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RADIATION DAMPING AND RADIATIVE SHIFTS
AS RELAXATION PROCESSES

BY
RAMZI A. RIHAN

Submitted in partial fulfillment of the requirements for the
degree of Master of Science at the American University of Beirut.

Beirut, Lebanon

18 May, 1964.

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A B S T R A C T

The formulation of relaxation theory developed by Fano is reviewed and then generalized to the case of a system interacting simultaneously with two thermal baths. When one of the baths is the vacuum electromagnetic field, this generalization permits the natural linewidth of the spectrum of the system to be taken into account in the study of various relaxation processes. The formalism is applied to the investigation of the interaction of an atomic system with electromagnetic radiation. The interaction with the vacuum field is found to result in spontaneous decay and in the Lamb shift. The interaction with an actual radiation field leads to stimulated emission and to a shift of the spectral frequencies of the atom; our results for both of these effects differ from previous results because of the inclusion of the natural linewidth, but reduce to them when this correction is ignored. The calculations are undertaken in the dipole approximation, and are carried out to second order in the interaction.

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I. INTRODUCTION

The accurate measurements of atomic spectra made possible by combined optical and radio-frequency techniques, such as those pioneered by W. E. Lamb and his coworkers, have encouraged theoretical investigation of radiation damping and radiative shifts. More recently, the advent of powerful and highly monochromatic light sources (lasers) in the optical region has given added impetus to these studies. The present work is an application of relaxation theory to the study of these phenomena. The formulation of relaxation theory adopted here was recently developed by Zwanzig¹ and Fano², and was applied by the latter author to the study of pressure broadening.

The work of Fano suggested that the techniques of relaxation theory might be profitably applied towards a systematic study of radiation damping and radiative shifts. The major motivation of the present paper was the corroboration of this conjecture. We have found that this new approach does indeed permit a unified treatment of these effects of the interaction of an atomic system with the electromagnetic field.

Part II is essentially a review of Fano's presentation of relaxation theory. However, we also discuss a modification of the theory that takes into account the natural lifetime of the atom. This modification is relevant to the study of all 'induced' effects, such as pressure broadening or stimulated emission.

¹ Robert Zwanzig, J. Chem. Phys. 33, 1338 (1960).
² U. Fano, Phys. Rev. 131, 259 (1963).

Part III summarizes the needed results from non-relativistic quantum electrodynamics. For a more complete presentation of the subject, the reader is referred to the standard works in the field.³

In Part IV the interaction of an atom with the vacuum radiation field is treated. The well-known expressions for the natural linewidth and the transverse self-energy contribution to the Lamb shift are derived.

In Part V the interaction of an atom with an 'actual' electromagnetic field is considered. Expressions for the rate of stimulated emission (Einstein B coefficient) and the radiative shift are obtained. Our results differ from previous results because of the inclusion of the natural linewidth that was mentioned above, but reduce to them when this correction is neglected.

³ For example, W. Heitler, The Quantum Theory of Radiation, 3rd ed., Oxford University Press, Oxford, 1954.

II. RELAXATION THEORY

1- General Considerations

The problem that we propose to consider may be stated as follows. A system, in which one is interested, is surrounded by a thermal bath. The interaction between these two components, which results in an approach to thermodynamic equilibrium, affects the system of interest, notably by perturbing its energy levels and by producing transitions between these levels. Information about these effects is sought.

The complete solution of the equation of motion of the total system⁴ presents one with a many-body problem, which is a forbidding task.⁵ Hence, one attempts to circumvent the need for a complete solution of the problem and endeavours to obtain the required information by other methods. The method adopted here employs the density matrix formulation of quantum statistical mechanics.⁶ It results in an exact equation describing the time-development of the system if the initial state of the total system satisfies certain conditions. The exact solution of this equation, the so-called master or kinetic equation, can be written down formally. However, for the purpose of explicit calculations, it is frequently necessary to resort to approximate

⁴ 'Total system' will henceforth indicate the system of interest plus the thermal bath; the system of interest will be frequently referred to simply as 'the system'.

⁵ For a recent treatment of the (classical) many-body problem, see D. Bohm and G. Carmi, Phys. Rev. 133, A319, A332 (1964). This work is an interesting contrast to the present approach.

⁶ U. Fano, Rev. Mod. Phys. 29, 74 (1957).

solution. The nature of the requisite approximations will be discussed and the range of their validity indicated. Finally, the application of the theory to the problems of radiation damping and radiative shifts is considered.

2- The Liouville Representation

In the density matrix formalism the time-development of a system is described non-relativistically by the equation

$$i\dot{\rho} = [H, \rho] \quad , \quad (1)$$

where $\rho(t)$ is the density matrix of the system and H its hamiltonian operator. It will be convenient to represent the right hand side of this equation as the result of a linear operator L acting on ρ ,

$$L\rho = [H, \rho] \quad . \quad (2)$$

The operator L thus defined is called the Liouville operator of the system.

When the state of the system is expressed in terms of the eigenstates of a complete set of compatible observables, the operators are represented by matrices. The elements of the product $L\rho$ are then

$$(L\rho)_{ab} = \sum_{cd} L_{ab,cd} \rho_{cd} \quad (3)$$

From this equation and the preceding one, the elements of L are found to be

$$L_{ab,cd} = H_{ac} \delta_{bd} - H_{bd}^* \delta_{ac} \quad (4)$$

Mathematically, L is a supermatrix. Supermatrices bear the same relation to matrices that the latter bear to vectors. Alternatively, the matrix elements of ρ may be considered as being the components of a vector;

* ρ and ω will be used in the written text to indicate ρ and ω .

according to this interpretation, L is an ordinary matrix that acts on this vector.

In a representation in which the hamiltonian is diagonal with the eigenvalues w_a , Eq.(4) becomes

$$L_{ab,cd} = w_{ab} \delta_{ac} \delta_{bd} , \quad (4')$$

$$w_{ab} = w_a - w_b . \quad (5)$$

The L operator involves energy differences only.

For an isolated system, H is independent of the time and Eq.(1) can be integrated immediately, thus:

$$\rho(t) = e^{-iLt} \rho(0) \quad (6)$$

Where the operator function may be interpreted by its power series expansion. More generally, when H depends upon the time, the formal solution of (1) can be written

$$\rho(t) = T e^{-i \int_0^t L(t') dt'} \rho(0) \quad (7)$$

where T is the Dyson time-ordering operator.⁷

In the situations that arise in the study of relaxation processes, the total system is decomposable into two interacting components: the system of interest, and a thermal bath. The total hamiltonian takes the form

$$H = H_0^{(s)} + H_0^{(b)} + H' = H_0 + H' \quad (8)$$

where $H_0^{(s)}$ and $H_0^{(b)}$ pertain to the non-interacting system and bath

⁷ F. J. Dyson, Phys. Rev. 75, 486 (1949). See also: G. C. Wick, Phys. Rev. 80, 268 (1950).

respectively, while H' represents the interaction between them. Since the total system is isolated, H and H' are independent of the time.

L is seen to split similarly

$$L = L_0^{(s)} + L_0^{(b)} + L' = L_0 + L' \quad (9)$$

A state of the total system is characterized by two sets of quantum numbers, one referring to the system and the other to the bath. System states will be labelled by a, b, \dots and bath states by m, n, \dots . Elements of the density matrix thus have the form $\rho_{am, bn}$. From this total density matrix a system density matrix can be extracted by taking the trace over the bath indices, viz.

$$\rho^{(s)} = \text{Tr}_b \rho \quad (10)$$

$$\rho_{ab}^{(s)} = \sum_m \rho_{am, bm} \quad (10')$$

$\rho^{(s)}$ gives the information about the system only that is contained in ρ . It is sufficient for the calculation of averages involving system variables only.

We adopt a representation in which H_0 is diagonal. L_0 is also diagonal, with matrix elements

$$(L_0)_{am, bn; a'm', b'n'} = (\omega_{ab} + \omega_{mn}) \delta_{aa'} \delta_{bb'} \delta_{mm'} \delta_{nn'} \quad (11)$$

3- Derivation of the Kinetic Equation

To obtain the kinetic equation which describes the time-development of the system of interest, we introduce the Fourier

transform of $p(t)$:⁸

$$\rho(\omega) = \int_0^{\infty} e^{i\omega t} \rho(t) dt. \quad (12)$$

For convergence purposes, ω is to be considered as a complex variable with a positive imaginary part; the limit $\text{Im } \omega \rightarrow 0$ is to be ultimately taken.

The transform of Eq.(6) is

$$L\rho(\omega) = (\omega - L)^{-1} \rho(0). \quad (13)$$

The factor $(\omega - L)^{-1}$, which is the resolvent operator in the Liouville representation, contains the interaction dynamics entangled with the non-interaction part; furthermore, it is the inverse of a matrix which is, in interesting cases, nondiagonal. The manipulation of the resolvent operator is facilitated by means of the identity

$$(\omega - L)^{-1} = (\omega - L_0)^{-1} [1 + M(\omega)(\omega - L_0)^{-1}], \quad (14)$$

$$M(\omega) = L' \sum_{h=0}^{\infty} [(\omega - L_0)^{-1} L']^h, \quad (14')$$

which is simply the generalization of

$$(a-b)^{-1} = a^{-1} \sum_{n=0}^{\infty} (a^{-1}b)^n$$

when a and b do not commute. Note that now only the inverse of the diagonal matrix $(\omega - L_0)$ occurs. Moreover, the interaction dynamics, given by the operator $M(\omega)$, are disentangled from the total resolvent.

⁸ Zwanzig, in reference 1, obtains the kinetic equation by a method that does not utilize this step. His derivation is essentially the Fourier transform of the present approach.

