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Forced Two-Level Oscillator

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Previously derived equations for the expectation values of the dynamical variables of a general two-level dipole system (TLS) coupled to a relaxation mechanism—of which the Bloch equations for a spin-$\frac{1}{2}$ magnetic-dipole system are a special case—are reformulated in the density-matrix formalism in order to point out the explicit difference in the relaxation terms between the present description, which includes electric-dipole systems, and that of conventional treatments that are based on the assumption that any TLS is equivalent to a spin-$\frac{1}{2}$ magnetic dipole. The original equations are then solved for a weak monochromatic driving field, and the frequency of maximum power absorption is shown to depend on the type of TLS under consideration. The case of a stronger monochromatic driving field and the resulting saturation effects are studied for a special TLS, a spatially linear electric dipole which may have permanent dipole moment. This case exhibits a strong-field resonance shift that depends on the magnitude of the permanent dipole moment. A driving field consisting of a strong component at resonance and a weak component near resonance is considered in connection with the same TLS. The polarization is shown to contain, in lowest order, a component at the difference frequency with an amplitude determined by the magnitude of the permanent dipole moment.

I. INTRODUCTION

In a recent article, hereafter referred to as II,[1] a set of differential equations were derived which describe the behavior of a completely general two-level dipole system driven by external fields and coupled to a fairly general relaxation mechanism. It was shown there that the Bloch equations for a magnetic dipole are a special case of these equations and that not all two-level systems—when coupled to a relaxation mechanism—are equivalent to a spin-$\frac{1}{2}$ magnetic-dipole system (in ordinary space), as is commonly thought. It is the purpose of the present article to investigate the difference between the description of two-level systems by these general equations and that of conventional treatments, and then to study the solution of these equations for certain special cases that are of interest.

II. GENERAL EQUATIONS

As shown in II, the properties of a general two-level system (TLS) possessing dipole moment are completely described by the dipole vectors $\mathbf{a}_\alpha$, $\alpha=1, 2, 3, 4$, which enter into the specification of the dipole-moment operator $\mathbf{d}$ given by the expression

$$\mathbf{d}=\mu\sum_{\alpha=1}^{4}\mathbf{a}_\alpha\sigma_\alpha\,, \tag{1}$$

where μ is the strength of the dipole moment, σ_1, σ_2, and σ_3 are the Pauli spin matrices—with $\frac{1}{2}\hbar\omega\sigma_3$ being the energy, referred to the midpoint between the two levels—and σ_4 is the unit matrix. The general TLS equations of motion [Eqs. II (43)] are

$$\dot{\sigma}_1=(-\omega+\tilde{\eta}\mathbf{a}_1\cdot\mathbf{a}_2)\sigma_2-\tilde{\eta}a_2^2\sigma_1+\eta\mathbf{a}_1\cdot\mathbf{a}_3(\sigma_3-\sigma_0)+\mathbf{a}_2\cdot\mathbf{f}\sigma_3-\mathbf{a}_3\cdot\mathbf{f}\sigma_2\,, \tag{2a}$$

$$\dot{\sigma}_2=(\omega+\tilde{\eta}\mathbf{a}_1\cdot\mathbf{a}_2)\sigma_1-\tilde{\eta}a_1^2\sigma_2+\eta\mathbf{a}_2\cdot\mathbf{a}_3(\sigma_3-\sigma_0)+\mathbf{a}_3\cdot\mathbf{f}\sigma_1-\mathbf{a}_1\cdot\mathbf{f}\sigma_3\,, \tag{2b}$$

$$\dot{\sigma}_3=-(a_1^2+a_2^2)\eta(\sigma_3-\sigma_0)+\mathbf{a}_1\cdot\mathbf{f}\sigma_2-\mathbf{a}_2\cdot\mathbf{f}\sigma_1\,, \tag{2c}$$

where σ_1, σ_2, and σ_3 now stand for the *expectation values* of the Pauli spin matrices, $\tilde{\eta}$ and η are two relaxation constants (expressions for which in terms of the relaxation mechanism parameters are given in II), $\mathbf{f}$ is the driving field in units of $-\hbar/2\mu$, and σ_0 is the equilibrium energy in units of $\frac{1}{2}\hbar\omega$ (measured from the midpoint between the two levels) in absence of a driving field. The units are chosen so that $\tilde{\eta}$, η, and f have the dimensions of frequency; the σ's and $\mathbf{a}$'s are dimensionless, of course. $\mathbf{a}_3$ and $\mathbf{a}_4$ determine the permanent dipole moment.[2] Since $\mathbf{a}_4$ does not enter into the equations of motion and does not, therefore, affect the dynamics of the TLS, we drop it, henceforth, from consideration. It can always be added at the end of any calculation.

The derivation of Eqs. (2) employed the assumption that σ_1 and σ_2 are approximately oscillatory functions with a frequency in the neighborhood of ω. As far as the spin *operators* (in the Heisenberg picture) are concerned, this assumption is justified by the operator equations of motion [Eqs. II (10)] and the condition that the forces due to both the driving field and relaxation mechanism are weak compared to the internal forces of the TLS. (In the notation of II, $\mathbf{f}$ and $\mathbf{F}$ are small compared to ω.) As far as the expectation values of σ_1 and σ_2 are concerned, however, this assumption is true only if the driving field frequency (or frequencies) are in the neighborhood of ω, for in the steady state, the intrinsic frequency is damped out and the frequencies of σ_1 and σ_2 are determined by the driving field, if one exists. (As shown in II, $\langle\sigma_1\rangle$ and $\langle\sigma_2\rangle$ are exponentially damped in

[1] I. R. Senitzky, Phys. Rev. **134**, A816 (1964). (This is the second of two articles dealing with a two-level system coupled to a relaxation mechanism, hence the symbol II.)

[2] The permanent dipole moment is the expectation value of the dipole moment when the TLS is in an energy state. Note that for an electric dipole system the "permanent" moment may be due to an external field.

absence of a driving field, but there cannot be any damping out of the operators, since $\sigma_{1\,\mathrm{op}}{}^2=\sigma_{1\,\mathrm{op}}{}^2=1$ for all times.) The case in which the driving field frequency is much different from ω will be discussed in a forthcoming article; in the present instance, we consider only driving fields near resonance.

It is reasonable to assume that Eqs. (2) may be applied not only to the case of a positive equilibrium temperature but also to that of a negative "equilibrium" temperature, that is, to a situation in which population inversion is achieved by a process that contains sufficient randomness, this process being considered part of the relaxation mechanism. The method employed in three-level masers, for example, that of pumping to a third level combined with thermal relaxation to the second level, is such a process. In the case of positive temperature, σ_0 is negative, and in the case of negative temperature, σ_0 is positive.

