# CONTRIBUTION
# TO THE QUANTUM THEORY
# OF LIGHT SCATTERING

## N. G. VAN KAMPEN

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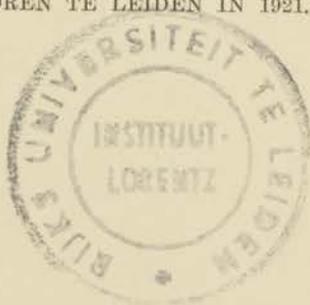
Promotor: Prof. Dr H. A. Kramers

# CONTRIBUTION TO THE QUANTUM THEORY OF LIGHT SCATTERING

BY

N. G. van KAMPEN

# CONTENTS

# Introduction and Summary.

**1.** In this work the theory of scattering and emission of light by an atom is developed on the basis of Kramers' method of quantizing the classical theory of the electron.[1,2] Accordingly, the calculations are non-relativistic and we shall confine ourselves throughout to electric dipole radiation. These restrictions will allow us to avoid all divergences.

Scattering will be described by means of stationary states of the compound system of atom and electromagnetic field, which bear a close analogy to the customary classical treatment. To emphasize this analogy the properties of each state are interpreted in terms of a classical radiation field. Emission is described by superposing these stationary states in such a way that initially the radiation field vanishes.

The scattering is calculated for incoming light with arbitrary frequency, either in resonance with an absorption line or not. In the latter case the result is equivalent to the well-known Kramers-Heisenberg formula. In the case of resonance—usually called resonance fluorescence—not only the usual line shape is found, but also a small line shift, which in the current treatment is infinite and has to be discarded. The behaviour of the Raman scattering inside the line width and the transition to non-resonance are also investigated.

**2.** Kramers' theory starts from the idea that in the classical electron theory all physically significant results depend only on the mass $m$ and the charge $e$ of the electron, and do not contain any reference to the structure of the electron. His program was to construct a structure-independent Hamiltonian that describes the actual behaviour with the best obtainable approximation. For this purpose the transverse electromagnetic field is decomposed

into a "proper field" and an "external field." The former is de-
fined as the non-retarded field, i. e. the field that follows from the
Biot-Savart rule.[3] It is determined by the instantaneous position
and velocity of the electron (in contrast with the sum of retarded
and advanced fields used by Dirac[4]). The vector potential $A'$
of the remaining external field is finite for a point-electron, so
that the average of $A'$ over the extended electron will be nearly
independent of the charge distribution. If now the equations of
motion of the electron are expressed in terms of $A'$, the effect
of the proper field being accounted for by an electromagnetic
mass $m_{el}$, they contain only the total or "experimental" mass
$m = m_0 + m_{el}$; they do not depend on the structure, except for
the very small wave lengths in $A'$. The equation for the external
field $A'$, however, still contains the proper field in such a way
that the formalism is only approximately structure-independent.

The next step consists of writing these equations in Hamil-
tonian form. First[1] Kramers used a Hamiltonian which had
practically the same form as the usual one, but with the external
field instead of the total field, and with the experimental mass $m$
instead of the mechanical mass $m_0$. He showed that it describes
the secular effects correctly to the first order of $e$, whereas certain
high-frequency vibrations, caused by the interaction, are neg-
lected. Later, Opechowski[5] found a Hamiltonian which is correct
in dipole approximation to the first order of $e$. Finally Kramers[2]
constructed in dipole approximation a Hamiltonian which is cor-
rect also to higher orders of $e$, and can therefore be applied to
the scattering of light.

**3.** In chapter I we obtain in dipole approximation a Hamil-
tonian which is correct in all powers of $e$, in the following way.
In the ordinary Hamiltonian the field is expanded in multi-
pole waves and only the electric dipole waves are retained. By
means of a canonical transformation this simplified Hamiltonian
is cast into a form which only contains the constants $m$ and $e$
and is practically structure-independent. This new form will be
the starting point of our calculations. We shall call it Kramers'
Hamiltonian, although it differs slightly from the form he used.

If there is *no binding force*, this new Hamiltonian appears as
the sum of an infinite number of oscillators, each referring to an

eigenvibration of the compound system. Hence the canonical transformation amounts to choosing the solutions for the free electron as basic elements. If the electron is *harmonically bound*, a further canonical transformation can be found which again transforms the Hamiltonian to normal modes, so that also in this case the rigorous solutions can be obtained. This is performed in chapter II, and some results are derived which are of later use.

If the binding force is of *a more general character* (ch. III), such a further transformation cannot be found, and one has to resort to perturbation theory. With the aid of the above mentioned solution of the free electron, however, the zeroth-order approximation can be chosen in such a way that the interaction of electron and radiation field is already partly included, namely as if the electron were free. The perturbation consists of the influence of the binding on the interaction, and will be small for the high-frequency quanta. Indeed, the shift of the energy levels caused by the perturbation now turns out to be finite and small. This has only a restricted physical significance, because the convergence becomes effective at energies for which relativistic effects should not be neglected. Mathematically, however, it seems that there are no longer fundamental obstacles in solving the Schrödinger equation by perturbation theory and obtaining physically significant results for the scattering of visible light.

**4.** In order to describe the scattering process we construct a stationary solution of the Schrödinger equation, satisfying the boundary condition that the ingoing radiation shall consist of a monochromatic wave. This solution will then also contain an outgoing wave of the same wave length, and the phase difference between both has to be found from the Schrödinger equation. This phase shift contains all relevant information about the physical quantities describing the scattering; indeed it is the counterpart for light waves of the phase matrix in Heisenberg's theory of the S-matrix.

The above solution may also contain outgoing waves of different wave lengths, namely Raman radiation. The intensities of the separate Raman lines follow, of course, from the coefficients of this solution, but these coefficients need not be computed explicitly. It appears that the Raman radiation is associated with

imaginary terms in the phase shift mentioned above, so that the
probability for Raman scattering can be calculated directly from
this phase shift.

Non-stationary solutions of the Schrödinger equation can be
obtained by superposing the stationary solutions. If the super-
position is chosen in such a way that at $t = 0$ the radiation
field vanishes, then the field that appears at $t > 0$ can only be
due to emission by the atom. Hence, such a non-stationary state
serves to describe spontaneous emission. Again the phase shift
(as a function of the incoming frequency) is sufficient to find
all data about the emission process. The scattering by an atom
in an excited state also requires a non-stationary solution, but
this problem is not treated in the present work.

The properties of the ingoing and outgoing electromagnetic
radiation fields have, of course, to be interpreted by computing
expectation values of certain field operators, for instance the
square of the field strength. However, it is possible to represent
all relevant features of the quantum-mechanical field by a classical
analogue. This classical field is constructed in such a way that
the (classical) time average of any relevant quantity is equal to
the expectation value of the same quantity in the quantum-
mechanical state.

**5.** With the method outlined above, the scattering by an atom
in the ground state is calculated (chs. III and IV) for the case of
non-resonance, i. e. for incoming frequencies that are not near
to an absorption frequency. The result is expressed in terms of
the phase shift, but it can be checked to be equivalent to the
Kramers-Heisenberg formula. The expression for the phase shift
contains real terms of order $e^2$, describing the Rayleigh scattering,
and imaginary terms of order $e^4$, associated with the Raman
radiation.

Chapter V is devoted to the case of resonance. Adopting tem-
porarily some simplifying assumptions, the phase shift is calcul-
ated for incoming waves with frequencies in the neighbourhood
of an absorption frequency. Just as in the classical treatment,
the phase shift strongly increases inside the line width, passes
through the value $\pi/2$ in the centre of the line and finally, on
the other side of the line, differs from the value $\pi$ by a small

amount of order $e^2$. However, the centre of the line does not exactly coincide with the atomic frequency, but shows a small line shift. With the ordinary Hamiltonian this so-called Lamb-Retherford shift[6] could only be computed by means of an ad hoc prescription for the subtraction of infinite terms.[7]

Inside the line width the Raman lines are very strong and their intensities are proportional to those of the corresponding emission lines. Therefore the scattering process may be visualized as the absorption of an incoming photon and subsequent spontaneous emission. This picture is, however, only partly true, because several details are not represented correctly.

In chapter VI the formulae obtained for resonance and non-resonance are combined into one formula for the phase shift, which holds for all values of the incoming frequency and for any binding force. This equation shows that the transition between resonance and non-resonance is rather involved. The simple device of inserting imaginary damping terms in the resonance denominators of the Kramers-Heisenberg formula has only a restricted validity.

**6.** One feature of the transformation that served to eliminate the electron structure has still to be mentioned. If the electron is chosen very small, and a fortiori in the limit of a point-electron, the new Hamiltonian contains one oscillator with an imaginary frequency. This corresponds to the well-known self-accelerating solution of the classical electron[8]. As emphasized by Bhabha[9], this solution of the equations of motion cannot be found by a perturbation calculation based on an expansion in $e$, because it is not analytic in $e = 0$.

As there is no proper way to quantize an oscillator with imaginary frequency, the transformed Hamiltonian cannot be carried over to quantum mechanics. Of course, even in classical theory the self-accelerating motion makes a rigorous solution of the equations of motion meaningless. A plausible procedure, however, consists of discarding the anomalous oscillator from the Hamiltonian; it will be shown that this leads to agreement with experimental results. It is important that no radiation is associated with this oscillator.

# Chapter I. Derivation of the Hamiltonian.

**7.** In this chapter Kramers' Hamiltonian is deduced from the usual one in the following way. In the non-relativistic Hamiltonian for an extended electron the transverse field is expanded in electric dipole waves, all other multipole waves being omitted. By means of a first canonical transformation the proper field of the electron is separated from the total field, so that only the external field occurs in the new Hamiltonian. By a second canonical transformation the remaining $A^2$ term is incorporated in the oscillators of the field.

The Hamiltonian thus obtained is, in dipole approximation, equivalent to the Hamiltonian given by Kramers. The electron is characterized only by the charge $e$ and the experimental mass $m$; the details of the structure have, for all practical purposes, been eliminated. Therefore one may take a simple model, and we shall choose a point-electron in order to get manageable formulae.

The formalism of the deduction is adapted to both classical theory and quantum mechanics.

**8.** After elimination of the longitudinal field the remaining transverse field can be described by a vector potential $A$ with div $A = 0$. The Hamiltonian of the system electron + field then takes the form[10]

$$\mathfrak{H} = \frac{1}{2\,m_0}(P - e\tilde{A})^2 + V(R) + \frac{1}{8\pi}\int \{E^2 + (\mathrm{rot}\,A)^2\}\,dr, \qquad (1)$$

where $- E/4\pi$ is the canonical conjugate of $A$.

R and P are the position and the momentum of the electron, $e$ and $m_0$ its charge and mechanical mass. The function $\varrho$ will describe the charge distribution, so that $\int \varrho\,dr = e$. We shall put $c = \hbar = 1$ throughout this work. A and E are the vector potential and the field strength of the transverse electromagnetic field, $V$ is the static potential resulting from the elimination of the longitudinal field. For the sake of simplicity we do not consider an external magnetic field, although it will be important in certain experiments. How it can be taken into account has been indicated by Kramers[1].

The symbol $\sim$ denotes the mean value over the extended electron, i. e.

$$e\widetilde{\mathbf{A}} = \int \mathbf{A}(\mathbf{r})\varrho(|\mathbf{r}-\mathbf{R}|)\,d\mathbf{r} = \int \mathbf{A}(\mathbf{R}+\mathbf{r})\varrho(|\mathbf{r}|)\,d\mathbf{r}.$$

If the motion of the electron is confined to a region around the origin that is small compared to the wave lengths present in the external field[11], then this mean value is practically independent of the position $\mathbf{R}$ of the electron, so that one may write

$$e\widetilde{\mathbf{A}} = \int \mathbf{A}(\mathbf{r})\varrho(|\mathbf{r}|)\,d\mathbf{r}. \tag{2}$$

This condition is certainly fulfilled when dealing with the scattering of visible light by atoms. Physically it amounts to neglecting the transport of (canonical) momentum from the transverse field to the electron; indeed from (1) and (2) follows

$$\dot{\mathbf{P}} = -\partial\mathfrak{H}/\partial\mathbf{R} = -\nabla V(\mathbf{R}). \tag{3}$$

When $\mathbf{A}$ is expanded in multipole waves, the result of this approximation is that only the electric dipole waves are coupled with the electron: all other multipole waves are zero in the origin and hence do not contribute to (2) if $\varrho$ falls off rapidly.

**9.** As far as electric dipole radiation is concerned the expansion of the field inside a large sphere of radius $L$ may be written

$$\mathbf{A}(\mathbf{r}) = \mathfrak{T}\sum_{n=1}^{\infty}\sqrt{\frac{3}{L}}\,\mathfrak{q}_n\frac{\sin \nu_n r}{r}, \qquad \nu_n = \frac{n\pi}{L}. \tag{4}$$

There are three directions of polarization corresponding to the three components of $\mathfrak{q}_n$. $\mathfrak{T}$ means "transverse part of" and may be defined by[12]

$$\mathfrak{T}\mathfrak{q}_n\frac{\sin \nu_n r}{r} = \left\{\mathfrak{q}_n + \frac{1}{\nu_n^2}(\mathfrak{q}_n\nabla)\nabla\right\}\frac{\sin \nu_n r}{r}. \tag{5}$$

It gives rise to a factor $\dfrac{2}{3}$ in the mean values over the electron, because for small $r$

$$\mathfrak{T}\mathfrak{q}_n(\sin \nu_n r)/r = \frac{2}{3}\mathfrak{q}_n\nu_n + Or;$$

and also in the normalization, because

$$\int\left\{\mathfrak{T}\mathfrak{q}_n(\sin \nu_n r)/r\right\}^2 d\mathbf{r} = \frac{2}{3}\int\left\{\mathfrak{q}_n(\sin \nu_n r)/r\right\}^2 \cdot 4\pi r^2 dr.$$

The orthogonal functions in the expansion (4) have the norm $\sqrt{4\pi}$; consequently, if $\mathbf{E}$ is similarly expanded:

$$-\mathbf{E}(\mathbf{r}) = \mathfrak{T} \varSigma \sqrt{\frac{3}{L}}\, \mathfrak{p}_n \frac{\sin \nu_n r}{r}, \tag{6}$$

then $\mathfrak{p}_n$ is canonically conjugate to $\mathfrak{q}_n$. From (4) follows furthermore

$$e\widetilde{\mathbf{A}} = \sqrt{4/3\, L}\, \varSigma\, \mathfrak{q}_n \int \sin \nu_n\, r \cdot \varrho(r) \cdot 4\pi r dr = \varSigma\, \varepsilon_n \mathfrak{q}_n, \tag{7}$$

where

$$\varepsilon_n = \delta_n \nu_n \sqrt{4\, e^2/3\, L},$$

$\delta_n$ being a convergence factor which depends on the structure $\varrho$ of the electron and tends to 1 for a point-electron. Substituting (4), (6) and (7) in the Hamiltonian (1), one gets

$$\mathfrak{H} = (1/2\, m_0)\, \mathbf{P}^2 + V(\mathbf{R}) - (1/m_0)\, \mathbf{P}\, \varSigma\, \varepsilon_n \mathfrak{q}_n$$
$$+ (1/2\, m_0)\, (\varSigma\, \varepsilon_n \mathfrak{q}_n)^2 + \frac{1}{2} \varSigma\, (\mathfrak{p}_n^2 + \nu_n^2 \mathfrak{q}_n^2).$$

**10.** If now new variables are introduced by means of the canonical transformation

$$\mathfrak{p}_n = \mathfrak{p}_n', \quad \mathfrak{q}_n = \mathfrak{q}_n' + \frac{\varepsilon_n}{m\nu_n^2} \mathbf{P}', \quad \mathbf{P} = \mathbf{P}', \quad \mathbf{R} = \mathbf{R}' + \varSigma \frac{\varepsilon_n}{m\nu_n^2} \mathfrak{p}_n', \tag{8}$$

where

$$m = m_0 + \varSigma\, (\varepsilon_n/\nu_n)^2, \tag{9}$$

then the Hamiltonian becomes

$$\left.\begin{array}{l} \mathfrak{H} = (1/2\, m)\, \mathbf{P}'^2 + V\big\{ \mathbf{R}' + \varSigma\, (\varepsilon_n/m\nu_n^2)\, \mathfrak{p}_n' \big\} \\[2mm] \quad + (1/2\, m_0)\, (\varSigma\, \varepsilon_n \mathfrak{q}_n')^2 + \frac{1}{2} \varSigma\, (\mathfrak{p}_n'^2 + \nu_n^2 \mathfrak{q}_n'^2). \end{array}\right\} \tag{10}$$

The third term on the right stems from the $\mathbf{A}^2$ term. Together with the fourth term it constitutes a quadratic form in the field variables $\mathfrak{q}_n'$:

$$\frac{1}{2} \varSigma\, A_{nn'}\, \mathfrak{q}_n' \mathfrak{q}_{n'}' = \frac{1}{2} \varSigma\, \big\{ \nu_n^2 \delta_{nn'} + (1/m_0)\, \varepsilon_n \varepsilon_{n'} \big\}\, \mathfrak{q}_n' \mathfrak{q}_{n'}', \tag{11}$$

which can be transformed to principal axes by means of an orthogonal transformation

$$q'_n = \Sigma X_{nn'} q''_{n'}, \quad p'_n = \Sigma X_{nn'} p''_{n'}. \tag{12}$$

This is carried out in Appendix A, sections 1 and 2, with the result

$$\mathfrak{H} = \frac{P'^2}{2m} + V\left(R' + \frac{e}{m}\Sigma\sqrt{\frac{4}{3L_n}\frac{\cos\eta_n}{k_n}}\,p''_n\right) + \frac{1}{2}\Sigma\,(p''^2_n + k^2_n q''^2_n), \tag{13}$$

where $k_n$ are the roots of a certain characteristic equation and $\eta_n$ and $L_n$ are defined by

$$\left.\begin{array}{ll} Lk_n = \eta_n + n\pi, & 0 < \eta_n < \pi/2; \\[4pt] L_n = L - (\cos\eta_n)^2/\varkappa, & 1/\varkappa = 2\,e^2/3\,m. \end{array}\right\} \tag{14}$$

The structure of the electron enters into the Hamiltonian (13) only through the equation for the $k_n$ (namely (A 6)). It may be expected that its influence on the physical phenomena we are interested in is small. Therefore we may choose a point-electron, in which case the characteristic equation becomes

$$\tan Lk = k/\varkappa \quad \text{or} \quad \tan\eta = k/\varkappa. \tag{15}$$

**11.** *For a free electron* $(V = 0)$, the Hamiltonian (13) furnishes the correct solution (of course in non-relativistic dipole approximation). The momentum $P' = P$ is constant (as a consequence of the dipole approximation, cf. (3)) and $R'$ is linear in $t$. The electron at the point $R$ fluctuates around the uniformly moving point $R'$. If no photons are present, then classically $R = R'$, but in quantum theory there is still a fluctuating motion, owing to the zero point fluctuations of the field.* In this case the square of the distance $R - R'$ has the expectation value

$$\langle (R - R')^2 \rangle = (2\,e^2/3\,m^2)\,\Sigma\,(2\cos^2\eta_n/Lk^2_n)\,(k_n/2). \tag{16}$$

Our factor $\cos^2\eta_n$ gives convergence for $k \to \infty$, but it becomes effective at too high values of $k$, owing to the neglect of

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* The influence of this fluctuation in the position of the electron on the physically measurable quantities has been studied by Welton[13].

recoil and relativistic effects (see also **40**). There is a logarithmic divergence for $k \to 0$, but any binding force will cut off the lower values of $k$ and thus make the expression finite (see ref. [13]). It may be added that fluctuations with infinite mean square amplitude are known in probability theory[14] and that the result for a free electron is not unacceptable, because the mean square amplitude is not an observable quantity. It will be shown in **15** that physically measurable quantities do not suffer from this infrared divergence.

**12.** The physical meaning of the transformation (8) can be seen from the corresponding decomposition of the field: $\mathbf{A} = \mathbf{A}' + \mathbf{A}^0$. Here $\mathbf{A}'$ is of the form (4) with $\mathbf{q}'_n$ instead of $\mathbf{q}_n$, and

$$\mathbf{A}^0(\mathbf{r}) = \mathfrak{T} \Sigma \sqrt{\frac{3}{L} \frac{\varepsilon_n}{m v_n^2}} \, \mathbf{P}' \frac{\sin v_n r}{r} = \mathfrak{T} \frac{\mathbf{P}'}{m} \int \frac{\varrho(|\mathbf{r}'|)}{|\mathbf{r} - \mathbf{r}'|} \, d\mathbf{r}' \quad (17)$$

(with the aid of (A 22)). We shall call $\mathbf{A}^0$ the proper field of the electron and $\mathbf{A}'$ the external field. If $\mathbf{P}'/m$ were the electron velocity, $\mathbf{A}^0$ would be identical with the proper field as defined by Kramers[3]. Now, however, this is only true in first approximation, because $\mathbf{P}'$ is the canonical momentum

$$\mathbf{P}'/m = \dot{\mathbf{R}}' = \dot{\mathbf{R}} + Oe.$$

Owing to this difference in the field that has been split off, (13) is slightly simpler than the Hamiltonian actually given by Kramers.

At first sight, Bloch and Nordsieck's transformation[15] seems to be rather the same as our transformation (8), but there is an essential difference. Since they used the unbound electron as zeroth approximation, they could replace with sufficient approximation $(\mathbf{P} - e\widetilde{\mathbf{A}})^2/2\,m_0$ by $\mathbf{v}\,(\mathbf{P} - e\widetilde{\mathbf{A}})$ and consider the velocity vector $\mathbf{v}$ as a constant:

$$\mathfrak{H} = \mathbf{v}\,(\mathbf{P} - \Sigma\,\varepsilon_n\mathbf{q}_n) + \Sigma\,(\mathbf{p}_n^2 + v_n^2\mathbf{q}_n^2).$$

Now the problem is not to transform this Hamiltonian to principal axes, but to get rid of the linear term in $\mathbf{q}_n$. This is achieved by the canonical transformation

$$\mathbf{p}_n = \mathbf{p}'_n, \quad \mathbf{q}_n = \mathbf{q}'_n + (\varepsilon_n/2\,v_n^2)\,\mathbf{v}, \quad \mathbf{P} = \mathbf{P}', \quad \mathbf{R} = \mathbf{R}'.$$

This transformation is much simpler than (8) since $\mathbf{R} = \mathbf{R}'$. On the other hand, Bloch and Nordsieck used a less trivial connection between $\mathbf{P}$ and $\mathbf{P}'$, because they did not confine themselves to dipole approximation.

Pauli and Fierz[16] supposed the electron to be so large that the electromagnetic mass is small compared to the mechanical mass. In this case, one can put in (8) $m = m_0$ and the transformation becomes identical to theirs. It is consistent with this approximation to omit the $\mathbf{A}^2$-term in the Hamiltonian, and accordingly they obtained the same Hamiltonian (13), but without the phase shifts $\eta_n$. The transition to the point-electron is, of course, excluded.

Welton[13] used the same Hamiltonian as Pauli and Fierz, with a rather sketchy justification. Schwinger's elaborate calculation of the self-energy[17] is based on the same idea, but meets all requirements of relativistic invariance and does not use dipole approximation. On the other hand, an expansion in $e$ is used for the canonical transformation and only the first power is computed.