The Fourier transform of $p^{(s)}(t)$ is found by taking the trace over the bath indices in Eq.(13). It is advisable, at this point, to introduce the explicit form of the initial total density matrix, which shall be taken to be

$$\rho(0) = \rho^{(s)}(0) \rho^{(b)}(0) ; \quad (15)$$

$$\rho_{mn}^{(b)}(0) = f_m \delta_{mn} . \quad (15')$$

The decomposability of $p(0)$ into a product of a system part and a bath part implies correlations between the states of the system and the bath are discarded at an initial time. Condition (15') means that $p^{(b)}(0)$ is stationary with respect to $H_0^{(b)}$. A discussion of the feasibility of the exact realization of these conditions in practice would involve a detailed analysis of statistical systems; it would not, however, lead to any results that are useful for the present purpose. The above conditions can be looked upon simply as resulting from an initial 'preparation' of the total system. Such a preparation is arbitrary, as long as it is consistent with the laws of quantum mechanics. Needless to say, $p(t)$ will not, in general, satisfy these conditions for $t \neq 0$.

Returning now to our main purpose, we note that when Eq.(14) is substituted in Eq.(13), the factor $(w-L_0)^{-1}$ on the right reduces to $(w-L_0^s)^{-1}$ because $p^{(b)}(0)$ is diagonal. Moreover, when the trace over the bath indices is taken, the same factor on the left is affected in the same manner. Hence, taking Eq.(15) into account, Eq.(13) yields:

$$i \rho^{(s)}(w) = (w-L_0^{(s)})^{-1} [1 + \langle M(w) \rangle (w-L_0^{(s)})^{-1}] \rho^{(s)}(0) , \quad (16)$$

where

$$\langle M(\omega) \rangle = \text{Tr}_b [M(\omega) \rho^{(b)}(0)] \quad (17)$$

It should be noted that, although L_0 and L' are usually hermitian, the same is not true of either $M(\omega)$ or $\langle M(\omega) \rangle$. The reason for this is that the resolvent operators $(\omega - L)^{-1}$ are themselves non-hermitian (Eq. III 7). Moreover, $\langle M \rangle$ is a function of the system variables only; all dependence on the bath variables being eliminated by the trace operation.

Equation (16) thus contains the system variables only. Its Fourier transformation would give an equation for $p^{(s)}(t)$. Before that step is taken, however, the following point should be considered. The factor that multiplies $p^{(s)}(0)$ in Eq. (16) is seen, by comparison with the general equation (13), to play the part of the effective resolvent of the system. The perturbation of the system by its interaction with the bath can thus be better exhibited by seeking a new operator $N(\omega)$ that satisfies

$$(\omega - L_0^{(s)} - N(\omega))^{-1} = (\omega - L_0^{(s)})^{-1} [1 + \langle M(\omega) \rangle (\omega - L_0^{(s)})^{-1}] \quad (18)$$

$N(\omega)$ is a frequency-dependent relaxation operator and represents the change of the system Liouville operator by the interaction; this operator is the central quantity of the formalism. The above equation may be solved for $N(\omega)$, thus:

$$N(\omega) = \langle M(\omega) \rangle \sum_{n=0}^{\infty} [-(\omega - L_0^{(s)})^{-1} \langle M(\omega) \rangle]^n \quad (19)$$

$N(\omega)$ is not, in general, hermitian because $\langle M(\omega) \rangle$ is not hermitian.

When Eq.(18) is substituted in (16) and the Fourier transformation carried out, the result is⁹

$$i\dot{\rho}(t) = \int_0^{t+} T(t-s) \rho(s) ds, \quad (20)$$

$$T(x) = L_0 \delta(x) + \frac{1}{2\pi} \int_{-\infty}^{\infty} N(\omega) e^{-i\omega x} d\omega. \quad (21')$$

The upper limit on the integral indicates that the singularity of $T(x)$ at $x=0$ is to be included in the range of integration. Equation (20), together with the definitions (14'), (19) and (21'), is the fundamental result of the theory.

The kinetic equation (20) has a number of interesting features. The only assumptions involved in its derivation are : 1) the additivity of the hamiltonian, Eq.(8); and 2) the structure of the initial total density matrix, Eq.(15) and (15'). It is correct to general order in the perturbation since the expansions for M and N are exact. It is a closed equation for the system density matrix and give information about the system only, not the bath.

Perhaps the most significant feature of the kinetic equation is that it ascribes non-Markoffian behaviour to the system. This is evident from the convolution on the right hand side of the equation. The state of the system at any particular instant of time T is a functional of its states at all preceding instants t' , $0 \leq t' \leq t$, (and, obviously, of the initial state of the bath.) The physical significance of this can be

⁹ The superscript (s) on p and L_0 has been omitted since all quantities now refer to the system of interest, and no ambiguity is likely to result from this notational simplification.

seen as follows. The state of the system at any instant is determined by its state and the state of the bath at an infinitesimally preceding instant. But the state of the bath is, in turn, determined by its state and the state of the system at an infinitesimally preceding instant. This chain of causal dependence extends back in time to the initial instant $t=0$. Hence, the state of the system can be alternatively considered as being determined by its state at all previous times and by the initial state of the bath.

4- Zero Memory Approximation

The kinetic equation describes a Markoffian process whenever the bath adjusts itself instantaneously to the action of the system on it. Hence there would be no correlation between the state of the bath at any particular instant and the previous states of the system. The causal chain described in the preceding section is cut after the first link. From Eq.(21'), this is seen to correspond to the case where $N(w)$ is independent of its argument, i.e.

$$i\dot{\rho}(t) = (L_0 + N)\rho(t). \quad (22)$$

The solution of this equation is

$$\rho(t) = e^{-i(L_0 + N)t} \rho(0). \quad (23)$$

This expression has the general form of Eq.(6). It follows that the system is described by an effective Liouville operator

$$\mathcal{L} = L_0 + N. \quad (24)$$

If the operator \mathcal{L} is normal (i.e. if \mathcal{L} and \mathcal{L}^\dagger commute), it

can be diagonalized. From Eq.(4') it is clear that the eigenvalues can be identified with the perturbed spectrum of the system. Since L is not necessarily hermitian, its eigenvalues are, in general, complex. The perturbed spectral frequencies can thus be written as

$$\omega'_{ab} = \omega_{ab} + d_{ab} - i\gamma_{ab} \quad (25)$$

where d and γ are real. The quantity d gives the shift of the spectral line caused by the interaction, while γ is the width of the line. As is well known, a spectrum described by Eq. (25) is a sum of Lorentzian lines.

The following consideration is of some importance. The unperturbed spectrum of the system obeys the Ritz combination law, Eq.(5). The question naturally arises as to whether this is also true of the perturbed spectrum; that is, whether it is true that

$$\omega'_{ab} = \omega'_a - \omega'_b \quad (26)$$

$$\omega'_a = \omega_a + d_a - i\gamma_a \quad (26')$$

To pursue this issue further, we consider the expansion for the eigenvalues of L :

$$\omega'_{ab} = \omega_{ab} + N_{ab,ab} + \sum_{\substack{a' \neq a \\ b' \neq b}} \frac{N_{ab,a'b'} N_{a'b',ab}}{\omega_{ab} - \omega_{a'b'}} + \dots \quad (27)$$

The last term is of higher order than the second if

$$|N_{ab,a'b'}| \ll |\omega_{ab} - \omega_{a'b'}|; \quad a' \neq a, \quad b' \neq b. \quad (28)$$

This condition breaks down when the system possesses a group of degenerate or nearly degenerate lines. This situation will not be treated here. However, when condition (28) is satisfied, the lowest

approximation to the perturbation is

$$d_{ab} = \text{Re } N_{ab,ab}, \quad (29)$$

$$\gamma_{ab} = -\text{Im } N_{ab,ab}. \quad (29')$$

In this approximation, the combination principle holds if the diagonal elements of N can be represented by a single-index set n such that

$$N_{ab,ab} = n_a - n_b^*. \quad (30)$$

It has been found¹⁰ that, for pressure broadening, in which the relaxation mechanism is intermolecular collisions, Eq. (26) holds only in the second order approximation for the series expansion of N . It will be seen, in Part V of the present paper, that, if the natural line-width is not neglected, the combination principle does not hold for induced radiation damping even in the lowest approximation.

5- Short Memory Approximation

From a physical point of view, $N(w)$ must depend on w since the bath cannot adjust itself instantaneously. It is therefore desirable to investigate the case in which N may be said to be a slowly varying function of w . A method that suggests itself for the treatment of this problem is to expand the matrix elements of $N(w)$ in a Taylor series and retain the first two terms only:

$$N(w)_{ab,cd} = N(w_{ab,cd}^0)_{ab,cd} + \left. \frac{dN(w)_{ab,cd}}{dw} \right|_{w=w_{ab,cd}^0} (w - w_{ab,cd}^0). \quad (31)$$

¹⁰ M. Baranger, Phys. Rev. 111, 481,494 (1958); 112, 855 (1958). Also, reference 2.

We shall find it convenient to expand elements of the same column of N around the same point, that is, $w_{ab,cd}^0 = w_{cd,cd}^0$. The above equation thus becomes

$$N(w)_{ab,cd} = N(w_{cd,cd}^0)_{ab,cd} + \left. \frac{dN(w)}{dw} \right|_{w=w_{cd,cd}^0} (w - w_{cd,cd}^0), \quad (31')$$

which may be written in the matrix form

$$N(w) = N(w^0) + \left. \frac{dN(w)}{dw} \right|_{w=w^0} (w - w^0) \equiv N^0 + \Delta (w - w^0). \quad (31'')$$

The resolvent operator for the system is then

$$(w - L_0 - N)^{-1} = (1 - \Delta)^{-1} [w - (L_0 + N^0 - \Delta w^0) (1 - \Delta)^{-1}]^{-1}. \quad (32)$$

The Fourier transformation of Eq. (16) may now be carried out:

$$\rho(t) = (1 - \Delta)^{-1} \exp[-i(L_0 + N^0 - \Delta w^0)(1 - \Delta)^{-1}t] \rho(0). \quad (33)$$

This solution is surprising since it obviously fails for $t=0$. Qualitatively, the reason for this is that the approximation (31) is valid only for small values of $(w - w^0)$; consequently its transform is valid only for large values of t . (See note at end of text.)