The study of quantum-mechanical systems coupled to a relaxation mechanism has been carried out in two different formalisms. In one, the equations of motion involve the dynamical variables (as either operators or expectation values) and in the other, the equations of motion involve density matrices. The first formalism is that of Bloch equations[3] and of the present treatment, and the second formalism is that of the large majority of treatments.[4] It is therefore of interest to recast Eqs. (2) into the density matrix formalism and compare the resulting equations of motion with that of other treatments.

The relationship between the expectation values of the Pauli spin matrices and the density matrix ρ for a TLS is

$$\sigma_1=\rho_{12}+\rho_{21}\,, \tag{3a}$$

$$\sigma_2=i(\rho_{12}-\rho_{21})\,, \tag{3b}$$

$$\sigma_3=\rho_{11}-\rho_{22}\,. \tag{3c}$$

Since $\rho_{11}+\rho_{22}=1$, the density matrix is specified by three numbers, which may conveniently be chosen as ρ_{12}, ρ_{21}, and $\rho_{11}-\rho_{22}$, the last being just σ_3. From Eqs. (3a) and (3b), we have

$$\rho_{12}=\tfrac{1}{2}(\sigma_1-i\sigma_2)\,, \tag{4a}$$

$$\rho_{21}=\tfrac{1}{2}(\sigma_1+i\sigma_2)\,, \tag{4b}$$

and Eqs. (2) become

$$\dot\rho_{12}=(-i\omega-2\tilde\eta\mathbf{a}_+\cdot\mathbf{a}_--i\mathbf{f}\cdot a_3)\rho_{12}+2\tilde\eta a_-^2\rho_{21}+\eta\mathbf{a}_-\cdot a_3(\sigma_3-\sigma_0)+i\mathbf{f}\cdot\mathbf{a}_-\sigma_3\,, \tag{5a}$$

$$\dot\rho_{21}=(i\omega-2\tilde\eta\mathbf{a}_+\cdot\mathbf{a}_-+i\mathbf{f}\cdot a_3)\rho_{21}+2\tilde\eta a_+^2\rho_{12}+\eta\mathbf{a}_+\cdot a_3(\sigma_3-\sigma_0)-i\mathbf{f}\cdot\mathbf{a}_+\sigma_3\,, \tag{5b}$$

$$\dot\sigma_3=-4\eta\mathbf{a}_+\cdot\mathbf{a}_-(\sigma_3-\sigma_0)+2i\mathbf{f}\cdot(\mathbf{a}_+\rho_{12}-\mathbf{a}_-\rho_{21})\,, \tag{5c}$$

where

$$\mathbf{a}_\pm\equiv\tfrac{1}{2}(\mathbf{a}_1\pm i\mathbf{a}_2)$$

and

$$a_\pm{}^2\equiv\mathbf{a}_\pm\cdot\mathbf{a}_\pm\,.$$

For a magnetic dipole system, $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are orthonormal. As shown in II, Eqs. (2) become, under these circumstances, the Bloch equations, and Eqs. (5) simplify to

$$\dot\rho_{12}=(-i\omega-\tilde\eta-if_3)\rho_{12}+if_-\sigma_3\,, \tag{6a}$$

$$\dot\rho_{21}=(i\omega-\tilde\eta+if_3)\rho_{21}-if_+\sigma_3\,, \tag{6b}$$

$$\dot\sigma_3=-2\eta(\sigma_3-\sigma_0)+2i(f_+\rho_{12}-f_-\rho_{21})\,, \tag{6c}$$

where the notation

$$f_\pm\equiv\mathbf{f}\cdot\mathbf{a}_\pm\,,\quad f_3\equiv\mathbf{f}\cdot\mathbf{a}_3$$

has been used. It is to be noticed that the relaxation terms (the terms containing $\tilde\eta$ and η) of Eqs. (6) are different, in general, from those of Eqs. (5). However, apparently because of the commonly accepted belief that any TLS is like a spin-$\frac{1}{2}$ magnetic-dipole system (even when coupled to a relaxation mechanism), the relaxation terms of Eqs. (6) have been used in the literature for a general TLS.[4] In the present article emphasis will be placed on situations where the dipole vectors are not orthonormal, and the relaxation terms of Eqs. (5), rather than those of Eqs. (6), must be used.

III. SOLUTION OF THE EQUATIONS

In II, the approach of the TLS to equilibrium (from given initial conditions) in the absence of a driving field was examined. The present discussion will concern itself with the steady-state response of the TLS to a stationary driving field. This response is specified by the expectation value of the dipole moment, which, through Eq. (1), is determined by the σ's. We return, therefore, to Eqs. (2) and seek their steady-state solutions for particular driving fields.

In order to have notational simplicity, Eqs. (2) will be rewritten in a more compact notation. Setting

$$\eta\mathbf{a}_i\cdot\mathbf{a}_j\equiv\eta_{ij}\,, \tag{7a}$$

$$\tilde\eta\mathbf{a}_i\cdot\mathbf{a}_j\equiv\tilde\eta_{ij}\,, \tag{7b}$$

$$\mathbf{f}\cdot\mathbf{a}_i\equiv f_i\,, \tag{7c}$$

we have

$$\dot\sigma_1=(-\omega+\tilde\eta_{12})\sigma_2-\tilde\eta_{22}\sigma_1+\eta_{13}(\sigma_3-\sigma_0)+f_2\sigma_3-f_3\sigma_2\,, \tag{8a}$$

$$\dot\sigma_2=(\omega+\tilde\eta_{12})\sigma_1-\tilde\eta_{11}\sigma_2+\eta_{23}(\sigma_3-\sigma_2)+f_3\sigma_1-f_1\sigma_3\,, \tag{8b}$$

$$\dot\sigma_3=-(\eta_{11}+\eta_{22})(\sigma_3-\sigma_0)+f_1\sigma_2-f_2\sigma_1\,. \tag{8c}$$

Equation (8c) may be rewritten in integral form adapted for the steady-state situation,

$$\sigma_3=\sigma_0+\int_{-\infty}^{t}dt_1\exp[-(\eta_{11}+\eta_{22})(t-t_1)]\times[f_1(t_1)\sigma_2(t_1)-f_2(t_1)\sigma_1(t_1)]\,. \tag{9}$$

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[3] F. Bloch, Phys. Rev. **70**, 460 (1946); R. K. Wangsness and F. Bloch, *ibid.* **89**, 728 (1953). The Bloch equations may be interpreted as relations between macroscopic variables or between expectation values of microscopic variables. The present discussion refers to the latter interpretation.

[4] See, for instance, N. Bloembergen and Y. R. Shen, Phys. Rev. **133**, A37 (1964) (additional references are given there); Yoh-Han Pao, J. Opt. Soc. Am. **52**, 871 (1962).

