

## 2. THE DAMPING PROBLEM IN WAVE MECHANICS

A formula is derived for the wave-mechanical treatment of damping, and is used to investigate some related problems; coherence phenomena also are explained. An expression is obtained for spontaneous emission, and the problem of the intensity of spectral lines is solved in this way.

### 1. COUPLED SYSTEMS IN WAVE MECHANICS

A system cannot be uniquely defined in wave mechanics; we always have a probability ensemble (statistical treatment).<sup>†</sup> If the system is coupled with another, there is a double uncertainty in its behaviour.

Let the state of the first system be described by the quantities  $a_n$  in

$$\psi = \sum a_n \psi_n, \quad (1)$$

and for the second system let

$$\psi' = \sum b_r \psi'_r. \quad (2)$$

The Schrödinger function for the two systems together is then

$$\Psi = \psi \psi' = \sum_n \sum_r a_n b_r \psi_n \psi'_r = \sum_n \sum_r c_{nr} \psi_n \psi'_r, \quad (3a)$$

where

$$c_{nr} = a_n b_r. \quad (3b)$$

If there is coupling, then  $c_{nr}$  is a function of time and can no longer be resolved as in equation (3b). Thus  $a_n$  and  $b_r$  can no longer be used separately.

For a function  $f$  of co-ordinates (and momenta) of the first system alone we have<sup>‡</sup>

$$\bar{f} = \int \Psi f \Psi^* d\tau d\tau' = \sum_n \sum_m \sum_r c_{nr}^* c_{mr} \int \psi_n^* f \psi_m d\tau = \sum_n \sum_m \alpha_{nm} f_{nm}, \quad (4a)$$

where

$$\alpha_{nm} = \sum_r c_{nr}^* c_{mr}, \quad (4b)$$

and

$$f_{nm} = \int \psi_n^* f \psi_m d\tau$$

L. Landau, Das Dämpfungsproblem in der Wellenmechanik, *Z. Phys.* **45**, 430 (1927).

<sup>†</sup> It has recently been shown by Heisenberg<sup>1</sup> that the reason for this is in the nature of the problem; this finally resolves the model problem in wave mechanics. The relationship with classical mechanics is discussed by Ivanenko and Landau<sup>2</sup>.

<sup>‡</sup>  $\bar{f}$  denotes the probability average value of  $f$ .

are the matrix components of  $f$ . Thus the "state" of the system can now be described by the quantities  $\alpha_{nm}$ . For a system defined by the quantities  $a_n$  it is well known that

$$\tilde{f} = \int \psi^* f \psi \, d\tau = \sum_n \sum_m a_n^* a_m f_{nm}. \quad (5)$$

In this particular case, therefore,  $\alpha_{nm} = a_n^* a_m$ ; in general such a representation is not possible, and  $\alpha_{nm}$  must then be regarded as a certain mean value of  $a_n^* a_m$ .

## 2. CAVITY RADIATION IN WAVE MECHANICS

Wave mechanics usually deals with objects having a limited number of degrees of freedom. The general problem of quantisation of the electromagnetic field (quantum electrodynamics) still presents insuperable difficulties. If the structure of the field is not involved, however, but only the properties of the radiation as a whole, the problem is considerably simpler.

If we imagine the radiation enclosed in a vessel of any shape, it is known to consist of independent eigen-oscillations, in general of different frequencies. Since each eigen-oscillation corresponds to a separate degree of freedom, such a system has a discrete, though infinite, series of degrees of freedom. Since they are independent, the eigen-oscillations can be quantised individually.

As the co-ordinate of an eigen-oscillation we take the phase of the corresponding electric (or magnetic) force for a particular point †. We have

$$\frac{d\varphi}{dt} = \omega, \quad (6)$$

where  $\varphi$  is the phase, and  $\omega$  the frequency of the eigen-oscillation multiplied by  $2\pi$ . If we now use the energy  $E$ , equation (6) may be written

$$\frac{d\varphi}{dt} = \frac{dE}{d(E/\omega)} = \frac{\partial H}{\partial p}, \quad (7)$$

where  $H = E$  is the Hamiltonian and

$$p = \frac{E}{\omega} \quad (8)$$

must be regarded as the momentum corresponding to the co-ordinate  $\varphi$ ; the second Hamiltonian equation gives an identity in consequence of the relation  $dE/dt = 0$ .