**13.** The orthogonal transformation (12) amounts to choosing a new set of orthogonal functions for the expansion of $\mathbf{A}'$. It is shown in A 4 that they are sine functions with wave number $k_n$ and phase shift $\eta_n$:

$$\mathbf{A}' = \mathfrak{T} \Sigma \sqrt{\frac{3}{L}} \, \mathfrak{q}_n' \frac{\sin \nu_n r}{r} = \mathfrak{T} \Sigma \sqrt{\frac{3}{L}} \, \mathfrak{q}_n'' \frac{\sin (k_n r - \eta_n)}{r}. \quad (18)$$

Owing to his slightly different definition of the proper field, Kramers found as the external field belonging to a stationary solution of the classical free electron, instead of (18),

$$\mathbf{A}_1 = \mathfrak{T} \sqrt{3/L_n} \, \mathfrak{q}_n'' \{ \sin (k_n r - \eta_n) + \sin \eta_n \}/r.$$

For a freely moving electron this field is finite at $r = 0$, in contrast with our "external" field (18). After having obtained these solutions, Kramers could write the Hamiltonian for the free electron simply as a sum of terms:

$$\frac{1}{2} \Sigma (\mathfrak{p}_n''^2 + k_n^2 \mathfrak{q}_n''^2),$$

each term referring to an oscillator associated with a stationary motion. The Hamiltonian which we obtained by means of two canonical transformations differs from this one only by the additional term $\mathbf{P}'^2/2\,m$, associated with the linear motion with constant velocity.

It is noteworthy that after the first transformation (8) the transition to the point-electron is not yet possible, because the Hamiltonian (10) still contains $m_0$. Since the term with $m_0$ has usually been omitted, the necessity of the second transformation did not appear. The factor $\cos^2 \eta_n$, however, which arises from it, will turn out to be useful in obtaining convergence (see 40; cf. also 11).

14. When the electron is very small, the electromagnetic mass is larger than the experimental mass $m$, and consequently $m_0$ is negative. Then (11) is no longer positive definite and not all the eigenvalues can be positive. In fact it is shown in A 2 that for the point-electron there is one negative eigenvalue $-\varkappa^2$, yielding two imaginary solutions $k_* = i\varkappa$ and $k^* = -i\varkappa$ of (15).

This anomalous eigenvalue gives rise in the Hamiltonian (13) to a term

$$\frac{1}{2}\,(\mathbf{p}_*^2 - \varkappa^2\mathbf{q}_*^2), \tag{19}$$

and to a term $(e/m)\sqrt{4/3}\,\varkappa\,\mathbf{p}_*$ in the argument of $V$. In the expansion (18) it gives a term

$$\mathfrak{X}\sqrt{3\,\varkappa}\,\mathbf{q}_*\,e^{-\varkappa r}/r;$$

this is a field which is appreciable only within a distance of the order of the classical electron radius, and hence does not contain a radiation field.

If the Hamiltonian (13) is used for the classical treatment of the free electron, then the term (19) gives rise to two solutions with time factors $e^{\varkappa t}$ and $e^{-\varkappa t}$. The former is the "self-accelerating" or "runaway" solution, well-known from the classical theory of the electron[8]. The latter comes in because, owing to the reflecting sphere, our treatment is symmetric in time. (The usual boundary condition that there is no ingoing radiation at infinity is, of course, not symmetric.)

The anomalous term (19) is not a structure-independent

feature, since it cannot occur if the electron is chosen so big that $m_0$ is positive. It may be expected therefore to be immaterial for the phenomena we are interested in, just as in Lorentz' theory, provided it is treated in a suitable manner. In his classical theory[4] Dirac gave the prescription that the initial situation should be chosen in such a way that the final velocity is finite. That means for our free electron that the initial $\mathbf{p}_*$ and $\mathbf{q}_*$ must be zero, because otherwise they will increase exponentially. This amounts to simply omitting the term (19) from the Hamiltonian of the free electron. The initial field can then no longer be chosen completely arbitrarily, but must be such that in (19) $\mathbf{q}_* = 0$ (and that $\mathbf{p}_* = 0$ in the analogous expansion of $\mathbf{E}'$). This restrictive condition affects only the field in the immediate neighbourhood of the electron, whereas the radiation field can still be chosen freely. The resulting Hamiltonian can be quantized without difficulty.

The bound electron in classical theory has also a self-accelerating solution, but in this case Dirac's prescription leads to difficulties[18]. Moreover, in order to apply it to quantum theory in the same way as above, one has to find a canonical transformation by which this solution is exhibited explicitly in a term like (19). This is only possible for a free or a harmonically bound electron.

A slightly different way of generalizing Dirac's prescription to bound electrons consists of dropping in the Hamiltonian (13) both the term (19) and the term with $\mathbf{p}_*$ in the argument of $V$. The remaining Hamiltonian can be used in quantum mechanics and may again be expected to give right results for the scattering of visible light by atoms. In the next chapter we shall apply both the first and the second procedure to the harmonically bound electron, and the results will turn out to be practically identical. In the later chapters the second procedure will be used for the electron in a general field of force.

**15.** The Hamiltonian (13) might give rise to "infrared" divergences of the kind encountered in (16). We shall here show that they are only formal and do not prevent a consistent solution of the Schrödinger equation. For this purpose we use the canonical transformation

$$\mathbf{p}_n'' = \overline{\mathbf{p}}_n, \quad \mathbf{q}_n'' = \overline{\mathbf{q}}_n - \vartheta_n \frac{e}{m} \sqrt{\frac{4}{3L_n} \frac{\cos \eta_n}{k_n}} \overline{\mathbf{P}}, \quad \mathbf{P}' = \overline{\mathbf{P}}, \quad \mathbf{R}' = \mathbf{R} - \varSigma \vartheta_n \frac{e}{m} \sqrt{\frac{4}{3L_n} \frac{\cos \eta_n}{k_n}} \overline{\mathbf{p}}_n,$$

where $\vartheta_n$ are arbitrary numbers, bounded for $n \to \infty$. The Hamiltonian (13) takes the form

$$\mathfrak{H} = \frac{\overline{\mathbf{P}}^2}{2\,m'} + V\left\{ \overline{\mathbf{R}} + \frac{e}{m}\, \varSigma(1-\vartheta_n)\sqrt{\frac{4}{3 L_n}}\, \frac{\cos \eta_n}{k_n}\, \overline{\mathbf{p}}_n \right\}$$
$$+ \frac{1}{2}\, \varSigma(\overline{\mathbf{p}}_n^2 + k_n^2 \overline{\mathbf{q}}_n^2) - \frac{e}{m}\, \overline{\mathbf{P}}\, \varSigma \vartheta_n \sqrt{\frac{4}{3 L_n}}\, k_n \cos \eta_n \overline{\mathbf{q}}_n , \tag{20}$$

with

$$\frac{1}{m'} = \frac{1}{m} + \frac{4\,e^2}{3\,m^2}\, \varSigma \vartheta_n^2 \frac{\cos^2 \eta_n}{L_n} .$$

If we now choose $\vartheta_n = 1$ for small $n$, there is no risk of divergence for $k \to 0$. If moreover $\vartheta_n = 0$ for large $n$, (20) will have the same features as (13) in the region of large $k$, that means (as will be seen later) that there are no divergences for $k \to \infty$. Consequently there is no difficulty in applying perturbation theory to (20). Any measurable quantity, however, must be independent of the arbitrary numbers $\vartheta_n$, so that one can put afterwards $\vartheta_n = 0$ for all $n$, without introducing any divergence.

A safe, but cumbersome, way to deal with (13) is to use its transform (20). Instead we may use (13) directly, because in the final result the divergences for $k \to 0$ will cancel. In intermediate stages any divergent term may be cut off temporarily at some low value of $k$.

Even with the choice $\vartheta_n = 1$ for all $n$ the results are still finite, owing to the factor $\cos \eta_n$ in the last term of (20). This choice might seem profitable because of the resemblance of the resulting Hamiltonian with the customary one. However, it is easily seen that then $m' = m/2$, so that half of the experimental mass has to be furnished by the interaction; hence we would get an unsuitable starting point for the application of perturbation theory.

## Chapter II. The Harmonic Oscillator.

**16.** In the case of a harmonically bound electron one has $V = \frac{1}{2}\, mK^2 \mathbf{R}^2$, and the Hamiltonian (13) reduces to a quadratic form

$$\mathfrak{H} = \frac{\mathbf{P}'^2}{2m} + \frac{m}{2} K^2 \left( \mathbf{R}' + \frac{e}{m} \Sigma \sqrt{\frac{4}{3L_n}} \frac{\cos \eta_n}{k_n} \mathbf{p}_n'' \right)^2 + \frac{1}{2} \Sigma (\mathbf{p}_n''^2 + k_n^2 \mathbf{q}_n''^2).$$

This is a sum of three similar terms, each referring to one direction in space. Therefore the problem can be reduced to a scalar one by writing

$$\mathbf{P}' = eP', \quad \mathbf{R}' = eR', \quad \mathbf{p}_n'' = ep_n'', \quad \mathbf{q}_n'' = eq_n'',$$

where $e$ is a unit vector in the $x$, $y$, or $z$ direction.

On introducing new canonical variables $P_\nu$, $Q_\nu$ by

$$P' = P_0 m^{\frac{1}{2}}, \quad R' = Q_0 m^{-\frac{1}{2}}, \quad p_n'' = Q_n k_n, \quad q_n'' = -P_n k_n^{-1},$$

and putting

$$k_0 = 0, \quad d_0 = 1, \quad d_n = \sqrt{2/\varkappa L_n} \cos \eta_n,$$

the Hamiltonian becomes simply

$$\mathfrak{H} = \frac{1}{2} \Sigma (P_\nu^2 + k_\nu^2 Q_\nu^2) + \frac{1}{2} K^2 (\Sigma d_\nu Q_\nu)^2. \tag{21}$$

The subscript $\nu$ takes the values $0, 1, 2, \ldots$ and also the "value" $*$ (at least in what is called in **14** the first procedure; in the second procedure, considered in **18**, the anomalous oscillator denoted by $*$ is discarded at this point).

The Hamiltonian (21) can be transformed to principal axes by means of an orthogonal transformation

$$Q_\nu = \Sigma Y_{\nu\nu'} Q_{\nu'}', \quad P_\nu = \Sigma Y_{\nu\nu'} P_{\nu'}',$$

with the result (see A **3**)

$$\mathfrak{H} = \frac{1}{2} \Sigma (P_\nu'^2 + \omega_\nu^2 Q_\nu'^2). \tag{22}$$

The shifted frequencies $\omega_\nu$ are the roots of the characteristic equation

$$\tan L\omega = \frac{\omega^3/\varkappa}{\omega^2 - K^2} = \frac{\omega}{\varkappa} \left( 1 + \frac{K^2}{\omega^2 - K^2} \right) \tag{23}$$

and a new phase shift $\zeta_\nu$ can be defined by

$$L\omega_\nu = \zeta_\nu + \nu\pi, \quad \tan \zeta_\nu = \tan L\omega_\nu. \tag{24}$$

It is seen from (23), (24), that $\zeta \approx \eta$ for $\omega \gg K$; that $\zeta$ is near to $\pi/2$ for $\omega \approx K$, and $\zeta \approx \pi$ for $\omega \ll K$. Hence there is resonance at the frequency $K$.

There is again one imaginary root $\omega_* \approx i\varkappa$, analogous to $k_*$ for the free electron. In the first procedure the corresponding term is discarded in the transformed Hamiltonian (22). The remaining part is positive definite and can be quantized.

**17.** In order to investigate the aspect of the eigensolutions, we express the original variables in terms of $P'_\nu$ and $Q'_\nu$. The position of the electron is given by (see A 3)

$$\mathbf{R} = \mathbf{e} \, \Sigma \, d_\nu Q_\nu m^{-\frac{1}{2}} = \mathbf{e} \, m^{-\frac{1}{2}} \Sigma \beta_\nu Q'_\nu,$$

$$\frac{\beta_\nu}{\sqrt{m}} = \sqrt{\frac{2\varkappa}{mL'_\nu}} K \frac{\sin \zeta_\nu}{\omega_\nu} = \frac{e}{m} \sqrt{\frac{4}{3 L'_\nu}} \frac{K\omega_\nu^2}{\sqrt{(\omega_\nu^2 - K^2)^2 + \omega_\nu^6/\varkappa^2}}.$$

In general this factor is small of order $e$, but for $\omega \approx K$ it becomes of order $1/e$.

The external field is described by

$$\mathbf{A}' = -\mathfrak{X} \, \mathbf{e} \, \Sigma \sqrt{3/L_n} \, P_n \sin (k_n r - \eta_n)/k_n r \tag{25}$$

and, with $P_n = \Sigma Y_{n\nu} P'_\nu$, this becomes (see A 5)

$$\mathbf{A}' = -\mathfrak{X} \, \mathbf{e} \, \Sigma \sqrt{\frac{3}{L'_\nu}} P'_\nu \frac{\sin (\omega_\nu r - \zeta_\nu)}{r} - \mathfrak{X} \frac{e\mathbf{P}}{mr}. \tag{26}$$

$\mathbf{P}$ is the momentum of the electron and the term with $\mathbf{P}$ is just the proper field $\mathbf{A}^0$, according to (17). Hence the first term on the right represents the total field; it is an electric dipole wave with phase $\zeta_\nu$, whose dependence on the frequency $\omega_\nu$ is given by (23) and (24).

It can be understood physically that the total field reappears in our formula. Contrary to the free electron, the harmonically bound electron can only perform an oscillatory motion and no translation. Hence the total field must be of the type of a dipole wave, and cannot contain a part with $1/r$. This essential difference with the free electron prevents a continuous transition if the binding tends to zero, i. e. if $K \to 0$. This paradox is caused, of course, by our dipole approximation.

**18.** The second procedure consists of discarding the anomalous terms in the untransformed Hamiltonian (21) and transforming the remaining Hamiltonian into (22). This is carried out in A **3** and, instead of (23), the characteristic equation

$$\tan \zeta(\omega) = \tan L\omega = \frac{\omega}{\varkappa}\left\{1 + \frac{K^2}{\omega^2 - K^2 - 2\omega^2 K^2/(\omega^2 + \varkappa^2)}\right\} \quad (27)$$

is now found. There is no complex root, because we started with a positive definite form, so that all eigenvalues $\omega^2$ must be positive.

Again the situation may be studied, and again

$$\mathbf{R} = \mathbf{e} \, \Sigma \sqrt{2\,\varkappa K^2/m\,\omega_\nu^2 L_\nu'} \, \sin \zeta_\nu \, Q_\nu',$$

$\zeta_\nu$ now being determined by (27). The expression (26) can also be maintained if a term with $e^{-\varkappa r}/r$ is neglected. The situation therefore is essentially the same as in **17**, the only difference being that between the expressions (23) and (27) for the phase $\zeta(\omega)$. This difference between the two values of $\zeta$ is always relatively small, except in the neighbourhood of $K$. Whereas (23) is infinite for $\omega = K$, (27) gives resonance for

$$\omega = K + K^3/(K^2 + \varkappa^2) + O\varkappa^{-4} \approx K + K \sin^2 \eta(K).$$

This shift of the resonance frequency is of order $(K/\varkappa)^2$ (for visible light about $137^{-6}$) with respect to $K$, which is much smaller than the natural line width and can therefore always be neglected.

Consequently, this second procedure is, to all intents and purposes, equivalent to the first one: it does not make any appreciable difference whether the problem is first solved rigorously and the new self-accelerating solution is discarded afterwards, or whether, alternatively, the self-accelerating solution of the free electron is discarded before the binding is taken into account. In this chapter we adopt the first procedure, because (23) is simpler than (27). As mentioned in **14**, we shall use the second procedure in the later chapters, because the first one cannot be applied to an electron in a more general field of force.

**19.** The investigation of the physical aspect of the solutions can be simplified by the following two remarks.

1°. In order to get a picture of the electromagnetic field in a quantum-mechanical state, it is convenient to construct a classical analogue[19]. Let $\Psi = \Sigma \, c_\nu \{\omega_\nu\} \, e^{-i\omega_\nu t}$ be a quantum-mechanical superposition of one-quantum states* $\{\omega_\nu\}$. The expectation values of quadratic expressions in the $P'$ and $Q'$ are

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* With $\{\omega_\nu\}$ we denote a state in which one quantum is present, with frequency $\omega_\nu$.

easily calculated; one finds, for instance, after subtraction of the vacuum part,

$$\langle P'_\lambda P'_\mu \rangle = \frac{1}{2}\sqrt{\omega_\lambda \omega_\mu}\left\{ c^*_\lambda c_\mu e^{i(\omega_\lambda - \omega_\mu)t} + c_\lambda c^*_\mu e^{-i(\omega_\lambda - \omega_\mu)t} \right\}. \quad (28)$$

Now consider a classical superposition of eigenvibrations, determined by[*]

$$P'_\nu(t) = \Re\sqrt{2\omega_\nu}c_\nu e^{-i\omega_\nu t} = \sqrt{\omega_\nu/2}\left( c_\nu e^{-i\omega_\nu t} + c^*_\nu e^{i\omega_\nu t} \right). \quad (29)$$

One finds for $P'_\lambda(t) P'_\mu(t)$ in this state the same expression (28), plus terms with frequency $\omega_\lambda + \omega_\mu$. The same agreement holds for $Q'_\lambda Q'_\mu$ and $P'_\lambda Q'_\mu + Q'_\mu P'_\lambda$ and, consequently, for any quadratic expression in $\mathbf{A}'$ and $\mathbf{E}'$. Hence the physical results are the same in both states, provided that in the classical one the high-frequency phenomena are omitted (e. g. by averaging over a time which is long compared to the period of the waves, but short compared to the macroscopical changes in the situation).

$2°$. In problems of *particle* scattering the wave function has necessarily an infinite norm. It may be considered as referring to an assembly of an infinite number of particles, such that the particle density is finite[20]. In the same way we shall choose an infinite norm in order to get a finite incoming energy current. In our finite sphere this amounts to omitting in all coefficients the factor $L^{-\frac{1}{2}}$, with the result that the ingoing field is independent of $L$. However, in the case of a perturbed state consisting of a superposition of the eigenstates in a certain energy interval, the number of these eigenstates increases proportional to $L$, and no extra power of $L$ needs to be added.

**20.** We are now in a position to investigate the physical aspect of the solutions. Any eigensolution, with frequency $\omega_\nu = \omega$ say, contains an ingoing and an outgoing wave and hence represents a stationary scattering process. According to (26) and (29), the incident electric dipole wave

$$\mathbf{A}_-(t) = \Re\mathfrak{T}\mathbf{e}\,e^{-i\omega(r+t)}/r$$

[*] $\Re$ denotes the real part.

(whose total ingoing energy per unit time is $I = \omega^2/3$) gives rise to an outgoing wave

$$\mathbf{A}_+(t) = -\Re e^{-2i\zeta} \mathfrak{T} e\, e^{i\omega(r-t)}/r.$$

The phase factor $e^{-2i\zeta}$; is connected with the cross-section for scattering of a plane wave by a well-known formula[21]

$$\sigma_s = \frac{3}{2}\frac{4\pi}{\omega^2}\sin^2\zeta(\omega) = \frac{6\pi}{\varkappa^2}\frac{\omega^4}{(\omega^2-K^2)^2+\omega^6/\varkappa^2}.$$

This is identical with the expression found in the classical theory of electrons[22].


**21.** Emission will be described by a superposition of stationary states, chosen in such a way that the field vanishes at $t = 0$. This is possible because the phase-shifted functions in (26) satisfy an identical relation (see A 6)*, viz.

$$\Sigma(2/L'_\nu\omega^2_\nu)\sin\zeta_\nu\sin(\omega_\nu r - \zeta_\nu) = 0.$$

If now, classically, one takes a superposition of eigenvibrations (29), the coefficients $c_\nu$ being determined by

$$\sqrt{2\omega_\nu}\,c_\nu = \sqrt{3/L'_\nu}\,\omega_\nu^{-2}\sin\zeta_\nu\cdot C,$$

one finds, according to (26),

$$\mathbf{A}(t) = -C\mathfrak{T}e\,\Sigma\frac{3}{L'_\nu}\frac{\sin\zeta_\nu}{\omega^2_\nu}\frac{\sin(\omega_\nu r - \zeta_\nu)}{r}\cos\omega_\nu t$$

as the classical analogue of the radiation field. At $t = 0$ both $\mathbf{A}(t)$ and $\mathbf{E}(t) = -\dot{\mathbf{A}}(t)$ vanish, so that there is no radiation present. Hence the field appearing at later times ($t > 0$) has to be interpreted as emission by the oscillator.

For the outgoing energy per unit time with frequency between $\omega$ and $\omega + d\omega$ one finds

$$I(\omega)d\omega = \frac{3\,C^2}{4\,L}\frac{\sin^2\zeta(\omega)}{\pi\omega^2}d\omega = \frac{3\,C^2}{4\,L}\frac{\omega^4}{(\omega^2-K^2)^2+\omega^6/\varkappa^2}\frac{d\omega}{\pi\varkappa^2}. \quad (30)$$

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* Whether the anomalous term is included in the sum or not is immaterial, since it decreases exponentially as $e^{-\varkappa r}$.

If $L$ tends to infinity (with constant $C$), this expression vanishes. Indeed, the field describes only one act of emission between $t = -\infty$ and $t = +\infty$, so that the outgoing intensity, averaged in time, must be zero. If $L$ is finite, however, the emitted radiation is reflected by the sphere and after a time $2 L$ the initial situation is restored. Thus, our non-stationary state then describes a sequence of emissions, one per time interval $2 L$. The emitted energy with frequency between $\omega$ and $\omega + d\omega$ for each emission is equal to (30), multiplied by $2 L$; for the total energy per emission one finds $3 C^2/4 \varkappa$. This value can be used to determine $C$, but, for convenience, we shall put $C = 1$ in the following.

The field for $t > 0$ can be calculated when the summation over $\nu$ is replaced by an integration over $\omega$:

$$\mathbf{A}(t) = -\mathfrak{T}(e/r) \int_0^\infty (3/\pi\omega^2) \sin\zeta(\omega) \sin\{\omega r - \zeta(\omega)\} \cos\omega t\, d\omega$$

$$= \mathfrak{T} \frac{3e}{8\pi r} \int_{-\infty}^{+\infty} \left\{ \frac{1 - e^{-2i\zeta}}{\omega^2} e^{i\omega(r-t)} + \frac{1 - e^{2i\zeta}}{\omega^2} e^{-i\omega(r+t)} \right\} d\omega.$$

In the last expression outgoing and ingoing fields appear separately. After substituting from (23), (24)

$$\frac{1 - e^{\pm 2i\zeta(\omega)}}{\omega^2} = \mp \frac{2i}{\varkappa} \frac{\omega}{\omega^2 - K^2 \mp i\omega^3/\varkappa},$$

one can carry out the integration in the complex plane. The poles $\omega \approx \pm i\varkappa$ give contributions $e^{-\varkappa r}$ and must be neglected. The two other poles are (omitting higher orders of $1/\varkappa$) $K \pm iK^2/2\varkappa$ and $-K \pm iK^2/2\varkappa$. One thus finds that the ingoing field is zero, of course, and so is the outgoing field for $r > t$. For $r < t$ the latter is, omitting terms of relative order $e^2$,

$$\mathbf{A}_+ = \mathfrak{T}(3e/2\varkappa r)\cos K(r-t)\exp(K^2/2\varkappa)(r-t). \quad (31)$$

This is the well-known expression for a damped wave with frequency $K$ and half-value breadth $K^2/\varkappa = 2e^2K^2/3\,m$.