A. Weak Field—General TLS

We consider, first, the case in which the TLS is driven by a weak field, and take $\mathbf{f}$ to be a small quantity of first order. The zeroth-order (steady-state) solution is

$$\sigma_1=\sigma_2=0, \quad \sigma_3=\sigma_0, \tag{10}$$

and Eq. (9) shows that σ_3 has no first-order contribution. The equations for the first-order solution are, therefore,

$$\dot{\sigma}_1=(-\omega+\tilde{\eta}_{12})\sigma_2-\tilde{\eta}_{22}\sigma_1+f_2\sigma_0, \tag{11a}$$

$$\dot{\sigma}_2=(\omega+\tilde{\eta}_{12})\sigma_1-\tilde{\eta}_{11}\sigma_2-f_1\sigma_0. \tag{11b}$$

These equations may be combined to yield differential equations for σ_1 and σ_2 individually:

$$\ddot{\sigma}_1+(\tilde{\eta}_{11}+\tilde{\eta}_{22})\dot{\sigma}_1+\omega'^2\sigma_1 =\sigma_0[(\omega-\tilde{\eta}_{12})f_1+\tilde{\eta}_{11}f_2+\dot{f}_2], \tag{12a}$$

$$\ddot{\sigma}_2+(\tilde{\eta}_{11}+\tilde{\eta}_{22})\dot{\sigma}_2+\omega'^2\sigma_2 =\sigma_0[(\omega+\tilde{\eta}_{12})f_2-\tilde{\eta}_{22}f_1-\dot{f}_1], \tag{12b}$$

where

$$\omega'^2=\omega^2-\tilde{\eta}_{12}{}^2+\tilde{\eta}_{11}\tilde{\eta}_{22}=\omega^2+\tilde{\eta}^2[a_1{}^2a_2{}^2-(\mathbf{a}_1\cdot\mathbf{a}_2)^2]. \tag{12c}$$

We see from Eqs. (12) that, when the driving field is sufficiently weak, σ_1 and σ_2 behave like the coordinates of a forced harmonic oscillator of (undamped) frequency ω' and damping coefficient $\tilde{\eta}(a_1{}^2+a_2{}^2)$, the forcing terms being given by the right-hand sides of Eqs. (12a) and (12b), respectively. It is clear that, for given magnitudes of $\mathbf{a}_1$ and $\mathbf{a}_2$, ω' is a maximum when $\mathbf{a}_1$ and $\mathbf{a}_2$ are orthogonal, and drops to its minimum ω, when $\mathbf{a}_1$ and $\mathbf{a}_2$ are parallel. The former case corresponds to a magnetic dipole TLS and the latter case corresponds to a (spatially) linear electric dipole TLS. The (steady-state) solution of Eqs. (12a) and (12b) for a linearly polarized monochromatic driving field and TLS of fixed orientation is a straightforward but somewhat tedious harmonic-oscillator type of calculation, and is given in Appendix A. The linearity of Eqs. (12a) and (12b) permits their solution for an arbitrary driving field (subject to the restrictions of the present article) by the superposition of the individual solutions for the Fourier components of the driving field.

The frequency response of the average power P absorbed by the TLS from a weak driving field is of interest. From the definition of the present notation (see Appendix B) this power is given by

$$\mathrm{P}=-\tfrac{1}{2}\hbar\textstyle\sum_i\langle f_i\dot{\sigma}_i\rangle_{\mathrm{av}}. \tag{13}$$

If we consider a field specified by

$$\mathbf{f}=\boldsymbol{\varphi}(e^{i\nu t}+e^{-i\nu t}), \tag{14}$$

where $\boldsymbol{\varphi}$ is a fixed vector, then it is shown in Appendix B that

$$P=-\frac{\hbar\nu^2\sigma_0\tilde{\eta}(a_1{}^2+a_2{}^2)}{(\nu^2-\omega'^2)^2+\nu^2\tilde{\eta}^2(a_1{}^2+a_2{}^2)}[\boldsymbol{\varphi}\cdot(\omega\mathfrak{M}+\tilde{\eta}\mathfrak{N})\cdot\boldsymbol{\varphi}], \tag{15}$$

where $\mathfrak{M}$ and $\mathfrak{N}$ are the dyadics

$$\mathfrak{M}\equiv\mathbf{a}_1\mathbf{a}_1+\mathbf{a}_2\mathbf{a}_2, \tag{15a}$$

$$\mathfrak{N}\equiv(\mathbf{a}_1\cdot\mathbf{a}_2)(\mathbf{a}_2\mathbf{a}_2-\mathbf{a}_1\mathbf{a}_1)-(a_2{}^2-a_1{}^2)\mathbf{a}_1\mathbf{a}_2. \tag{15b}$$

The expression in the square brackets of Eq. (15) depends, obviously, on the orientation (assumed fixed) of the TLS relative to the driving field. As the driving field frequency ν is varied, P reaches a maximum at

$$\nu=\omega'. \tag{16}$$

This frequency of maximum absorption is often used as the definition of resonant frequency. It may be compared with the frequency of free decay Ω in the absence of a driving field, which was obtained in II [and can also be obtained from Eqs. (12) by setting $\mathbf{f}=0$], and is given by

$$\Omega^2=\omega^2-\tilde{\eta}^2[(\mathbf{a}_1\cdot\mathbf{a}_2)^2+\tfrac{1}{4}(a_1{}^2-a_2{}^2)^2]. \tag{17}$$

It is to be noted that

$$\omega'^2-\Omega^2=\tfrac{1}{4}\tilde{\eta}^2(a_1{}^2+a_2{}^2), \tag{18}$$

a relationship between frequency of maximum absorption, frequency of free decay, and damping coefficient that is characteristic of harmonic oscillators. We see that both the frequency of maximum absorption ω' and frequency of free decay Ω depend on the configuration of the dipole vectors, and the difference between these two frequencies depends only on the damping coefficient. Also, $\omega'\geqslant\omega$ and $\Omega\leqslant\omega$, so that for systems with the same damping coefficient, these two frequencies may be thought of as two end points of an interval of fixed length on the frequency axis situated so as to contain ω. If $\mathbf{a}_1$ and $\mathbf{a}_2$ have equal magnitudes, and if the angle between them is varied from 0 to $\frac{1}{2}\pi$, this interval slides from one extreme position to the other.