In order now to derive Schrödinger's equation, we use the operator method. From

$$\omega p - E = 0$$

we have

$$\frac{\hbar}{i} \omega \frac{\partial \psi}{\partial \varphi} + \frac{\hbar}{i} \frac{\partial \psi}{\partial t} = 0$$

† Here I follow the ideas of Dirac<sup>3</sup>. The introduction of light quanta is, however, arbitrary and not necessary.

or

$$\omega \frac{\partial \psi}{\partial \varphi} + \frac{\partial \psi}{\partial t} = 0. \quad (9)$$

Since  $\varphi$  is a cyclic co-ordinate, the permissible solutions of (9) must have the period  $2\pi$ ; the quantity  $E$ , being the energy, must be positive for every combination of such solutions. Separation of the variables gives

$$\psi_r = \frac{1}{\sqrt{2\pi}} e^{i r(\varphi - \omega t)}, \quad (10)$$

where  $r$  is a constant which, by the first condition, takes only integral values. The energy is

$$E_r = r \hbar \omega, \quad (11)$$

and  $r$  must therefore be positive †. We shall also use the quantities  $e^{i\varphi}$  and  $e^{-i\varphi}$ ; in the matrices corresponding to them, all elements are zero except

$$|e^{i\varphi}|_{r, r-1} = e^{i\omega t} \quad \text{and} \quad |e^{-i\varphi}|_{r-1, r} = e^{-i\omega t}. \quad (12)$$

### 3. DAMPING IN ATOMIC STRUCTURES

In view of the results of section 2 the methods of ordinary perturbation theory are applicable here, since the damping phenomena are caused by the reaction of the atomic radiation field.

The perturbation function is known to be

$$\eta = (\mathbf{C} \cdot \mathbf{E}), \quad (13)$$

where  $\mathbf{C}$  denotes the polarisation vector and  $\mathbf{E}$  the electric force at the centre of the atom. The latter can be represented as a sum of electric forces corresponding to the individual eigen-oscillations:

$$\mathbf{E} = \sum_x \mathbf{E}_x, \quad \eta = (\mathbf{C} \cdot \sum_x \mathbf{E}_x). \quad (14)$$

If we take the centre as the point which determines the phase, then

$$\mathbf{E}_x = \mathbf{e}_x \cos \varphi_x, \quad (15)$$

with  $\mathbf{e}_x$  independent of time. The total energy of an eigen-oscillation is ‡

$$E_x = \int \frac{1}{8\pi} \overline{(\mathbf{E}_x^2 + \mathbf{H}_x^2)} dV = \int \frac{1}{4\pi} \overline{\mathbf{E}_x^2} dV = \int \frac{1}{4\pi} \mathbf{e}_x^2 \overline{\cos^2 \varphi_x} dV = \frac{1}{8\pi} \int \mathbf{e}_x^2 dV, \quad (16)$$

and the space average of  $\mathbf{e}_x^2$  is given by

$$E_x = \frac{1}{8\pi} V \overline{\mathbf{e}_x^2}, \quad \overline{\mathbf{e}_x^2} = 8\pi \frac{E_x}{V},$$

† From equation (11) Planck's radiation formula can be obtained by direct application of Planck statistics (see also ref. 4).