**22.** It is useful to consider a more general formula for the phase shift, viz.

$$\tan\zeta(\omega) = \sum_j \frac{\omega^3/\varkappa_j}{\omega^2 - K_j^2} = \frac{\omega}{\varkappa} \sum_j \frac{\omega^2 f_j}{\omega^2 - K_j^2} = \frac{\omega}{\varkappa} \Phi(\omega). \quad (32)$$

This is the phase shift caused by a number of oscillators with frequencies $K_j$ and oscillator strengths $f_j = \varkappa/\varkappa_j$.

To each zero $\Omega_l$ of $\Phi$ corresponds an identical relation (A 21) and hence a state in which there is no radiation at $t = 0$. At any time $t > 0$ there is a radiation field, but it will be seen that it contains all frequencies $K_j$, so that the initial situation is one in which all oscillators are excited. Indeed, choosing in (29)

$$\sqrt{2\,\omega_\nu}\,c_\nu = \sqrt{3/L_\nu'}\sin\zeta_\nu/(\Omega_l^2 - \omega_\nu^2), \tag{33}$$

one finds from (26) the field

$$\left.\begin{aligned}
A(t) &= -\mathfrak{T}\frac{e}{r}\sum \frac{3}{L_\nu'}\frac{\sin\zeta_\nu}{\Omega_l^2 - \omega_\nu^2}\sin(\omega_\nu r - \zeta_\nu)\cos\omega_\nu t\\
&= \mathfrak{T}\frac{3\,e}{8\,\pi r}\int_{-\infty}^{+\infty}\left\{\frac{1 - e^{-2i\zeta}}{\Omega_l^2 - \omega^2}\,e^{i\omega(r-t)} + \frac{1 - e^{2i\zeta}}{\Omega_l^2 - \omega^2}\,e^{-i\omega(r+t)}\right\}d\omega.
\end{aligned}\right\} \tag{34}$$

The integration can again be performed in the complex plane. From (32) follows

$$\frac{1 - e^{\pm 2i\zeta}}{\Omega_l^2 - \omega^2} = \frac{\mp 2\,i\omega/\varkappa}{1 \mp (i\omega/\varkappa)\,\Phi}\,\frac{\Phi}{\Omega_l^2 - \omega^2}$$

and the only singularities are the zeros of $1 \mp (i\omega/\varkappa)\Phi$. Those with $\omega \approx \pm i\varkappa$ must be neglected and the others are $K_j \pm iK_j^2 f_j/2\,\varkappa$ and $-K_j \pm iK_j^2 f_j/2\,\varkappa$. Thus one finds an outgoing field for $r < t$, viz.

$$A(t) = \mathfrak{T}\frac{3\,e}{2\,\varkappa r}\sum_j \frac{K_j^2 f_j}{\Omega_l^2 - K_j^2}\cos K_j(r - t)\exp(K_j^2 f_j/2\,\varkappa)(r - t).$$

This field corresponds to simultaneous emission by all the oscillators.

In order to describe emission by only one of the oscillators, one has to choose a suitable linear combination of these states. For this purpose we use the theory of A 1 and substitute $s = \omega^2$ and $F(s) = \Phi(\omega)$. The poles $t_n$ of $F(s)$ are now $K_j^2$ and the residues are $\alpha_j^2 = K_j^2 f_j$. The roots of the equation $F(s) = 0$ are $\Omega_l^2$ and the normalization constants are

$$\beta_l^{-2} = -F'(\Omega_l^2) = \Sigma K_j^2 f_j/(\Omega_l^2 - K_j^2),$$

so that (A 5) becomes

$$\sum_l{}' \frac{\beta_l^2}{(\Omega_l^2 - K_h^2)(\Omega_l^2 - K_j^2)} = \frac{\delta_{hj}}{K_j^2 f_j}.$$

Now let the states given by (33) be added, each being multiplied by $\beta_l^2/(\Omega_l^2 - K_h^2)$. In other words, we consider a new state given by new coefficients $c$, determined by

$$\sqrt{2\,\omega_\nu}\,c_\nu = \sqrt{3/L_\nu'}\sin\zeta_\nu\,\Sigma_l\,\beta_l^2/(\Omega_l^2 - K_h^2)(\Omega_l^2 - \omega_\nu^2).$$

Then the field follows from (26) and (29):

$$\mathbf{A}(t) = \mathfrak{T}(3\,\mathbf{e}/2\,\varkappa r)\cos K_h(r-t)\exp(K_h^2 f_h/2\,\varkappa)(r-t). \quad (35)$$

This is exactly the field (31) of an oscillator with frequency $K_h$ whose probability for emission is reduced by a factor $f_h$.

It should be emphasized that these results follow from the equation (32) for the phase shift, and that it is immaterial whether this phase shift is caused by oscillators or by any other scattering centre. In fact, in this section we have derived the existence and properties of decaying excited states from the behaviour of the $S$-matrix, in our case defined by

$$S(\omega) = -e^{-2i\zeta(\omega)} = -\frac{1 - i\tan\zeta}{1 + i\tan\zeta}.$$

The connection with the usual treatment[23] follows from the remark that the poles which contribute to (34) are the zeros of $1 + (i\omega/\varkappa)\Phi = 1 + i\tan\zeta$, and hence also the poles of $S(\omega)$.

It is noteworthy that $\tan\zeta$, rather than the multiple valued function $\zeta$ itself, describes the properties of the scattering centre in a simple way[24].

## Chapter III. Arbitrary Binding Force.

**23.** In this chapter the Hamiltonian (13) is employed to compute the scattering of light by an electron in a general field of force with potential $V(\mathbf{R})$. As $V$ is no longer a quadratic function in $\mathbf{R}$, the Schrödinger equation cannot be solved by a linear canonical transformation of the variables, and perturbation theory becomes necessary. Accordingly, the term $V$ in (13) must be expanded in powers of $e$ and the zero-order Hamiltonian is

$$\mathfrak{H}^0 = \mathbf{P}'^2/2\,m + V\,(\mathbf{R}') + \frac{1}{2}\,\Sigma\,(\mathfrak{p}_n''^2 + k_n^2\,\mathfrak{q}_n''^2).$$

Following the program outlined in **14**, the anomalous term is omitted in the sum, so that $n$ takes the values 1, 2, $\cdots$. This Hamiltonian $\mathfrak{H}^0$ describes a motion of $\mathbf{R}'$ as if there were no coupling, whereas the electron at $\mathbf{R}$ fluctuates around $\mathbf{R}'$ in the same way as the unbound electron. The higher terms in $e$ describe the effect of the binding force on the fluctuation. Since for high-frequency vibrations this effect will be small, the convergence may be expected to be better than in the usual treatment, where the whole interaction with the transverse electromagnetic field is treated as a perturbation.

**24.** Each of the field quanta corresponds not only to a certain oscillation of the field, but contains a vibratory motion of the electron as well*. They are labelled by $n$ and their polarization $v$ ($v = x$, $y$, $z$ for the three components of $\mathfrak{q}_n$ and $\mathfrak{p}_n$). Instead of the pair $n, v$ we shall often use n. Creation and annihilation operators are introduced by

$$p_{nv}'' = \sqrt{k_n/2}\,(a_{nv} + a_{nv}^{\dagger}), \quad q_{nv}'' = i\,(a_{nv} - a_{nv}^{\dagger})/\sqrt{2\,k_n}.$$

The Hamiltonian (13) then becomes, to the second order,**

$$\left. \begin{aligned} \mathfrak{H} = \mathbf{P}'^2/2\,m &+ V\,(\mathbf{R}') + \Sigma\,k_n\,a_{nv}^{\dagger}\,a_{nv} + \Sigma\,\tau_n\,(a_{nv} + a_{nv}^{\dagger})\partial_v V \\ &+ \frac{1}{2}\,\Sigma\,\tau_n\tau_{n'}\,(a_{nv} + a_{nv}^{\dagger})\,(a_{n'v'} + a_{n'v'}^{\dagger})\,\partial_v\partial_{v'}V, \end{aligned} \right\} \quad (36)$$

where

$$\tau_n = \frac{e}{m}\sqrt{\frac{2}{3\,k_n L_n}}\,\cos\eta_n \quad (= Oe). \quad (37)$$

Let $E_N$ be the eigenvalues of the operator $\mathbf{P}'^2/2\,m + V\,(\mathbf{R}')$. The eigenfunctions will be labelled by $N$ and an additional subscript $\mu$ to cover the case of degeneracy. Writing N for $N, \mu$ we shall denote the eigenfunctions by $\varphi_N(\mathbf{R}')$. The eigenstates of the operator $\Sigma\,k_n\,a_n^{\dagger}\,a_n$ will be denoted by $\{\}$, $\{n\}$, $\{n, n'\} = \{n', n\}, \cdots$,

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\* This is the reason why we prefer not to call them photons.
\*\* $\partial_v$ denotes derivation in the direction $v$.

according as there are 0, 1, 2, $\cdots$ quanta present. A state vector $\Psi$ of the whole system can be expanded as follows:

$$\Psi = \sum_N c_N \varphi_N \{\ \} + \sum_{Nn} c_N^n \varphi_N \{n\} + (1/2!) \sum_{Nnn'} c_N^{nn'} \varphi_N \{n, n'\} + \cdots,$$

with $c_N^{nn'} = c_N^{n'n}$, etc.[25] Finally, for the matrix elements of $V$ we use the abbreviations

$$\tau_n \langle N | \partial_v V | N' \rangle = \langle N n v N' \rangle = \langle N n N \rangle \quad (= Oe),$$

$$\tau_n \tau_{n'} \langle N | \partial_v \partial_{v'} V | N' \rangle = \langle N n n' N' \rangle \qquad (= Oe^2).$$

Then the Schrödinger equation $(\mathfrak{H} - W)\, \Psi = 0$ takes the form*

$$(E_N - W) c_N + \langle Nn'N' \rangle c_{N'}^{n'} + \frac{1}{2} \langle Nn'n''N' \rangle c_{N'}^{n'n''} + \frac{1}{2} \langle Nn'n'N' \rangle c_{N'} = 0 \quad (38\ a)$$

$$\left.\begin{aligned} &(E_N - W + k_n) c_N^n + \langle NnN' \rangle c_{N'} + \langle Nn'N' \rangle c_{N'}^{nn'} + \langle Nnn'N' \rangle c_{N'}^{n'} + \\ &\qquad + \frac{1}{2} \langle Nn'n'N' \rangle c_{N'}^n + \frac{1}{2} \langle Nn'n''N' \rangle c_{N'}^{nn'n''} = 0 \end{aligned}\right\} \quad (38\ b)$$

$$\left.\begin{aligned} &(E_N - W + k_n + k_m) c_N^{nm} + \langle NnN' \rangle c_{N'}^m + \langle NmN' \rangle c_{N'}^n + \\ &+ \langle NnmN' \rangle c_{N'} + \langle Nn'N' \rangle c_{N'}^{nmn'} + \frac{1}{2} \langle Nn'n''N' \rangle c_{N'}^{nmn'n''} + \\ &+ \langle Nnn'N' \rangle c_{N'}^{n'm} + \langle Nmn'N' \rangle c_{N'}^{n'n} + \frac{1}{2} \langle Nn'n'N' \rangle c_{N'}^{nm} = 0. \end{aligned}\right\} \quad (38\ c)$$

It should be noted that an infinite constant $(3/2) \Sigma k_n$ has been dropped in (36). This is the zero-point energy of the *shifted* oscillators and differs from the usually subtracted term $(3/2) \Sigma v_n$ by an infinite amount (cf. ref. [2]),

$$(3/2) \Sigma (k_n - v_n) = (3/2\ L) \Sigma \eta_n = (3/2\ \pi) \int \eta(k)\, dk,$$

which represents the non-relativistic fluctuation energy of the free electron. In the usual treatment this infinite energy shift has to be furnished by the perturbation calculation and causes divergence. In the exact treatment of the *harmonic oscillator* in ch. II the subtracted zero-point energy $(3/2) \Sigma \omega_v$ differs from that for the free electron by a finite amount

$$\left.\begin{aligned} (3/2) \Sigma (\omega_n - k_n) &= (3/2\ \pi) \int \{\zeta(k) - \eta(k)\}\, dk \\ &= 3\ K/2 + (3\ K^2/2\ \pi\varkappa) \log (\varkappa/K). \end{aligned}\right\} \quad (39)$$

* Summation over all primed letters is implied. Similarly in the following, summation over primed letters is not indicated explicitly, when no confusion can arise.

The first term represents the zero-point energy of the harmonic oscillator, and the second term is an additional fluctuation energy. It has the same form as the Lamb-Retherford shift, but in this particular case it does not give rise to a frequency shift, because it is the same for all levels. In the present case of a non-harmonically bound electron, an analogous term must result from the perturbation calculation; as it is no longer the same for all levels, a frequency shift does arise.

It should also be noted that in the right-hand side of (36) a term occurs with $a_{nv} a_{nv}^\dagger$. Here the operators cannot be reordered with the creation operators on the left, because this would amount to discarding a term in the Hamiltonian which is not a constant. In fact, this term will turn out in **39** to be essential for the cancellation of the infra-red divergence.

**25.** In the same way as in ch. II we shall describe the scattering process by means of a stationary scattering state. For this purpose an eigenfunction $\Psi$ will be constructed, satisfying the boundary condition that the ingoing field at large distance shall consist of a monochromatic wave with given frequency $\omega$ and given polarization $w$. The outgoing field then consists of waves with frequencies $\omega$, $\omega_1$, $\omega_2$, $\cdots$, describing the Rayleigh scattering and the various Raman lines.

This method of stationary scattering states has the physical advantage that it is a direct translation of the customary classical treatment. Mathematically it is simpler than the time-dependent method, because the latter is unduly complicated by irrelevant terms arising from the initial conditions for the intermediate states[26]. Moreover, it describes the time-dependence in greater detail than required for the actual experiments (cf. **50**). On the other hand, the interpretation of a stationary scattering state is rather subtle. It should be emphasized in particular that it must not be visualized as a steady stream of photons, scattered by one atom, but as an assembly of identical systems, each containing one scattering center and one incoming photon[20].

In the theory of particle collisions, the eigenfunction $\Psi$ is constructed by starting from an unperturbed wave function $\Psi^0$ which has the required ingoing waves. In order to satisfy the perturbed Schrödinger equation one adds a perturbation term $\Psi'$ containing outgoing waves only. This means that the $k$-representative of this term must have a factor

$$2\pi i \delta_+(k - \omega) = (k - \omega)^{-1} + i\pi\delta(k - \omega). \qquad (40)$$

This method, however, will not be suitable when the scattering is very large, for instance when $\omega$ is in resonance with an absorption frequency of the atom. To cover the case of resonance as well, we shall here use a different line of approach, which can be outlined as follows.

Since the above mentioned unperturbed wave function contains a factor $\delta(k - \omega)$, the total wave function is of the form

$$\Psi = \Psi^0 + \Psi' = C\left\{(k - \omega)^{-1} + \lambda\delta(k - \omega)\right\}. \qquad (41)$$

(In general $C$ and $\lambda$ will be functions of the direction in space, but in our dipole approximation they only depend on the polarization of the incoming radiation.) Our method consists of finding a stationary solution of the Schrödinger equation which has this form (41). The total energy $W$ can then be considered as a prescribed quantity, determined by the given incoming frequency $\omega$. The parameter $\lambda$, however, has to be found from a characteristic equation. The coefficients $c$ in (38) can then easily be computed. It turns out that $\lambda$ is directly connected with the phase difference between the ingoing and outgoing waves, and hence with the physical quantities we are interested in. In the same way as in ch. II, it will be convenient sometimes to choose the normalization constant $C$ such that $\Psi$ corresponds to a given ingoing energy current.

On solving the Schrödinger equation other singular terms will appear, of the type $(k - \omega_1)^{-1}, (k - \omega_2)^{-1}, \ldots,$ where $\omega_1, \omega_2, \cdots$ are frequencies lower than $\omega$. They represent Raman lines, and, in order to obtain a state in which there is no ingoing radiation with these frequencies, they have to be supplemented with terms $i\pi\delta(k - \omega_1), i\pi\delta(k - \omega_2), \ldots,$ similar to (40).

The $\delta$-functions, of course, refer to continuous variables. It is shown in A 7 that our procedure follows directly from the discontinuous treatment, when the enclosing sphere goes to infinity. Discrete spectra in connection with stationary eigenfunctions have been used in similar problems by Rice[27] and more recently by Hamilton[28]. They constitute a reliable basis, but the actual calculations are much simplified by the use of $\delta$-functions. Nevertheless, we shall sometimes for convenience in writing use discrete spectra.

**26.** We try to find a solution of (38) whose zeroth order approximation represents a state with the electron in the ground state $N = 0$ (which for simplicity we suppose to be non-degenerate), and with one quantum present of frequency $\omega$ and polarization $w$. Accordingly we put

$$\Psi = \Sigma\, c_0^{n'}\, \varphi_0\, \{n'\} + Oe, \quad W = E_0 + \omega + Oe^2. \qquad (42)$$

It may also be expected that $c_0^n$ is of the first (or higher) order in $e$, except for those n for which $v = w$, $k_n \approx \omega$. In this chapter, we shall show that this "Ansatz" leads indeed to a solution, if the energy is too small for excitation

$$E_0 < W < E_1 \quad \text{or} \quad \omega < E_1 - E_0 = K_{10} \qquad (43)$$

and outside the level width (which may be expected, from the particular case in **21**, to be of order $K_{10}^2/\varkappa$)

$$K_{10} - \omega \gg K_{10}^2/\varkappa. \qquad (44)$$

One then finds to the first order from (38 a) and (38 c)

$$c_N = -\frac{\langle Nn'0\rangle}{E_N - W}\, c_0^{n'}, \quad c_N^{nm} = -\frac{\langle Nn\,0\rangle\, c_0^m + \langle Nm\,0\rangle\, c_0^n}{E_N - W + k_n + k_m}, \qquad (45)$$

all other coefficients being of higher order. Substituting this in (38 b) and omitting orders higher than the second, one gets

$$
(E_N - W + k_n)\, c_N^n = \left\{ \frac{\langle NnN'\rangle\,\langle N'n'\,0\rangle}{E_{N'} - W} + \frac{\langle Nn'N'\rangle\,\langle N'n\,0\rangle}{E_{N'} - W + k_n + k_{n'}} - \langle Nnn'0\rangle \right\} c_0^{n'} \left.\vphantom{\frac{1}{2}}\right\}
$$
$$
+ \left\{ \frac{\langle Nn'N'\rangle\,\langle N'n'\,0\rangle}{E_{N'} - W + k_n + k_{n'}} - \frac{1}{2}\langle Nn'n'0\rangle \right\} c_0^n. \tag{46}
$$

This shows that all $c_N^n$ are $Oe^2$, except perhaps when $E_n - E + k_n$ is small. Owing to (43) and (44) this can only occur if $N = 0$, $k_n \approx \omega$, and in that case (46) becomes

$$
(k_n - \omega)\, c_0^n = \left\{ \frac{\langle 0\,nN'\rangle\,\langle N'n'w\,0\rangle}{E_{N'} - W} + \frac{\langle 0\,n'wN'\rangle\,\langle N'n\,0\rangle}{E_{N'} - W + 2\,\omega} - \langle 0\,n'n'0\rangle \right\} c_0^{n'w}. \tag{47}
$$

Here the value $k_n = \omega$ is used in the factor $\{\,\}$; and also $k_{n'} = \omega$, because in the sum over $n'$ only terms with $k_{n'} \approx \omega$ are of order

$e^2$. Moreover, only the coefficients $c_0^{nw}$ referring to the polarization of the incoming radiation are retained, since the other coefficients are $Oe^2$. The second term in (46) has been omitted; it would yield a contribution

$$\left\{ \frac{|\langle 0\,n'N'\rangle|^2}{E_{N'} - E_0 + k_{n'}} - \frac{1}{2}\langle 0\,n'n'\,0\rangle \right\} c_0^n,$$

which can be absorbed in the term with $E_0$ on the left. Thus it would give rise to a shift of order $e^2$ in the atomic energy levels, analogous to the last term in (39). Outside the resonance region, however, it is a term of relative order $e^2$ and may be neglected.

Taking $v = w$ in (47) one gets the equation

$$(k_n - \omega)\,c_0^{nw} = \tau_n \Theta(\omega)\, \Sigma\, \tau'_n\, c_0^{n'w}, \tag{48}$$

where (see App. C)*

$$\left. \begin{aligned} \Theta(\omega) &= \frac{|\langle 0\,|\,\partial_w V\,|\,N'\rangle|^2}{E_{N'} - E_0 - \omega} + \frac{|\langle 0\,|\,\partial_w V\,|\,N'\rangle|^2}{E_{N'} - E_0 + \omega} - \langle 0\,|\,\partial_w^2 V\,|\,0\rangle \\ &= 2\,\omega^2 \sum_N \frac{K_{N0}\,|\langle 0\,|\,P_w\,|\,N\rangle|^2}{K_{N0}^2 - \omega^2}. \end{aligned} \right\} \tag{49}$$

**27.** (48) is a set of homogeneous equations for the unknown $c_0^{nw}$, which has the form (A 1) except for the factor $\Theta$ depending on the eigenvalue $\omega$. It can be treated in the same way, but it is convenient to perform now the transition to the limit $L \to \infty$ in order to use the formalism for continuous spectra. Introducing continuous functions $\tau(k)$ and $c(k)$ by

$$\tau(k_n) = \sqrt{\frac{L_n}{\pi}}\,\tau_n = \frac{e}{m}\sqrt{\frac{2}{3\pi k_n}}\,\cos\eta_n, \quad c(k_n) = \sqrt{\frac{L_n}{\pi}}\,c_0^{nw},$$

one can write for (48)

$$(k - \omega)\,c'(k) = \tau(k)\Theta(\omega)\int_0^\infty \tau(k')c(k')\,dk'. \tag{50}$$

Now, as is shown in A 7, *the solution of this equation is*

$$c(k) = \tau(k)\left\{(k - \omega)^{-1} + \lambda\delta(k - \omega)\right\}C, \tag{51}$$

* $P_w$ is the component of the momentum in the direction $w$.

where $C$ is an arbitrary constant and *the eigenvalue $\lambda$ is determined by the equation*

$$\frac{1}{\Theta(\omega)} = \int_0^\infty \frac{\tau(k)^2}{k-\omega}\,dk + \lambda\tau(\omega)^2, \tag{52}$$

obtained by substituting (51) in (50).

In the integral the principal value has to be taken at $k = \omega$. It is, however, of order $e^2$ and is negligible compared to the left-hand side, which is of order 1. It does not matter that the integral is logarithmically divergent at $k = 0$, because other terms of the same order have already been neglected and from **15** we know that they will cancel the divergence (see **39**). The solution for $\lambda$ can then be written with the aid of a new quantity $\xi$

$$\lambda = -\pi\cot\xi, \quad \tan\xi = -\pi\tau(\omega)^2\Theta(\omega). \tag{53}$$

Clearly $\xi = Oe^2$, $\lambda = Oe^{-2}$, and $C$ will be of order $e$.

At this point the problem of determining $\Psi$ has been solved in principle. For a given $\omega$ one can find $\lambda$ from (53) and then $c(k)$ from (51). All other coefficients then follow in successive approximations, the first step being written explicitly in (45). By means of the conditions (43) and (44) it can easily be verified that they are small of the order anticipated in (42).