A suitable choice for the diagonal elements of w^0 is L_0 ; hence we set

$$N^0_{ab,cd} = N(w_{cd})_{ab,cd}. \quad (34)$$

This choice is dictated by the following circumstance: if $N(w)$ is much less than L_0 , $p(w)$ is peaked around the region $w = L_0$. Thus the values of w that are nearly equal to L_0 are those that contribute most. It is also seen from the expansion of $N(w)$, Eq. (19), that the derivative of N may be expected to have a nearly minimal value at $w = L_0$; thus this value is a nearly optimal point for the approximation to the Taylor series.

With this choice of w_0 , Eq.(33) becomes

$$\rho(t) = (1-\Delta)^{-1} \exp[-i\{L_0 + N_0(1-\Delta)^{-1}\}t] \rho(0). \quad (33')$$

Taking into account that this solution is valid only to first order in Δ , we see that the effective Liouville operator of the system is approximately

$$\mathcal{L} \doteq L_0 + N_0(1+\Delta) \doteq L_0 + (1+\Delta)N_0. \quad (35)$$

The part $N_0\Delta$ represents the correction due to the variation of N with w . The correction to each term in the series expansion for N is of higher order than the term itself. Thus the 'derivative correction' $N_0\Delta$ does not contribute to lowest order.

The above equation may be said to give the best Markoffian approximation to the behaviour of the system. If the next term in the Taylor series is retained in Eq.(31) and the above procedure repeated, it is found impossible to derive a better Markoffian approximation than Eq.(35) because of the occurrence of a term in the resolvent that is quadratic in w . Hence, a Markoffian approximation is justified only if the first derivative of $N(w)$ at L_0 is small and the higher derivatives are negligible.

6- The Density Matrix - General Case

In this section we discuss the complete formal solution of the kinetic equation derived in Section 2. Such a thorough treatment is required when either the Markoffian approximation or condition (28)

are inapplicable. The kinetic equation is

$$i\dot{\rho}(t) = \int_0^{t+} T(t-s)\rho(s)ds, \quad (20)$$

$$T(x) = L_0 \delta(x) + \frac{1}{2\pi} \int_{-\infty}^{\infty} N(\omega) e^{-i\omega x} d\omega. \quad (21)$$

Equation (20) can be integrated once to give

$$\rho(t) = \rho(0) - i \int_0^t dt' \int_0^{t'+} ds T(t'-s)\rho(s). \quad (36)$$

Since the operator $T(x)$ occurs with non-negative argument only, it may be defined for negative arguments arbitrarily. The most suitable choice is

$$T(x) \equiv 0, \quad x < 0. \quad (37)$$

The upper limit on the integral over the variable s can now be replaced by infinity. This allows an interchange of the order of integration.

Equation (36) now becomes

$$\rho(t) = \rho(0) - i \int_0^{\infty} K(t,s)\rho(s)ds, \quad (38)$$

$$K(t,s) = \int_0^{t+} T(t'-s) dt', \quad t \geq s, \quad (38')$$

$$= 0, \quad t < s.$$

Equation (38) is a Fredholm integral equation of the second kind,¹¹ and has the general form of a scattering equation.¹²

¹¹ H. Margenau and G. M. Murphy, The Mathematics of Physics and Chemistry, D. Van Nostrand, N.Y., 1949. Chapter 14.

¹² P. A. M. Dirac, The Principles of Quantum Mechanics, Oxford University Press, Oxford, 4th ed., 1958; Section 49. Also: L. I. Schiff, Quantum Mechanics, McGraw-Hill, N.Y., 1955; Section 26.

The general formal solution of Eq.(38) is

$$\rho(t) = S(t) \rho(0) , \quad (39)$$

$$S(t) = 1 + \sum_{n=1}^{\infty} (-i)^n \int_0^t K_n(t,s) ds , \quad ii$$

$$K_1(t,s) = K(t,s) , \quad iii$$

$$K_n(t,s) = \int_0^{\infty} K(t,t') K_{n-1}(t',s) dt' . \quad iv$$

With the aid of the time-ordering operator T , the above solution may be written as

$$\rho(t) = \left(T e^{-i \int_0^t K(t,s) ds} \right) \rho(0) . \quad (40)$$

For a Markoffian process, the kernel is found to be

$$\begin{aligned} K(t,s) &= L_0 + N , \quad t \geq s , \\ &= 0 , \quad t < s . \end{aligned} \quad (41)$$

The solution (39) reduces, in this case, to

$$S(t) = e^{-i(L_0 + N)t} , \quad (42)$$

which agrees with the result of Section 4.

If, as usual, the relaxation interaction does not 'create' or 'annihilate' the system, the density matrix maintains a constant trace equal to unity at all times; hence

$$\text{Tr} [S(t) \rho(0)] = 1 . \quad (43)$$

This equation can be expressed as a condition on the time-development

operator $S(t)$ if the initial density matrix is chosen to correspond to a pure state of the system. This gives

$$\sum_b S_{bb,aa}(t) = 1 \quad (44)$$

In other words, S is a stochastic matrix. This feature can be shown to be a consequence of the fact that the interaction Liouville operator L' , being essentially a commutator, has a vanishing trace.

The matrix element $S_{bb,aa}(t)$ gives the probability of a transition from state a to state b in time t . Hence, the stochastic property of S merely asserts that the sum of the transition probabilities from any initial states into all states is one. It is interesting to note that a corresponding sum-over-rows rule cannot be derived. The derivation of such a rule would require that $p(t)$ be assumed to be a pure state. However, there is no guarantee that, starting from any initial state whatsoever, the system will ever be in a pure state at a later time. Thus the above assumption cannot be made. The lack of symmetry between the rows and columns of S is intimately connected with the irreversibility of the system.

7- Inclusion of the Natural Linewidth

In this section, a slight, but significant, modification of the theory outlined in the preceding sections will be discussed. This modification is relevant to all problems in which the system of interest has a finite natural lifetime and, consequently, a natural linewidth. Specifically, we shall have in mind the study of the broadening and shifting of atomic spectral lines by various relaxation mechanisms.

An isolated atom in an excited state is not stable; it decays because of its interaction with the vacuum electromagnetic field. This phenomenon, which can itself be treated as a relaxation process (Part IV), is always coexistent with any other relaxation mechanism that might also affect the atom. Hence the study of any relaxation process, other than spontaneous decay, necessarily entails the simultaneous investigation of two problems: the interaction with the vacuum electromagnetic field, and the 'other' process in which one is really interested. It follows that the theory developed previously can be applied without modification only to the phenomenon of spontaneous decay. For all other processes, the theory has to be generalized so as to take into account the simultaneous interaction of the system with two thermal baths.

This modification is most easily achieved if it is assumed that there is no interaction between the two baths. The validity of this assumption can usually be decided upon from physical considerations. If the interaction between the two baths cannot be neglected, the problem can be handled in an approximate manner that will be indicated later.

Each state of the total system is labelled by three sets of quantum numbers, referring to the system of interest, the first bath and the second bath respectively. The total Liouville operator is

$$L = L_0^{(s)} + L_0^{b1} + L_0^{b2} + L'1 + L'2, \quad (45)$$

where $L'1$ indicates the interaction of the system with the first bath and $L'2$ its interaction with the second bath. The lack of interaction between the two baths has two consequences. In the first

place, L does not contain a term corresponding to a bath1-bath2 interaction. It also implies that L^{11} is independent of and diagonal in the second bath. The corresponding considerations hold, of course, for L^{22} .

The initial density matrix for the total system is, by the assumption of initial phase randomization,

$$\rho^{(0)} = \rho^{(s)(0)} \rho^{b1(0)} \rho^{b2(0)}, \quad (46)$$

Where the bath density matrices are, as before, taken diagonal.

The problem becomes more transparent if the two baths are formally adjoined to each other by the definitions

$$L_o^{(b)} = \begin{pmatrix} L_o^{b1} & 0 \\ 0 & L_o^{b2} \end{pmatrix}, \quad L' = \begin{pmatrix} L'^{11} & 0 \\ 0 & L'^{22} \end{pmatrix}, \quad \rho^{(b)(0)} = \begin{pmatrix} \rho^{b1(0)} \\ \rho^{b2(0)} \end{pmatrix}. \quad (47)$$

The problem is thereby cast into a form that can be handled by the previously discussed methods.

As before, we can define an operator $\langle M(w) \rangle$,

$$\langle M(w) \rangle = \text{Tr}_b \left\{ L' \sum_{n=0}^{\infty} [(\omega - L_o)^{-1} L']^n \rho^{(b)(0)} \right\}. \quad (48)$$

The fact that L_o is diagonal and that the baths do not interact with each other has the consequence that the two baths are not entangled in this expression. Thus, we can write

$$\langle M(w) \rangle = \langle M_1(w) \rangle + \langle M_2(w) \rangle. \quad (49)$$

This separation is not, however, true of the relaxation operator $N(w)$:

$$N(w) = (\langle M_1 \rangle + \langle M_2 \rangle) \sum_{n=0}^{\infty} [-(\omega - L_o^{(s)})^{-1} (\langle M_1 \rangle + \langle M_2 \rangle)]^n. \quad (50)$$

Nevertheless, $N(w)$ does separate in lowest order. Hence, to lowest order, if the interaction of the system with the first bath is nearly Markoffian, the interaction with the second bath can be handled by assigning to the system an effective Liouville operator

$$L_0^{(s)} = L_0^{(s)} + \langle M_1 \rangle, \quad (51)$$

and then applying the theory of the preceding sections. $L_0^{(s)}$ is generally not hermitian,¹³ but, in the lowest order approximation, it is diagonal:

$$(L_0^{(s)})_{ab, a'b'} = (\omega_{ab} + d_{ab} - i\gamma_{ab}) \delta_{aa'} \delta_{bb'}, \quad (52)$$

where ω_{ab} is an eigenvalue of $L_0^{(s)}$ while d_{ab} and γ_{ab} are the shifts and widths caused by the first bath.