In the case for which Eqs. (11) are applicable, that is, in the case of weak driving fields, differential equations may be obtained from the sum of the dipole moments of a large number of identical two-level systems with various orientations. (This is not possible in general, as pointed out in II.) From Eqs. (1) and (12), we have for the $\mathbf{j}$th TLS,

$$d^2\mathbf{d}^{(j)}/dt^2=\mu\textstyle\sum_\alpha\mathbf{a}_\alpha{}^{(j)}d^2\sigma_\alpha{}^{(j)}/dt^2, \tag{19}$$

$$d^2\mathbf{d}^{(j)}/dt^2+(\tilde{\eta}_{11}+\tilde{\eta}_{22})d\mathbf{d}^{(j)}/dt+\omega'^2\mathbf{d}^{(j)}=\mathbf{F}^{(j)}, \tag{20}$$

where

$$\mathbf{F}^{(j)}=\mu\sigma_0(\mathfrak{R}^{(j)}\cdot\mathbf{f}+\mathfrak{S}^{(j)}\cdot d\mathbf{f}/dt-\mathbf{a}_3{}^{(j)}\omega'^2), \tag{20a}$$

$\mathfrak{R}^{(j)}$ and $\mathfrak{S}^{(j)}$ being dyadics given by

$$\mathfrak{R}^{(j)}=(\omega-\tilde{\eta}_{12})\mathbf{a}_1{}^{(j)}\mathbf{a}_1{}^{(j)}+(\omega+\tilde{\eta}_{12})\mathbf{a}_2{}^{(j)}\mathbf{a}_2{}^{(j)} +\tilde{\eta}_{11}\mathbf{a}_1{}^{(j)}\mathbf{a}_2{}^{(j)}-\tilde{\eta}_{22}\mathbf{a}_2{}^{(j)}\mathbf{a}_1{}^{(j)}, \tag{20b}$$

$$\mathfrak{S}^{(j)}=\mathbf{a}_1{}^{(j)}\mathbf{a}_2{}^{(j)}-a_2{}^{(j)}a_1{}^{(j)}. \tag{20c}$$

Setting

$$\mathbf{D}=\textstyle\sum_j\mathbf{d}^{(j)}, \tag{21}$$

we have

$$d^2\mathbf{D}/dt^2+(\tilde{\eta}_{11}+\tilde{\eta}_{22})d\mathbf{D}/dt+\omega'^2\mathbf{D}=\sum_j\mathbf{F}^{(j)}. \quad (22)$$

Equation (22) is the differential equation for the macroscopic dipole moment.

B. Stronger Field—Spatially Linear TLS

We consider now the case in which the driving field is not sufficiently weak for the use of first-order perturbation theory, and saturation effects are important. The solution of Eqs. (8) for a general TLS under these conditions, even for a monochromatic driving field, can be carried out only approximately, is very tedious, and the result is too complicated for easy inspection. It is prudent, therefore, to select a special TLS for consideration. In accordance with the motivation of the present article, we will consider a TLS that is different from the magnetic dipole TLS, for which equations of motion have been available and which has already been studied in detail.[5] In the magnetic dipole TLS, the dipole vectors are orthogonal (and also equal in magnitude). It is, therefore, not unreasonable to select for present discussion a TLS in which the dipole vectors are parallel. The magnitudes of the dipole vectors are left arbitrary, so that we have under consideration the most general spatially linear electric-dipole TLS.

We express the parallel dipole vectors in terms of a unit vector $\hat{a}$ as follows:

$$\mathbf{a}_1=r_1\hat{a}, \quad \mathbf{a}_2=r_2\hat{a}, \quad \mathbf{a}_3=\epsilon\hat{a}, \quad (23)$$

and also set

$$\mathbf{f}\cdot\hat{a}=f. \quad (24)$$

Equations (2) then become

$$\dot{\sigma}_1=(-\omega+\tilde{\eta}r_1r_2)\sigma_2-\tilde{\eta}r_2^2\sigma_1+\eta r_1\epsilon(\sigma_3-\sigma_0)+r_2f\sigma_3-\epsilon f\sigma_2, \quad (25a)$$

$$\sigma_2=(\omega+\tilde{\eta}r_1r_2)\sigma_1-\tilde{\eta}r_1^2\sigma_2+\eta r_2\epsilon(\sigma_3-\sigma_0)+\epsilon f\sigma_1-r_1f\sigma_3, \quad (25b)$$

$$\dot{\sigma}_3=-(r_1^2+r_2^2)\eta(\sigma_3-\sigma_0)+r_1f\sigma_2-r_2f\sigma_1. \quad (25c)$$

The transformation

$$\sigma_\alpha=r_1\sigma_1+r_2\sigma_2, \quad (26a)$$

$$\sigma_\beta=-r_2\sigma_1+r_1\sigma_2, \quad (26b)$$

together with the normalization condition

$$r_1^2+r_2^2=1 \quad (27)$$

(which makes the transformation orthogonal), can be used to obtain the much simpler set of equations

$$\dot{\sigma}_\alpha=-\omega\sigma_\beta+\eta\epsilon(\sigma_3-\sigma_0)-\epsilon f\sigma_\beta, \quad (28a)$$

$$\dot{\sigma}_\beta=\omega\sigma_\alpha-\tilde{\eta}\sigma_\beta-f\sigma_3+\epsilon f\sigma_\alpha, \quad (28b)$$

$$\dot{\sigma}_3=-\eta(\sigma_3-\sigma_0)+f\sigma_\beta. \quad (28c)$$

In terms of the new variables, the dipole moment is given by

$$\mathbf{d}=\mu\hat{a}(\sigma_\alpha+\epsilon\sigma_3). \quad (29)$$

It is interesting to note that if r_2 were set equal to zero (and r_1 equal to unity) in Eqs. (25), they would reduce to Eqs. (28) with σ_α replaced by σ_1 and σ_β replaced by σ_2. This means that the description of the system for which $\mathbf{a}_1$ and $\mathbf{a}_2$ are parallel ($\mathbf{a}_3$ is not involved in the above transformation) is connected to the description of the system for which $\mathbf{a}_2$ is zero by a unitary transformation, and the two systems are essentially equivalent.[6]

Equation (28a) can be rewritten in a more compact form by noting that the last two terms are a multiple of $\dot{\sigma}_3$. We thus have

$$\dot{\sigma}_\alpha=-\omega\sigma_\beta-\epsilon\dot{\sigma}_3. \quad (30)$$

Further simplification can be achieved by considering a new variable defined by

$$\sigma=\sigma_\alpha+\epsilon(\sigma_3-\sigma_0), \quad (31)$$

and in terms of which we have

$$\mathbf{d}=\mu\hat{a}(\sigma+\epsilon\sigma_0). \quad (32)$$

The physical significance of σ is clear. It is the magnitude (in units of μ) of the deviation of the TLS dipole moment from equilibrium value. Substitution for σ_α in terms of σ and σ_3 in Eqs. (28a) and (28b) yields

$$\dot{\sigma}=-\omega\sigma_\beta, \quad (33a)$$

$$\dot{\sigma}_\beta=(\omega+\epsilon f)[\sigma-\epsilon(\sigma_3-\sigma_0)]-\tilde{\eta}\sigma_\beta-f\sigma_3. \quad (33b)$$

In analogy with the introduction of σ, we introduce σ', the deviation of σ_3—the energy, in units of $\frac{1}{2}\hbar\omega$—from equilibrium value:

$$\sigma'=\sigma_3-\sigma_0. \quad (34)$$

Substituting for σ_3 from Eq. (34) and for σ_β from Eq. (33a) into Eqs. (28c) and (33b), we obtain, in terms of dipole moment and energy measured from equilibrium value in appropriate units,

$$\ddot{\sigma}+\tilde{\eta}\dot{\sigma}+\omega^2(1+\epsilon f/\omega)\sigma=\omega\sigma_0 f+\epsilon\omega^2\sigma'+(1+\epsilon^2)\omega f\sigma', \quad (35a)$$

$$\dot{\sigma}'=-\eta\sigma'-(f/\omega)\dot{\sigma}. \quad (35b)$$

These equations describe completely the behavior of the spatially linear TLS.[7] It is readily noted that a pair of differential equations for macroscopic dipole moment

[5] A. Abragam, *The Principles of Nuclear Magnetism* (Oxford University Press, New York, 1961); N. Bloembergen and Y. R. Shen, Phys. Rev. **133**, A37 (1964).