It might seem from (38) that $c_0^{nv}$ for $v \neq w$ can also become large when $k_n \approx \omega$. These coefficients correspond to scattering with the incoming frequency but different polarization, which can be treated in the same way as the Raman scattering (see **35**). In the next chapter it will be shown that our solution is not invalidated by such singularities in the coefficients.

**28.** In order to investigate the physical aspect of the stationary state, it is again (cf. **19**) convenient to construct a classical analogue. Let a classical field be defined by*

$$\mathbf{A}(t) = \mathfrak{T}(e^w/r)\,\Sigma\sqrt{3/2\,L_n k_n}\,\sin(k_n r - \eta_n).\ i\{c_0^{nw}e^{-i\omega t} - c_0^{nw*}e^{i\omega t}\}; \tag{54}$$

then it can easily be checked by direct calculation that the time average of $\mathbf{A}(t)^2$ is equal to the expectation value of the operator $\mathbf{A}'^2$ in the state $\Psi_0 = \Sigma_n c_0^{nw}\{n,w\}$, provided the vacuum ex-

* $e^w$ is a unit vector in the direction $w$.

pectation value is subtracted. Owing to the singularity of $c_0^{nw}$ at $k_n = \omega$, (54) satisfies the wave equation for large $r$; consequently, $\mathbf{E}(t)$ need not be introduced separately, but can be replaced by $-\dot{\mathbf{A}}(t)$. The expectation value of any quadratic expression in $\mathbf{A}'$ and $\dot{\mathbf{A}}'$ is equal to the time average of the same quantity for the classical field (54). The non-singular terms in $\Psi$ do not give any radiation at large distance, nor does the proper field $\mathbf{A}^0$. Thus $\mathbf{A}(t)$ may be used to find the ingoing and outgoing radiation.

In order to compute the field, we write (54) as an integral and substitute (51)

$$
\left.
\begin{aligned}
\mathbf{A}(t) &= \mathfrak{T}\,(\mathbf{e}^w/r) \int \sqrt{3/2\,\pi k}\,\sin\{kr - \eta(k)\}\,c(k)dk \cdot 2\sin\omega t \\
&= \mathfrak{T}(\mathbf{e}^w/r)(2e/m\omega)\cos\eta(\omega)\,[\cos\{\omega r - \eta(\omega)\} - \cot\xi\sin\{\omega r - \eta(\omega)\}]\,C\sin\omega t \\
&= -\mathfrak{T}\,\frac{\mathbf{e}^w}{r}\,\frac{2\,e}{m\omega}\cos\eta(\omega)\,\frac{\sin(\omega r - \eta - \xi)}{\sin\xi}\,C\sin\omega t.
\end{aligned}
\right\} \quad (55)
$$

An elementary calculation now gives for the total incoming energy per unit time $I$ the value

$$
I = (2\,\varkappa m)^{-1}\,\{\cos\eta(\omega)/\sin\xi\}^2\,C^2,
$$

and the normalization constant can be expressed in $I$:

$$
C = \{\sin\xi/\cos\eta(\omega)\}\sqrt{2\,\varkappa mI}. \tag{56}
$$

The field now becomes

$$
\mathbf{A}(t) = -\sqrt{12\,I}\,\mathfrak{T}\,(\mathbf{e}^w/\omega r)\sin(\omega r - \eta - \xi)\sin\omega t
$$

and $\xi$ appears as a new phase shift to be added to the phase shift $\eta$ of the free electron.

**29.** For this phase shift $\xi$ follows from (53) and (49) the value

$$
\tan\xi = \frac{\omega}{\varkappa}\sum_N \frac{K_{N0}^2 f_{N0}^w}{\omega^2 - K_{N0}^2}\cos^2\eta(\omega),
$$

where the oscillator strength $f_{N0}^w$ has been introduced by[29]

$$
|\langle 0|P_w|N\rangle|^2 = \frac{1}{2}mK_{N0}f_{N0}^w, \quad \sum_\mu f_{N\mu,0}^w = f_{N0}^w, \quad \sum_N f_{N0}^w = 1.
$$

Since both $\eta$ (the phase shift of the free electron) and $\xi$ (the shift caused by the binding) are of the order $e^2$, the total phase shift $\zeta = \xi + \eta$ becomes, omitting terms $Oe^4$,

$$\tan \zeta_w = \frac{\omega^3}{\varkappa} \sum_N{}' \frac{f_{N0}^w}{\omega^2 - K_{N0}^2}. \tag{57}$$

The subscript $w$ has been added to remind that this is the shift for the radiation with polarization in the direction $w$. For a central field of force one has $f_{N0}^x = f_{N0}^y = f_{N0}^z$, so that the phase shift is independent of the polarization. In that case (57) is identical to the expression (32) for the phase shift caused by a set of independent oscillators. By using anisotropic oscillators, one can also construct a model with the more general phase shift (57). Hence, in this respect the atom in the ground state can be represented by a set of oscillators; but (57) is only approximate (see ch. IV), whereas (32) is true to all orders of $e$.

**30.** It is convenient to define the *region of resonance* for each atomic frequency $K_{N0}$ as those values of $\omega$, for which in the sum (57) the term with $K_{N0}$ predominates, so that the terms with different $K$ may be neglected. In general it is sufficient that $|\omega - K_{N0}| \ll K_{N0}$, but if the line is very weak, or very near to another line, the resonance region may be narrower.

The *natural line* width is the region where $\tan \zeta$ is not small, i. e. where $\omega - K_{N0} \sim K_{N0}^2/\varkappa$. Outside the line width the omission of the principal-value integral in (52) is justified. For visible light the line width is of the order $137^{-3} K_{N0}$; this is in general much narrower than the resonance region[30]. Hence it is always possible to apply either the simplification for the resonance region, or the simplification for outside the line width, except if the distance between two lines is comparable to their widths.

Now (57) has been derived under the restriction (44), that means outside the line width. In this approximation there is no reason to write $\tan \zeta$ rather than $\zeta$ or $\sin \zeta$. In ch. V, however, the region of resonance will be studied, with the result that owing to the choice $\tan \zeta$, (57) also holds inside the line width (apart from a small frequency shift). It is noteworthy that our derivation should yield a more precise formula than is warranted by the calculation.

Granted this validity of (57) inside the line width, it is possible to derive the formulae for emission from this expression for the

phase shift, as has been shown in **22**. The probability per unit time of transition from the state N to the ground state 0, under emission of radiation with polarization $w$, was there (eq. (35)) found to be $K_{N0}^2 f_{N0}^w / \varkappa$, in agreement with the usual result[29].

**31.** The influence of the presence of the atom on the field can be described by a polarizability tensor $\alpha^{vw}$, expressing the electric moment **M** of the atom in terms of the incoming field strength **E**:

$$M_v = \alpha^{vw} E_w.$$

The diagonal elements $\alpha^{ww}$ are related to the phase shifts $\zeta_w$ according to (B 12). Thus we find outside the line width

$$\alpha^{ww} = \frac{e^2}{m} \sum_N {}' \frac{f_{N0}^w}{K_{N0}^2 - \omega^2},$$

in agreement with the Kramers-Heisenberg formula[31]. The phase shift is also connected with a cross-section for coherent scattering (with the same polarization), viz.

$$\sigma_s = \frac{8\pi e^4}{3 m^2} \omega^4 \left( \sum {}' \frac{f_{N0}^w}{\omega^2 - K_{N0}^2} \right)^2.$$

For the non-diagonal elements $\alpha^{vw}$ the coefficients $c_0^{nv}$ for $v \neq 0$ have to be solved from (47). This will be done in the next chapter, because the calculation is the same as for the Raman radiation. For a central potential field $V$ they are, of course, zero. Otherwise some of the energy of the ingoing radiation is lost in radiation with different polarization. This energy loss can be described by an "absorption" cross-section $\sigma_a$, which, according to App. B, is associated with an imaginary term in the phase shift. This term, however, will turn out to be of higher order (see **35**).

## Chapter IV. The Raman Effect.

**32.** We shall now consider the case where the frequency of the incident light is higher than one or more of the absorption frequencies of the atom. Thus we suppose, instead of (43),

$$E_M < W < E_{M+1} \quad \text{or} \quad K_{M0} < \omega < K_{M+1,0}$$

and we shall use the subscript L for the states that can be excited $(L = 1, 2, \ldots, M)$. The region of the line width is still excluded:

$$\omega - K_{M0} \gg K_{M0}^2/\varkappa, \qquad K_{M+1,0} - \omega \gg K_{M+1,0}^2/\varkappa. \tag{59}$$

In this case, some of the energy factors on the left-hand side of (38) may vanish and the solution found in ch. III seems to break down. It will be shown, however, that the order of magnitude of the coefficients is not altered by this singularity, so that actually the solution is not invalidated.

First take the expression (45) for $c_L^{nm}$. As only the first order is required, and $c_0^n = Oe^2$ except if $k_n \approx \omega$, it may be replaced by

$$c_L^{nm} = -\frac{\langle Ln\,0\rangle}{E_L - E_0 + k_n}\, c_0^m - \frac{\langle Lm\,0\rangle}{E_L - E_0 + k_m}\, c_0^n + Oe^2.$$

Hence the vanishing denominators do not occur in the first order expression of $c_L^{nm}$, which has been used in deriving (57). Therefore the formulae of the preceding chapter can be maintained, provided that it is shown that the higher order terms may still be considered to be small. That this is indeed justified, in spite of such vanishing denominators, is due to the fact that wherever these denominators occur in the Schrödinger equation (38), one has to sum over $k_n$. The resulting sum will turn out to be of the same order as it was supposed to be in ch. III.

Take, for example, the expression (46) for $c_L^n$. As we are interested in the behaviour for those values of $k_n$ for which $E_L - W + k_n$ is small, it is possible to insert in the right-hand member the value $k_n = W - E_L \equiv \omega_L$. Omitting terms $Oe^4$ one gets

$$(k_n - \omega_L)\, c_L^{nv} = \tau_n \Theta_{L0}^{vw} \tau_{n'} c_0^{n'w},$$

where (App. C)

$$\Theta_{L0}^{vw} = \frac{\langle L\,|\,\partial_v V\,|\,N'\rangle \langle N'\,|\,\partial_w V\,|\,0\rangle}{E_{N'} - E_0 - \omega} + \frac{\langle L\,|\,\partial_w V\,|\,N'\rangle \langle N'\,|\,\partial_v V\,|\,0\rangle}{E_{N'} - E_0 + \omega_L} - \langle L\,|\,\partial_v \partial_w V\,|\,0\rangle$$

$$= \omega \omega_L \left\{ \frac{\langle L\,|\,P_v\,|\,N'\rangle \langle N'\,|\,P_w\,|\,0\rangle}{K_{N'0} - \omega} + \frac{\langle L\,|\,P_w\,|\,N'\rangle \langle N'\,|\,P_v\,|\,0\rangle}{K_{N'L} + \omega} \right\}. \tag{60}$$

Going to the limit of a continuous spectrum and substituting (51), one finds

$$(k - \omega_L) \, c_L^v(k) = \tau(k) \, \Theta_{L0}^{vw} \, \tau(\omega)^2 \lambda \, C.$$

Hence $c_L(k)$ has a singularity for $k = \omega_L$, which will give rise to a radiation field that extends to infinity. On dividing by $k - \omega_L$ a term $i\pi\delta\,(k - \omega_L)$ must be added in order to get only outgoing radiation:

$$c_L^v(k) = -\tau(k)\,\Theta_{L0}^{vw}\,\{(k - \omega_L)^{-1} + i\pi\delta\,(k - \omega_L)\}\sqrt{2\,I/\varkappa\,m\,\omega^2}\,\cos\xi \quad (61)$$

(with the use of (56) and (37)).

It is now clear that in any summation over $k$, such as occurs in (38), $c_L(k)$ can be considered as a quantity of order $e^2$ (one factor $e$ from $\tau(k)$ and one from $\varkappa^{-\frac{1}{2}}$), in spite of the singularity. The same holds for the other higher order coefficients: each time a denominator vanishes it gives rise to a radiation field; as ingoing radiation of any frequency other than $\omega$ is precluded by the boundary condition, the singular term must be supplemented by an $i\pi\delta$-term, and the order of magnitude after integration over $k$ is not increased. But if there were also ingoing radiation of the same frequency, then instead of $i\pi$ an arbitrary parameter would appear, which might take large values.

**33.** The radiation field belonging to the frequency $\omega_L$ may again be represented by a classical field, which can be found from (54) by replacing $c_0^{nw}$ by $c_L^{nv}$ and $\omega$ by $\omega_L$:[*]

$$\left.\begin{aligned}
A_L(t) &= -\mathfrak{T}\,(e^v/r)\int\sqrt{3/2\,\pi k}\,\sin\,(kr - \eta)\,\mathfrak{I}\,c_L^v(k)\,e^{-i\omega_L t}\,dk \\
&= \mathfrak{T}\,\frac{e^v}{r}\,\frac{2}{\varkappa\,m\,\omega\omega_L}\,\sqrt{3\,I}\,\cos\xi\,\mathfrak{I}\,\Theta_{L0}^{vw}\,e^{i\omega_L(r-t)-i\eta(\omega_L)}.
\end{aligned}\right\} \quad (62)$$

This shows explicitly that there is no ingoing radiation. For the total outgoing energy per unit time one finds by an elementary calculation

$$I_L^v = 4\,(\varkappa m\omega)^{-2}\,\big|\Theta_{L0}^{vw}\big|^2\,I\cos^2\xi(\omega). \quad (63)$$

This formula has been derived only outside the line width and in that case $\cos^2\xi$ is indistinguishable from 1. It is interesting, however,

* $\mathfrak{I}$ denotes the imaginary part (without the factor $i$).

that (63) can be extrapolated to the region of a line width ($\omega \approx K_{M0}$ say), because $\Theta_{L0}^{vw} \cos \xi$ remains finite. One would thus find for the intensity of the Raman lines in resonance

$$I_L^v = 4 \frac{K_{ML}^3 f_{ML}^v}{K_{M0}^3 f_{M0}^v} \sin^2 \xi.$$

Here $f_{ML}^v$ is the total oscillator strength for the transition from the level $E_M$ to the state L for the polarization $v$:

$$f_{ML}^v = (2/mK_{ML}) \sum_\mu |\langle L|P_v| M\mu\rangle|^2.$$

In **42** it will be shown that this expression for $I_L^v$ in resonance is nearly correct. On substituting for L the value M, it gives $I_M^v = 0$, so that this Raman line disappears without discontinuity when $\omega$ drops below $K_{M0}$.

In order to compare (63) with well-known results, a connection has to be established between the energy flow $J$ of a plane wave and the ingoing energy per unit time in its dipole component. According to App. B this relation is $I = (3\pi/2\,\omega^2)\,J$. Hence, the energy in the Raman line with polarizarion $v$ is found to be

$$I_L^v = \frac{8\pi}{3}\left(\frac{e}{m}\right)^4 \left(\frac{\omega_L}{\omega}\right)^2 \left|\sum_N \left\{ \frac{\langle L|P_v|N\rangle\langle N|P_w|0\rangle}{K_{N0}-\omega} + \frac{\langle L|P_w|N\rangle\langle N|P_v|0\rangle}{K_{NL}+\omega} \right\}\right|^2 J \cos^2 \xi.$$

This is the radiated energy for a given final state L. The total energy with frequency $\omega_L$ is obtained by summing over the different states with the same energy $E_L$ and over the polarization $v$. The result agrees with the usual expression[32], apart from the factor $\cos^2 \xi$.

**34.** The question may be asked how this energy loss is taken into account in the Rayleigh radiation. It is true that, owing to the phase shift $\zeta$, the intensity in the forward direction is decreased, but the corresponding amount of energy is found in the scattered Rayleigh light. However, in the next section we shall show that each Raman line gives rise to an imaginary term in $\zeta$. Such an imaginary phase shift causes a decrease in the intensity in the forward direction without a corresponding increase in the Rayleigh scattering, and is therefore connected with an "absorption" cross-section $\sigma_a$. This imaginary term in $\zeta$ will turn out to

be of the order $e^4$ and has therefore consistently been neglected in the foregoing. The absorption cross-section $\sigma_a$ is linear in this term and consequently also of the order $e^4$. On the other hand, the real part of $\zeta$ has been found to be of the order $e^2$, but as the scattering cross-section $\sigma_s$ is quadratic in this term, it is also of the order $e^4$. Thus the energy decrease due to Raman scattering is of the same order of magnitude as that due to Rayleigh scattering.

Of an incoming plane wave with energy flow $J$ the energy $\sigma_s J$ is lost in Rayleigh scattering. The energy $\sigma_a J$ is lost due to Raman scattering, but only part of it is found in the radiation, the remaining part being used to excite the atom. If $\sigma_{aL}$ is the cross-section for the Raman line $\omega_L$, then clearly

$$I_L = \sigma_{aL} J (\omega_L/\omega) \quad \text{or} \quad I_L/\omega_L = \sigma_{aL} J/\omega. \tag{64}$$

This equation can also be interpreted as the conservation of the number of photons. We shall now check that it is indeed satisfied.

**35.** For this purpose we calculate the higher order correction in (57) due to the imaginary term in (61), but still omit real terms of higher order. Repeating the calculation in **26** one finds new terms in (46), which result in an additional term in (47), viz.

$$\left\{ \frac{\langle 0\,nN' \rangle \langle N'n'L' \rangle}{E_{N'} - W} + \frac{\langle 0\,n'N' \rangle \langle N'nL' \rangle}{E_{N'} - W + k_n + k_{n'}} - \langle 0\,nn'L' \rangle \right\} c_{L'}^{n'}.$$

On substituting from (61) this becomes

$$\tau_n \Theta_{0L'}^{vv'} \tau_{n'}^2 \Theta_{L'0}^{v'w} i\pi\delta (k_{n'} - \omega_{L'}) \tau_{n'} c_0^{n'w} = i\pi\tau_n \tau(\omega_{L'})^2 \Theta_{0L'}^{vv'} \Theta_{L'0}^{v'w} \int \tau(k)c(k)\,dk.$$

With this addition (50) becomes

$$(k-\omega)c(k) = \tau(k)\Theta(\omega)\int \tau(k')c(k')\,dk' + i\pi\tau(k)\tau(\omega_{L'})^2 \left| \Theta_{0L'}^{vv'} \right|^2 \int \tau(k')c(k')\,dk'.$$

Solving as before by means of the "Ansatz" (51) one finds

$$\Theta + i\,\pi\tau(\omega_{L'})^2 \left| \Theta_{0L'}^{vv'} \right|^2 = \frac{1}{\lambda\tau(\omega)^2} = -\frac{\tan\xi}{\pi\tau(\omega)^2} \tag{65}$$

(summed over L' and v').

Writing $\xi = \xi' - i\xi''$ one finds for the imaginary part

$$\xi'' = \pi^2\tau(\omega)^2\tau(\omega_{L'})^2 \left| \Theta_{0L'}^{vv'} \right|^2.$$

The corresponding cross-section for one final state L is (App. B)

$$\sigma_{aL} = \frac{3\pi}{2\omega^2}(1 - e^{-4\xi''}) = \frac{8\pi}{3\omega^2}\left(\frac{e}{m}\right)^4 \frac{1}{\omega\omega_L}|\Theta_{0L}^{wv'}|^2. \tag{66}$$

Comparison with (63) shows that indeed (64) holds.

The scattered radiation with the original frequency $\omega$ but with different polarization can be treated on equal footing with the Raman radiation. Its intensity is given by (63) when $L = 0$, $v \neq w$. It also contributes to $\sigma_a$. The radiation with the original frequency and the original polarization, however, contributes to the real part of $\zeta$ and hence to $\sigma_s$.

It is noteworthy that the damping by the Raman radiation is represented by imaginary terms added to $\Theta$, and not by damping terms in the denominators of $\Theta$. This is due to the fact that the Raman effect does not damp the excited states of the atom, but only the state with the primary radiation. (Actually there are terms in the Schrödinger equation (38) connecting the $c_N$ with the $c_N^n$ other than $c_0^n$, but they are of higher order and have been neglected in (45).) In case of resonance, however, both damping effects cannot be separated and we shall find an imaginary energy shift caused by the Raman effect.

**36.** For a complete description of the situation the higher coefficients, describing the probability of finding more than one radiation quantum, must also be computed. We shall here briefly consider the two-quantum coefficients $c_N^{nm}$. They consist of a series in odd powers of $e$, and the first-power terms were shown in **32** to be free from singularities. The singularities in the third-power terms describe the radiation field after the atom, left in an excited state by Raman scattering, has emitted a subsequent quantum. Accordingly, it may be expected that they will furnish the breadth of the Raman lines, due to the broadening of the final level by the possibility of emission.

Instead of doing the complete calculation we shall retain only the most important terms, namely those connecting $c_0^{nm}$ with $c_L^n$. They can be visualized as the emission of a quantum by the atom in the state L, whereas the other terms are just mathematical details. One thus obtains, just as in (45),

$$c_0^{vv'}(k,k') = -\{\tau(k)\langle 0|\partial_v V|L'\rangle c_{L'}^{v'}(k') + \\ + \tau(k')\langle 0|\partial_{v'}V|L'\rangle c_{L'}^{v}(k)\}\{(k+k'-\omega)^{-1} + i\pi\delta(k+k'-\omega)\}. \tag{67}$$

Again an $i\pi\delta$-term has been added in order to obtain outgoing radiation only[33]. Inserting this in the equation (38 b) for $c_N^n$ one finds the following additional terms in the right-hand member of (46)

$$\left.\begin{aligned}
\tau(k)\langle N|\partial_v V|0\rangle\langle 0|\partial_v V|L'\rangle \int \tau(k')c_{L'}^v(k')\{(k+k'-\omega)^{-1}+ \\
+ i\pi\delta(k+k'-\omega)\}dk' + \\
+\langle N|\partial_v V|0\rangle\langle 0|\partial_v V|L'\rangle c_{L'}^v(k)\int\tau(k')^2\{(k+k'-\omega)^{-1}+ \\
+ i\pi\delta(k+k'-\omega)\}\, dk'.
\end{aligned}\right\} \quad (68)$$

As we are only interested in imaginary terms of order $e^4$, we may write for the second term

$$i\pi\langle N|\nabla V|0\rangle\langle 0|\nabla V|L'\rangle\tau(\omega-k)^2\,c_{L'}^v(k)$$
$$\text{(summed over } 0 < L' \le M).$$

It is found that the non-diagonal elements ($N \ne L'$) give rise to real terms $Oe^4$ in the solution and hence may be neglected. The diagonal elements can be brought to the left-hand side of (46), yielding (for $N = L$, $L \le M$)

$$(k-\omega_L-i\Gamma_L^0)\,c_L^v(k), \qquad (69)$$

where $\Gamma_L^0 = \pi\tau(K_{L0})^2\,|\langle L|\nabla V|0\rangle|^2$ is the well-known expression for the transition probability from the state L to the ground state 0.

From (69) it is clear that $c_L^v(k)$ is no longer a singular function, but that one has to put

$$c_L^v(k) = \gamma_L^v(k)(k-\omega_L-i\Gamma_L^0)^{-1},$$

where $\gamma_L^v(k)$ is slowly varying for $k$ in the neighbourhood of $\omega_L$. Hence the first term in (68) vanishes, because

$$\int(k'-\omega_L-i\Gamma_L^0)^{-1}\{(k+k'-\omega)^{-1}+i\pi\delta(k+k'-\omega)\}\,dk' = 0.$$

Since $\Gamma_L^0$ is small, the sum $\int\tau(k)c_L^v(k)\,dk$ remains the same as before. Consequently one finds now instead of (61) the solution

$$c_L^v(k) = -\tau(k)\Theta_{L0}^{vw}(k-\omega_L-i\Gamma_L^0)^{-1}\sqrt{2\,I/\varkappa m\omega^2}\cos\xi,$$

which shows indeed that the Raman radiation has a width $\Gamma_L^0$.