The interaction of an atom with the vacuum radiation field will be seen to be nearly Markoffian in lowest order (Part IV). Thus the above modification is sufficient for the approximate treatment of other relaxation mechanisms to lowest order also. This procedure corresponds to the usual practice in microwave spectroscopy where one introduces phenomenological damping constants.¹⁴ However, judging by the number of approximations that must be made in order to arrive at such a simplified description of the situation, one is tempted to feel that this description has, perhaps, been used somewhat too trustingly in problems where it is not sufficiently accurate.

¹³ Note that the hermiticity of L_0 is nowhere needed in the derivation of the kinetic equation.

¹⁴ For example: Robert Karplus and Julian Schwinger, Phys. Rev. 73, 1020 (1948). Also: V. M. Kontorovich and A. M. Prokhorov, J.E.T.P. 6, 1100 (1958).

The most important consequence of the above modification is that, when the limit $\Gamma \rightarrow 0+$ is taken, singularities that may otherwise occur in $N(w)$ are circumvented by the imaginary (non-hermitian) part of $L_0^{(s)}$. The finite natural lifetime of the atom introduces an effective cutoff of the interaction which serves to render its effects convergent. However, when the interaction of the atom with the vacuum electromagnetic field is being considered, the above argument fails since it is just this interaction that leads to a finite lifetime. Hence, the singularities that arise from this particular interaction (the self-energy problem) cannot be properly discussed in the present context. Their convergence is achieved by a deeper study of the interaction itself rather than from any general considerations of relaxation theory.

We return briefly to the question of the interaction between the baths. If this interaction is independent of the time, it merely adds a term to $L_0^{(b)}$ which would thus become, in general, non-diagonal. The addition to $L_0^{(b)}$ can be considered as a perturbation of one of the baths. The perturbed eigenvalues of that bath can (in principle) be obtained if the system of interest is momentarily neglected. The diagonalized bath Liouville operators can then be inserted in Eq.(45) and the previous method followed. Such a procedure is extremely approximate since the three interactions (system-bath 1, system-bath 2, and bath 1-bath 2) are liable to get 'entangled' with each other.

The preceding observations would gain clarity if their application to a specific situation is outlined. Consider the problem of pressure broadening. The two baths in this case are the vacuum radiation field and the 'other' atoms that are perturbing the atom of interest. The

interaction of the atom with the radiation field results in the complex spectral frequencies (52). The interaction between the radiation field and the other atoms results in a similar perturbation of their spectral frequencies. With the inclusion of the perturbed frequencies for both the atom of interest and the other atoms, the problem can then be treated in the usual manner.

8- Application to Radiation Damping and Radiative Shifts

We conclude this outline of relaxation theory with a few remarks concerning its application to the study of the interaction of an atom with the electromagnetic field.

The system of interest is an atom (ion, molecule) whose unperturbed energy levels are assumed to be given. The bath is a radiation field with an arbitrary initial spectral distribution. Only the pure radiation (transverse) will be quantized. The primary quantities on which the calculations are based are the total Hamiltonian and the initial spectral distribution of the radiation.

We shall be interested in calculating the linewidths and the shifts of the spectrum of the atom only. The spectral distribution of the radiation emitted by the atom will not be discussed. The dipole approximation will be assumed. Moreover, since the calculations are carried out to lowest order only, we shall focus our attention on the diagonal elements of the first relevant term in the series expansion of $N(\omega)$.

III. THE INTERACTION OF MATTER WITH RADIATION

1- Representation of the Field

Since,¹⁵ in the preceding part, the hamiltonian of the bath was assumed diagonal, we shall take the radiation field in the energy representation. It is convenient, at first, to consider radiation in a 'box'. The potential and field intensities can then be expanded in terms of the normal modes of oscillation of the box. Each state of the field is specified by the number of photons present in each mode. These states are a product of the single-mode states $|n\rangle$ and will be written as $|N\rangle$, where N stands for the set $\{n\}$.

Different normalized energy eigenstates are related to each other by the annihilation and creation operators $a_{k\lambda}$, $a_{k\lambda}^\dagger$:

$$\begin{aligned} a_{k\lambda} |N\rangle &= n_{k\lambda}^{1/2} |n_1, n_2, \dots, n_{k\lambda}-1, \dots\rangle, \\ a_{k\lambda}^\dagger |N\rangle &= (n_{k\lambda}+1)^{1/2} |n_1, n_2, \dots, n_{k\lambda}+1, \dots\rangle, \end{aligned} \quad (1)$$

where k is the wave number and λ indicates the state of polarization.

The vacuum state, in which no photons are present, satisfies

$$a_{k\lambda} |0\rangle = 0. \quad (2)$$

¹⁵ For a detailed exposition of the material outlined in this section and the next one, see Heitler, op. cit., especially Sections 6, 7 & 14. See also: R. L. Douglass, Lectures on Quantum Electrodynamics, American University of Bierut, Beirut, 1963 (unpublished).

The hamiltonian operator is

$$H = \frac{1}{2} \sum_{\mathbf{k}\lambda} \hbar \omega_{\mathbf{k}} (a_{\mathbf{k}\lambda} a_{\mathbf{k}\lambda}^{\dagger} + a_{\mathbf{k}\lambda}^{\dagger} a_{\mathbf{k}\lambda}), \quad (3)$$

and has the eigenvalues

$$\langle N|H|N\rangle = \sum_{\mathbf{k}\lambda} \hbar \omega_{\mathbf{k}} (n_{\mathbf{k}\lambda} + 1/2). \quad (3')$$

The vector potential \underline{A} and the electric and magnetic fields \underline{E} and \underline{B} are given by the operators

$$\vec{A} = (\hbar/2\epsilon_0 V)^{1/2} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}}^{-1/2} (a_{\mathbf{k}\lambda} e^{i\vec{k}\cdot\vec{r}} + a_{\mathbf{k}\lambda}^{\dagger} e^{-i\vec{k}\cdot\vec{r}}) \hat{e}_{\mathbf{k}\lambda}, \quad (4) \text{ i}$$

$$\vec{E} = i(\hbar/2\epsilon_0 V)^{1/2} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}}^{1/2} (a_{\mathbf{k}\lambda} e^{i\vec{k}\cdot\vec{r}} - a_{\mathbf{k}\lambda}^{\dagger} e^{-i\vec{k}\cdot\vec{r}}) \hat{e}_{\mathbf{k}\lambda}, \quad \text{ii}$$

$$\vec{B} = i(\hbar/2\epsilon_0 V)^{1/2} \sum_{\mathbf{k}\lambda} \omega_{\mathbf{k}}^{-1/2} (a_{\mathbf{k}\lambda} e^{i\vec{k}\cdot\vec{r}} - a_{\mathbf{k}\lambda}^{\dagger} e^{-i\vec{k}\cdot\vec{r}}) (\vec{k} \times \hat{e}_{\mathbf{k}\lambda}), \quad \text{iii}$$

where V is the volume of the box in which the radiation is enclosed, and $\hat{e}_{\mathbf{k}\lambda}$ is a unit polarization vector. It is clear that these operators are non-diagonal in the energy representation.

Since each state of the field is labelled by a set N , the components of the density matrix have the form ρ_{MN} . In particular, a stationary state of the field with the occupation index set X has the density matrix

$$\rho_{MN} = \delta_{MX} \delta_{NX}, \quad (5)$$

where $\delta_{MX} = \delta_{m_1, x_1} \delta_{m_2, x_2} \dots$ (5')

As the size of the box that contain the radiation increases indefinitely, the distribution of normal frequencies approaches a continuum. The transition to a continuous representation of the

field is effected by the replacement

$$\frac{1}{V} \sum_{k\lambda} \rightarrow \frac{1}{\pi^2 c^3} \int \omega^2 d\omega. \quad (6)$$

2- The Interaction Hamiltonian

The interaction between radiation and a particle of mass m , electric charge e and magnetic dipole moment $\vec{\mu}$ is described by the interaction hamiltonian

$$H' = -\frac{e}{m} \vec{p} \cdot \vec{A} - \vec{\mu} \cdot \vec{B} + \frac{e^2}{2m} A^2, \quad (7)$$

where \vec{p} is the momentum of the particle. For an atomic electron, the dipole approximation is usually sufficient. This consists in neglecting the spatial dependence of the fields. The justification for this approximation can be seen from the fact that, for an atomic electron interacting with radiation in the optical region, $kr \approx 2 \times 10^{-4}$; thus the exponential factors $e^{+ik \cdot r}$ in the expressions for the fields may be replaced by unity.

Each state of the total system (atom and radiation) is characterized by a set of quantum numbers referring to the atom and a set of occupation numbers for the field. Thus a typical state vector may be labelled $|aN\rangle$, and is a product of the non-interacting states $|a\rangle$ and $|N\rangle$. It will be remembered that the states $|a\rangle$ are energy eigenstates of the free atom with eigenvalues w_a .

In evaluating the matrix elements of H' , use is made of the relation

$$\vec{p} = \frac{im}{\hbar} [H_0^a, \vec{r}], \quad (8)$$

where H_0^a is the free atom hamiltonian. This gives the matrix elements

of \vec{p} in terms of the position matrix (i.e. dipole matrix/e):

$$\vec{P}_{ab} = i m \omega_{ab} \vec{r}_{ab} \quad (8')$$

Furthermore, it is convenient to define the set N_i as the complement of n_i in N . Similarly, N_{ij} will indicate the complement of n_i and n_j in N .

