''') x_r(J''J')}{\nu(J''J') + \nu_r} \right\} \right|,$$

again in agreement with Kramers and Heisenberg.

§ 6. The Case of Resonance.

The dispersion formulæ obtained in the preceding section can no longer hold when the frequency of the incident radiation coincides with that of an absorption or emission line of the atom, on account of a vanishing denominator. One easily sees where a modification must be made in the deduction of the formulæ. Since one of the intermediate states n now has the same energy as the initial state k , the term in the second summation in (21) referring to this n becomes large and can no longer be neglected.

In investigating this case of resonance one must, for generality, suppose the incident radiation to consist of a distribution of light-quanta over a range of frequencies including the resonance frequency, instead of entirely of light-quanta of a single frequency, as the results will depend very considerably on how nearly monochromatic the incident radiation is. Thus one must take the initial state k of the system to be given by $J = J'$ and $N_s = N_s'$, where N_s' is zero except for light-quanta of a specified direction, and is for these light-quanta (roughly speaking) a continuous function of the frequency, so that the rate of flow of incident energy per unit area per unit frequency range is given by (5). The final state m for a process of coherent scattering is one for which $J = J'$ again, and a light-quantum s has been absorbed and one r of approximately the same frequency emitted. Thus we have

$$W_m - W_k = h(\nu_r - \nu_s). \quad (32)$$

As before, the intermediate states n will be those for which $J = J''$ (arbitrary) and either the s -quantum has already been absorbed or the r -quantum has already been emitted. If we take for definiteness the case when the range of incident frequencies includes only one resonance frequency, and this is an

absorption frequency to the state of the atom $J = J^l$, say, then that intermediate state of the system for which $J = J^l$ and for which the s -quantum has already been absorbed will have very nearly the same proper energy as the initial state. Calling this intermediate state l we have

$$W_l - W_k = h(\nu_0 - \nu_s) \quad W_m - W_l = h(\nu_r - \nu_0) \quad (33)$$

where ν_0 is the resonance frequency, equal to $[H(J^l) - H(J')]/h$.

In equation (21) we can now neglect only those terms of the second summation for which $n \neq l$. This gives

$$a_m = \left(v_{mk} - \sum_{n \neq l} \frac{v_{mn} v_{nk}}{W_n - W_k} \right) \frac{1 - e^{2\pi i (W_m - W_k) t/h}}{W_m - W_k} \\ + \frac{v_{ml} v_{lk}}{W_l - W_k} \left\{ \frac{1 - e^{2\pi i (W_m - W_l) t/h}}{W_m - W_l} - \frac{1 - e^{2\pi i (W_m - W_k) t/h}}{W_m - W_k} \right\},$$

which, with the help of (32) and (33), may be written

$$a_m = \left(v_{mk} - \sum_{n \neq l} \frac{v_{mn} v_{nk}}{W_n - W_k} \right) \frac{1 - e^{2\pi i (\nu_r - \nu_s) t}}{h(\nu_r - \nu_s)} \\ + \frac{v_{ml} v_{lk}}{h^2(\nu_0 - \nu_s)} \left\{ \frac{1 - e^{2\pi i (\nu_r - \nu_0) t}}{\nu_r - \nu_0} - \frac{1 - e^{2\pi i (\nu_r - \nu_s) t}}{\nu_r - \nu_s} \right\}.$$

We must now determine the total probability of a specified light-quantum r being emitted with the absorption of any one of the incident light-quanta s , which is given by $\sum_s |a_m|^2$, equal to $\int (\Delta\nu_s)^{-1} |a_m|^2 d\nu_s$. To evaluate this we require the following integrals

$$\int_0^\infty \frac{|1 - e^{2\pi i (\nu_r - \nu_s) t}|^2}{(\nu_r - \nu_s)^2} d\nu_s = 4\pi^2 t \\ \int_0^\infty \frac{1}{(\nu_0 - \nu_s)^2} \left| \frac{1 - e^{2\pi i (\nu_r - \nu_0) t}}{\nu_r - \nu_0} - \frac{1 - e^{2\pi i (\nu_r - \nu_s) t}}{\nu_r - \nu_s} \right|^2 d\nu_s \\ = 4\pi \frac{2\pi(\nu_r - \nu_0)t - \sin 2\pi(\nu_r - \nu_0)t}{(\nu_r - \nu_0)^3} \\ \int_0^\infty \frac{1 - e^{2\pi i (\nu_r - \nu_s) t}}{(\nu_r - \nu_s)(\nu_0 - \nu_s)} \left\{ \frac{1 - e^{-2\pi i (\nu_r - \nu_0) t}}{\nu_r - \nu_0} - \frac{1 - e^{-2\pi i (\nu_r - \nu_s) t}}{\nu_r - \nu_s} \right\} d\nu_s \\ = 2\pi \left\{ \frac{2\pi(\nu_r - \nu_0)t - \sin 2\pi(\nu_r - \nu_0)t}{(\nu_r - \nu_0)^2} + i \frac{1 - \cos 2\pi(\nu_r - \nu_0)t}{(\nu_r - \nu_0)^2} \right\},$$