‡ Here we average over the time.

so that

$$\mathbf{e}_x = \sqrt{8\pi \frac{E_x}{V}} \mathbf{n}_x, \quad (17)$$

where  $\mathbf{n}_x$  depends only on the position of the centre and satisfies the condition

$$\overline{\mathbf{n}_x^2} = 1. \quad (18)$$

Substitution of (17) in (15) gives

$$\mathbf{E}_x = \sqrt{8\pi \frac{E_x}{V}} \cos \varphi_x \mathbf{n}_x. \quad (19)$$

If now we regard  $E_x$  and  $\cos \varphi_x$  as matrices,  $\eta$  and therefore  $\mathbf{E}_x$  must be symmetrised:

$$\mathbf{E}_x = \sqrt{\frac{2\pi}{V}} (\sqrt{E_x} e^{i\varphi_x} + e^{-i\varphi_x} \sqrt{E_x}) \mathbf{n}_x \quad (20)$$

According to general perturbation theory, the coefficients  $c_N$  in  $\varphi = \sum c_N \varphi_N$  are such that

$$\frac{dc_N}{dt} = \frac{i}{\hbar} \sum_M \eta_{NM} c_M. \quad (21)$$

If we use radiation quantum numbers  $r_x$  as well as the atomic quantum numbers  $n(m, k, \dots)$ , we have in our case from (14) and (19), and (11) and (12),

$$\begin{aligned} \frac{d}{dt} c(r_x, n) = i \sum_y \sum_m \left\{ c(r_x - \delta_{xy}, m) \sqrt{\frac{2\pi r_y \omega_y}{\hbar V}} e^{i\omega_y t} \right. \\ \left. + c(r_x + \delta_{xy}, m) \sqrt{\frac{2\pi (r_y + 1) \omega_y}{\hbar V}} e^{-i\omega_y t} \right\} (\mathbf{n}_y \cdot \mathbf{C}_{nm}), \quad (22) \end{aligned}$$

where

$$\begin{aligned} \delta_{xy} &= 0 \quad \text{for } x \neq y, \\ &= 1 \quad \text{for } x = y. \end{aligned}$$

For simplicity we take as the initial state a "state" of the atom determined in the usual way (see section 1); the final formulae can be immediately applied to the general case. Since the previously emitted field has no effect on the atom, we also suppose that no radiation field is present at the initial instant. Then all the coefficients  $c$  except the  $c(0, n)$  are zero. At the next instant the  $c(\delta_{xy}, n)$  must be brought in, since (22) shows that only they have a non-zero time derivative:

$$\left. \begin{aligned} \frac{d}{dt} c(\delta_{xy}, n) &= i \sqrt{\frac{2\pi \omega_y}{\hbar V}} e^{i\omega_y t} \sum_m c(0, m) (\mathbf{n}_y \cdot \mathbf{C}_{nm}), \\ \frac{d}{dt} c(0, n) &= i \sum_y \sum_m c(\delta_{xy}, m) \sqrt{\frac{2\pi \omega_y}{\hbar V}} e^{-i\omega_y t} (\mathbf{n}_y \cdot \mathbf{C}_{nm}). \end{aligned} \right\} \quad (23)$$

The state of the atom is described, according to (4), by the quantities

$$\alpha_{nm} = c^*(0, n) c(0, m) + \sum_y c^*(\delta_{xy}, n) c(\delta_{xy}, m). \quad (24)$$

The time derivative of  $\alpha_{nm}$  is

$$\begin{aligned} \frac{d\alpha_{nm}}{dt} = & i \sum_k \sum_y \left\{ c^*(0, n) c(\delta_{xy}, k) \sqrt{\frac{2\pi\omega_y}{\hbar V}} e^{-i\omega_y t} (\mathbf{n}_y \cdot \mathbf{C}_{mk}) \right. \\ & - c^*(\delta_{xy}, k) c(0, m) \sqrt{\frac{2\pi\omega_y}{\hbar V}} e^{i\omega_y t} (\mathbf{n}_y \cdot \mathbf{C}_{kn}) \\ & + c^*(\delta_{xy}, n) c(0, k) \sqrt{\frac{2\pi\omega_y}{\hbar V}} e^{i\omega_y t} (\mathbf{n}_y \cdot \mathbf{C}_{mk}) \\ & \left. - c^*(0, k) c(\delta_{xy}, m) \sqrt{\frac{2\pi\omega_y}{\hbar V}} e^{-i\omega_y t} (\mathbf{n}_y \cdot \mathbf{C}_{kn}) \right\}. \quad (25) \end{aligned}$$