The matrix elements of H' are found to be

$$\langle aN | H' | bM \rangle = \sum_i f(a n_i, b m_i) \delta_{N_i M_i} + \sum_i g(a n_i, b m_i) \delta_{N_i M_i} \quad (9) \text{ i}$$

$$+ \sum_{ij} K(n_i n_j, m_i m_j) \delta_{ab} \delta_{N_{ij} M_{ij}},$$

where

$$f(a n_i, b m_i) = -i e (\hbar / 2 \epsilon_0 V)^{1/2} \frac{\omega_{ab}}{\omega_i^{1/2}} \vec{r}_{ab} \cdot \hat{e}_i [(n_i + 1)^{1/2} \delta_{m_i, n_i + 1} + n_i^{1/2} \delta_{m_i, n_i - 1}] \quad \text{ii}$$

$$g(a n_i, b m_i) = -i (\hbar / 2 \epsilon_0 V)^{1/2} \frac{\omega_i^{1/2}}{c} \vec{\mu}_{ab} \times \hat{k} \cdot \hat{e}_i [(n_i + 1)^{1/2} \delta_{m_i, n_i + 1} - n_i^{1/2} \delta_{m_i, n_i - 1}] \quad \text{iii}$$

$$K(n_i n_j, m_i m_j) = -\frac{e^2 \hbar}{4 \epsilon_0 m V} \hat{e}_i \cdot \hat{e}_j \left[\frac{(n_i + 1) n_j}{\omega_i \omega_j} \right]^{1/2} \delta_{m_i, n_i + 1} \delta_{m_j, n_j - 1} \quad \text{iv}$$

The first term gives the interaction of the electric dipole moment of the atom with the radiation; similarly, the second term describes the magnetic dipole interaction. The third term, which arises from the $\frac{e^2}{2m} \mathbf{A}^2$ part of H' , will be found not to contribute to the subsequent calculations.

3- The Relaxation Operator

The non-interaction part of the Liouville operator, L_0 , is, from Eq. II(4'),

$$\begin{aligned} & \langle aM, bN | L_0 | a'M', b'N' \rangle \\ & = [\omega_{ab} + \sum_i (m_i - n_i) \omega_i] \delta_{aa'} \delta_{bb'} \delta_{MM'} \delta_{NN'} \end{aligned} \quad (10)$$

The ω_{ab} part contributes $L_0^{(a)}$ and the other part contributes $L_0^{(b)}$.

The interaction Liouville operator L' is found from Eq.(9)

and Eq. II(4) :

$$\langle aM, bN | L' | a'M', b'N' \rangle \quad (11)$$

$$= \sum_i \left\{ [f(a_{m_i}, a'_{m'_i}) \delta_{bb'} \delta_{n_i n'_i} - f(b'_{n'_i}, b_{n_i}) \delta_{aa'} \delta_{m_i m'_i}] \right. \\ \left. + [g(a_{m_i}, a'_{m'_i}) \delta_{bb'} \delta_{n_i n'_i} - g(b'_{n'_i}, b_{n_i}) \delta_{aa'} \delta_{m_i m'_i}] \right\} \delta_{M_i M'_i} \delta_{N_i N'_i} \\ + \sum_{ij} [K(m_i m'_j, m'_i m_j) \delta_{n_i n'_i} \delta_{n_j n'_j} - K(n'_i n'_j, n_i n_j) \delta_{m_i m'_i} \delta_{m_j m'_j}] \\ \times \delta_{aa'} \delta_{bb'} \delta_{M_{ij} M'_{ij}} \delta_{N_{ij} N'_{ij}} .$$

L' is seen to split into three parts corresponding to the three terms in H' .

In the evaluation of the relaxation operator $N(w)$, one needs, in addition to L , the initial radiation density matrix. According to Eq.II(15'), this is diagonal. Thus

$$\rho_{MN}^{(b)}(0) = \delta_{MX} \delta_{NX} \quad (12)$$

The initial set of occupation numbers of the radiation oscillators will henceforth always be indicated by $X = \{x\}$.

Before proceeding with the calculation of the matrix elements of $N(w)$, we shall demonstrate that all terms in the series expansion for $\langle M(w) \rangle$ that are odd in L' vanish. The n -th order term in $\langle M(w) \rangle$ is (Eq.II(14') and II(17))

$$\langle M(w) \rangle^{(n)} = \text{Tr}_b \left\{ L' [(w - L_0)^{-1} L']^{n-1} \rho^{(b)}(0) \right\} . \quad (13)$$

The system indices are irrelevant in the present context and will be

momentarily suppressed; furthermore, the factors $(w-L_0)^{-1}$ are diagonal and do not contribute new summations to the matrix product, they can be, therefore, neglected. Hence, we can write, somewhat schematically

$$\langle M(w) \rangle^{(n)} \propto \sum_Y \sum_{\substack{A_1, \dots, A_{n-1} \\ B_1, \dots, B_{n-1}}} L'_{Y, A_1 B_1} L'_{A_1 B_1, A_2 B_2} \dots L'_{A_{n-1} B_{n-1}, X X}, \quad (13')$$

where Y and the A_i and B_i indicate occupation number sets. It is seen from Eq.(11) that different modes are not coupled in L' . Thus the sums in $\langle M \rangle$ can be divided into a sum over occupation numbers for a single mode followed by a sum over modes, i.e.

$$\langle M(w) \rangle^{(n)} \propto \sum_{\text{modes}} \sum_Y \sum_{\substack{a_1, \dots, a_{n-1} \\ b_1, \dots, b_{n-1}}} L'_{Y, a_1 b_1} L'_{a_1 b_1, a_2 b_2} \dots L'_{a_{n-1} b_{n-1}, X X}, \quad (13'')$$

where the indices now refer to the same mode.

It is now possible to verify the above assertion. For terms that are odd in L' , n is even. This means that there is an odd number of 'steps' from y to x . However, the selection rules are symmetrical in the a and b indices, namely,

$$\text{either } |a_{i+1} - a_i| = 1, \quad b_{i+1} = b_i, \quad (14)$$

$$\text{or } |b_{i+1} - b_i| = 1, \quad a_{i+1} = a_i. \quad (14')$$

Since, for even n , the runs of a and b indices cannot be both reconciled to the same indices y and x at the ends, it follows that these terms vanish.

We shall concern ourselves only with the first nonvanishing term in the series for $N(w)$. This term is of second order in L' and

is given by

$$N(w) \doteq \langle M(w) \rangle \doteq \text{Tr}_b [L'(w-L_0)^{-1} L' \rho^{(b)}(0)] \quad (15)$$

In the evaluation of this expression, the sum over occupation sets is split, as above, into a sum for a single mode followed by a sum over modes. The Kronecker deltas in L_0 , L' and $\rho_0^{(b)}$ allow the first sum to be carried out explicitly. We obtain:

$$\begin{aligned} & (ab|N(w)|a'b') \quad (16) \\ &= \sum_i \sum_c \left\{ [f(a, x_i; c, x_i - 1) f(c, x_i - 1; a', x_i) (w - \omega_{cb} + \omega_i)^{-1} \right. \\ & \quad \left. + f(a, x_i; c, x_i + 1) f(c, x_i + 1; a', x_i) (w - \omega_{cb} - \omega_i)^{-1}] \delta_{bb'} \right. \\ & \quad \left. + [f(b', x_i; c, x_i - 1) f(c, x_i - 1; b, x_i) (w - \omega_{ac} - \omega_i)^{-1} \right. \\ & \quad \left. + f(b', x_i; c, x_i + 1) f(c, x_i + 1; b, x_i) (w - \omega_{ac} + \omega_i)^{-1}] \delta_{aa'} \right\} \\ &= \sum_i \left\{ f(a, x_i - 1; a', x_i) f(b', x_i; b, x_i - 1) [(w - \omega_{ab} + \omega_i)^{-1} + (w - \omega_{ab} - \omega_i)^{-1}] \right. \\ & \quad \left. + f(a, x_i + 1; a', x_i) f(b', x_i; b, x_i + 1) [(w - \omega_{ab} - \omega_i)^{-1} + (w - \omega_{ab} + \omega_i)^{-1}] \right\} \\ & \quad + \text{similar expression with } f \text{ replaced by } g. \end{aligned}$$

The sum over i is the sum over the radiation modes while c runs over all the states of the atom. It is to be noted that $k(n_1, n_j; m_1, m_j) - \frac{e^2}{2m} A^2$ part of H' - does not contribute.

Remembering that w is complex and that the limit $\text{Im } w \rightarrow 0+$ is to be taken, we make use of the relation¹⁶

$$\lim_{\epsilon \rightarrow 0} (w + i\epsilon - \omega_0)^{-1} \doteq \zeta(w - \omega_0) = (w - \omega_0)^{-1} - i\pi \delta(w - \omega_0). \quad (17)$$

¹⁶ Heitler, op. cit., Section 8.

The ζ -function thus defined plays an important role in the theory of scattering¹⁷ and satisfies

$$\zeta(-x) = -\zeta^*(x). \quad (17^*)$$

In the lowest approximation we are interested only in the diagonal elements of N , $N_{ab,ab}$, evaluated at the transition frequency ω_{ab} . These are given by

$$\begin{aligned} & (ab|N(\omega_{ab})|ab) \quad (18) \\ &= \sum_{i,c} \left\{ \left[|f(a, x_i; c, x_i - 1)|^2 \zeta(\omega_{ac} + \omega_i) + |f(a, x_i; c, x_i + 1)|^2 \zeta(\omega_{ac} - \omega_i) \right] \right. \\ & \quad \left. - \left[|f(b, x_i; c, x_i - 1)|^2 \zeta^*(\omega_{bc} + \omega_i) + |f(b, x_i; c, x_i + 1)|^2 \zeta^*(\omega_{bc} - \omega_i) \right] \right\} \\ & \quad + \text{similar expression with } f \text{ replaced by } g, \end{aligned}$$

where we have used the property (17'). Upon performing the transition to a continuous representation of the field, Eq.(6), we obtain

$$\begin{aligned} & (ab|N(\omega_{ab})|ab) \quad (18') \\ &= \frac{V}{\pi^2 c^3} \sum_c \int_0^\infty d\omega \omega^2 \left\{ \left[|f(a, x; c, x - 1)|^2 \zeta(\omega_{ac} + \omega) + |f(a, x; c, x + 1)|^2 \zeta(\omega_{ac} - \omega) \right] \right. \\ & \quad \left. - \left[|f(b, x; c, x - 1)|^2 \zeta^*(\omega_{bc} + \omega) + |f(b, x; c, x + 1)|^2 \zeta^*(\omega_{bc} - \omega) \right] \right\} \\ & \quad + \text{similar expression with } f \text{ replaced by } g. \end{aligned}$$

The occupation number x is now a function of the continuous variable w .