[6] It is seen that the relaxation terms in Eqs. (25a) and (25b) which are absent in the case of a magnetic dipole are needed for this equivalence, in general.

[7] If $\mathbf{a}_3=0$, then $\epsilon=0$, and Eq. (35a) becomes

$$\ddot{\sigma}+\tilde{\eta}\dot{\sigma}+\omega^2\sigma=\omega f(\sigma_0+\sigma').$$

This equation and Eq. (35b) have been used by J. Fontana, R. Pantell, and R. Smith, *Advances in Quantum Electronics*, edited by J. R. Singer (Columbia University Press, New York, 1961), and by L. W. Davis, Proc. IEEE **51**, 76 (1963). These authors consider a free two-level system without permanent dipole moment and insert damping terms phenomenologically into the equations for the expectation value of dipole moment and energy.

and energy *cannot* be constructed if the orientation of all the microscopic systems is not the same, for f and, therefore, σ' (as well as σ, of course) depend on orientation, and the sum of $f\sigma'$ cannot be expressed in terms of the sum of σ', the macroscopic energy.

For a steady-state situation, Eq. (35b) may be put into the integral form

$$\sigma'=-\frac{1}{\omega}\int_{-\infty}^{t}dt_1e^{-\eta(t-t_1)}f(t_1)\dot{\sigma}(t_1)\,, \tag{36}$$

which may then be substituted into Eq. (35a) to yield an integrodifferential equation for σ only.

$$\ddot{\sigma}+\bar{\eta}\dot{\sigma}+\omega^2(1+\epsilon f/\omega)\sigma =\omega\sigma_0f-[\epsilon\omega+f(1+\epsilon^2)]\int_{-\infty}^{t}dt_1e^{-\eta(t-t_1)}f(t_1)\dot{\sigma}(t_1)\,. \tag{37}$$

1. *Monochromatic Driving Field*

If the driving field is monochromatic and the TLS orientation fixed, we have

$$f=f_0(e^{i\nu t}+e^{-i\nu t})\,. \tag{38}$$

A method of solution now consists of expanding σ into a Fourier series,

$$\sigma=\sum_{n=-\infty}^{\infty}A_ne^{in\nu t}, \tag{39}$$

where

$$A_{-n}=A_n^*, \tag{39a}$$

and substituting from Eq. (39) in Eq. (37). Equating equal powers of $\exp(i\nu t)$, we obtain an infinite set of simultaneous equations,

$$\left\{\omega^2-n^2\nu^2+in\bar{\eta}\nu+(1+\epsilon^2)\,n\nu f_0^2\left[\frac{1}{(n-1)\nu-i\eta}+\frac{1}{(n+1)\nu-i\eta}\right]\right\}A_n=\omega\sigma_0f_0(\delta_{n1}+\delta_{n,-1})$$
$$-\epsilon\omega\nu f_0\frac{(n-1)A_{n-1}+(n+1)A_{n+1}}{n\nu-i\eta}-\epsilon\omega f_0(A_{n-1}+A_{n+1})-(1+\epsilon^2)\nu f_0^2\left[\frac{(n-2)A_{n-2}}{(n-1)\nu-i\eta}+\frac{(n+2)A_{n+2}}{(n+1)\nu-i\eta}\right]. \tag{40}$$

Let us consider f_0/ω to be a small quantity of first order. If we take ϵ to be of the order of magnitude of unity, then Eq. (40) is satisfied by the following order of magnitude relationships:

$$A_0\sim(f_0/\eta)A_1\,, \tag{41a}$$

$$A_1\sim(f_0/\bar{\eta})\sigma_0\,, \tag{41b}$$

$$A_n\sim(f_0/\omega)^{n-1}A_1\,,\quad n\geqslant1\,. \tag{41c}$$

If $\epsilon=0$, all even harmonics vanish, and Eq. (41c) applied only the the odd harmonics.

Our interest lies mainly in $A_{\pm1}$, since these two coefficients determine the average effects of the interaction between TLS and field. Setting $n=1$ in Eq. (40), we see that in order to calculate possible frequency shifts at resonance, we must retain terms as high as the order of $f_0^2A_1$, since f_0^2 is the order of magnitude of the real part of the coefficient of A_1 for $\nu=\omega$, and it is the vanishing of the real part that accounts (mathematically) for resonance. The ωf_0A_2 terms must therefore be retained, but the $f_0^2A_3$ term may be dropped. The only coefficients that concern us, altogether, are A_0, $A_{\pm1}$, $A_{\pm2}$, and Eq. (40) furnishes a set of equations for their deviation. With some obvious approximation, based on the relationship $\eta\ll\omega$, we have

$$[\omega^2-\nu^2+i\bar{\eta}\nu+(1+\epsilon^2)\nu f_0^2(i\eta^{-1}+\tfrac{1}{2}\nu^{-1})]A_1 =\omega\sigma_0f_0-\epsilon\omega f_0A_0-3\epsilon\omega f_0A_2+i(1+\epsilon^2)\nu f_0^2\eta^{-1}A_{-1}\,. \tag{42}$$

It is clear that for use in Eq. (42), A_0 is needed up to the order of $(f_0/\omega)\,A_1$, and A_2 is needed only in lowest order. We obtain from Eq. (40), with these approximations,

$$A_0=-\epsilon(f_0/\omega)[A_1+A_{-1}+i(\nu/\eta)(A_1-A_{-1})]\,, \tag{43}$$

$$A_{\pm2}=\tfrac{1}{2}\epsilon(f_0/\omega)A_{\pm1}\,, \tag{44}$$

where an additional approximation based on the relationship $|\omega-\nu|\ll\omega$ has been introduced in the latter equation. Substitution from Eqs. (43) and (44) into Eq. (42) yields an equation in A_1 and A_{-1}, which, together with its complex conjugate and Eq. (39a), provides two equations for these coefficients. The solution gives

$$A_{\pm1}=\omega\sigma_0f_0[\omega^2-\nu^2+\tfrac{1}{2}f_0^2(1+4\epsilon^2)\mp i\nu\bar{\eta}]\mathfrak{D}^{-1}\,, \tag{45}$$

where

$$\mathfrak{D}=(\omega^2-\nu^2+\tfrac{1}{2}f_0^2)^2+2\epsilon^2f_0^2(\omega^2-\nu^2+\tfrac{1}{2}f_0^2) +\nu^2\bar{\eta}^2(1+2f_0^2/\eta\bar{\eta})\,. \tag{45a}$$

From Eq. (43) we have

$$A_0\approx-2\epsilon\sigma_0f_0^2\nu^2(\bar{\eta}/\eta)\mathfrak{D}^{-1}. \tag{46}$$

As was already evident from Eq. (41a), the zero-frequency "harmonic" is of the same order of magnitude as the fundamental (if f_0 and η are considered to be of the same order). For $\epsilon\neq0$, therefore, we can regard zero as a resonant frequency of the system. If an analogy is made between nonlinear susceptibility and nonlinear conductance, A_0 may be considered as the "rectified" polarization. Equation (46) shows that the TLS is a square-law "rectifier" for $\epsilon\neq0$.