By inserting this into (67) one obtains the probability of finding two quanta with frequencies $k$ and $k'$. It is seen from the resulting expression that one of the quanta has a frequency in a neighbourhood of the order $\Gamma_L^0$ around $\omega_L$, and that the frequency of the other is such that the sum of both is exactly $\omega$. By taking into account still higher coefficients, one can find in the same way situations with more than two quanta; it then turns out that all but one of the frequencies have certain probability distributions around atomic frequencies, while the sum of all is exactly equal to the incoming frequency.

## Chapter V. Resonance.

**37.** In the region of the line width, (44) and (59) no longer hold and $\Theta$ can become very large. In that case the principal-value integral in (52) is no longer small compared to $1/\Theta$ and cannot be neglected. Thus we are faced with the divergence of this integral for small values of $k$, and according to **15** we have to look for other terms which cancel this divergence.

On the other hand, if only the region of resonance is considered, it is possible to neglect in $\Theta$ all terms referring to other atomic frequencies, so that one may write (for $\omega \approx K_{M0}$)

$$\Theta(\omega) = m\omega^2 \frac{K_{M0}^2 f_{M0}}{K_{M0}^2 - \omega^2} = \frac{mK_{M0}^3 f_{M0}/2}{K_{M0} - \omega}. \tag{70}$$

This is the usual approximation for resonance (cf. **30**); we have to resort to it in **38**, but it will be possible afterwards to correct the result.

To avoid irrelevant complications, we suppose all levels to be non-degenerate and consider only one direction of polarization. More precisely, we assume

$$V(\mathbf{R}) = V_x(R_x) + V_y(R_y) + V_z(R_z) \tag{71}$$

with the result that the Hamiltonian (36) is separable. In the same way as for the harmonic oscillator we only consider one of the three parts, omitting superfluous indexes. The same Schrö-

dinger equation (38) holds, but instead of $N, n$ may now be written $N, n$.

Thus we suppose that the incoming frequency is near to the atomic frequency $K_{M0}$, namely

$$\omega - K_{M0} \sim K_{M0}^2/\varkappa, \quad \text{or} \quad W - E_M \sim K_{M0}^2/\varkappa.$$

If again $c_0^n$ is assumed to be of the order 1 for $k_n \approx \omega$ it now follows from (38 a) that $c_M$ may be large. A closer inspection of the example of the harmonic oscillator suggests $c_M = Oe^{-1}$ and then follows from (38 b) $c_N^n = O1$ (except perhaps for $N = M$). We further put $c_N = Oe$ for $N \neq M$ and also $c_N^{nm} = Oe$, and proceed to construct a solution satisfying these assumptions.

**38.** Instead of (45) one now finds from (38 a) and (38 c), to the first order,

$$c_N = -\frac{\langle Nn'N' \rangle}{E_N - W} c_{N'}^{n'} - \frac{1}{2} \frac{\langle Nn'n'M \rangle}{E_M - W} c_M, \qquad (N \neq M)$$

$$c_N^{nm} = -\frac{\langle NnN' \rangle c_{N'}^m + \langle NmN' \rangle c_{N'}^n + \langle NnmM \rangle c_M}{E_N - W + k_n + k_m},$$

$$(E_M - W) c_M = -\langle Mn'N' \rangle c_{N'}^{n'} - \frac{1}{2} \langle Mn'n'M \rangle c_M. \qquad (72)$$

Inserting the first two expressions into (38 b) one gets an equation for $c_N^n$ of the form

$$(E_N - W + k_n) c_N^n = A_N^n c_M + B_{NN'}^{nn'} c_{N'}^{n'} + C_{NN'}^{(n)} c_{N'}^n. \qquad (73)$$

(73) and (72) together are a set of homogeneous linear equations with eigenvalue parameter $W$. They can be simplified in several respects.

1°. Since $C_{NN'}^{(n)} = Oe^2$, the non-diagonal elements $(N \neq N')$ may be neglected, because they would give rise to terms $Oe^4$ in the solution. The diagonal terms (with $C_{NN}^{(n)}$) may also be neglected in the presence of the term with $E_N - W + k_n$, except when the latter is small. Hence the value $k_n = W - E_N = \omega_N$ may be used in the expression for $C_{NN}^{(n)}$, yielding

$$C_{NN}^{(\omega_N)} = \frac{|\langle Nn'N' \rangle|^2}{E_{N'} - E_N + k_{n'}} - \frac{1}{2} \langle Nn'n'N \rangle \equiv -\Lambda_N. \qquad (74)$$

2°. The terms with $B_{NN'}^{nn'}$ can also be neglected for $N \neq N'$, but the effect of $B_{NN}^{nn'}$ cannot be seen so easily. Provisionally we omit that term too, and it will be shown in **43** that this amounts to the approximation (70) for the resonance region.

3°. To the first order, $A_N^n = -\langle NnM \rangle$; and the higher orders (viz. $Oe^3$) may be neglected. (It can be checked that this is also true for $N = M$, although in that case the first-order term vanishes.)

With these simplifications, and writing

$$E_N - C_{NN}^{(\omega_N)} = E_N + \Lambda_N = E_N',$$

equations (73) and (72) become

$$(E_{N'}' - W + k) c_N(k) = -\tau(k) \langle N | \partial V | M \rangle c_M \qquad (75\,\mathrm{a})$$

$$\left( E_M - W + \frac{1}{2} \langle Mn'n'M \rangle \right) c_M = -\langle M | \partial V | N' \rangle \int \tau(k) c_{N'}(k)\, dk. \quad (75\,\mathrm{b})$$

**39.** Solving (75 a) for $c_N(k)$ one obtains

$$c_N(k) = -\tau(k) \langle N | \partial V | M \rangle (E_N' - W + k)^{-1} c_M \qquad (N > M) \qquad (76\,\mathrm{a})$$

$$c_L(k) = -\tau(k) \langle L | \partial V | M \rangle \{ (E_L' - W + k)^{-1} + i\pi\delta (E_L' - W + k) \} c_M \left. \vphantom{\int} \right\} \atop (M > L > 0) \qquad (76\,\mathrm{b})$$

$$c_0(k) = -\tau(k) \langle 0 | \partial V | M \rangle \{ (E_0' - W + k)^{-1} + \lambda\delta (E_0' - W + k) \} c_M. \qquad (76\,\mathrm{c})$$

After substituting this in (75 b) the common factor $c_M$ can be cancelled and we are left with a characteristic equation for $\lambda$:

$$
\left.
\begin{aligned}
E_M - W + \frac{1}{2} \langle Mn'n'M \rangle &= |\langle M | \partial V | N' \rangle|^2 \int_0^\infty \frac{\tau(k)^2\, dk}{E_{N'}' - W + k} \\
&+ i\pi |\langle M | \partial V | L' \rangle|^2 \tau(\omega_{L'})^2 + \lambda |\langle M | \partial V | 0 \rangle|^2 \tau(\omega)^2
\end{aligned}
\right\} \quad (77)
$$

(summation over all $N'$ and over $0 < L' < M$).

In order to compare this with (52) we simplify the latter by using (70), and write it in the form

$$(E_M - W) = |\langle M | \partial V | 0 \rangle|^2 \int_0^\infty \frac{\tau(k)^2\, dk}{E_0 - W + k} + \lambda |\langle M | \partial V | 0 \rangle|^2 \tau(\omega)^2. \qquad (78)$$

$1°$. Whereas (78) contains one integral, (77) contains an integral for each level $E_N$. For each singularity in these integrals a term with $i\pi$ is added, except for the singularity in the integral with $N = 0$, as that is already accounted for by the term with $\lambda$. All these terms with $N \neq 0$ do not occur in (78), because in ch. III the coefficients $c_N^n$ ($N \neq 0$) have been neglected, since they are small if there is no resonance.

$2°$. In the denominators in (77) occur the shifted energy values $E_N'$ instead of the $E_0$ in (78). The difference, however, is of the order $e^2$ and may certainly be neglected in a principal-value integral. (Actually it has .already been neglected in the other terms by writing $\omega_L$ for $W - E_L'$.) Also the $W$ in the denominator may be replaced by $E_M$ inside the resonance region.

$3°$. The new term on the left-hand side of (77)

$$\frac{1}{2} \langle Mn'n'M) \rangle = \frac{1}{2} \langle M | \partial^2 V | M \rangle \int \tau(k)^2 dk$$

cancels the divergence in the integrals on the right*. Indeed, the coefficient of $1/k$ for small $k$ is now

$$\frac{1}{2} \langle M | \partial^2 V | M \rangle - \frac{|\langle M | \partial V | N' \rangle|^2}{E_{N'} - E_M},$$

which can easily be seen to vanish (see, e. g., App. C). Both terms together give a small shift of the level $E_M$, which turns out to be just $\Lambda_M$, defined in (74).

**40.** According to App. C one can write for $\Lambda_M$

$$\Lambda_M = \frac{2 e^2}{3 \pi m^2} \sum_N K_{NM} |\langle M | P | N \rangle|^2 \int_0^\infty \frac{\cos^2 \eta(k)}{K_{NM} + k} dk. \qquad (79)$$

This is nearly Bethe's expression for the electromagnetic shift[34], but owing to the factor $\cos^2 \eta$ it is convergent. The effect of this factor can roughly be represented by a cut-off at $k = \varkappa$. From Bethe's work, however, it is known that the right numerical result is obtained by cutting off at the Compton frequency $m = \frac{2}{3} \varkappa/137$.

---

* This is the term mentioned in the last paragraph of **24**, which arises from the term with $a_{nv} a_{nv}^\dagger$ in (36).

This can be justified by relativistic considerations[35], and a cut-off of the same order can also be found by taking into account the recoil of the electron[36]. Since both effects have been neglected in the present treatment, it is not astonishing that our result is wrong. On the other hand, we have not used any subtraction prescription ad hoc, but Bethe's subtraction of the free electron self-energy is here automatically performed by the elimination of the proper field $A^0$; that means that it is implied in the subtraction of the self-action of the electron. Moreover, the convergence factor $\cos^2 \eta$ is obtained by using in the zeroth approximation the field quanta that are adapted to the unbound electron.

The line between two levels $E_M$ and $E_N$ suffers a frequency shift $\Lambda_M - \Lambda_N$. This shift was shown by Oppenheimer[37] to be divergent on the usual theory. In fact, it exhibits the same divergence as the shifts $\Lambda$ themselves, since in general the divergent terms do not cancel. Serpe[38] showed that it is finite on Kramer's theory in the special case of a harmonically bound electron.

Unfortunately his proof has no general value, because for the harmonic oscillator the shift is actually zero, as was shown in ch. II. (It can, of course, also be deduced from Bethe's expression.) In fact, in the general case he should have found a logarithmic divergence, because of the omission of the $A^2$-term. It may be added that he only found the first term in (74) and cut off the divergence at $k = 0$.

**41.** For the phase shift $\xi$ one finds from (77)

$$\tan \xi = \frac{K_{M0}^2 f_{M0}/2 \varkappa}{W - E_M - \Lambda_M + i \Gamma'_M}, \tag{80}$$

where

$$\Gamma'_M = \frac{2 e^2}{3 m^2} \sum_{L=1}^{M-1} K_{ML} |\langle M|P|L\rangle|^2 \cos^2 \eta \, (K_{ML})$$

$$= \Sigma K_{ML}^2 f_{ML}/2 \varkappa.$$

This "imaginary level shift" is caused by the damping of the state $M$ due to transition to lower levels $L$, the ground state excluded. The transition to the ground state does not give rise to an imaginary damping term, because in our stationary state it is balanced by transitions from the ground state. It does give rise,

though, to a widening of the level in the same way as the width

$$K^2_{M0} f_{M0}/2 \varkappa = \Gamma^0_M$$

resulted from (57).

The imaginary term in the phase shift is again associated with a cross-section for absorption (App. B)

$$\sigma_a = \frac{6\pi}{\omega^2} \frac{\Gamma^0_M \Gamma'_M}{(\omega - K'_{M0})^2 + (\Gamma^0_M + \Gamma'_M)^2},$$

where $K'_{M0} = K_{M0} + \Lambda_M - \Lambda_0$, $\omega = W - E_0 - \Lambda_0$. In this expression the total line width

$$\Gamma_M = \Gamma^0_M + \Gamma'_M = \sum_{L=0}^{M-1} K^2_{ML} f_{ML}/2\varkappa$$

appears. Adding the cross-section for Rayleigh scattering one obtains the total cross-section

$$\sigma_t = \frac{6\pi}{\omega^2} \frac{\Gamma^0_M \Gamma_M}{(\omega - K'_{M0})^2 + \Gamma^2_M}.$$

This is the Breit-Wigner formula. Indeed, in our case the Raman radiation plays the same part as the $\gamma$-ray emission in the case of neutron scattering. Thus, the Breit-Wigner formula is contained in the above expression for the phase shift:

$$\tan \xi = \Gamma^0_M/(\omega - K'_{M0} + i\Gamma'_M).$$

Clearly $\Gamma_M$ is just the sum of the residues of the integrand in (79), multiplied by $-\pi$. $\Gamma'_M$ is obtained by omitting the residue at $K_{M0}$. Hence the "complex level shift" $\Lambda_M - i\Gamma'_M$ in (80) can be found from (79) by taking the principal value at $K_{M0}$ and avoiding the other poles by shifting the integration path into the lower half plane. If the denominator in $\sigma_a$ and $\sigma_t$ is written as $|W - E_M - \Lambda_M + i\Gamma_M|^2$, the total complex shift $\Lambda_M - i\Gamma_M$ of the level $E_M$ appears; it can be found from (79) by shifting the whole integration path into the lower half plane.

**42.** Once $\lambda$ is found, the solution is immediately given by (76). $c_M$ may be used as an arbitrary factor, and on writing

$$-\langle 0|\partial V|M\rangle c_M = C,$$

(76 c) takes the form (51). The radiation field associated with the singularity in these coefficients can again be described by a classical analogue (54), which instead of (55) now becomes*

$$\mathbf{A}(t) = \mathfrak{T}\frac{e}{r}\frac{2e}{m\omega}\,\mathfrak{J}\frac{\sin(\omega r - \eta - \xi)}{\sin \xi}\,Ce^{-i\omega t}.$$

From this follows for the ingoing energy per unit time

$$I = (2\varkappa m)^{-1}\,\big|\sin \xi\big|^{-2}\,e^{2\xi''}\,\big|C\big|^2.$$

From (76 b) one finds the coefficients $c_L(k)$, which determine the Raman radiation. The outgoing radiation with frequency $\omega_L$ can be described by a classical field (comp. (62))

$$\mathbf{A}_L(t) = \mathfrak{T}\frac{e}{r}\frac{2e}{m\omega_L}\,\mathfrak{J}e^{i\omega_L(r-t)-i\eta(\omega_L)}\langle L\,|\,\partial V\,|\,M\rangle\,c_M.$$

The outgoing energy per unit time is found to be

$$\left.\begin{aligned} I_L &= (2/\varkappa m)\big|\langle L\,|\,\partial V\,|\,M\rangle\,c_M\big|^2 \\ &= 4\frac{K_{ML}^3\,f_{ML}}{K_{M0}^3\,f_{M0}}\big|\sin \xi\big|^2\,e^{-2\xi''}\,I. \end{aligned}\right\} \quad (81)$$

A nearly identical expression was found in **33** by extrapolating the formula obtained for non-resonance. However, the influence of the damping of the level $E_M$, exhibited by the imaginary phase $\xi''$, could not be found in that way.

Let again (see **34**) $\sigma_{aL}$ be the partial cross-sections and $J$ the intensity of the plane wave whose electric-dipole part has an ingoing energy $I$. Then (81) can simply be written

$$I_L/K_{ML} = \sigma_{aL}J/K_{M0},$$

showing that for each emitted Raman photon an incoming photon is absorbed. (81) has only been derived for $0 < L < M$, but for $L = 0$ it takes the form

$$I_0 = 4\,\big|\sin \xi\big|^2\,e^{-2\xi''}\,I = \sigma_s J,$$

which is obviously true if $I_0$ is interpreted as the outgoing energy of the Rayleigh scattering.

* The difference with (55) is that $\xi$ is now complex.

In the customary picture[39] the scattering in resonance is visualized as the absorption of an incoming photon—after which the atom is in the state $M$—and a subsequent spontaneous emission of a photon, either with the same frequency $K_{M0}$ or with a lower frequency $K_{ML}$. Now, an atom in the state $M$ would spontaneously emit waves with frequencies $K_{ML}$, whose intensities are, according to **30**, $K_{ML}^3 f_{ML}/\varkappa$. The fact that this is just proportional to the Raman intensities $I_L$ in (81) is the justification for the customary picture. For the probability of the atom being in the excited state $M$ one then has to take

$$\frac{4\varkappa}{K_{M0}^3 f_{M0}} |\sin \xi|^2 e^{-2\xi''} I = \frac{\sigma_t J}{2 K_{M0} \Gamma_M}.$$

Since $\sigma_t J/K_{M0}$ is the number of photons absorbed per unit time, $1/2\,\Gamma_M$ has to be interpreted as the average time during which the atom remains in the excited state $M$.

However, this picture fails to make clear that the sum of the frequencies which the atom emits on its way back to the ground state is exactly equal to the incoming frequency, as shown in **36**[40]. Neither does it represent the interference phenomena correctly; but we shall not discuss that here (cf. **51**)[41].

**43.** In this section it is shown that the omission of the terms $B_{NN}^{nn'} c_N^{n'}$ in (73) is equivalent to using the approximation (70) for the resonance region.

For each particular $N$ let $Z_{(N)}^{nm}$ be the orthogonal matrix that transforms the matrix $k_n \delta_{nm} - B_{NN}^{nm}$ to principal axes:

$$k_n Z_{(N)}^{nm} - B_{NN}^{nn'} Z_{(N)}^{n'm} = \bar{k}_m Z_{(N)}^{nm}.$$

Here $\bar{k}_m$ denotes the new eigenvalues. Clearly $Z_{(N)}^{nm} = \delta_{nm} + Oe^2$. Now if the $c_N^n$ are transformed by

$$c_N^n = Z_{(N)}^{nn'} \bar{c}_N^{n'}, \tag{82}$$

then (73) becomes, omitting terms $Oe^3$,

$$(E_N - W + \bar{k}_n) \bar{c}_N^n = A_N^n c_M + C_{NN}^{(n)} \bar{c}_N^n.$$

(72) remains the same equation with $\bar{c}_N^n$ instead of $c_N^n$. Hence

the omission of the term $B_{NN}^{nn'} c_N^{n'}$ in (73) is justified, provided the unknowns $c_N^n$ are replaced by the transformed ones $\bar{c}_N^n$.

Consequently the equation (77) for $\lambda$ is still valid, because it does not contain the $c$'s. However, the connection of $\lambda$ with the phase shift between ingoing and outgoing radiation is altered. Indeed, since $B_{NN}^{nn'}$ varies slowly with $n$ and $n'$, the theory of A **1** can again be applied, and for $Z_{(N)}^{nm}$ is then found a matrix of the type (A 3). Hence, according to A **4**, (82) is a transformation to new quanta whose phase is shifted with respect to the old ones. With the method of A **7** it is found that this additional phase shift $\xi_N$ is given by

$$\tan \xi_N = -\pi B_{NN}(\omega_N, \omega_N).$$

Since the Rayleigh radiation is described by the $c_0^n$, the total phase shift for the coherent scattering now becomes $\zeta = \eta + \xi + \xi_0$ ($\eta$ for the unbound electron, $\xi$ given by (80)). Using the explicit value of $B_{00}(\omega, \omega)$ one finds

$$\tan \xi_0 = \frac{\omega}{\varkappa} \sideset{}{'}\sum_{N \neq M} \frac{K_{N0}^2 f_{N0}}{\omega^2 - K_{N0}^2} + \frac{1}{2\varkappa} \cdot \frac{K_{M0}^2 f_{M0}}{\omega + K_{M0}}.$$

These are just the terms that are omitted in $\Theta(\omega)$ by using the approximation (70).

Combining the results one obtains for the total phase shift

$$\tan \zeta = \frac{\omega^3}{\varkappa} \sideset{}{'}\sum \frac{f_{N0}}{\omega^2 - (K_{N0}' - i\Gamma_N')^2}.$$

*This expression is correct to the order $e^2$ for all values of $\omega$.* As mentioned in **34**, however, the imaginary terms of the order $e^4$ are also needed for the correct value of the total cross-section. They cannot be found so simply by a combination of the formula for non-resonance and those for resonance with the different levels. The right expression is found in the next chapter.

# Chapter VI. General Result.

**44.** In chs. III and IV we have considered the case where the incoming frequency $\omega$ does not coincide (within the line width) with one of the atomic frequencies; whereas in ch. V the region of resonance was considered. Both cases had to be treated separately, because for an explicit solution of the Schrödinger equation either of the simplifications mentioned in **30** had to be employed. Fortunately the regions where these approximations are valid overlap, so that for each value of $\omega$ a scattering formula could be obtained.

Nevertheless there are some difficulties in linking up these expressions. It is not clear how the imaginary damping in the denominator of the resonance formula (80) merges into the imaginary term in the non-resonance formula (65). Moreover, the latter has different values on both sides of the resonance region, corresponding to the disappearing of one Raman line when the incoming frequency drops below an absorption frequency. Therefore it is of interest to find one formula for all values of $\omega$—which is the purpose of this chapter.

In the choice of the approximations to be used we shall be guided by the calculations in the previous chapters. All those terms which were shown to contribute only to the small level shifts will be omitted, since we are not interested in them now*. Then it is possible to write a general equation (96) for the phase shift, which comprises the previous results, and in addition describes the transition between them.

**45.** We take again the simple case of the previous chapter, namely a separable potential field (71). Furthermore we suppose

$$E_M \leq W < E_{M+1} \quad \text{and} \quad E_{M+1} - W \gg K^2_{M+1,0}/2 \varkappa,$$

but we do not exclude the width of the level $E_M$. The subscript $L$ will again be used for levels between $E_0$ and $E_M$.

Again $c_0(k)$ will be of the form

$$c_0(k) = \gamma_0(k) \left\{ (k-\omega)^{-1} + \lambda\delta(k-\omega) \right\}$$

---

* Consequently, from a formal point of view the calculations of this chapter could also be based on the usual Hamiltonian.

and $c_N(k)$ for $N > 0$

$$c_N(k) = \gamma_N(k) \{(k - \omega_N)^{-1} + i\pi\delta (k - \omega_N)\}. \tag{83}$$

Whenever in the Schrödinger equation $c_N(k)$ is integrated over $k$, the term with $(k - \omega_N)^{-1}$ gives rise to a principal-value integral. Since we have seen in the previous chapter that these integrals are of importance only for the level shifts, they will be omitted here. The $\delta$-term vanishes for $N > M$, so that in the summations $c_N(k)$ may be neglected altogether for $N > M$.