The electric and magnetic parts are clearly separated. Since only the squares of the absolute values of f and g appear, it is seen, from Eq.(9,ii,iii) that the magnetic analogue of an electric effect is obtained by the replacement

$$e^2 \omega_{ab}^2 |\vec{r}_{ab} \cdot \hat{e}|^2 \rightarrow \frac{\omega^2}{c^2} |\vec{u}_{ab} \times \hat{k} \cdot \hat{e}|^2. \quad (19)$$

¹⁷ Dirac, op. cit., Section 50.

IV. SPONTANEOUS RADIATION DAMPING
AND RADIATIVE CORRECTIONS

1- Spontaneous Emission and the Natural Linewidth

Spontaneous radiation damping results from the interaction of the atom with the vacuum radiation field. It is obtained from the general expressions III(18') by setting the initial occupation number function $x(\omega) = 0$. This gives

$$(a|N(\omega_{ab})|a) = \frac{V}{\pi^2 c^3} \sum_c \int_0^\infty d\omega \omega^2 \left[|f(a, 0; c)|^2 \zeta(\omega_{ac} - \omega) - |f(b, 0; c)|^2 \zeta^*(\omega_{bc} - \omega) \right]. \quad (1)$$

We concentrate our attention now on the electric part.

This expression contains factors of the form $|\vec{r}_{ab} \cdot \hat{e}|^2$. Now, for an atom in vacuum, the orientation of the polarization base vectors is completely arbitrary. Hence, these factors are to be averaged over all possible directions of the polarization, i.e.

$$|\vec{r}_{ab} \cdot \hat{e}|^2 = |r_{ab}|^2 \cos^2 \theta \rightarrow |r_{ab}|^2 \frac{1}{2} \int_{-1}^{+1} \cos^2 \theta d \cos \theta = \frac{1}{3} |r_{ab}|^2. \quad (2)$$

It will be shown in Section 3 that the Markoffian approximation is valid for the present problem. Hence, the width of the spectral line $a \rightarrow b$ is the negative of the imaginary part of Eq.(1). This is found to be

$$\gamma_{ab} = \frac{2\alpha}{3c^2} \left(\sum_{\omega_{ac} > 0} \omega_{ac}^3 |r_{ac}|^2 + \sum_{\omega_{bd} > 0} \omega_{bd}^3 |r_{bd}|^2 \right), \quad (3)$$

where α is the fine-structure constant.

The particular case

$$\gamma_a \equiv \gamma_{aa} = \frac{4\alpha}{3c^2} \sum_{\omega_{ac} > 0} \omega_{ac}^3 |r_{ac}|^2 \quad (3')$$

is worth noting. (In these expressions a factor of \hbar^{-2} has been inserted; ω_{ac} stands now for frequency and not, as before, for energy.)

The width of each line is half the sum of the widths of the initial and final levels,

$$\gamma_{ab} = \frac{1}{2} (\gamma_a + \gamma_b) . \quad (4)$$

This is the expression of the combination principle for the decay rates. Equation (4) was assumed by Weisskopf and Wigner in their original treatment of the natural linewidth.¹⁸

Equation (3') implies that an atom in state a decays into all lower states with partial decay rates

$$\gamma_{a \rightarrow b} = \frac{4\alpha}{3c^2} \omega_{ab}^3 |r_{ab}|^2 . \quad (5)$$

This result can be obtained by more conventional perturbation-theoretic techniques.¹⁹

For magnetic dipole transitions the partial decay rates are, by Eq. II(19),

$$\gamma_{a \rightarrow b} = \frac{4\alpha}{3e^2 c^2} \omega_{ab}^3 |\mu_{ab}|^2 . \quad (5')$$

This result is also well-known.

¹⁸ V. Weisskopf and E. P. Wigner, *Zeit. f. Phys.* **63** (1930).

¹⁹ Heitler, *op. cit.*, Section 14.

2- Radiative Correction to the Energy Levels

The real part of expression (1) gives a shift of the spectral line ab by an amount

$$d_{ab} = \frac{V}{\pi^2 c^3} \sum_c \int_0^\infty d\omega \omega^2 \left[|f(a, 0; c)|^2 (\omega_{ac} - \omega)^{-1} - |f(b, 0; c)|^2 (\omega_{bc} - \omega)^{-1} \right]. \quad (6)$$

Performing the average over polarization directions, Eq.(2), we get

$$d_{ab} = \frac{2\alpha}{3\pi c^2} \int_0^\infty d\omega \omega \left\{ \sum_c \left(\frac{\omega_{ac}^2 |r_{ac}|^2}{(\omega_{ac} - \omega)} - \frac{\omega_{bc}^2 |r_{bc}|^2}{(\omega_{bc} - \omega)} \right) \right\}. \quad (6')$$

This indicates a shift of the level a given by

$$d_a = \frac{2\alpha}{3\pi c^2} \int_0^\infty d\omega \omega \sum_c \frac{\omega_{ac}^2 |r_{ac}|^2}{(\omega_{ac} - \omega)}. \quad (7)$$

This shift, which represents the transverse self-energy of the atomic electron, diverges. It was thus consistently deleted from all calculations until 1947, when Bethe²⁰ showed that a finite result could be extracted from it. Furthermore, Bethe's calculation indicated that this shift could be identified as the cause of the slight separation between the $2^2S_{1/2}$ and $2^2P_{1/2}$ states of hydrogen that had been suspected for a long time²¹ and which was finally confirmed by the famous experiments of Lamb and Retherford.²²

Bethe's evaluation of the transverse self-energy is based on two observations. In the first place, a free electron also possesses

²⁰ H. A. Bethe, Phys. Rev. 72, 339 (1947). This article forms the basis for this section.

²¹ W. V. Houston, Phys. Rev. 51, 446 (1937).

²² W. E. Lamb and R. C. Retherford, Phys. Rev. 72, 241 (1947).

a divergent self-energy due to its interaction with the vacuum field. The observable shift of the energy levels of a bound electron is its self-energy minus the self-energy of a free electron with the same total energy. Secondly, Bethe argued that the upper limit on the integral should be replaced by $m_0 c^2/h$, in the expectation that a fully relativistic treatment of the problem would provide justification for such a 'cutoff'.

To apply these ideas it is convenient to express Eq.(7) in terms of the velocity by using Eq.III(8') :

$$d_a = \frac{2\alpha}{3\pi c^2} \int_0^\infty d\omega \omega \sum_c \frac{|V_{ac}|^2}{(\omega_{ac} - \omega)} \quad (7')$$

The corresponding expression for a free electron with the same energy is

$$d_o = -\frac{2\alpha}{3\pi c^2} \int_0^\infty \omega d\omega \frac{(V^2)_{aa}}{\omega} \quad (8)$$

The sum rule

$$(V^2)_{aa} = \sum_c |V_{ac}|^2, \quad (9)$$

allows the free electron self-energy to be written in the form

$$d_o = -\frac{2\alpha}{3\pi c^2} \int_0^\infty \omega d\omega \sum_c \frac{|V_{ac}|^2}{\omega} \quad (8')$$

To obtain the observable shift of the energy of the bound electron, expression (8') is subtracted from (7') and the upper limit on the integral is then replaced by $m_0 c^2/h$. This gives a finite result:

$$\begin{aligned} \Delta_a &= \frac{2\alpha}{3\pi c^2} \int_0^{m_0 c^2/h} d\omega \sum_c \frac{|V_{ac}|^2 \omega_{ca}}{(\omega_{ca} + \omega)} = \frac{2\alpha}{3\pi c^2} \sum_c |V_{ac}|^2 \omega_{ca} \ln \left| \frac{m_0 c^2}{h \omega_{ca}} \right| \\ &= -\frac{2\alpha}{3\pi c^2} \sum_c \omega_{ac}^3 |V_{ac}|^2 \ln \left| \frac{m_0 c^2}{h \omega_{ca}} \right|. \end{aligned} \quad (10)$$

To render this expression more amenable to numerical evaluation, it is noted that all energy differences $\hbar\omega_{ca}$ for a bound electron are much less than the rest energy of the electron, m_0c^2 . Hence the dependence of the logarithm on the index c may be safely neglected. Thus, one may write, approximately,

$$\Delta_a = -\frac{2\alpha}{3\pi c^2} \lambda_a \sum \omega_{ac}^3 |r_{ac}|^2, \quad (11)$$

$$\lambda_a = \ln \left| \frac{m_0 c^2}{\hbar \omega'_a} \right|, \quad (11')$$

where ω'_a is the average of ω_{ca} for all bound states c . Finally, the shift of the spectral line ab is

$$\Delta_{ab} = \Delta_a - \Delta_b. \quad (12)$$

The Ritz combination principle is satisfied. It should be noted that this assertion could not be made before the shifts were ~~rendered~~ finite.

Bethe's calculation yielded a shift of about 1040 Mcps for the $2^2S_{\frac{1}{2}} - 2^2P_{\frac{1}{2}}$ transition in hydrogen, in good agreement with the experimental result of 1058 Mcps.

The validity of this calculation was vindicated by fully relativistic calculations²³ which also accounted for all of the observed shift.

The intimate connection between the linewidth and the energy correction is noteworthy. This relation arises from the combination of the inverse function and the delta function in the ζ -function as given by Eq. III(17).

²³ N. M. Kroll and W. E. Lamb, Phys. Rev. 75, 338 (1949).

3- The Validity of the Markoffian Approximation

The applicability of the Markoffian approximation in the evaluation of the natural linewidth and the Lamb shift will now be demonstrated. According to Section 5 of Part II, this approximation is justified if the derivative of $N(w)$ at $w = L_0$ is much less than one. Since, in the lowest order, only the diagonal elements of $N(w)$ are relevant, it suffices to investigate the derivatives of these elements.