If we substitute directly in (25) the initial conditions  $c_0(\delta_{xy}, n) = 0$ , we arrive at the absurd conclusion that  $d\alpha_{nm}/dt = 0$ . The reason for this is evidently that the infinite frequency sums  $\sum_y$  are divergent. In order to obtain a more plausible result, we apply (25) not to the initial instant but to a later instant  $T$ . In the same approximation we have

$$\left. \begin{aligned} c(\delta_{xy}, n) &= i \sqrt{\frac{2\pi\omega_y}{\hbar V}} \sum_m c_0(0, m) \int_0^T (\mathbf{n}_y \cdot \mathbf{C}_{nm}) e^{i\omega_y t} dt, \\ c(0, n) &= c_0(0, n), \end{aligned} \right\} \quad (26)$$

and so, using the relation  $\alpha_{nm}^0 = c_0^*(0, n) c_0(0, m)$ ,

$$\begin{aligned} \frac{d\alpha_{nm}}{dt} = & \sum_k \sum_e \sum_y \frac{2\pi\omega_y}{\hbar V} \left\{ -\alpha_{ne}^{(0)} (\mathbf{n}_y \cdot \mathbf{C}_{mk}) e^{-i\omega_y T} \int_0^T (\mathbf{n}_y \cdot \mathbf{C}_{ke}) e^{i\omega_y t} dt \right. \\ & - \alpha_{em}^{(0)} (\mathbf{n}_y \cdot \mathbf{C}_{kn}) e^{i\omega_y T} \int_0^T (\mathbf{n}_y \cdot \mathbf{C}_{ek}) e^{-i\omega_y t} dt \\ & + \alpha_{ek}^{(0)} (\mathbf{n}_y \cdot \mathbf{C}_{mk}) e^{i\omega_y T} \int_0^T (\mathbf{n}_y \cdot \mathbf{C}_{en}) e^{-i\omega_y t} dt \\ & \left. + \alpha_{ke}^{(0)} (\mathbf{n}_y \cdot \mathbf{C}_{kn}) e^{-i\omega_y T} \int_0^T (\mathbf{n}_y \cdot \mathbf{C}_{me}) e^{i\omega_y t} dt \right\}. \quad (27) \end{aligned}$$

Since the volume  $V$  is regarded as infinite, the frequency sums can be replaced by integrals. The number of eigen-oscillations between  $\omega$  and  $\omega + d\omega$  is known to be

$$N_\omega d\omega = V \frac{\omega^2}{\pi^2 c^3} d\omega. \quad (28)$$

Instead of each expression of the type  $(\mathbf{n} \cdot \mathbf{A})(\mathbf{n} \cdot \mathbf{B})$  we must put

$$\frac{1}{3} (\mathbf{A} \cdot \mathbf{B}) \quad (29)$$

in consequence of the averaging, having regard to (18). Equation (27) may therefore be written

$$\begin{aligned} \frac{d\alpha_{nm}}{dt} = & \sum_k \sum_e \int_0^\infty \left\{ \alpha_{ek}^{(0)} \left( \mathbf{C}_{mk} e^{i\omega T} \cdot \int_0^T \mathbf{C}_{en} \right) e^{i\omega t} dt \right. \\ & + \alpha_{ke}^{(0)} \left( \mathbf{C}_{kn} e^{-i\omega T} \cdot \int_0^T \mathbf{C}_{me} \right) e^{i\omega t} dt \\ & - \alpha_{ne}^{(0)} \left( \mathbf{C}_{mk} e^{-i\omega T} \cdot \int_0^T \mathbf{C}_{ke} \right) e^{i\omega t} dt \\ & \left. - \alpha_{em}^{(0)} \left( \mathbf{C}_{kn} e^{i\omega T} \cdot \int_0^T \mathbf{C}_{ek} \right) e^{-i\omega t} dt \right\} \frac{2\omega^3}{\pi \hbar c^3} d\omega. \quad (30) \end{aligned}$$