for large t , and with their help obtain,

$$\begin{aligned} \Sigma_{\nu_s} |a_m|^2 = & \left| v_{mk} - \Sigma_{n \neq l} \frac{v_{mn} v_{nk}}{W_n - W_k} \right|^2 \frac{4\pi^2 t}{\hbar^2 \Delta \nu_s} \\ & + \frac{|v_{ml} v_{lk}|^2}{\hbar^4} \frac{4\pi}{\Delta \nu_s} \frac{2\pi (\nu_r - \nu_0) t - \sin 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^3} \\ & + 2R \left(v_{mk} - \Sigma_{n \neq l} \frac{v_{mn} v_{nk}}{W_n - W_k} \right) \frac{v_{kl} v_{lm}}{\hbar^3 \Delta \nu_s} 2\pi \left\{ \frac{2\pi (\nu_r - \nu_0) t - \sin 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^2} \right. \\ & \left. + i \frac{1 - \cos 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^2} \right\} \quad (34) \end{aligned}$$

where the quantities on the right now refer to that incident light-quantum s for which $\nu_s = \nu_r$, and R means the real part of all that occurs in the term after it.

The first of these three terms is just the contribution of those terms of the dispersion formula (22) that remain finite, the second is that which replaces the contribution of the infinite term,* and the third gives the interference between the first two, and replaces the cross terms obtained when one squares the dispersion electric moment. One can see the meaning of the second term more clearly if one sums it for all frequencies ν_r of the scattered radiation in a small frequency range $\nu_0 - \alpha'$ to $\nu_0 + \alpha''$ about the resonance frequency ν_0 (which frequency range must be large compared with the theoretical breadth of the spectral line in order that the approximations may be valid). This is equivalent to multiplying the term by $(\Delta \nu_r)^{-1}$ and integrating through the frequency range. If, for brevity, one denotes the quantity $4\pi |v_{ml} v_{lk}|^2 / \hbar^4 \Delta \nu_r \Delta \nu_s$ by $f(\nu_r)$, the result is, neglecting terms that do not increase indefinitely with t or that tend to zero as the α 's tend to zero,

$$\begin{aligned} & \int_{\nu_0 - \alpha'}^{\nu_0 + \alpha''} f(\nu_r) \frac{2\pi (\nu_r - \nu_0) t - \sin 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^3} d\nu_r \\ & = f(\nu_0) \int_{\nu_0 - \alpha'}^{\nu_0 + \alpha''} \frac{2\pi (\nu_r - \nu_0) t - \sin 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^3} d\nu_r \\ & \quad + f'(\nu_0) \int_{\nu_0 - \alpha'}^{\nu_0 + \alpha''} \frac{2\pi (\nu_r - \nu_0) t - \sin 2\pi (\nu_r - \nu_0) t}{(\nu_r - \nu_0)^2} d\nu_r \\ & = f(\nu_0) (2\pi t)^2 \left[\frac{1}{2} \pi - \frac{1}{2\pi t \alpha''} - \frac{1}{2\pi t \alpha'} \right] + f'(\nu_0) 2\pi t \log \alpha'' / \alpha'. \end{aligned}$$

* It should be noticed that this second term does not reduce to the square of the l term in the summation (22) when ν_r is not a resonance frequency, but to double this amount. This difference is due to the fact that processes involving a change of proper energy are not entirely negligible for the initial conditions used in the present paper, and one such scattering process, which was neglected in § 5, becomes in the resonance case a process with no change of proper energy and is included in the calculation.

Thus the contribution of the second term in (34) to the small frequency range $\nu_0 - \alpha'$ to $\nu_0 + \alpha''$ consists of two parts, one of which increases proportionally to t^2 and the other proportionally to t . The part that increases proportionally to t^2 , namely,

$$\frac{1}{2}\pi f(\nu_0) (2\pi t)^2 = \frac{1}{2} (2\pi)^4 |v_{ml}v_{lk}|^2 / \hbar^4 \Delta\nu_r \Delta\nu_s \cdot t^2,$$

is just that which would arise from actual transitions to the higher state of the atom and down again governed by Einstein's laws, since the probability that the atom has been raised to the higher state by the time τ is* $(2\pi)^2 |v_{lk}|^2 / \hbar^2 \Delta\nu_s \cdot \tau$, and when it is in the higher state the probability per unit time of its jumping down again with emission of a light-quantum in the required direction is $(2\pi)^2 |v_{ml}|^2 / \hbar^2 \Delta\nu_r$, so that the total probability of the two transitions taking place within a time t is

$$\frac{(2\pi)^2 |v_{lk}|^2}{\hbar^2 \Delta\nu_s} \cdot \frac{(2\pi)^2 |v_{ml}|^2}{\hbar^2 \Delta\nu_r} \int_0^t \tau d\tau = \frac{(2\pi)^4 |v_{ml}v_{lk}|^2}{\hbar^4 \Delta\nu_r \Delta\nu_s} \frac{1}{2} t^2.$$

The part that increases linearly with the time may be added to the contributions of the first and third terms, which also increase according to this law. For values of t large compared with the periods of the atom, the terms proportional to t will be negligible compared with those proportional to t^2 , and hence the resonance scattered radiation is due practically entirely to absorptions and emissions according to Einstein's laws.

* This result and the one for the emission follow at once from formula (32) of *loc. cit.*