Thus, writing for brevity

$$\gamma_N(\omega_N) = \gamma_N, \quad \tau(\omega_N) = \tau_N, \quad \lambda_0 = \lambda, \quad \lambda_N = i\pi \quad (N > 0),$$

one obtains from (38 a) and (38 c), analogous to (45),

$$c_N = - \frac{\langle N | \partial V | N' \rangle}{E_N - W} \tau_{N'} \lambda_{N'} \gamma_{N'} \tag{84 a}$$

$$c_N(k, k') = - \frac{\langle N | \partial V | N' \rangle}{E_N - W + k + \omega_{N'}} \tau(k) \lambda_{N'} \gamma_{N'} \delta (k' - \omega_{N'}). \tag{84 b}$$

The last term in (46) contributed only to the level shift and therefore the corresponding term in the expression for $c_N(k, k')$ has been omitted here. Inserting (84) into (38 b) one gets an equation of the form

$$(E_N - W + k) c_N(k) = \tau(k) F_{NN'}(k)\tau_{N'} \lambda_{N'} \gamma_{N'}$$

(summed over $N'$ from 0 to $M$).

The complete expression for $F_{NN'}(k)$ is not required, because we now substitute (83) on the left and take $k = \omega_N$. It turns out that $F_{NN'}(\omega_N)$ is the compound matrix element $\Theta_{NN'}$, which occurred in the Raman effect (see **32** and App. C), and we find

$$\gamma_N = \tau_N \Theta_{NN'} \lambda_{N'} \gamma_{N'}. \tag{85}$$

Now (85) is a set of homogeneous equations for the $\gamma_N$ $(N = 0, 1, \cdots, M)$ with one adjustable parameter $\lambda_0 = \lambda$. The condition for solubility is, writing $\tau_N \Theta_{NN'} \tau_{N'} = T_{NN'}$,

4*

$$
\begin{vmatrix}
1-\lambda T_{00} & -i\pi T_{01} & -i\pi T_{02} & \cdots & -i\pi T_{0M} \\
-\lambda T_{10} & 1-i\pi T_{11} & -i\pi T_{12} & \cdots & -i\pi T_{1M} \\
-\lambda T_{20} & -i\pi T_{21} & 1-i\pi T_{22} & \cdots & -i\pi T_{2M} \\
\cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots & \cdots\cdots\cdots\cdots & \cdots\cdots & \cdots\cdots \\
-\lambda T_{M0} & \cdots\cdots & \cdots\cdots\cdots & & 1-i\pi T_{MM}
\end{vmatrix} = 0 . \; (86)
$$

This is a linear equation for $\lambda$, or for $\tan\xi = -\pi/\lambda$. We shall now show that it contains the formulae (65) and (80) as special cases.

**46.** First, consider the case that $\omega$ is not inside the line width, so that all $T_{NN'}$ are small, namely $Oe^2$. The evaluation of the determinant (86) with omission of the terms $Oe^2$ is trivial and yields

$$
0 = 1 - \lambda T_{00} = 1 - \lambda\tau(\omega)^2 \Theta_{00},
$$

which is identical to (53). Retaining also terms of relative order $e^2$ one finds

$$
1/\lambda = T_{00} + i\pi (T_{01} T_{10} + T_{02} T_{20} + \cdots + T_{0M} T_{M0}), \quad (87)
$$

which is identical to (65).

Secondly, let $W$ be so near to $E_M$ that in the sums over $M$ the terms with $W - E_M = \omega_M$ in the denominator are large and the other terms negligible. Then, according to App. C, one has

$$
T_{NN'} = -u_N u_{N'}^*/\omega_M \quad \text{with} \quad u_N = \tau_N \langle N|\partial V|M\rangle. \quad (88)
$$

Instead of evaluating the determinant (86) it is more convenient to solve (85) directly. These equations are now

$$
-\omega_M \gamma_0 = |u_0|^2 \lambda\gamma_0 + u_0 \cdot i\pi \cdot u_{L'}^* \gamma_{L'},
$$
$$
-\omega_M \gamma_L = u_L u_0^* \lambda\gamma_0 + u_L \cdot i\pi \cdot u_{L'}^* \gamma_{L'}.
$$

From the second line:

$$
-\omega_M (u\gamma) = (uu) u_0^* \lambda\gamma_0 + i (uu)(u\gamma),
$$

with the abbreviations

$$
(uu) = \pi\sum_{L=1}^{M} u_L^* u_L, \qquad (u\gamma) = \pi\sum_{L=1}^{M} u_L^* \gamma_L.
$$

This, together with the first line, makes two homogeneous equations for $\gamma_0$ and $(u\gamma)$, which yield for the parameter $\lambda$

$$\tan \xi = -\frac{\pi}{\lambda} = \frac{\pi |u_0|^2}{\omega_M + i(uu)}. \tag{89}$$

This equation is identical with (80), but for the level shift, which has been neglected in the present chapter.

**47.** The equation (86) for $\lambda$ is still not general, because it only holds between the levels $E_M$ and $E_{M+1}$. When $W$ drops below $E$, one row and one column have to be obliterated in the determinant, and when $W$ increases beyond $E_{M+1}$, a row and a column have to be added.

This discontinuity is related to Stokes' phenomenon for asymptotic expansions[42]. Indeed, our boundary condition that the radiation with frequency $\omega_M$ should contain only outgoing waves, refers to the asymptotic behaviour of the radiation field at large distance. The decomposition of the field in ingoing and outgoing waves is practically unique only in the wave zone. When $\omega_M$ tends to zero, the wave zone recedes to larger and larger distances. When it is beyond the observing apparatus, the boundary condition is no longer an appropriate expression of the experimental conditions. In that case the scattering centre and the observing apparatus cannot be treated as separate systems. (In actual experiments, of course, these long waves would not be detected by the spectroscope.) Consequently, there is a "region of discontinuity":

$$\omega_M \sim (\text{distance scattering centre—observer})^{-1} \sim 10^{-6} K_{M0} \tag{90}$$

where our formulae are physically insignificant.

It seems that there are also mathematical difficulties, because the neglected principal-value integral

$$\int_0^\infty \gamma_M(k)(k - \omega_M)^{-1} dk$$

might become large for small $\omega_M$. However, it is clear from (83) in connection with (61) and (37) that $\gamma_M(k)$ contains a factor $k^{-\frac{1}{2}}$, and can be expanded for small $k$ in the form

$$\gamma_M(k) = k^{-\frac{1}{2}}(a_0 + a_1 k + \cdots).$$

Now we have

$$\int_0^\infty k^{-\frac{1}{2}}(k - \omega_M)^{-1} dk = 0,$$

and the higher terms are certainly finite for $\omega_M = 0$; hence the integral is always a small quantity, even when $\omega_M$ is small.

The above considerations are only valid if the level $E_M$ is sharp, i. e. if the state $M$ is metastable. If it has a finite width $\Gamma_M$, then the expression for $c_M(k)$ contains a factor $(k - \omega_M - i\,\Gamma_M)^{-1}$ instead of the $\delta$-function (see **36**), and no discontinuity arises.

Accordingly, (86) can be written in a more general form by introducing a function $p(\omega)$ defined outside the region of discontinuity (90) by

$$p(\omega) = \pi \quad (\omega > 0), \quad p(\omega) = 0 \quad (\omega < 0);$$

inside this region it is necessarily indeterminate. On replacing $\lambda_N$ in (85) by $p(\omega_N)$ one finds instead of (86)

$$\begin{vmatrix} 1 - \lambda T_{00} & -ip_1 T_{01} & -ip_2 T_{02} \cdots \\ -\lambda T_{10} & 1 - ip_1 T_{11} & -ip_2 T_{12} \cdots \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \end{vmatrix} = 0, \qquad (91)$$

where $p_N = p(\omega_N)$. It is clear that for $E_M < W < E_{M+1}$ this reduces to (86).

For the phase shift in resonance one now finds from (91) the same formula (89), but with

$$(uu) = \sum_{L=1}^{\infty} p\,(\omega_L)\, u_L^* u_L.$$

Owing to $u_M = 0$, this result amounts to exactly the same as before.

**48.** Although (91) completely determines $\lambda$ as a function of $\omega$, it is not yet fully satisfactory. It is unduly complicated by higher order terms, which are meaningless since terms of the same order have already been neglected in obtaining (91) from the Schrödinger equation. As a consequence the results of the previous chapters could only be derived from (91) by rather lengthy manipulations. Therefore we shall now transform (91) into a form that resembles more closely the formulae of the previous chapters.

For $T_{NN'}$ we use an expression similar to (88), but more complete:

$$T_{NN'} = \sum_J{}' \frac{u_N^J u_{N'}^{J*}}{-\omega_J}, \qquad u_N^J \equiv \omega_N \tau_N \langle N \,|\, P \,|\, J \rangle. \qquad (92)$$

Here the first summand in (C 1) is taken into account, but the second one has still been omitted. It can easily be added afterwards, since it does not give rise to resonance. (85) now becomes

$$\gamma_N = - \Sigma_J (u_N^J/\omega_J) \Sigma_{N'} u_{N'}^{J*} \lambda_{N'} \gamma_{N'},$$

from which, writing $\Sigma_{N'} u_{N'}^J \lambda_{N'} \gamma_{N'} \equiv \omega_J \gamma_J'$, we get

$$\omega_J \gamma_J' = - \Sigma_{NI} u_N^{J*} \lambda_N u_N^I \gamma_I'.$$

This is a set of homogeneous equations for the $\gamma_J'$, whose characteristic equation determines $\lambda \,(= \lambda_0)$:

$$\mathrm{Det.}\, \| \omega_J \delta_{JI} + \lambda u_0^{J*} u_0^I + i\,(u^J u^I) \| = 0.$$

Here $(u^J u^I)$ is defined by

$$(u^J u^I) = \sum_{L=1}^{\infty} p(\omega_L)\, u_L^{J*} u_L^I.$$

The determinant can be expanded in powers of $\lambda$ and it is easily seen that only the zeroth and the first power survive. With the abbreviation $\omega_J + i(u^J u^J) = \omega_J'$ one finds

$$0 = \frac{1}{\lambda}
\begin{vmatrix}
\omega_0' & i(u^0 u^1) & i(u^0 u^2) & \cdots \\
i(u^1 u^0) & \omega_1' & i(u^1 u^2) & \cdots \\
i(u^2 u^0) & i(u^2 u^1) & \omega_2' & \cdots \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{vmatrix} +$$

$$+
\begin{vmatrix}
u_0^{0*} u_0^0 & i(u^0 u^1) & \cdots \\
u_0^{1*} u_0^0 & \omega_1' & \cdots \\
u_0^{2*} u_0^0 & i(u^2 u^1) & \cdots \\
\cdots\cdots\cdots\cdots\cdots
\end{vmatrix}
+
\begin{vmatrix}
\omega_0' & u_0^{0*} u_0^1 & i(u^0 u^2) & \cdots \\
i(u^1 u^0) & u_0^{1*} u_0^1 & i(u^1 u^2) & \cdots \\
i(u^2 u^0) & u_0^{2*} u_0^1 & \omega_2' & \cdots \\
\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots
\end{vmatrix} + \cdots$$

The determinants can easily be worked out if real terms of relative order $e^2$ and imaginary terms of relative order $e^4$ are omitted. After dividing by $\omega_0' \omega_1' \omega_2' \ldots$ one thus gets

$$\frac{1}{\lambda} = -\sum_{N}{}' \frac{u_0^N u_0^{N*}}{\omega'_N} + i \sum_{L}{}' p(\omega_L) \sum_{N \neq N'}{}' \frac{u_0^{N'*} u_L^{N'}}{\omega'_{N'}} \frac{u_L^{N*} u_0^N}{\omega'_N} \left.\vphantom{\sum}\right\}$$

$$\omega'_N = \omega_N + i \Sigma_L p(\omega_L) u_L^{N*} u_L^N. \tag{93}$$

In the approximation for resonance (with the level $E_M$) this equation reduces to

$$\frac{1}{\lambda} = -\frac{u_0^M u_0^{M*}}{\omega'_M} = \frac{K_{M0}^2 f_{M0}/2\varkappa}{\omega_M + i \Gamma_M}.$$

It should be noted that the imaginary term in $\omega'_M$ is equal to $\Gamma_M$ only inside this resonance region.

Outside the line width the denominator in the second term of (93) can be replaced by $\omega_{N'}\omega_N$; in the first term it can be expanded, yielding

$$-\sum_{N}{}' \frac{u_0^N u_0^{N*}}{\omega_N} + i \sum_{NL}{}' p(\omega_L) \frac{u_0^N u_0^{N*} u_L^{N*} u_L^N}{\omega_N^2}.$$

This imaginary term just furnishes the terms with $N = N'$ that are missing in the double sum in (93). With the aid of (92) our general equation (91) thus reduces to (65) outside the line width.

When Kramers and Heisenberg (ref. [31]) constructed their scattering formula, they considered resonance fluorescence as partly due to spontaneous emission by the excited atom (cf. **42**). This gave rise to the question how this radiation combines with the Rayleigh scattering that is also present outside the line width. The present treatment shows that, basically, there is only one kind of scattering process, which in resonance has some features in common with spontaneous emission.

**49.** The equation (93) has been derived under certain simplifying assumptions, but it can be generalized, without performing any new calculations, by following up the analogy with the results of the previous chapters.

1°. The terms that have been dropped when writing (92) can be supplemented by comparing (93) with (65). Both equations can be combined into

$$\tan \xi = -\pi \tau(\omega)^2 \left\{ \Theta_{00} + i \Sigma p(\omega_L) \tau(\omega_L)^2 \overline{\Theta'_{0L} \Theta'_{L0}} \right\}.$$

Here the prime means that all denominators $\omega_N$ are to be replaced by

$$\omega_N' = \omega_N + i \Sigma p(\omega_L) \tau(\omega_L)^2 \omega_L^2 |\langle N|P|L\rangle|^2; \qquad (94)$$

and the bar means that all terms with denominators $\omega_N^{-2}$ are to be discarded:

$$\overline{\Theta_{0L}' \Theta_{L0}'} = \Theta_{0L}' \Theta_{L0}' - \Sigma_N (\omega^2 \omega_L^2 / \omega_N^2) |\langle 0|P|N\rangle|^2 |\langle N|P|L\rangle|^2. \quad (95)$$

2°. The assumption (71) of the potential being separable can be dropped if also radiation with different polarization direction is taken into account. From (65) it is clear where polarization superscripts have to be added.

3°. Degeneracy can be accounted for by writing L instead of $L$, following the example of (65). The result is an expression for the phase shift $\xi_w$ of the radiation with frequency $\omega$ and polarization $w$, caused by an atom in the state $N = 0, \mu = \mu_0$, viz.

$$\tan \xi_w = -\pi\tau(\omega)^2 \left\{ \Theta_{0\mu_0;0\mu_0}'^{ww} + i \sum_{L} p(\omega_L) \tau(\omega_L)^2 \sum_{v} \overline{\Theta_{0\mu_0;L}'^{wv} \Theta_{L;0\mu_0}'^{vw}} \right\}. \quad (96)$$

The sum over $L = (L, \mu)$ includes $L = 0$, $\mu \neq \mu_0$, but not the initial state $L = 0$, $\mu = \mu_0$ (cf. 35). In (94) one should now write $\omega_{N,\mu}' = \omega_N'$ to exhibit the dependence on $\mu$, and $\mathbf{P}$ rather than $P$ to account for the three directions of polarization. Then

$$\Theta_{0\mu_0;N}'^{wv} = \omega\omega_N \sum_{N'}{}' \left\{ \frac{\langle 0\mu_0|P_w|N'\rangle\langle N'|P_v|N\rangle}{-\omega_{N'}'} + \frac{\langle 0\mu_0|P_v|N'\rangle\langle N'|P_w|N\rangle}{\omega + K_{N'N}} \right\}. \quad (97)$$

4°. From ch. V it seems that also the level shift can be embodied in (96) by a slight alteration of the definition of $\omega_N'$. However, the interaction with the electromagnetic field constitutes a perturbation which splits up each degenerate level into a number of components with distances of the order of the electromagnetic level shift. The matrix elements of this perturbation follow from (73) and (79); they are for the level $E_N$ (see App. C)

$$-C_{N\mu;N\mu'}^{(\omega_N)} = \frac{2e^2}{3\pi m^2} \sum_{N'}{}' K_{N'N} \langle N\mu|\mathbf{P}|N'\rangle\langle N'|\mathbf{P}|N\mu'\rangle \int_0^\infty \frac{\cos^2\eta(k)}{K_{N'N}+k} \, dk. \quad (98)$$

Let us suppose that for each level this perturbation is cast into a diagonal form, with diagonal elements $\Lambda_{N\mu}$ say*. Then each state $N, \mu$ has the shifted energy value $E_N + \Lambda_{N,\mu} = E'_N$ and these shifts can be taken into account by putting

$$\omega'_N = \omega_N - (\Lambda_{N\mu} - \Lambda_{0\mu_0}) + i\Sigma_L p(\omega_L) \tau(\omega_L)^2 \omega_L^2 |\langle N|\mathbf{P}|L\rangle|^2. \quad (99)$$

*The formula* (96), *together with* (97), (99) *and* (95), *describes the scattering by an electron in an arbitrary field of force, for all values of $\omega$ except the region of discontinuity* (90). *The imaginary terms are given to the order $e^4$, so that it yields the correct values for the cross-sections* $\sigma_s$, $\sigma_a$, $\sigma_t$.

**50.** The formula (96) will now be compared with the results obtained by previous authors. Outside the line width (96) was shown to reduce to (65), which according to **33** is equivalent to the Kramers-Heisenberg formula. Actually our result is more restricted, since it has only been derived for scattering by an atom in the ground state. The Rayleigh scattering is described by the phase shift (57) and the Raman scattering by (65). The corresponding cross-sections are (58) and (66).

The dispersion in the case of resonance has been treated by Weisskopf[43] and by Breit[44], using time-dependent perturbation theory. This method consists of taking an initial situation with the atom in the ground state and some radiation present. Since that is not a stationary state, other states are built up in the course of time and from the rate of increase of their coefficients follows the probability for scattering of the radiation present in the initial situation. Because of the difficulty of solving the resulting set of first-order differential equations, they had to resort to a simplified model with only two possible states for the atom. Hence the Raman radiation does not enter into the picture. Of course, also the line shift had to be neglected, because it would be infinite.

Weisskopf[43] first calculated the Rayleigh scattering in resonance and found a line width $\Gamma^0$ (in the notation we used in **41**), corresponding to the transition from the excited state to the ground level. Our additional line width $\Gamma'$ is due to the transition

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* In case of a central force, when there is no other degeneracy than with respect to the direction in space, this is automatically fulfilled if $\mu$ is the magnetic quantum number.

probability to other excited states, which he had omitted. Consequently his result is equivalent to (80), if in the latter $\Lambda_M$ and $\Gamma'_M$ are dropped.

It should be noted that in Weisskopf's formulae the frequencies of the incoming and the scattered photons may differ by an amount $\gamma^A$ (his notation). The reason is that he considers a state of the whole system which is not stationary, but whose energy has an uncertainty $\gamma^A$. That in our stationary state treatment such a quantity does not occur, may be considered as an advantage, because it has no bearing on actual observations.

Breit, in his review on dispersion[44], gives the same calculation of the scattering in resonance. In addition he analyzes the behaviour in time of atom and radiation field after the moment when the interaction is switched on. Again this is immaterial for actual scattering experiments: at most the decay of an excited state can be observed by specially designed experiments[45], but not the decay of the initial state of the whole system.

Weisskopf[43] also gives—without calculation—a formula for the resonance scattering in the case where more levels are present. This result is practically identical with ours; only the width of the initial level does not appear in our formula, because we supposed it to be the ground level. He also omits the width of the final level, just as we did (except in 36).

In a later paper[46] Weisskopf obtained a general formula by writing the Kramers-Heisenberg formula for the induced dipole moment, and adding terms $i\Gamma$ in the resonance denominators. This formula is correct when terms of relative order $e^2$ are disregarded. However, since the imaginary terms $Oe^4$ in this formula are not correct, it cannot be used to compute the total cross-section for instance, from the polarizability by means of the relation (B 12)*. Therefore it was impossible for us to generalize the expression (57) for the phase shift in this simple way.

Hamilton[28] derived the usual results for emission and for scattering outside the line width by solving the time independent Schrödinger equation. For the physical interpretation, however, he made use of time dependent states, which he obtained by

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* Of course the total cross-section can be found by computing the partial cross-sections for Rayleigh scattering and for all Raman lines:

$$\sigma_t = \sigma_s + \Sigma_L \, \sigma_{aL}.$$

superposition of the stationary solutions. In his calculations again only one higher level is taken into account and, of course, the usual divergences occur.

**51.** The problem of finding the states of steady scattering by arbitrary atoms, which Kramers[2] raised in 1948, has now been solved. Nevertheless the present theory of emission and scattering is incomplete on several points, even within the limits of non-relativistic dipole approximation. We here list these points in the order in which they seem to be logically connected.

1°. *Second order emission* can be described by a superposition of stationary states, chosen in such a way that at $t = 0$ the whole radiation field vanishes. Hence one has to find linear dependence relations of the kind (A 21) for quantum states whose phase shift is given by (96). Since this is just a matter of algebra, there does not seem to be any fundamental difficulty in describing in this way the two-photon emission studied by M. Göppert-Mayer[47]. For the emission of three of more photons, one has first to find the expression for the phase shift in which the singularities in the coefficients $c_N(k, k', k'')$ etc. are taken into account.

2°. *Higher order scattering processes*, in which the incoming photon is broken up into three or more photons, can be calculated along the lines of **36**. The result may be expected to be identical with that of Güttinger[48] and Weisskopf[46], except that the line shift is included. However, processes in which several photons are simultaneously absorbed and one or more photons emitted, cannot be treated readily, owing to the incoherence of the incoming photons. It is true that by putting in (85) $\lambda_N = -\pi \cot \xi_N$ (instead of taking all $\lambda$'s but one equal to $i\pi$) one obtains stationary states containing several ingoing waves with different frequencies. But these waves have definite frequencies $\omega_N$ and even definite phase relations, and therefore do not correspond to an incoherent mixture of incoming photons. Hence it is necessary to use the many-photon states for the description of the incoming field and, accordingly, to introduce adjustable parameters $\lambda$ into the singularities of the coefficients $c_N(k, k')$, $c_N(k, k', k'')$, $\cdots$.

3°. *Scattering by an excited atom* has not been treated, because it cannot be described by a stationary state. It seems possible, however, to construct an appropriate decaying state in the

following way. First one has to find the stationary states describing the scattering of two photons, one with the frequency $\omega$ of the incoming radiation and one with a frequency $k$ in the neighbourhood of the absorption frequency, $K_{M0}$ say. These states—for different values of $k$—have to be superposed in such a way that at $t = 0$ the radiation with frequency in the neighbourhood of $K_{M0}$ vanishes. Since $\omega$ has a fixed value for these states, they have different energies $\omega + k + E_0$ with a peak in the neighbourhood of $\omega + E_M$. Consequently the superposition will describe a non-stationary state with ingoing radiation of frequency $\omega$, in which initially the atom has the energy $E_M$.

4°. The *classical analogue of the quantized electromagnetic field* has only been used for one-quantum states. It is desirable that for the many-photon states a similar classical picture will be developed. The solution of this problem is not obvious, but presumably it is possible to describe every state of the photon field by an appropriate mixture of partially coherent classical waves.