A number of considerations which will not be given here show that the double integrals occurring in this formula (which are divergent) must be independent of the upper limit  $T$ . If we raise the latter to infinity, apply the theory of the Fourier integral, and return to the initial instant, the result is

$$\begin{aligned} \frac{d\alpha_{nm}}{dt} = & \sum_k \sum_e \frac{2i}{3\hbar c^3} \left\{ \alpha_{ek} \left( \mathbf{C}_{mk} \cdot \frac{d^3}{dt^3} \mathbf{C}_{en}^+ \right) - \alpha_{ke} \left( \mathbf{C}_{kn} \cdot \frac{d^3}{dt^3} \mathbf{C}_{me}^- \right) \right. \\ & \left. + \alpha_{ne} \left( \mathbf{C}_{mk} \cdot \frac{d^3}{dt^3} \mathbf{C}_{ke}^- \right) - \alpha_{em} \left( \mathbf{C}_{kn} \cdot \frac{d^3}{dt^3} \mathbf{C}_{ek}^+ \right) \right\} \end{aligned}$$

or

$$\begin{aligned} \frac{d\alpha_{nm}}{dt} = & \sum_k \sum_e \frac{2i}{3\hbar c^3} \left\{ \alpha_{ke} \left( \mathbf{C}_{me} \cdot \frac{d^3}{dt^3} \mathbf{C}_{kn}^+ \right) - \left( \mathbf{C}_{kn} \cdot \frac{d^3}{dt^3} \mathbf{C}_{me}^- \right) \right. \\ & \left. + \alpha_{nk} \left( \mathbf{C}_{me} \cdot \frac{d^3}{dt^3} \mathbf{C}_{ek}^- \right) - \alpha_{em} \left( \mathbf{C}_{kn} \cdot \frac{d^3}{dt^3} \mathbf{C}_{ek}^+ \right) \right\}; \quad (31) \end{aligned}$$

the signs + and - signify that only the part containing positive and negative frequencies respectively is taken. This is because the integration is only over positive  $\omega$ .

Formula (31) is of fundamental importance in the theory of damping phenomena. The quantities  $a_n$  cannot be used in this problem; the "state of the atom" must be described by means of the quantities  $\alpha_{nm}$ .

If the external influences on the atom are quasi-periodic, the quantities  $\alpha_{nm}$  change in a definite manner under the action of damping and tend (in the first approximation) asymptotically to definite values. The "state of the atom" corresponding to such values of  $\alpha_{nm}$  will be called the *zero state*. In some cases there are several such states, of which some may be metastable.

For any quantity  $f$  with matrix  $f_{nm}$  we obtain from (4b)

$$\begin{aligned} \frac{d\tilde{f}}{dt} &= \frac{d}{dt} \sum_n \sum_m \alpha_{nm} f_{nm} = \sum_n \sum_m \left( \alpha_{nm} \frac{df_{nm}}{dt} + \frac{d\alpha_{nm}}{dt} f_{nm} \right) \\ &= \frac{d_0 f}{dt} + \sum_n \sum_m \frac{d\alpha_{nm}}{dt} f_{nm}; \end{aligned} \quad (32)$$

$d_0 f/dt$  denotes the time derivative of  $f$  without allowance for damping. Substitution of (31), gives, in matrix notation,

$$\begin{aligned} \frac{d\hat{f}}{dt} &= \frac{d_0 \hat{f}}{dt} + \frac{2i}{3\hbar c^3} \left[ \left( \frac{d^3 \hat{C}^+}{dt^3} \cdot \hat{f} \hat{C} \right) - \left( \hat{C} f \cdot \frac{d^3 \hat{C}^-}{dt^3} \right) \right. \\ &\quad \left. + \left( \hat{f} \hat{C} \cdot \frac{d^3 \hat{C}^-}{dt^3} \right) - \left( \frac{d^3 \hat{C}^+}{dt^3} \cdot \hat{C} f \right) \right] \\ &= \frac{d^0 \hat{f}}{dt} + \frac{2}{3c^3} \left[ \left( \frac{d^3 \hat{C}^+}{dt^3} \cdot \hat{F} \right) + \left( \hat{F} \cdot \frac{d^3 \hat{C}^-}{dt^3} \right) \right], \end{aligned} \quad (33)$$

where  $\hat{f} \hat{C} - \hat{C} f = \frac{\hbar}{i} \hat{F}$ .