The expression for the average power absorbed from the field, from Eqs. (13) and (39), is

$$P=-\tfrac{1}{2}i\hbar f_0\nu(A_1-A_{-1})\,, \tag{47}$$

which, by the use of Eq. (45), becomes

$$P=-\hbar\omega\sigma_0\tilde{\eta}\nu^2 f_0^2\mathfrak{D}^{-1}. \tag{48}$$

It is interesting to compare Eq. (48) with Eq. (15), which, it is recalled, is the expression for power absorption by a general TLS from a very weak field. If we ignore the f_0^2 terms in $\mathfrak{D}$, and let $\mathbf{a}_1$ and $\mathbf{a}_2$ be parallel and subject to the normalization condition $a_1^2+a_2^2=1$ in Eq. (15), then (noting that $\boldsymbol{\varphi}\cdot\hat{a}=f_0$) the two expressions become identical. The frequency of maximum absorption, in the present instance, is given by

$$\nu_0^2=[(\omega^2+\tfrac{1}{2}f_0^2)^2+2\epsilon^2 f_0^2(\omega^2+\tfrac{1}{2}f_0^2)]^{1/2} \approx\omega^2[1+(\tfrac{1}{2}+\epsilon^2)f_0^2/\omega^2]. \tag{49}$$

Comparison with Eq. (16) shows that the shift due to the nonparallelism of $\mathbf{a}_1$ and $\mathbf{a}_2$ is absent, but we now have a shift that depends on the strength of the driving field. It is the analog of the Bloch-Siegert shift[8] in the case of a magnetic dipole. As Eq. (49) shows, it is affected, in the present case, by the magnitude of the permanent dipole moment.

2. *Superposition of Two Driving Frequencies*

We will consider now a driving field containing two frequencies, ω_1 and ω_2, both close to ω, with the amplitude of one being large and that of the other small. Let

$$f(t)=2f_1\cos\omega_1 t+2f_2\cos\omega_2 t\,, \tag{50}$$

with

$$f_2\gg f_1\,, \tag{50a}$$

where ω_2 is the resonant frequency and ω_1 is in the neighborhood of resonance. The resonant frequency may be defined in several ways: as ω, or as the frequency of maximum power absorption from a monochromatic field, or as the frequency for which $A_{\pm1}$ of Eq. (45) (the amplitude of the fundamental of polarization for a monochromatic field) has a maximum absolute value, or as the frequency for which $A_{\pm1}$ is a pure imaginary, or as the frequency of free decay. These frequencies are all sufficiently close together so that we can approximate the expression for $A_{\pm1}$ and A_0 by

$$A_{\pm1}=\frac{\mp i\sigma_0 f_0}{\tilde{\eta}(1+2f_0^2/\eta\tilde{\eta})}\,, \tag{51a}$$

$$A_0=\frac{-2\epsilon\sigma_0 f_0^2}{\eta\tilde{\eta}(1+2f_0^2/\eta\tilde{\eta})}\,. \tag{51b}$$

These expressions will be utilized later.

We focus our attention on the steady-state solution of Eq. (37) with f given by Eq. (50). Expanding σ into a double series,

$$\sigma=\sum_{m,n=-\infty}^{\infty}A_{mn}e^{i\Omega_{mn}t}\,, \tag{52}$$

where

$$\Omega_{mn}=m\omega_1+n\omega_2\,, \tag{52a}$$

and

$$A_{-m,-n}=A_{mn}{}^*\,,$$

we substitute from Eq. (52) into Eq. (37). The approximation to be used consists of neglecting powers higher than the first in f_1 and retaining only the lowest necessary power of f_2/ω. Using the first of these approximations, one obtains an iterative expression for the A_{mn}'s—in the same manner as that in which Eq. (40) was obtained for a single frequency—which is rather lengthy but of fairly simple structure:

$$\begin{aligned}
&(\omega^2-\Omega_{mn}^2+i\tilde{\eta}\Omega_{mn})A_{mn}\\
&\quad=\omega\sigma_0[f_1\delta_{n0}(\delta_{m1}+\delta_{m,-1})+f_2\delta_{m0}(\delta_{n1}+\delta_{n,-1})]-\epsilon\omega\{[f_1(A_{m-1,n}+A_{m+1,n})+f_2(A_{m,n-1}+A_{m,n+1})]\\
&\qquad+(\Omega_{m,n}-i\eta)^{-1}[f_1(\Omega_{m-1,n}A_{m-1,n}+\Omega_{m+1,n}A_{m+1,n})+f_2(\Omega_{m,n-1}A_{m,n-1}+\Omega_{m,n+1}A_{m,n+1})]\}\\
&\qquad-(1+\epsilon^2)\{f_1f_2[(\Omega_{m-1,n}-i\eta)^{-1}(\Omega_{m-1,n-1}A_{m-1,n-1}+\Omega_{m-1,n+1}A_{m-1,n+1})+(\Omega_{m+1,n}-i\eta)^{-1}\\
&\qquad\times(\Omega_{m+1,n-1}A_{m+1,n-1}+\Omega_{m+1,n+1}A_{m+1,n+1})+(\Omega_{m,n-1}-i\eta)^{-1}(\Omega_{m-1,n-1}A_{m-1,n-1}+\Omega_{m+1,n-1}A_{m+1,n-1})\\
&\qquad+(\Omega_{m,n+1}-i\eta)^{-1}(\Omega_{m-1,n+1}A_{m-1,n+1}+\Omega_{m+1,n+1}A_{m+1,n+1})]+f_2^2[(\Omega_{m,n-1}-i\eta)^{-1}(\Omega_{m,n-2}A_{m,n-2}+\Omega_{m,n}A_{m,n})\\
&\qquad+(\Omega_{m,n+1}-i\eta)^{-1}(\Omega_{m,n}A_{m,n}+\Omega_{m,n+2}A_{m,n+2})]\}\,.
\end{aligned} \tag{53}$$

It is seen that if f_1 is set equal to zero, then the equation for A_{0n} becomes identical to the equation for A_n in the case of the monochromatic driving field. A similar consideration applies if f_2 is set equal to zero, except that terms in f_1^2 are dropped.