5°. *Interference phenomena* in the current time-dependent theory require special calculations[49]. In the present theory, owing to the close resemblance with the classical picture, they can be analyzed immediately. Indeed, the Rayleigh scattered waves of two scattering atoms are both coherent with the incoming light and therefore also with each other. However, if the ground level is degenerate, incoherent scattering is also possible (see **35**) and the two scattered waves will only be partially coherent[50]. The interference of Raman light can be studied in the same way, but a complete account is only possible after the problem 4° has been solved.

## Appendix A.

**A 1.** The purpose of this section is to find the principal axes of the quadratic form

$$\Sigma A_{nn'} x_n x_{n'} = \Sigma (t_n \delta_{nn'} + \alpha_n \alpha_{n'}) x_n x_{n'},$$

where for definiteness $t_n$ and $\alpha_n$ are supposed to be real. The equation for the eigenvectors is

$$s x_n = \Sigma A_{nn'} x_{n'} = t_n x_n + \alpha_n \Sigma \alpha_{n'} x_{n'}. \tag{A 1}$$

From this follows

$$x_n = \alpha_n \beta/(s - t_n) \quad \text{with} \quad \beta = \Sigma \, \alpha_{n'} x_{n'},$$

and by substituting the former in the latter one finds the characteristic equation for the eigenvalues

$$\sum{}' \frac{\alpha_n^2}{s - t_n} = 1. \tag{A 2}$$

There is one real root between each pair of successive $t_n$. If there is only a finite number of $t_n$, there is one root larger than all $t_n$, and there are no other roots. If there is an infinite number of $t_n$, other roots may occur, e. g. complex roots.

To each root $s_\nu$ corresponds an eigenvector $X_n$:

$$X_{n\nu} = \alpha_n \beta_\nu/(s_\nu - t_n), \tag{A 3}$$

which may be normalized by a suitable choice of $\beta$:

$$\frac{1}{\beta_\nu^2} = \sum{}' \frac{\alpha_n^2}{(s_\nu - t_n)^2} = -\left[ \frac{d}{ds} \sum{}' \frac{\alpha_n^2}{s - t_n} \right]_{s=s_\nu}. \tag{A 4}$$

From the orthogonality of the matrix $X_{n\nu}$ follow

$$\sum_n{}' \frac{\alpha_n^2}{(s_\nu - t_n)(s_\mu - t_n)} = \frac{\delta_{\mu\nu}}{\beta_\nu^2}, \qquad \sum_\nu{}' \frac{\beta_\nu^2}{(s_\nu - t_n)(s_\nu - t_m)} = \frac{\delta_{nm}}{\alpha_n^2}. \tag{A 5}$$

The transformation to principal axes takes the form

$$x_n = \Sigma X_{n\nu} y_\nu, \qquad \Sigma A_{nn'} x_n x_{n'} = \Sigma s_\nu y_\nu^2;$$

and in particular one has

$$\Sigma X_{n\nu} \alpha_n = \beta_\nu, \qquad \Sigma \alpha_n x_n = \Sigma \beta_\nu y_\nu.$$

It is useful for the calculations in 22 to associate with this transformation an analytic function of $s$

$$F(s) = \sum{}' \frac{\alpha_n^2}{s - t_n} - 1$$

with the following properties. It has poles $t_n$ with residues $\alpha_n^2$.

The characteristic equation can be written $F(s) = 0$, and the normalization constants are given by $\beta_\nu^{-2} = -F'(s_\nu)$.

A 2. For the transformation of (11) one has to take $t_n = \nu_n^2 = (n\pi/L)^2$ and $\alpha_n = \varepsilon_n m_0^{-\frac{1}{2}}$. If for $s$ we now write $k^2$, the characteristic equation becomes (using (9))

$$m_0 = \sum{}' \frac{\varepsilon_n^2}{k^2 - \nu_n^2}, \qquad m = k^2 \sum{}' \frac{\varepsilon_n^2}{\nu_n^2(k^2 - \nu_n^2)}. \qquad (A6)$$

The latter form of the equations has been chosen so that it is possible to put $\delta_n = 1$ (transition to the point-electron). Subsequently, the series can be summed:

$$m = \frac{4\,e^2}{3\,L} k^2 \sum_{n=1}^{\infty}{}' \frac{1}{k^2 - (n\pi/L)^2} = \frac{2\,e^2}{3} k \left( \cot kL - \frac{1}{kL} \right)$$

and for large $L$ this reduces to (15).

With the abbreviations $L_n$ and $\eta_n$ according to (14) one finds from (A 4)

$$\frac{m_0}{\beta_n^2} = -\left[ \frac{d}{ds} \left( \sum_{n'}{}' \frac{\varepsilon_{n'}^2}{s - \nu_{n'}^2} + \sum_{n'}{}' \frac{\varepsilon_{n'}^2}{\nu_{n'}^2} \right) \right]_{s=k_n^2} = \frac{e^2}{3} \frac{L_n}{\sin^2 \eta_n}. \qquad (A7)$$

The transformation (12) is according to (A 3)

$$X_{nn'} = \frac{2\,\nu_n \sin \eta_{n'}}{\sqrt{LL_{n'}}(k_{n'}^2 - \nu_n^2)} = \frac{2}{\varkappa} \frac{\nu_n k_{n'} \cos \eta_{n'}}{\sqrt{LL_{n'}}(k_{n'}^2 - \nu_n^2)}. \qquad (A8)$$

Finally, using (A 3), (A 6) and (A 7) one finds

$$\sum{}' \frac{\varepsilon_n}{\nu_n} \mathbf{p}_n' = \sum{}' \frac{\varepsilon_n^2}{\nu_n^2 \sqrt{m_0}} \frac{\beta_{n'} \ddot{\mathbf{p}}_{n'}}{k_{n'}^2 - \nu_n^2} = \sum{}' \sqrt{\frac{4\,e^2}{3\,L_{n'}}} \frac{\cos \eta_{n'}}{k_{n'}} \ddot{\mathbf{p}}_{n'},$$

which completes the proof of (13).

With $k = ik'$ the characteristic equation (15) becomes Tnh $Lk' = k'/\varkappa$, and this equation has one positive root very near to $\varkappa$. This eigenvalue $ik' \approx i\varkappa$ will be denoted by $k_*$ and the corresponding $\eta_*$ is defined by $\eta_* = Lk_* \approx iL\varkappa$. Hence

$$\cos \eta_* \approx \mathrm{Csh}\, L\varkappa \approx \frac{1}{2} e^{L\varkappa}, \qquad L_* = L - \cos^2 \eta_*/\varkappa \approx -e^{2L\varkappa}/4\varkappa. \qquad (A9)$$

In all summations over $n$ this anomalous term must be included, i. e. $n$ also takes the value $*$.

A 3. For the transformation of (21) one has to replace $t_n$ and $a_n$ by $k_\nu^2$ and $K d_\nu$, the subscript $\nu$ being used to remind that the value $\nu = 0$ is included. Writing for the eigenvalue parameter $\omega^2$, one finds the characteristic equation

$$\frac{1}{K^2} = \sum_{\nu=0}^{\infty} \frac{d_\nu^2}{\omega^2 - k_\nu^2} = \frac{1}{\omega^2} + \sum_{n=1}^{\infty} \frac{2}{\varkappa L_n} \frac{\cos^2 \eta_n}{\omega^2 - k_n^2}. \tag{A 10}$$

In order to evaluate this sum we now construct an analytic function of $\omega$ with the same poles and residues.

First we define the function $\eta(k)$ by

$$\cos \eta(k) = \frac{\varkappa}{\sqrt{\varkappa^2 + k^2}}, \quad \sin \eta(k) = \frac{k}{\sqrt{\varkappa^2 + k^2}}, \quad \tan \eta(k) = \frac{k}{\varkappa},$$

so that $\eta(k_n) = \eta_n$. Then the equation (15) for the $k_n$ is equivalent to $\tan \{L k - \eta(k)\} = 0$ and one can easily verify

$$\sum_{-\infty}^{+\infty} \frac{\cos^2 \eta_n}{L_n(\omega - k_n)} = \frac{\cos^2 \eta(\omega)}{\tan \{L \omega - \eta(\omega)\}} - \frac{\varkappa \omega}{\varkappa^2 + \omega^2}. \tag{A 11}$$

The second term is required for subtracting the additional poles due to $\cos^2 \eta(\omega)$. After some calculations one finds from (A 10) and (A 11) the equation (23).

Furthermore, from (A 4) with the aid of (A 11) is found after laborious calculations

$$\beta_\nu = \sqrt{2 \varkappa / L_\nu'} \, (K/\omega_\nu) \sin^2 \zeta_\nu, \tag{A 12}$$

where

$$L_\nu' = L - \sin \zeta_\nu \cos \zeta_\nu / \omega_\nu + 2 \varkappa K^2 \sin^2 \zeta_\nu / \omega_\nu^4 = L - (d\zeta/d\omega)_{\omega_\nu}.$$

Substituting all this in (A 3) one finds the transformation matrix (now denoted by $Y$)

$$Y_{n\nu} = \frac{2\varkappa K^2}{\sqrt{L_n L_\nu'}} \frac{\sin \eta_n}{k_n} \frac{\sin \zeta_\nu}{\omega_\nu} \frac{1}{\omega_\nu^2 - k_n^2}, \qquad (n \neq 0)$$

$$Y_{0\nu} = K^2 \sqrt{\frac{2\varkappa}{L_\nu'} \frac{\sin \zeta_\nu}{\omega_\nu^3}} = \sqrt{\frac{2}{\varkappa L_\nu'}} \frac{K^2}{\sqrt{(\omega_\nu^2 - K^2)^2 + \omega_\nu^6/\varkappa^2}}.$$

(A 13)

Again, putting $\omega = i\omega'$ in (23) one finds an imaginary root $\omega_* \approx i\varkappa$, which is not quite the same as the root $k_*$ for the free electron. The values of $Y_{n*}$ and $Y_{0*}$ can be found from (A 13) by taking, like in (A 9),

$$\zeta_* = iL\varkappa, \quad L_*' = -e^{L\varkappa}/4\varkappa.$$

The values of $Y_{*\nu}$ are found by means of (A 9).

When the second procedure is applied (in 18), the sum in (A 10) does not contain the term with $n = *$. The corresponding terms in (A 11) have to be subtracted on the right and the result is that the sign of the last term in (A 11) is reversed. One then finds (27) instead of (23), and both (A 12) and (A 13) hold, provided $L'$ is replaced by

$$L_\nu'' = \left(1 - \frac{2K^2}{\omega_\nu^2 + \varkappa^2}\right)^2 \left[L - \left(\frac{d\zeta}{d\omega}\right)_{\omega_\nu}\right].$$

Here the derivative has to be computed from (27), but its explicit expression is rather complicated.

A 4. In this section it will be shown that the transformation (12) is indeed a transformation to phase-shifted light quanta, as stated in 13. For this purpose consider the boundary problem given by

$$v''(r) + k^2 v(r) = 0, \quad v(L) = 0, \quad v'(0) + \varkappa v(0) = 0.$$

The solution is trivial and furnishes the normalized eigenfunctions

$$v_n(r) = \sqrt{2/L_n} \, \sin(k_n r - \eta_n), \tag{A 14}$$

where $k_n$, $\eta_n$, $L_n$ are again given by (15) and (14). In particular, for $\varkappa = \infty$ one finds the orthogonal functions

$$u_n(r) = \sqrt{2/L} \, \sin \nu_n r.$$

Both orthogonal sets are connected by an orthogonal transformation

$$v_n(r) = \sum B_{nn'} u_{n'}(r), \quad B_{nn'} = \int_0^L v_n(r) u_{n'}(r) \, dr.$$

The integration can readily be performed, and $B_{nn'}$ turns out to be equal to $X_{nn'}$ given by (A 8). This proves (18).

A 5. When the equation for the phase is more complicated, as e. g. in (23), there is no corresponding boundary problem. Nevertheless, if a phase function $\zeta(\omega)$ is given by

$$\tan \zeta(\omega) = (\omega/\varkappa) \, \Phi(\omega),$$

we may consider the set of functions

$$w_n(r) = \sqrt{2/L'_n} \sin(\omega_n r - \zeta_n),$$

where $\zeta_n = \zeta(\omega_n)$, and $\omega_n$ is determined by the condition $w_n(L) = 0$. For convenience, a factor with

$$L'_n = L - (d\zeta/d\omega)_{\omega_n} \tag{A 15}$$

has been added, but that does not mean that the functions are normalized. They can be expressed in the complete orthogonal set $v_n(r)$:

$$w_n(r) = \sum C_{nn'} v_{n'}(r), \quad C_{nn'} = \int_0^L w_n(r) v_{n'}(r) \, dr, \tag{A 16}$$

and one finds readily

$$C_{nn'} = \frac{2\varkappa}{\sqrt{L'_n L_{n'}}} \frac{\sin \zeta_n \sin \eta_{n'}}{\omega_n^2 - k_{n'}^2} \left\{ 1 - \frac{1}{\Phi(\omega_n)} \right\}.$$

For the harmonic oscillator $\Phi(\omega) = \omega^2/(\omega^2 - K^2)$ and

$$C_{\nu n} = (k_n/\omega_\nu) Y_{n\nu} = (\omega_\nu/k_n) \left\{ Y_{n\nu} - \sqrt{2\varkappa/L_n} (\sin \eta_n/k_n) Y_{0\nu} \right\}, \tag{A 17}$$

according to (A 13)[*].

In order to prove (26) we deduce from (25), using successively (A 14), (A 17) and (A 16),

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[*] The same equation holds in the second procedure, where $\Phi$ is determined by (27), provided the derivative in (A 15) is accordingly computed from (27).

$$\begin{aligned}
\mathbf{A}' &= -\mathfrak{I}\mathfrak{e}\sqrt{3/2}\,\Sigma_{n\nu}\{v_n(r)/k_n r\}\,Y_{n\nu}P'_\nu \\
&= -\mathfrak{I}\mathfrak{e}\sqrt{3/2}\,\Sigma_{n\nu}\{v_n(r)/\omega_\nu r\}\,C_{\nu n}P'_\nu - \\
&\quad -\mathfrak{I}\mathfrak{e}\,\Sigma_{n\nu}\sqrt{3\varkappa/L_n}\{v_n(r)\sin\eta_n/k_n^2 r\}\,Y_{0\nu}P'_\nu \\
&= -\mathfrak{I}\mathfrak{e}\sqrt{3/2}\,\Sigma_\nu\{w_\nu(r)/\omega_\nu r\}\,P'_\nu - \\
&\quad -\mathfrak{I}\mathfrak{e}\,\Sigma_n\sqrt{3\varkappa/L_n}\{v_n(r)\sin\eta_n/k_n^2 r\}\,\Sigma_\nu Y_{0\nu}P'_\nu.
\end{aligned} \qquad \text{(A 18)}$$

On the other hand

$$\mathbf{P} = \mathbf{P}' = \mathfrak{e}P_0 m^{\frac{1}{2}} = \mathfrak{e}\sqrt{m}\,\Sigma Y_{0\nu}P'_\nu$$

and with the aid of the relation

$$\sum\sqrt{2/L_n}\{v_n(r)\sin\eta_n/k_n^2\} = 1/\varkappa, \qquad \text{(A 19)}$$

which will be proved presently, (A 18) reduces to (26).

A 6. In this section an identical relation between the $w_n(r)$ will be derived, which proves that they are not independent. Let $\Phi(z)$ be a one-valued analytic function in the complex $z$-plane, whose only singularities are simple poles and which tends to a limit different from zero when $|z|$ tends to infinity. Then

$$G(z) \equiv \frac{\sin\{Lz - \zeta(z)\}}{\sin\zeta(z)} = \frac{\varkappa\sin Lz}{z\Phi(z)} - \cos Lz$$

is also one-valued analytic and its only singularities are the zeros $\Omega_l$ of $\Phi$. The zeros of $G(z)$ are the characteristic values $\omega_n$ and the values of the derivative in these points are

$$G'(\omega_n) = L'_n/\sin L\omega_n,$$

$L'_n$ being defined by (A 15).

If $J$ is a closed path of integration that does not pass through any point $\omega_n$, then

$$\frac{1}{2\pi i}\int_J \frac{\sin zx\,dz}{G(z)(z-\omega)} = \frac{\sin\omega x}{G(\omega)} + \sum \frac{\sin\omega_n L\sin\omega_n x}{L'_n(\omega_n - \omega)},$$

the sum being extended over all $\omega_n$ inside $J$. The integral on the left vanishes for $J \to \infty$, $|x| < L$. Hence, with $x = L - r$,

$$\frac{\sin \omega x}{G(\omega)} = \sum_{-\infty}^{+\infty} \frac{\sin \omega_n L \sin \omega_n x}{L_n'(\omega - \omega_n)} = -2\omega \sum_{1}^{\infty} \frac{\sin \zeta_n \sin(\omega_n r - \zeta_n)}{L_n'(\omega^2 - \omega_n^2)}, \quad (A\,20)$$

the last member being valid if $\Phi$ is an even function, so that $\omega_{-n} = -\omega_n$. Substituting $\omega = \Omega_l$,

$$0 = \sum_{n=1}^{\infty} \frac{2 \sin \zeta_n \sin(\omega_n r - \zeta_n)}{L_n'(\Omega_l^2 - \omega_n^2)} = \sum_{n=1}^{\infty} \sqrt{\frac{2}{L_n'}} \frac{\sin \zeta_n}{\Omega_l^2 - \omega_n^2} w_n(r). \quad (A\,21)$$

In this way one finds a relation between the $w_n(r)$ for each zero of $\Phi$.

Incidentally the relation (A 19) can be proved on choosing $\Phi = 1$ (so that $\omega_n = k_n$, $\zeta_n = \eta_n$, $L_n' = L_n$) and taking in (A 20) $\omega = 0$ and $L$ very large. Moreover, if in this relation $x$ goes to infinity, it becomes

$$\Sigma (2 \sin \nu_n r)/L \nu_n = 1, \qquad (A\,22)$$

which proves (17).

A 7.  In this section the work of A 1 is reformulated for the case of a continuous spectrum. First suppose that the $t_n$ are very dense on the real axis; introducing functions $\varepsilon(t)$ and $\alpha(t)$ by

$$t_{n+1} - t_n = \varepsilon(t_n), \qquad \alpha_n = \sqrt{\varepsilon(t_n)}\, \alpha(t_n),$$

we suppose that they vary slowly:

$$d\varepsilon/dt \ll 1, \qquad d\alpha/dt \ll \alpha/\varepsilon.$$

Then, with $x_n = x(t_n)\sqrt{\varepsilon(t_n)}$ equation (A 1) can be written

$$(s - t)x(t) = \alpha(t)\int \alpha(t')x(t')dt' = \alpha(t) \cdot \beta.$$

The formal solution, given in 27, is

$$x(t) = \alpha(t)\{(s - t)^{-1} - \lambda \delta(s - t)\}\beta, \qquad (A\,23)$$

$\lambda$ being determined by

$$\int \frac{\alpha(t)^2}{s - t}dt - \lambda \alpha(s)^2 = 1. \qquad (A\,24)$$

For a justification we consider (A 2) for our nearly continuous spectrum.

The (real) roots $s$ are, from a macroscopical point of view, continuously distributed, but microscopically the position of each root between two successive $t$'s is determined by the equation (A 2). Let $s$ be the root between $t_m$ and $t_{m+1}$, and put $s = t_m + \sigma$, $0 < \sigma < \varepsilon$. Then

$$\sum{}' \frac{\alpha_n^2}{s - t_n} = \sum_n{}' \frac{\alpha_n^2}{t_m + \varepsilon/2 - t_n} + \sum_n{}' \alpha_n^2 \left( \frac{1}{t_m + \sigma - t_n} - \frac{1}{t_m + \varepsilon/2 - t_n} \right).$$

It is readily seen that the first sum on the right tends to a principal-value integral

$$\sum_n{}' \frac{\alpha_n^2}{t_m + \varepsilon/2 - t_n} \rightarrow \int \frac{\alpha(t)^2 \, dt}{t_m + \varepsilon/2 - t} \rightarrow \int \frac{\alpha(t)^2 \, dt}{s - t},$$

which does not depend on the microscopical position of $s$.

The second sum is convergent, so that the higher terms, with $|n - m| > N$ say, may be neglected. The other terms cover an interval $2 N \varepsilon$, which is small for small $\varepsilon$, so that $\alpha_n^2$ may be taken constant in it. Hence this sum can be written

$$\alpha_m^2 \sum_{-\infty}^{+\infty}{}' \left( \frac{1}{\sigma - n\varepsilon} - \frac{1}{\varepsilon/2 - n\varepsilon} \right) = \alpha_m^2 \frac{\pi}{\varepsilon} \cot \frac{\pi}{\varepsilon} \sigma = \pi \alpha(s)^2 \cot \frac{\pi}{\varepsilon} \sigma.$$

Since the cotangent can assume all values from $-\infty$ to $+\infty$, one can use instead of $\sigma$ the parameter

$$\lambda = -\pi \cot \pi\sigma/\varepsilon.$$

The characteristic equation (A 2) for $s$ then takes the form (A 24) with $\lambda$ as eigenvalue parameter to be determined.

The solution (A 23) can now easily be justified in the same way.

## Appendix B.

Since we employ an expansion in multipole waves rather than in the customary plane waves, the mathematical connection between both pictures has to be established. We shall first derive

the relation between the intensity $J$ of the plane wave and the outgoing energy $I$ associated with its electric dipole component. Next we express the cross-sections in terms of the polarizability $\alpha$ and, subsequently, we derive the relation between $\alpha$ and the phase shift $\zeta$. Finally we shall apply the resulting formulae to the classical damped harmonic oscillator.