For  $f = \text{constant}$ , the damping term in (33) is zero, as we should expect. The same is true of any function of co-ordinates only, on account of the commutation relations. For an electron moment  $\mathbf{H}$  we have

$$\frac{d\hat{H}}{dt} = \frac{d_0 \hat{H}}{dt} - \frac{2e}{3c^3} \left( \frac{d^3 \hat{C}^+}{dt^3} + \frac{d^3 \hat{C}^-}{dt^3} \right) = \frac{d_0 \hat{H}}{dt} - \frac{2e}{3c^3} \frac{d^3 \hat{C}}{dt^3}, \quad (34)$$

where  $e$  is the electron charge. This equation agrees entirely with the classical theory. Since linear relations always appear in wave mechanics unchanged, this conclusion can be used to justify (31). If  $f$  is taken as the energy  $\varepsilon$  of the atomic system, then

$$\hat{F} = \frac{d\hat{C}}{dt},$$

$$\frac{d\hat{\varepsilon}}{dt} = \frac{2}{3c^3} \left[ \left( \frac{d^3 \hat{C}^+}{dt^3} \cdot \frac{d\hat{C}}{dt} \right) + \left( \frac{d\hat{C}}{dt} \cdot \frac{d^3 \hat{C}^-}{dt^3} \right) \right]. \quad (35)$$

In order to derive from this formula an expression for the energy radiated, we follow the classical theory; elimination of a complete derivative gives

$$\hat{J} = -\frac{d\hat{E}}{dt} = \frac{2}{3c^3} \left[ \left( \frac{d^2\hat{C}^+}{dt^2} \cdot \frac{d^2\hat{C}}{dt^2} \right) + \left( \frac{d^2\hat{C}}{dt^2} \cdot \frac{d^2\hat{C}^-}{dt^2} \right) \right]. \quad (36)$$

This formula is of importance not only in damping theory but also in the wave mechanics representation of the radiation intensity, which can not be derived from the expression for the "mean" field (in the sense of the comment following equation (5)).†

In the continuous "spectrum" the sums in (31) must be replaced by integrals.

#### 4. SOME PARTICULAR APPLICATIONS

Let us now apply the above results to systems which, apart from the damping, are conservative. In such systems, as we know, for any quantity  $f$  which does not depend explicitly on time,

$$f_{nm} = f^{nm} e^{i\omega_{nm}t}, \quad (37a)$$

$$\tilde{f} = \sum_n \sum_m \alpha_{nm} f_{nm} = \sum_n \sum_m \alpha_{nm} f^{nm} e^{i\omega_{nm}t}, \quad (37b)$$

where  $\omega_{nm} = (E_n - E_m)/\hbar$  and the  $f^{nm}$  are independent of time.

In order to obtain an expression for the intensity of spectral lines, we use formula (36):

$$\left. \begin{aligned} J^{nm} &= \frac{2}{3c^3} \sum_k^{E_k < E_n} \omega_{nk}^2 \omega_{km}^2 (C^{nk} \cdot C^{kn}) + \sum_k^{E_k < E_m} \omega_{nk}^2 \omega_{km}^2 (C^{nk} \cdot C^{km}) \\ \tilde{J} &= \sum_n \sum_m a_n^* a_m J^{nm} e^{i\omega_{nm}t} \end{aligned} \right\} \quad (38)$$

or, after averaging over time,

$$\bar{J} = \sum_n |a_n|^2 J^{nm} = \sum_n \sum_k^{E_n < E_k} \frac{2}{3c^3} \omega_{nk}^4 |C_{n\mathbf{k}}|^2 |a_n|^2. \quad (39)$$

Each term in this formula is to be regarded as the intensity of the radiation of the corresponding frequency. The characteristic properties of intensity (including, of course, polarisation etc.) of a spectral line thus correspond entirely to the amplitude coefficient of the radiation field (matrix component of  $d^2C/dt^2$ ). In addition, the intensity of radiation for a frequency  $\omega_{nk}$  is, as we should expect, proportional to the quantity  $|a_n|^2$  or, in the usual terminology, to the number of atoms in the initial state (the state with the higher energy value).