An examination of Eq. (53) shows that the lowest powers of f_1 and f_2 contained in A_{mn}, with m and n not both zero, are $f_1{}^{|m|}f_2{}^{|n|}$. We therefore retain only coefficients with $m=0$, ±1. The fundamentals, corresponding to the frequencies of the driving field, have the coefficients $A_{\pm1,0}$ and $A_{0,\pm1}$; all other coefficients refer to harmonics. Further study of Eq. (53) shows that the harmonics are of higher order in f_2/ω than the fundamentals except for A_{00}, $A_{\pm1,\mp1}$, and $A_{\pm1,\mp2}$. These particular harmonics may be called the "resonant" hzrmonics, since, for these (and only these, if $m=0$, ±1) $m\omega_1+n\omega_2$ is either in the neighborhood of ω or 0, and it was mentioned previously that, for $\epsilon\neq0$, zero may be

[8] F. Bloch and A. Siegert, Phys. Rev. **57**, 522 (1940).

regarded as a resonant frequency. Thus, the only terms we need retain are the fundamentals and the resonant harmonics.

Equation (53) may be considered an expression for A_{mn} in terms of the other coefficients. It is easily seen that in the expression for A_{1n}, the coefficients $A_{0n'}$ enter only with the multiplicative factor f_1. The weak field may therefore be neglected in $A_{0n'}$ when it is used to obtain A_{1n}. Furthermore, the weak field effects $A_{0n'}$ only slightly, and for vanishing f_1, $A_{0n'}$ becomes equal to $A_{n'}$ in the single-frequency case. We therefore have, approximately, from Eqs. (51),

$$A_{0,\pm1}=\mp i\sigma_0 f_2/\tilde{\eta}(1+2\beta)\,, \tag{54a}$$

$$A_{00}=-2\epsilon\sigma_0\beta/(1+2\beta)\,, \tag{54b}$$

where

$$\beta\equiv f_2^2/\eta\tilde{\eta}\,. \tag{54c}$$

The only unknowns remaining are $A_{\pm1,0}$, $A_{\pm1,\mp1}$ and $A_{\pm1,\mp2}$. These are three quantities and their complex conjugates. Equation (53) shows that A_{mn} and $A_{m'n'}$ occur in the same equation only if $m-1\leqslant m'\leqslant m+1$. Thus, of the six coefficients, those with $m=1$ occur in one set of equations and those with $m=-1$ occur in another set. Our problem has therefore been reduced to one of solving three simultaneous equations for three unknowns, the equations being immediately obtainable from Eq. (53).

This problem can now be solved in a straightforward manner. For the sake of simplicity, however, we consider only the situation in which

$$|\omega_1-\omega_2|\ll\eta\,. \tag{55}$$

Approximations based on this inequality[9] [as well as on the previously used (stronger) inequality $\eta\ll\omega$] simplify the computation considerably. The three equations for A_{10}, $A_{1,-1}$, and $A_{1,-2}$ become

$$aA_{10}+bA_{1,-1}-cA_{1,-2}=k_1\,, \tag{56a}$$

$$dA_{10}+A_{1,-1}-dA_{1,-2}=k_2\,, \tag{56b}$$

$$cA_{10}+bA_{1,-1}-aA_{1,-2}=k_3\,, \tag{56c}$$

where

$$\begin{aligned}&a\equiv i\tilde{\eta}[1+(1+\epsilon^2)\beta]\,,\quad b\equiv\epsilon f_2\,,\\&c\equiv i\tilde{\eta}(1+\epsilon^2)\beta\,,\quad d\equiv i\epsilon f_2/\eta\,,\\&k_1\equiv\sigma_0 f_1[1-\beta(1+\epsilon^2)]/(1+2\beta)\\&k_2\equiv-\epsilon\sigma_0 f_1 f_2/\eta\tilde{\eta}(1+2\beta)\,,\quad k_3\equiv-\sigma_0 f_1\beta(1+\epsilon^2)/(1+2\beta)\,.\end{aligned}$$

Their solution gives

$$A_{10}=-i\sigma_0 f_1/\tilde{\eta}(1+2\beta)^2\,, \tag{57a}$$

$$A_{1,-1}=-2\epsilon\sigma_0 f_1 f_2/\eta\tilde{\eta}(1+2\beta)^2\,, \tag{57b}$$

$$A_{1,-2}=-2i\sigma_0 f_1\beta/\tilde{\eta}(1+2\beta)^2\,. \tag{57c}$$

We see that A_{10} and $A_{1,-2}$ are unaffected, in lowest order, by the permanent dipole moment, while $A_{1,-1}$ is different from zero only in the presence of a permanent dipole moment. If one sets

$$\omega_1=\omega_2+\delta\,, \tag{58}$$

Eqs. (52), (54), and (57) yield, in lowest order,

$$\sigma=\frac{2\sigma_0}{1+2\beta}\bigg\{-\epsilon\beta+\frac{f_2}{\tilde{\eta}}\sin\omega_2 t+\frac{f_1}{\tilde{\eta}(1+2\beta)}\times\bigg[\sin(\omega_2+\delta)t-\beta\sin(\omega_2-\delta)t+\epsilon\frac{f_2}{\eta}\cos\delta t\bigg]\bigg\}\,. \tag{59}$$

It is to be noted that in addition to the fundamentals, the polarization exhibits the three frequencies 0, δ, and $\omega_2-\delta$. These, of course, are the previously mentioned resonant harmonics Ω_{00}, $\Omega_{\pm1,\mp1}$, and $\Omega_{\pm1,\mp2}$, respectively. The power absorbed from the weak field is given by

$$\begin{aligned}P&=-\tfrac{1}{2}i\hbar f_1\omega_1(A_{10}-A_{-10})\\&=-\frac{\sigma_0\hbar\omega_1 f_1^2}{\tilde{\eta}(1+2\beta)^2}\,,\end{aligned} \tag{60}$$

which is positive (for positive temperature); the weak field is therefore attenuated. If there were imposed, however, a third driving field $2f_1\cos(\omega_2-\delta)t$, it is easy to see that the $\omega_2-\delta$ component of σ in Eq. (59) would amplify it, and, for sufficiently large β, this amplification would overcome the attenuation of the third field due to its own polarization. This is the basis of an amplifier described by Benjamin Senitzky *et al.*[10]

The analogy between nonlinear susceptibility and nonlinear conductance, made earlier, may be continued in the present instance of the superposition of two neighboring frequencies. The strong field corresponds to a local oscillator, the weak field corresponds to a signal, and the electric dipole TLS with permanent dipole moment corresponds to a mixer, the output at the difference frequency being given by the $\cos\delta t$ term of Eq. (59).