1°. Let a monochromatic plane wave in the $z$-direction be represented by the vector potential

$$\mathbf{A}(t) = \Re \mathbf{e}\, e^{i\omega(z-t)}. \qquad (\text{B 1})$$

The expansion in multipole waves can be written

$$\mathbf{e}\, e^{i\omega z} = \Sigma_{lu}\, b_{lu}\, \mathbf{A}_{lu}(r,\vartheta,\varphi),$$

where the subscript $l$ refers to the order of the multipole and $u$ distinguishes the different waves of the same order. Since the multipole waves are orthogonal on the surface of a sphere with large radius $r$, one finds the coefficients $b_{lu}$ from

$$b_{lu} \int \mathbf{A}_{lu}(r,\vartheta,\varphi)^2\, d\Omega = \int \mathbf{e}\, \mathbf{A}_{lu}(r,\vartheta,\varphi)\, e^{i\omega r\cos\vartheta}\, d\Omega. \qquad (\text{B 2})$$

We are only interested in the electric dipole wave: $l = 1$, $u = x,y,z$; in this case we have

$$\mathbf{A}_{1u}(r,\vartheta,\varphi) = \mathfrak{T}\mathbf{e}^u \sin \omega r/r. \qquad (\text{B 3})$$

Performing the elementary integrations in (B 2) one finds $b_{1u} = (3/2\,\omega)\,(\mathbf{e}^u\mathbf{e})$ so that the expansion takes the form

$$\Re \mathbf{e}\, e^{i\omega(z-t)} = \frac{3}{2}\,\Re\mathfrak{T}\mathbf{e}\,\frac{\sin \omega r}{\omega r}\, e^{-i\omega t} + \cdots . \qquad (\text{B 4})$$

Now the plane wave (B 1) has the intensity $J = \omega^2/8\,\pi$, whereas the outgoing (and also the ingoing) energy per unit time in (B 3) is $\omega^2/12$. Thus from (B 4) follows

$$J = (2\,\omega^2/3\,\pi)\, I.$$

2°. Suppose there is a scattering centre at the origin which has an induced dipole moment $\mathbf{M}$ proportional to the field strength $\mathbf{E}$ of the incident plane wave:

$$\left.\begin{array}{ll} \mathbf{E} = \Re\,\mathbf{E_0}\,e^{-i\omega t}, & \mathbf{E_0} = i\,\omega\,\mathbf{e}; \\[4pt] \mathbf{M} = \Re\,\mathbf{M_0}\,e^{-i\omega t}, & \mathbf{M_0} = \alpha\,\mathbf{E_0} = i\,\omega\,\alpha\,\mathbf{e}. \end{array}\right\} \quad (\text{B 5})$$

The work done by the field force per unit time is

$$\overline{\mathbf{E}\dot{\mathbf{M}}} = \frac{1}{4}\,i\,\omega\,(\mathbf{E_0}\mathbf{M_0^*} - \mathbf{E_0^*}\mathbf{M_0}) = \frac{1}{2}\,\omega\,|\mathbf{E_0}|^2\,\Im\alpha. \qquad (\text{B 6})$$

On the other hand, the dipole emits, according to a well-known calculation[51], per unit time the energy

$$I = (\omega^4/3)\,|\mathbf{M_0}|^2 = (\omega^4/3)\,|\alpha|^2\,|\mathbf{E_0}|^2. \qquad (\text{B 7})$$

Since $J = |\mathbf{E_0}|^2/8\,\pi$, (B 6) and (B 7) give respectively

$$\sigma_t = 4\,\pi\omega\,\Im\alpha, \qquad \sigma_s = (8\,\pi\omega^4/3)\,|\alpha|^2. \qquad (\text{B 8})$$

As the field is now singular in the origin, its dipole component will not only contain the regular dipole term $\sin\omega r/r$, but also $\cos\omega r/r$. Therefore it can be written

$$\mathbf{A}(t) = \Re\,\Im\,\mathbf{C}\frac{\sin(\omega r - \zeta)}{r}\,e^{-i\omega t}. \qquad (\text{B 9})$$

The singularity caused by the dipole moment $\mathbf{M}$ has, according to classical formulae, the form

$$\mathbf{A} = \Re\,\Im - i\,\omega\,\mathbf{M_0}\,e^{-i\omega t}/r + \text{finite terms},$$

so that one finds

$$-\mathbf{C}\sin\zeta = -i\,\omega\,\mathbf{M_0}. \qquad (\text{B 10})$$

On the other hand, the constants $\mathbf{C}$ and $\zeta$ have to be adjusted so that (B 9) contains the same ingoing dipole wave as (B 4):

$$\mathbf{C}e^{i\zeta} = 3\,\mathbf{e}/2\,\omega. \qquad (\text{B 11})$$

Combining (B 5), (B 10), and (B 11) one finds

$$\alpha = \frac{3\,i}{4\,\omega^3}\,(1 - e^{-2i\zeta}). \qquad (\text{B 12})$$

From this, together with (B 8) follow[52]

$$\sigma_{\rm t} = \frac{3\,\pi}{\omega^2}\ \Re\,(1 - e^{-2i\zeta}) = \frac{6\,\pi}{\omega^2}\,\Re\,\frac{i\tan\zeta}{1 + i\tan\zeta},$$

$$\sigma_{\rm s} = \frac{3\,\pi}{2\,\omega^2}\ |1 - e^{-2i\zeta}|^2 = \frac{6\,\pi}{\omega^2}\left|\frac{\tan\zeta}{1 + i\tan\zeta}\right|^2,$$

$$\sigma_{\rm a} = \frac{3\,\pi}{2\,\omega^2}(1 - |\,e^{-2i\zeta}\,|^2) = \frac{3\,\pi}{2\,\omega^2}\left(1 - \left|\frac{1 - i\tan\zeta}{1 + i\tan\zeta}\right|^2\right).$$

3°. For a damped harmonic oscillator the equation of motion is

$$\ddot{\mathbf{R}} + \gamma\dot{\mathbf{R}} + K^2\mathbf{R} = (e/m)\,\Re\,\mathbf{E}_0 e^{-i\omega t}. \tag{B 13}$$

The damping term $\gamma$ is the sum of the radiation damping and the damping due to energy dissipation by other processes[53]

$$\gamma = \gamma^0 + \gamma', \qquad \gamma^0 = 2\,e^2\omega^2/3\,m = \omega^2/\varkappa.$$

From (B 13) follows in the ordinary way for the polarizability

$$\alpha = (e^2/m)\,(K^2 - \omega^2 - i\gamma\omega)^{-1},$$

and the phase shift can then be found from (B 12):

$$\tan\zeta = \frac{\omega^3/\varkappa}{\omega^2 - K^2 + i\gamma'\omega}.$$

This formula takes the form (80) in the neighbourhood of the resonance frequency. The expressions one obtains for the cross-sections are also similar to those in **41**.

## Appendix C.

Here we shall derive a general relation between matrix elements of the unperturbed atom, which has been used several times to prove the equivalence of the results obtained by Kramers' Hamiltonian with the usual results. If $H$ is the Hamiltonian $\mathbf{P}^2/2\,m + V(\mathbf{R})$ and $\Omega$ an arbitrary constant, one finds successively

$$\begin{aligned}
\dot{P}_v\,(H - \Omega)^{-1}\,\dot{P}_w &= i\{\dot{P}_v P_w - \dot{P}_v\,(H - \Omega)^{-1}\,P_w\,(H - \Omega)\} \\
&= i\{(H - \Omega)\,P_v\,(H - \Omega)^{-1}\,\dot{P}_w - P_v\dot{P}_w\} \\
&= \frac{1}{2}\,i\,(\dot{P}_v P_w - P_v\dot{P}_w) + (H - \Omega)\,P_v\,(H - \Omega)^{-1}\,P_w\,(H - \Omega) \\
&\quad - \frac{1}{2}\{P_v P_w\,(H - \Omega) + (H - \Omega)\,P_v P_w\}.
\end{aligned}$$

In the first term on the right one can write

$$\dot{P}_v P_w - P_v \dot{P}_w = \dot{P}_v P_w - \dot{P}_w P_v - [P_v, \dot{P}_w]$$
$$= \dot{P}_v P_w - \dot{P}_w P_v - i \partial_v \partial_w V.$$

Hence, the eigenstates being labelled by $N, M, J$,

$$\langle N | \dot{P}_v (H - \Omega)^{-1} \dot{P}_w | M \rangle \equiv \sum_J{}' \frac{\langle N | \partial_v V | J \rangle \langle J | \partial_w V | M \rangle}{E_J - \Omega}$$

is found to be equal to

$$\frac{1}{2} \sum_J (E_J - E_N) \{ \langle N | P_v | J \rangle \langle J | P_w | M \rangle - \langle N | P_w | J \rangle \langle J | P_v | M \rangle \} + \frac{1}{2} \langle N | \partial_v \partial_w V | M \rangle$$

$$- \frac{1}{2} \sum_J{}' \frac{(E_N - \Omega)(E_J - E_M) + (E_M - \Omega)(E_J - E_N)}{E_J - \Omega} \langle N | P_v | J \rangle \langle J | P_w | M \rangle.$$

This identity will now be specialized in various ways.

1°. On taking $N = M = 0$, $v = w$, and $\Omega = E_0 + \omega$ and $\Omega = E_0 - \omega$ respectively, one obtains two identities, which added together yield the equality used in (49).

2°. On taking $M = N$, $v = w$, and $\Omega = E_N - k$ one finds the equivalence of (74) and (79). If all three directions in space are taken into account, one has to sum over $v$, which amounts to writing in (79) the vector $\mathbf{P}$.

3°. In the same way, by writing $N = N, \mu$ and $M = N, \mu'$, taking $\Omega = E_N - k$ and summing over $v = w$, one finds (98).

4°. Finally write the identity with $\Omega = E_M + \omega_M$, and also with $\Omega = E_N - \omega_M$ and $v$ and $w$ interchanged; the sum of both equalities thus obtained is

$$\vartheta_{NM}^{vw} = \sum_J{}' \left\{ \frac{\langle N | \partial_v V | J \rangle \langle J | \partial_w V | M \rangle}{E_J - E_M - \omega_M} + \frac{\langle N | \partial_w V | J \rangle \langle J | \partial_v V | M \rangle}{E_J - E_N + \omega_M} \right\} - \langle N | \partial_v \partial_w V | M \rangle$$

$$= -\frac{1}{2} \sum_J{}' \frac{(K_{NM} - \omega_M) K_{JM} - \omega_M K_{JN}}{K_{JM} - \omega_M} \langle N | P_v | J \rangle \langle J | P_w | M \rangle$$

$$- \frac{1}{2} \sum_J{}' \frac{\omega_M K_{JM} + (K_{MN} + \omega_M) K_{JN}}{K_{JN} + \omega_M} \langle N | P_w | J \rangle \langle J | P_v | M \rangle.$$

Adding to this the identity

$$0 = \langle N|P_v P_w - P_w P_v|M\rangle = \sum_J \{\langle N|P_v|J\rangle\langle J|P_w|M\rangle - \langle N|P_w|J\rangle\langle J|P_v|M\rangle\}$$

after multiplying with $-\frac{1}{2}(2\,\omega_M + K_{MN})$, one gets on the right-hand side

$$\omega_M(\omega_M + K_{MN}) \sum_J{}' \left\{ \frac{\langle N|P_v|J\rangle\langle J|P_w|M\rangle}{K_{JM} - \omega_M} + \frac{\langle N|P_w|J\rangle\langle J|P_v|M\rangle}{K_{JN} + \omega_M} \right\}. \quad (C\,1)$$

This includes (60)—and also (49)—as special cases.

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## Acknowledgement.

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## Notes and References.

[1] H. A. Kramers, Grundlagen der Quantentheorie II (Leipzig 1938) § 89. See for a short account: H. A. Kramers, Nuovo Cim. 15, 108 (1938).

[2] H. A. Kramers' Report at the Solvay Congress 1948.

[3] Kramers[2] defined this proper field as the (transverse) field of a uniformly moving electron having the same $R$ and $\dot{R}$ as the actual electron at the time considered.

[4] P. A. M. Dirac, Proc. Roy. Soc. 167, 148 (1938).

[5] W. Opechowski, Physica 8, 161 (1941).

[6] W. E. Lamb and R. C. Retherford, Phys. Rev. 72, 241 (1947); 79, 549 (1950); 81, 222 (1951); S. Pasternack, Phys. Rev. 54, 1113 (1938).

[7] The computation was first given—in elementary form—by Bethe[34], and later developed by many others[35].

[8]  It was first studied by DIRAC[4], but, of course it was known before, see e. g. W. WESSEL, Zeits. für Phys. **92**, 407 (1934).

[9]  H. J. BHABHA, Phys. Rev. **70**, 759 (1946). See also the discussion at the Solvay Congress, ref. [2].

[10] To be quite correct one should write in the first term $\tilde{\mathfrak{T}}\mathbf{A}$ rather than $\tilde{\mathbf{A}}$ (the symbol $\mathfrak{T}$ is defined in [9]), because the transversality of $\mathbf{A}$ is only imposed as a supplementary condition. However, there is no harm in dropping the $\mathfrak{T}$, since we shall only deal with solutions satisfying this condition.

[11] It is indeed sufficient that the *external* field varies smoothly, because the field produced by the charge distribution $\varrho$ itself furnishes a contribution to $\tilde{\mathbf{A}}$ which does not depend on $\mathbf{R}$, provided the velocity $\dot{\mathbf{R}}$ is small compared to the velocity of light.

[12] Cf. F. J. BELINFANTE, Physica **12**, 1 (1946). It is easily seen that, for vector fields of the form $\mathfrak{q}\sin vr/r$, his definition reduces to (5).

[13] T. A. WELTON, Phys. Rev. **74**, 1157 (1948).

[14] E. g. F. ZERNIKE, Geiger and Scheel's Handb. der Phys. **3** (Berlin 1928) p. 443.

[15] F. Bloch and A. NORDSIECK, Phys. Rev. **52**, 54 (1937).

[16] W. PAULI and M. FIERZ, Nuovo Cim. **15**, 167 (1938).

[17] J. SCHWINGER, Phys. Rev. **75**, 651 (1949).

[18] C. J. ELIEZER, Rev. Mod. Phys. **19**, 147 (1947).

[19] This has been done for free fields by KRAMERS (Quantentheorie II, § 87).

[20] P. A. M. DIRAC, Quantum mechanics (3rd ed., Oxford 1947) ch. VIII.

[21] N. F. MOTT and H. S. W. MASSEY, Theory of Atomic Collisions (Oxford 1933, 1949) p. 24.

[22] W. HEITLER, Quantum Theory of Radiation (Oxford 1936, 1944) p. 38.

[23] C. MØLLER, Dan. Mat. Fys. Medd. **22**, no. 19 (1946).

[24] Cf. PAULI's remark in the Report Conf. Camb. 1946. Vol. I, p. 9.

[25] See V. FOCK, Phys. Zeits. der Sowjetunion **6**, 425 (1934), in particular eq. (20) together with (6). The connection between our coefficients $c$ and his is

$$\Sigma_N c_N^{r_1 r_2 \cdots r_n} \varphi_N = \sqrt{n!}\, c\,(r_1, r_2, \cdots r_n).$$

[26] In his calculation of the scattering of light by free electrons, I. WALLER (Zeits. für Phys. **88**, 436 (1934)) dropped these terms. E. GÓRA (Acta Phys. Pol. **7**, 159 and 374 (1939)) justified this omission by an adiabatic switching on of the coupling. This is indeed a plausible justification from a physical point of view, but his mathematical proof has no meaning. H. A. WILSON (Proc. Camb. Phil. Soc. **37**, 301 (1941)) showed that these terms vanish when the electron is subject to a binding force, however small. It would have been sufficient to take for the electron a wave packet instead of a plane wave.

[27] O. K. RICE, Phys. Rev. **33**, 748 (1929).

[28] J. HAMILTON, Proc. Phys. Soc. **59**, 917 (1947).

[29] See e. g. Geiger and Scheel's Handb. der Phys. **24**—1, (2nd ed., Berlin 1933) p. 431.

[30] WEISSKOPF[46] calls these regions "weitere Umgebung" and "engere Umgebung".

[31] H. A. KRAMERS and W. HEISENBERG, Zeits. für Phys. **31**, 681 (1925) eq. 29. The second term (with the emission frequencies) does not occur in our formula, because we only consider scattering by an atom in the ground state.

[32] G. WENTZEL, Geiger and Scheel's Handb. der Phys. **24**—1 (2nd ed., Berlin 1933) § 19.

[33] W. HEISENBERG (Zeits. für Phys. **120**, 513 (1943)) has shown that if several particles are present, such a factor guarantees that all particles are outgoing. We here assume the same for the radiation field, although it ought to be proved separately.

[34] H. A. BETHE, Phys. Rev. **72**, 339 (1947).

[35] N. M. KROLL and W. E. LAMB, Phys. Rev. **75**, 388 (1949).
J. B. FRENCH and V. F. WEISSKOPF, Phys. Rev. **75**, 1240 (1949).
See also H. A. BETHE's Report at the Solvay Congress 1948.

[36] See the paper by KROLL and LAMB in ref. [35], footnote 1.

[37] J. R. OPPENHEIMER (Phys. Rev. **35**, 461 (1930)) used relativistic one-particle theory. For the non-relativistic electron I. WALLER (Zeits. für Phys. **62**, 673 (1930)) computed the self-energy, and his result shows that the shift is logarithmically divergent. In dipole approximation it would be linearly divergent.

[38] J. SERPE, Physica **8**, 226 (1941).

[39] E. g. W. PAULI, Geiger and Scheel's Handb. der Phys. **23** (Berlin 1926) § 5; P. PRINGSHEIM, Fluorescence and Phosphorescence (New York 1949) p. 2.

[40] Also ref. [22] § 15.

[41] Other defects of this picture have been pointed out by G. PLACZEK (Zeits. für Phys. **58**, 585 (1929)).

[42] G. N. WATSON, Theory of Bessel Functions (Cambridge 1922) p. 201; T. J. I'A BROMWICH, Infinite Series (2nd ed., London 1947) p. 347.

[43] V. WEISSKOPF, Ann. der Phys. **9**, 23 (1931).

[44] G. BREIT, Rev. Mod. Phys. **5**, 91 (1933).

[45] These experiments have been discussed by WEISSKOPF[46]. He showed that only experiments in which the interaction actually ceases at a definite time (as is the case in experiments with cathode rays) can be considered as direct measurements of the decay time.

[46] V. WEISSKOPF, Zeits. für Phys. **85**, 451 (1933); Phys. Zeits. der Sowjetunion **4**, 97 (1933).

[47] M. GÖPPERT-MAYER, Ann. der Phys. **9**, 273 (1931).

[48] P. GÜTTINGER, Helv. Phys. Acta **5**, 237 (1932); J. BLATON, Zeits. für Phys. **69**, 835 (1931).

[49] See e. g. ref. [22], p. 133; ref. [32], p. 758.

[50] Cf. G. Placzek, Marx' Handbuch der Radiologie 6—2 (2nd ed., Leipzig 1934) p. 223.

[51] R. Becker, Theorie der Elektrizität II (Leipzig 1933) p. 75.

[52] These formulae are the same as those given in N. F. Mott and H. S. W. Massey, Theory of Atomic Collisions (2nd ed., Oxford 1949) p. 134.

[53] See ref. [51], p. 86.

# STELLINGEN

## I

De kanonieke transformatie die in hoofdstuk I van dit proef-schrift werd toegepast, kan ook door middel van velden worden geschreven, zonder tussenkomst van een ontwikkeling naar eigen-trillingen.

## II

Hoewel men moet toegeven dat de storingstheorie voor niet-ontaarde toestanden niet zonder nadere rechtvaardiging op continue spectra mag worden toegepast, is de bewering van Peng dat zij tot verkeerde resultaten zou leiden, onjuist. Integendeel, het kan worden aangetoond dat zij nagenoeg de juiste uitdrukking oplevert voor bijvoorbeeld de storingsenergie.

H. W. Peng, Proc. Roy. Soc. (A) **186**, 119 (1946).

## III

De berekening van Ma en Hsüeh kan niet aanvaard worden als een afleiding van de integraalvergelijking van Heitler voor de stralingsdemping.

S. T. Ma en C. F. Hsüeh, Proc. Camb. 40, 167 (1944).

## IV

Wanneer bij de beschrijving van een electromagnetisch veld de vectorpotentiaal gebruikt wordt, pleegt men te eisen dat de theorie ijkinvariant zij. In het geval van een gequantiseerd veld heeft dit echter geen zin, indien voor de ijkfuncties $c$-getallen gekozen wor-den: in plaats daarvan moeten ijkfuncties beschouwd worden die lineaire combinaties zijn van de creatie- en annihilatie-operatoren.

## V

De gevolgtrekking van S c h w i n g e r dat een electromagnetische golf geen vacuumpolarisatie teweeg brengt, volgt niet uit zijn daaraan voorafgaande beschouwing. Met een aanvullende berekening echter kan men aantonen dat de bewering wel juist is.

J. S c h w i n g e r, Phys. Rev. **75**, 651 (1949).

## VI

De door T o l l en W h e e l e r gevonden voorlopers van electromagnetische golffronten in een dispergerend medium zijn te verklaren, doordat in de begintoestand de verstoring ook al geen scherp begrensd front heeft. Het is noodzakelijk het probleem mathematisch nauwkeuriger te formuleren; in het bijzonder moet gepreciseerd worden welke beginvoorwaarden gesteld kunnen worden.

J. S. T o l l en J. A. W h e e l e r, Precursors and the relation between absorption, refraction and scattering. („Preliminary draft", ongepubliceerd.)

## VII

Tegen de verklaring die R u b i n o w i c z geeft voor het feit, dat het buigingslicht afkomstig schijnt te zijn van de buigende rand, kunnen zowel bezwaren van mathematische als van physische aard ingebracht worden.

W. R u b i n o w i c z, Ann. Phys. (4) **73**, 339 (1924).

## VIII

Ten onrechte beschouwen natuurkundigen veelal een exacte formulering van de voorwaarden, waaronder de door hen toegepaste wiskundige bewerkingen geoorloofd zijn, als wiskundige haarkloverij. Bij juiste behandeling hebben deze voorwaarden dikwijls een physische ondergrond, en soms kunnen zij een vingerwijzing voor verdere ontwikkeling vormen.

## IX

De toepassing van de methode der stationnaire phase op dubbele integralen van de gedaante

$$\int \int_D g(x,y)\, e^{ikf(x,y)}\, dx\, dy,$$

zoals die geformuleerd werd in een vroeger artikel, leidt tot een mathematisch correcte asymptotische ontwikkeling voor grote waarden van $k$. De critiek van W o l f is niet gerechtvaardigd.

N. G. v a n K a m p e n, Physica **14**, 575 (1949).

E. W o l f, Reports on Progress in Physics **14**, 95 (1951).

## X

Als $g(x)$ door de zgn. Hilbert-transformatie toegevoegd is aan $f(x)$, dan bestaat een analytische functie $H(z)$, die regulier is in de bovenhelft van het complexe vlak, aan zekere voorwaarden in het oneindige voldoet, en op de reële as in $f(x) + ig(x)$ overgaat. Dit is bewezen door M. R i e s z voor het geval dat $f(x)$ tot de klasse $L''$ behoort $(p > 1)$. Een dergelijke stelling geldt ook, indien de integraal van $f(x)$ over elk begrensd interval bestaat en eindig blijft als de integratiegrenzen oneindig worden. Bovendien kan deze stelling uitgebreid worden voor het geval dat de reële as door een andere kromme vervangen wordt.

E. C. T i t c h m a r s h, Theory of Fourier Integrals (Oxford 1937) Hoofdst. V.

## XI

De gebruikelijke, op de klassieke lichttheorie gebaseerde verklaring van het bestaan van incoherente lichtbundels, is onjuist.

## XII

In de theorie van de Stark-verbreding van waterstoflijnen moet ook de richting van het storende veld in acht genomen worden. Daardoor zal men een kleinere verbreding vinden dan uit de berekening van S p i t z e r volgt.

L. S p i t z e r, Phys. Rev. **55**, 699; **56**, 39 (1939).

## XIII

Voor zover de verklaring, die G o r t e r gegeven heeft voor de door V a n I t t e r b e e k en anderen gevonden weerstandsverandering van dunne metaallaagjes, afwijkt van de verklaring van M o s t o v e t c h en V o d a r, verdient de laatste de voorkeur.

C. J. G o r t e r, Physica **17**, 777 (1951).

N. M o s t o v e t c h en B. V o d a r, Comptes Rendus 230, 2008 (1950); **233**, 360 (1951).

## XIV

Het gedrag van de „tippetop" kan begrepen worden, indien men de wrijvingskracht ten gevolge van de glijding over het ondervlak als een kleine storing in rekening brengt.

## XV

Door aan de physiologische maatbepaling een fundamentele betekenis toe te kennen, miskent R e e n p ä ä het willekeurige karakter van de keuze van een maatbepaling.

Y. R e e n p ä ä, Über Wahrnemen, Denken und messendes Versuchen (Bibliotheca Biotheoretica, ser. D, vol. 3; Leiden 1947).

## XVI

Het existentialisme van S a r t r e vertoont aanrakingspunten met de positivistische opvatting in de moderne natuurkunde.