† The expression for the square of a quantity is, in wave mechanics, not equal to the square of the expression for that quantity; the quantities  $a_n$  must always appear homogeneously in the second degree. The results of Joos<sup>5</sup> are therefore unsatisfactory.

In order to analyse the damping process, we use the basic formula (31):

$$\begin{aligned}
 \frac{d\alpha_{nm}}{dt} &= \sum_k \sum_e^{E_k > E_n} \frac{2\omega_{kn}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{me}) e^{i(\omega_{ke} + \omega_{mn})t} \alpha_{ke} \\
 &+ \sum_k \sum_e^{E_e > E_m} \frac{2\omega_{em}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{me}) e^{i(\omega_{ke} + \omega_{mn})t} \alpha_{ke} \\
 &- \sum_k \sum_e^{E_k > E_e} \frac{2\omega_{ke}^3}{3\hbar c^3} (\mathbf{C}^{me} \cdot \mathbf{C}^{ek}) e^{i\omega_{mk}t} \alpha_{nk} \\
 &- \sum_k \sum_e^{E_k < E_e} \frac{2\omega_{ek}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{ek}) e^{i\omega_{en}t} \alpha_{em}, \tag{40a}
 \end{aligned}$$

and for  $m = n$

$$\begin{aligned}
 \frac{d\alpha_{nn}}{dt} &= \sum_k \sum_e^{E_k > E_n} \frac{2\omega_{kn}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{ne}) e^{i\omega_{ke}t} \alpha_{ke} \\
 &+ \sum_k \sum_e^{E_e > E_n} \frac{2\omega_{en}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{ne}) e^{i\omega_{ke}t} \alpha_{ke} \\
 &- \sum_k \sum_e^{E_k > E_e} \frac{2\omega_{ke}^3}{3\hbar c^3} (\mathbf{C}^{ne} \cdot \mathbf{C}^{ek}) e^{i\omega_{nk}t} \alpha_{nk} \\
 &- \sum_k \sum_e^{E_k < E_e} \frac{2\omega_{ek}^3}{3\hbar c^3} (\mathbf{C}^{kn} \cdot \mathbf{C}^{ek}) e^{i\omega_{en}t} \alpha_{en}. \tag{40b}
 \end{aligned}$$

If all the frequencies  $\omega_{nm}$  are different †, averaging over time gives

$$\overline{\frac{d\alpha_{nm}}{dt}} = - \left\{ \sum_e^{E_m > E_e} \frac{2\omega_{me}^3}{\hbar c^3} |\mathbf{C}^{me}|^2 + \sum_k^{E_n > E_k} \frac{2\omega_{nk}^3}{3\hbar c^3} |\mathbf{C}^{nk}|^2 \right\} \alpha_{nm}, \tag{41a}$$

$$\overline{\frac{d\alpha_{nn}}{dt}} = \sum_k^{E_k < E_n} \frac{4\omega_{kn}^3}{3\hbar c^3} |\mathbf{C}^{kn}|^2 \alpha_{kk} - \alpha_{nn} \sum_k^{E_k < E_n} \frac{4\omega_{nk}^3}{3\hbar c^3} |\mathbf{C}^{nk}|^2. \tag{41b}$$

The latter formula also follows from elementary arguments ( $\alpha_{nm}$  corresponds to the quantity  $|a_n|^2$ ). The relation

$$J(\omega_{nm}) = |a_n|^2 A_{nm} \hbar \omega_{nm},$$

where

$$A_{nm} = \frac{4\omega_{nm}^3}{3\hbar c^3} |\mathbf{C}^{nm}|^2 \tag{42}$$

is the Einstein transition probability for spontaneous emission, is also in agreement with this. The time spent in the  $n$ th state is given from (41 b) as

$$\frac{1}{\tau_n} = \sum_k^{E_k < E_n} A_{nk}. \tag{43}$$

† The majority of the following results are valid also for ordinary cases of eigenvalue degeneracy (directional degeneracy, the many-body problem).