APPENDIX A

The steady-state solution of Eqs. (12a) and (12b) for a linearly polarized monochromatic driving field will be obtained. We set

$$\mathbf{f}=2\boldsymbol{\varphi}\cos\nu t\,, \tag{A1}$$

where $\boldsymbol{\varphi}$ is a fixed vector, and

$$\sigma_1=A_+e^{i\nu t}+A_-e^{-i\nu t}\,, \tag{A2}$$

where

$$A_-=A_+^*\,. \tag{A3}$$

[9] Had the inequality (55) been assumed at the beginning, another, and perhaps simpler, method of solution could have been used. The two frequencies could have been combined into a single oscillation with both amplitude and phase modulation. If the modulation frequency is sufficiently low, the expressions for a single frequency can be used approximately (see Ref. 10) in an adiabatic approximation. It is worthwhile, however, to develop a method of solution for the case in which the frequency difference is comparable to the relaxation constant (linewidth)—even though it is not applied in the present article—and where the significance of the resonant harmonics is apparent.

[10] B. Senitzky, G. Gould, and S. Cutler, Phys. Rev. **130**, 1460 (1963). The effect of the third field on σ may be obtained immediately by taking the terms of the square bracket of Eq. (59), replacing δ by $-\delta$, and adding them to the terms already there, since the weak fields do not interact and their effects are, therefore, additive.

Substitution of σ_1 from Eq. (A2) into Eq. (12a) and the equating of coefficients of $\exp i\nu t$ gives

$$A_+ = \frac{\sigma_0[\varphi_1(\omega-\tilde{\eta}_{12})+\tilde{\eta}_{11}\varphi_2+i\nu\varphi_2]}{-\nu^2+i(\tilde{\eta}_{11}+\tilde{\eta}_{22})\nu+\omega'^2}, \quad \text{(A4)}$$

where

$$\varphi_i = \mathbf{a}_i\cdot\boldsymbol{\varphi}. \quad \text{(A5)}$$

From Eq. (A4) we obtain

$$\mathrm{Re}A_+ = (\sigma_0/D)[\varphi_1(\omega-\tilde{\eta}_{12})(\omega'^2-\nu^2) + \varphi_2(\tilde{\eta}_{22}\nu^2+\tilde{\eta}_{11}\omega'^2)], \quad \text{(A6)}$$

and

$$\mathrm{Im}A_+ = i(\sigma_0/D)\nu[-\varphi_1(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\omega-\tilde{\eta}_{12}) + \varphi_2(\omega^2-\nu^2-\tilde{\eta}_{12}^2-\tilde{\eta}_{11}^2)], \quad \text{(A7)}$$

where

$$D = (\omega'^2-\nu^2)^2+\nu^2(\tilde{\eta}_{11}+\tilde{\eta}_{22})^2. \quad \text{(A8)}$$

Setting

$$\sigma_2 = B_+e^{i\nu t}+B_-e^{-i\nu t}, \quad \text{(A9)}$$

with

$$B_- = B_+{}^*, \quad \text{(A10)}$$

we obtain, in an entirely analogous manner

$$\mathrm{Re}B_+ = (\sigma_0/D)[\varphi_2(\omega+\tilde{\eta}_{12})(\omega'^2-\nu^2) - \varphi_1(\tilde{\eta}_{11}\nu^2+\tilde{\eta}_{22}\omega'^2)], \quad \text{(A11)}$$

and

$$\mathrm{Im}B_+ = -i\nu(\sigma_0/D)[\varphi_2(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\omega+\tilde{\eta}_{12}) + \varphi_1(\omega^2-\nu^2-\tilde{\eta}_{12}^2-\tilde{\eta}_{22}^2)]. \quad \text{(A12)}$$

APPENDIX B

The average power P absorbed by the TLS from the field is given by $\langle\mathfrak{F}\cdot\mathbf{d}\rangle_{\mathrm{av}}$, where $\mathfrak{F}$ is the field vector. Since

$$\mathfrak{F} = -(\hbar/2\mu)\mathbf{f}, \quad \text{(A13)}$$

we have, from Eq. (1),

$$P = -\tfrac{1}{2}\hbar\textstyle\sum_i\langle f_i\dot{\sigma}_i\rangle_{\mathrm{av}}, \quad \text{(A14)}$$

which is Eq. (13) of the text. In first order, σ_3 is constant, and we therefore have, for a weak field.

$$P = -\tfrac{1}{2}\hbar\langle f_1\dot{\sigma}_1+f_2\dot{\sigma}_2\rangle_{\mathrm{av}} = -i\hbar\nu(\varphi_1\,\mathrm{Im}A_+ + \varphi_2\,\mathrm{Im}B_+). \quad \text{(A15)}$$

Utilizing Eqs. (A7) and (A12), we obtain

$$P = -\hbar\nu^2(\tilde{\eta}_{11}+\tilde{\eta}_{22})(\sigma_0/D)[\omega(\varphi_1^2+\varphi_2^2) + \tilde{\eta}_{12}(\varphi_2^2-\varphi_1^2)+\varphi_1\varphi_2(\tilde{\eta}_{11}-\tilde{\eta}_{22})], \quad \text{(A16)}$$

which—with the notational definitions of Eqs. (7), and in dyadic notation—is identical to Eq. (15).

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Theory of Thermal Transport Coefficients*

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A simple proof of the usual correlation-function expressions for the thermal transport coefficients in a resistive medium is given. This proof only requires the assumption that the phenomenological equations in the usual form exist. It is a "mechanical" derivation in the same sense that Kubo's derivation of the expression for the electrical conductivity is. That is, a purely Hamiltonian formalism with external fields is used, and one never has to make any statements about the nature or existence of a local equilibrium distribution function, or how fluctuations regress. For completeness the analogous formulas for the viscosity coefficients and the heat conductivity of a simple fluid are given.

I. INTRODUCTION

In recent years there has been considerable interest in certain general formulas for transport coefficients. These formulas express the transport coefficients in terms of certain correlation functions and are in principle more general than the use of any transport equation. Such general expressions seem to have been first given by Green[1] for transport in fluids. For the electrical transport coefficients the analogous formulas seem first to have been published by Kubo.[2] Since the latter's formula for the electrical conductivity tensor is perhaps the most widely used of these formulas, they are often known as "Kubo" formulas.

In obtaining such formulas, two different approaches have been used. For the electrical conductivity problem one can simply study the linear response of the system to an external electrical field and calculate the currents that flow. This leads unambiguously to Kubo's formula for the electrical conductivity tensor and seems very hard to object to. Such derivations we will call "mechanical" because they arise from studying a problem with a well-defined Hamiltonian (that of system plus interaction with external field). On the other hand, to obtain, say, the thermal conductivity, there exists no mechanical formulation, since there is no

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[1] M. S. Green, J. Chem. Phys. 20, 1281 (1952); 22, 398 (1954). From a quite different point of view, equivalent formulas were obtained by H. Mori, Phys. Rev. 112, 1829 (1958).

[2] R. Kubo, J. Phys. Soc. Japan 12, 570 (1957); R. Kubo, M. Yokota, and S. Nakajima, *ibid.*, p. 1203.