Consider first the imaginary part of the matrix element $(ab|N(w)|ab)$. Its derivative can be evaluated from Eq.III(9), (16) and (17), then computed in the manner used to derive the natural linewidth. We find

$$C_{ab} \equiv \frac{d}{dw} \text{Im} N(w)_{ab,ab} \Big|_{w=L_0} = -\frac{2\alpha}{3c^2} \left[\sum_{\substack{c \\ \omega_{ac} > 0}} \omega_{ac}^2 |r_{ac}|^2 + \sum_{\substack{d \\ \omega_{bd} > 0}} \omega_{bd}^2 |r_{bd}|^2 \right]. \quad (13)$$

This may be expressed in terms of the velocity by Eq.III(8'), thus:

$$C_{ab} = -\frac{2\alpha}{3c^2} \left[\sum_{\substack{c \\ \omega_{ac} > 0}} |v_{ac}|^2 + \sum_{\substack{d \\ \omega_{bd} > 0}} |v_{bd}|^2 \right]. \quad (13')$$

The sum rule, Eq.(9), indicates an upper bound on C_{ab} :

$$|C_{ab}| < \frac{2\alpha}{3c^2} \left[(v^2)_{aa} + (v^2)_{bb} \right]. \quad (14)$$

A rough estimate of the magnitude of this quantity may be obtained from the Bohr theory of atomic structure. According to this theory, the velocity of an electron with principal quantum number n_a

in an atom with nuclear charge Z is

$$(v^2)_{aa} = \frac{Z^2 \alpha^2}{2n_a^2} c^2, \quad (15)$$

Equation (14) thus becomes

$$|C_{ab}| < \frac{Z^2 \alpha^3}{3} (1/n_a^2 + 1/n_b^2). \quad (14')$$

The right hand side is indeed much less than unity, being proportional to α^3 .

In the evaluation of the derivative of the real part of $(ab|N(w)|ab)$ the Bethe cutoff has to be employed. However, there is no need for subtracting the free electron energy. Following the procedure of the preceding section, one obtains

$$D_{ab} \equiv \frac{d}{dw} \text{Re } N(w)_{ab,ab} \Big|_{w_{ab}} = -\frac{2\alpha}{3\pi c^2} [(\lambda_a - 1)(v^2)_{aa} - (\lambda_b - 1)(v^2)_{bb}], \quad (16)$$

where λ_a is defined in Eq.(11'). Using the Bohr model again, we find

$$D_{ab} = -\frac{Z^2 \alpha^3}{3\pi} \left(\frac{\lambda_a - 1}{n_a^2} - \frac{\lambda_b - 1}{n_b^2} \right). \quad (16')$$

The logarithmic factors λ vary from 0 to about 8 for hydrogen in the $n = 2$ state and are not expected to vary greatly from element to element.²⁴ Hence, again, the derivative is much less than unity.

It should be emphasized that the above results, Eq.(14') and (16'), are order of magnitude estimate only. These estimates are, however, excellent for hydrogen since, in this case, the quantum mechanical corrections to the Bohr energy levels are quite small.

²⁴ Bethe, op. cit.

An obvious upper bound on the derivative of $N(\omega)$ that is valid for all cases may be obtained from Eq.(14) and (16) by setting $v = c$.

This gives

$$|C_{ab}| < 4\alpha, \quad (14'')$$

$$|D_{ab}| < \frac{2\alpha}{3\pi} |\lambda_a - \lambda_b|. \quad (16'')$$

These relations show clearly that the derivative of N is less than one in all cases.

A consequence of the validity of the Markoffian approximation and the combination principle for the interaction of an atom with the vacuum radiation field is that the 'natural' spectrum of the atom has a Lorenzian line shape.

V. STIMULATED EMISSION
AND RADIATIVE SHIFTS

1- General Formulation

The presence of an 'actual' electromagnetic field induces resonant emission of radiation by the atom. It also causes a shift of the spectral lines of the atom. The first effect has been known for nearly half a century, while the second effect came into prominence only recently. Both effects are most spectacularly¹ exhibited in the operation of the laser. These effects will be calculated here to lowest order, with the assumption of Markoffian behaviour. The natural linewidth of the atom will, however, be taken into account.

The relaxation operator has diagonal elements (see Eq. III (9), (16) and (18'))

$$\begin{aligned}
 & (ab|N(\omega_0)|ab) \\
 &= \frac{2\alpha}{\pi c^2} \int_0^\infty d\omega \omega \sum_c \left\{ \omega_{ac}^2 |\vec{r}_{ac}|^2 \hat{E}(\omega) \left[\chi(\omega) \zeta(\omega_0 - \omega_c + \omega) + (\chi+1) \zeta(\omega_0 - \omega_c - \omega) \right] \right. \\
 & \quad \left. - \omega_{bc}^2 |\vec{r}_{bc}|^2 \hat{E}(\omega) \left[\chi(\omega) \zeta(\omega_c - \omega_0 + \omega) + (\chi+1) \zeta(\omega_c - \omega_0 - \omega) \right] \right\}
 \end{aligned} \tag{1}$$

where $\hat{E}(\omega)$ is a unit vector in the direction of the spectral component of the electric field with frequency ω . We focus our attention, for the time being, on electric dipole transitions. The results for magnetic dipole interactions follow immediately by Eq. III(19).

The above expression contains both spontaneous and induced relaxation. The spontaneous part is given by the '1' in $(x(\omega) + 1)$. In calculating induced relaxation this part is to be deleted. However, as mentioned in Part II, the spectral frequencies of the 'bare' atom must be replaced by the (complex) frequencies of the atom interacting with the vacuum field, i.e.

$$\omega_{ac} \rightarrow \omega_{ac} + d_{ac} - i\gamma_{ac} \quad (2)$$

where d_{ab} is the Lamb shift and γ_{ab} is the natural linewidth. Moreover, the relaxation operator is to be evaluated at the 'corrected' frequency $\omega_{ab} + d_{ab}$. To simplify the appearance of the equations, we introduce a slight change in notation: the corrected frequency $\omega_{ab} + d_{ab}$ will henceforth be written as ω_{ab} . Note also that the factors ω_{ac}^2 and ω_{bc}^2 in Eq.(1) are really $-\omega_{ac}\omega_{ca}$ and $-\omega_{bc}\omega_{cb}$ respectively (see Eq.III (9) and III (16).) These are thus to be replaced by

$$\begin{aligned} \omega_{ac}^2 &\rightarrow \omega_{ac}^2 + \gamma_{ac}^2 \equiv \Omega_{ac}^2, \\ \omega_{bc}^2 &\rightarrow \omega_{bc}^2 + \gamma_{bc}^2 \equiv \Omega_{bc}^2. \end{aligned} \quad (3)$$

The induced shifts and widths can now be found by separating the real and imaginary parts of the induced relaxation operator which, due to the above observations, takes the form

$$\begin{aligned} & (ab|N(\omega_{ab})|ab) \quad (4) \\ &= \frac{2\alpha}{\pi c^2} \int_0^\infty d\omega \omega \chi(\omega) \sum_c \left\{ \Omega_{ac}^2 |\vec{r}_{ac}|^2 \hat{E}^2 \left[\zeta(\omega_{ac} + i\gamma_{ab} + \omega) + \zeta(\omega_{ac} + i\gamma_{cb} - \omega) \right] \right. \\ & \quad \left. - \Omega_{bc}^2 |\vec{r}_{bc}|^2 \hat{E}^2 \left[\zeta^*(\omega_{bc} - i\gamma_{ac} + \omega) + \zeta^*(\omega_{bc} - i\gamma_{ac} - \omega) \right] \right\} \end{aligned}$$

It is desirable, at this point, to express the occupation number function $x(\omega)$ in terms of the spectral distribution of the field strengths. This is achieved by the following replacement (which is, perhaps, more obvious when stated in words than in symbols) :

$$\begin{aligned} & \text{number of photons in interval } d\omega \text{ around } \omega & (5) \\ & \times \text{ energy per photon } \times \text{ density of modes at } \omega \\ & = \text{energy density at } \omega \times d\omega, \end{aligned}$$

or:
$$\frac{\hbar}{\pi^2 c^3} \omega^3 \chi(\omega) d\omega = U(\omega) d\omega, \quad (5')$$

where U is the energy density. As is well known, the energy density is divided equally between the electric and magnetic fields. Thus

$$U(\omega) = \epsilon_0 |E(\omega)|^2 = \frac{1}{\mu_0} |B(\omega)|^2, \quad (6)$$

where the first equality is to be used for electric interactions and the second for magnetic interactions.

For an atom with electric dipole moment \underline{P} in an electric field $\underline{E}(\omega)$, Eq.(5') and (6), when substituted in Eq.(4), imply a shift B and a width Γ given by

$$\begin{aligned} D_{ab}^{(e)} &= \int_0^\infty d\omega \frac{|E(\omega)|^2}{2} & (7) \\ & \times \sum_c \left\{ (\Omega_{ac}/\omega)^2 |\vec{P}_{ac} \cdot \hat{E}|^2 \left[\frac{(\omega_{ac} + \omega)}{(\omega_{ac} + \omega)^2 + \gamma_{cb}^2} + \frac{(\omega_{ac} - \omega)}{(\omega_{ac} - \omega)^2 + \gamma_{cb}^2} \right] \right. \\ & \left. - (\Omega_{bc}/\omega)^2 |\vec{P}_{bc} \cdot \hat{E}|^2 \left[\frac{(\omega_{bc} + \omega)}{(\omega_{bc} + \omega)^2 + \gamma_{ac}^2} + \frac{(\omega_{bc} - \omega)}{(\omega_{bc} - \omega)^2 + \gamma_{ac}^2} \right] \right\}, \end{aligned}$$

$$\Gamma_{ab}^{(e)} = \int_0^{\infty} d\omega \frac{|E(\omega)|^2}{2} \quad (8)$$

$$\times \sum_c \left\{ (\Omega_{ac}/\omega)^2 |\vec{P}_{ac} \cdot \hat{E}|^2 \gamma_{bc} \left(\frac{1}{[(\omega_{ac} + \omega)^2 + \gamma_{bc}^2]} + \frac{1}{[(\omega_{ac} - \omega)^2 + \gamma_{bc}^2]} \right) \right. \\ \left. + (\Omega_{bc}/\omega)^2 |\vec{P}_{bc} \cdot \hat{E}|^2 \gamma_{ac} \left(\frac{1}{[(\omega_{bc} + \omega)^2 + \gamma_{ac}^2]} + \frac{1}{[(\omega_{bc} - \omega)^2 + \gamma_{ac}^2]} \right) \right\}.$$