The state of minimum energy (the ground state of the atom) here evidently represents the zero state. States of higher energy which show no transitions to the zero state are, of course, only metastable; a further approximation in equation (31) gives the corresponding time for these states also.

Equation (40a) shows that the quantities  $a_{nm}$  always decrease on average in the course of time. The reason is that the intensity of the radiation behaves quite differently according to (39) and (41b), evidently, in the increasing uncertainty of the phase, which causes a reduced coherence of the radiation.† The “duration” of coherence  $\tau_{nm}$  is given by equation (41a) as

$$\frac{1}{\tau_{nm}} = \lambda_{nm} = \frac{1}{2} \left( \frac{1}{\tau_n} + \frac{1}{\tau_m} \right). \quad (44)$$

Instead of the quantities  $\alpha_{nm}$  which correspond to the unperturbed system and are now functions of time, we can also use quantities independent of time:

$$\tilde{f} = \sum_n \sum_m \alpha'_{nm} f'_{nm}, \quad (45)$$

where  $\alpha'_{nm}$  are the arbitrary constants. If new quantities

$$\gamma_{nm} = \alpha_{nm} e^{i\omega_{nm}t} \quad (46)$$

are introduced in order to eliminate the time from (37), then (40) becomes

$$\begin{aligned} \frac{d\gamma_{nm}}{dt} = i\omega_{nm}\gamma_{nm} &+ \sum_k \sum_e^{E_k > E_n} \frac{2\omega_{kn}^3}{3\hbar c^3} (C^{kn} \cdot C^{me}) \gamma_{ke} \\ &+ \sum_k \sum_e^{E_e > E_m} \frac{2\omega_{em}^3}{3\hbar c^3} (C^{kn} \cdot C^{me}) \gamma_{ke} \\ &- \sum_k \sum_e^{E_k > E_e} \frac{2\omega_{ke}^3}{3\hbar c^3} (C^{me} \cdot C^{ek}) \gamma_{nk} \\ &- \sum_k \sum_e^{E_k < E_e} \frac{2\omega_{ek}^3}{3\hbar c^3} (C^{kn} \cdot C^{ek}) \gamma_{km}. \end{aligned} \quad (47)$$

Exponential solutions of this linear differential equation with constant coefficients correspond to certain relations between the  $\gamma$  and therefore also certain expressions  $f'_{nm}$  for  $\tilde{f}$ . In the first approximation we have, with  $f'^{nm}$  a constant,

$$\left. \begin{aligned} f'_{nm} &= e^{(i\omega_{nm} - \lambda_{nm})t} f'^{nm} = e^{[i(E_n - E_m) - j_n - j_m]t/\hbar} f'^{nm}, \\ \text{where} \quad j_n &= \frac{1}{2} \hbar \sum_k^{E_k < E_n} A_{nk} = \sum_k^{E_k < E_n} \frac{2\omega_{nk}^3}{3c^3} |C^{nk}|^2. \end{aligned} \right\} \quad (48)$$

† This phenomenon is only partly related to the damping process; the agency which keeps the emission in a steady state (e.g. black-body radiation, optical excitation, etc.) also causes a perturbation of coherence.

The quantities  $f'^{nm}$  are evidently linear combinations of the  $f^{nm}$ . They can easily be derived from equation (46). For the zero state we evidently have

$$f'^{00} = f^{00} \quad (49)$$

and

$$\alpha'_{00} = 1, \quad (50)$$

replacing the usual condition  $\sum_n \alpha_{nm} = 1$ .

For the line width (to which the preceding remark applies also) we find

$$\Delta \omega_{nm} = \pi \lambda_{nm} = \frac{1}{\hbar} (\pi j_n + \pi j_m), \quad (51)$$

and so we can define a "term width"  $\Delta E_n = \pi j_n$ .

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