The induced shift and width of the spectral lines of a magnetic dipole $\vec{\mu}$ in a magnetic field $\underline{B}(\omega)$ may be deduced from the above expressions with the aid of Eq.III(19) :

$$D_{ab}^{(m)} = \int_0^{\infty} d\omega \frac{|B(\omega)|^2}{2} \quad (9)$$

$$\times \sum_c \left\{ |\vec{\mu}_{ac} \cdot \hat{B}|^2 \left[\frac{(\omega_{ac} + \omega)}{(\omega_{ac} + \omega)^2 + \gamma_{cb}^2} + \frac{(\omega_{ac} - \omega)}{(\omega_{ac} - \omega)^2 + \gamma_{cb}^2} \right] \right. \\ \left. - |\vec{\mu}_{bc} \cdot \hat{B}|^2 \left[\frac{(\omega_{bc} + \omega)}{(\omega_{bc} + \omega)^2 + \gamma_{ac}^2} + \frac{(\omega_{bc} - \omega)}{(\omega_{bc} - \omega)^2 + \gamma_{ac}^2} \right] \right\},$$

$$\Gamma_{ab}^{(m)} = \int_0^{\infty} d\omega \frac{|B(\omega)|^2}{2} \quad (10)$$

$$\times \sum_c \left\{ |\vec{\mu}_{ac} \cdot \hat{B}|^2 \gamma_{bc} \left(\frac{1}{[(\omega_{ac} + \omega)^2 + \gamma_{bc}^2]} + \frac{1}{[(\omega_{ac} - \omega)^2 + \gamma_{bc}^2]} \right) \right. \\ \left. + |\vec{\mu}_{bc} \cdot \hat{B}|^2 \gamma_{ac} \left(\frac{1}{[(\omega_{bc} + \omega)^2 + \gamma_{ac}^2]} + \frac{1}{[(\omega_{bc} - \omega)^2 + \gamma_{ac}^2]} \right) \right\}.$$

Expressions 7 - 10 have several noteworthy features. A significant aspect of these equations is that they indicate a spectrum that does not obey the combination principle (Eq.II(30)). This means that

we are now justified in talking about spectral frequencies (i.e. energy differences) only and not about definite energy levels. From a purely physical point of view, such a limitation is not objectionable.

In the second place, all 'resonance denominators' in the above expressions are Lorentzian and non-singular. This, however, is not sufficient to guarantee the convergence of the integrals, since this convergence depends also on the spectral distributions $\underline{E}(\omega)$ and $\underline{B}(\omega)$. It is clear that convergence is assured for fields that are nowhere singular and that are cut off at a finite high frequency limit (and, for electric fields, at a non-vanishing low frequency limit also.) The convergence of the sum-over-states cannot be discussed in a general, and simple manner since it depends on the details of the spectrum of the system, on the natural linewidth and on the magnitudes of the dipole matrix elements.

The Markoffian approximation, which was assumed above, may be accepted if the derivative of $(ab|N(\omega)|ah)$ at ω_{ab} is much less than unity. The expression for this derivative is rather involved and does not repay detailed analysis. Suffice it to say that the derivative is proportional to the intensity of the radiation. Moreover, it may be expected to be relatively large at resonance. Hence, our results would tend to be too rough for strong fields and for resonant fields. Since the inclusion of the natural linewidth is of particular significance only for resonant, or nearly resonant radiation, it would seem that the present treatment of the frequency shifts due to strong resonant radiation may be inadequate.

2- Particular Cases

The expressions for the shifts and widths derived in the preceding section assume a simpler form under certain conditions. Some of these simplified forms are worth mentioning.

In previous derivations of these results the natural linewidth was ignored.²⁵ In this approximation, the electric shifts and widths are

$$D_{ab}^{(e)} = \int_0^\infty d\omega \frac{|E(\omega)|^2}{2} \sum_c \left\{ (\omega_{ac}/\omega)^2 |\vec{P}_{ac}| \hat{E}^2 \left[(\omega_{ac} + \omega)^{-1} + (\omega_{ac} - \omega)^{-1} \right] \right. \\ \left. - (\omega_{bc}/\omega)^2 |\vec{P}_{bc}| \hat{E}^2 \left[(\omega_{bc} + \omega)^{-1} + (\omega_{bc} - \omega)^{-1} \right] \right\} \quad (11)$$

$$\Gamma_{ab}^{(e)} = \pi \sum_c \left\{ |E(\omega_{ac})|^2 |\vec{P}_{ac}| \hat{E}(\omega_{ac})^2 + |E(\omega_{bc})|^2 |\vec{P}_{bc}| \hat{E}(\omega_{bc})^2 \right\} \quad (12)$$

The corresponding expressions for the magnetic interaction are analogous, and differ only in the absence of the factors $(\omega_{ac}/\omega)^2$ and $(\omega_{bc}/\omega)^2$ in the expression for the frequency shift. The combination principle holds in this approximation, but the shifts are singular for resonant radiation.

If the radiation is purely monochromatic, the general results

(7) and (8) reduce to

$$D_{ab}^{(e)} = \frac{1}{2} \sum_c \left\{ (\Omega_{ac}/\omega)^2 |\vec{P}_{ac}| \hat{E}^2 \left[\frac{(\omega_{ac} + \omega)}{(\omega_{ac} + \omega)^2 + \gamma_{cb}^2} + \frac{(\omega_{ac} - \omega)}{(\omega_{ac} - \omega)^2 + \gamma_{cb}^2} \right] \right. \\ \left. - (\Omega_{bc}/\omega)^2 |\vec{P}_{bc}| \hat{E}^2 \left[\frac{(\omega_{bc} + \omega)}{(\omega_{bc} + \omega)^2 + \gamma_{ac}^2} + \frac{(\omega_{bc} - \omega)}{(\omega_{bc} - \omega)^2 + \gamma_{ac}^2} \right] \right\} \quad (13)$$

$$\Gamma_{ab}^{(e)} = \frac{1}{2} \sum_c \left\{ (\Omega_{ac}/\omega)^2 |\vec{P}_{ac}| \hat{E}^2 \gamma_{bc} \left[\frac{1}{[(\omega_{ac} + \omega)^2 + \gamma_{bc}^2]^{-1}} + \frac{1}{[(\omega_{ac} - \omega)^2 + \gamma_{bc}^2]^{-1}} \right] \right. \\ \left. + (\Omega_{bc}/\omega)^2 |\vec{P}_{bc}| \hat{E}^2 \gamma_{ac} \left[\frac{1}{[(\omega_{bc} + \omega)^2 + \gamma_{ac}^2]^{-1}} + \frac{1}{[(\omega_{bc} - \omega)^2 + \gamma_{ac}^2]^{-1}} \right] \right\} \quad (14)$$

²⁵ Masakata Mizushima, Phys. Rev. 133, A414 (1964).

with the corresponding results for magnetic interactions, namely

$$D_{ab}^{(m)} = \frac{1}{2} \sum_c \left\{ |\vec{\mu}_{ac} \cdot \vec{B}|^2 \left[\frac{(\omega_{ac} + \omega)}{(\omega_{ac} + \omega)^2 + \gamma_{cb}^2} + \frac{(\omega_{ac} - \omega)}{(\omega_{ac} - \omega)^2 + \gamma_{cb}^2} \right] \right. \\ \left. - |\vec{\mu}_{bc} \cdot \vec{B}|^2 \left[\frac{(\omega_{bc} + \omega)}{(\omega_{bc} + \omega)^2 + \gamma_{ac}^2} + \frac{(\omega_{bc} - \omega)}{(\omega_{bc} - \omega)^2 + \gamma_{ac}^2} \right] \right\}, \quad (15)$$

$$\Gamma_{ab}^{(m)} = \frac{1}{2} \sum_c \left\{ |\vec{\mu}_{ac} \cdot \vec{B}|^2 \gamma_{bc}^2 \left(\frac{1}{[(\omega_{ac} + \omega)^2 + \gamma_{bc}^2]} + \frac{1}{[(\omega_{ac} - \omega)^2 + \gamma_{bc}^2]} \right) \right. \\ \left. + |\vec{\mu}_{bc} \cdot \vec{B}|^2 \gamma_{ac}^2 \left(\frac{1}{[(\omega_{bc} + \omega)^2 + \gamma_{ac}^2]} + \frac{1}{[(\omega_{bc} - \omega)^2 + \gamma_{ac}^2]} \right) \right\}. \quad (16)$$

ACKNOWLEDGMENTS

The author takes pleasure in expressing his thanks to Professor L. R. Wilcox for suggesting the above problem to him and for his constant interest in this work. He also wishes to acknowledge the benefit of several stimulating discussions with Professor R. L. Douglass. Professors F. Bruin and F. W. Heineken read parts of the manuscript and suggested some improvements.

Note added in proof: The discussion of the short memory approximation given in Section II-5 seems to leave much to be desired in the way of emphasis of the relevant physical concepts. The same problem has been treated by E. T. Jaynes (Phys. Rev. 108, 171 (1957)), who uses the correlation-function technique. His analysis shows that the system density matrix decays in a manner that is dominated by Gaussian time-dependence for times smaller than the correlation time of the bath; while for times larger than the correlation time the time-dependence is exponential (curve A in the diagram below). Our solution, Eq. II(33), ignores the details of the time-dependence of $p(t)$ for periods of time less than the correlation time and extrapolates the exponential decay back to $t=0$ (curve B in diagram). This gives rise to the factor $(1-\Delta)^{-1}$ in that expression.

