Theory of Quadratic Response Functions

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The general quantum theory of quadratic response functions, such as the optical-frequency quadratic polarizability of dielectrics, is developed on the lines of Kubo's density matrix—Green's function theory of linear response functions. Sum rule series are obtained, and applied to the quadratic polarizability. A suitable form of Kramers-Kronig relations for quadratic response functions is developed.

$\mathbf{I}$N experiments by Franken *et al.*,[1] and others, they observed radiation from dielectrics due to polarization proportional to the square of the amplitude of an incident optical Maxwell wave from a laser, or proportional to the product of the wave amplitudes of two laser beams, the radiation, therefore, being at the second-harmonic frequency or at the sum and difference frequencies. The quantum theory of this quadratic polarization, as a generalization of the theory of the linear optical-frequency polarization of matter, has been investigated by several people.[2-4] The present paper concerns the general formulation of the theory in terms of the response of the density matrix to "impulse" perturbations, on the lines of Kubo's treatment of linear response functions,[5,6] and the derivation from this point of view of sum-rule formulas and dispersion relations.

1. LINEAR THEORY

This section outlines the general linear theory, as a preparation for the following sections. The density matrix, $\rho(t)$, satisfies

$$d\rho/dt = [H(t), \rho].\tag{1}$$

Now let the Hamiltonian, $H(t)$, be given by

$$H = H_0 + h_1\delta(t - t_1),\tag{2}$$

where H_0 and h_1 are independent of t, and let

$$\begin{aligned}\rho &= \rho_0(H_0), &t < t_1; \\ \rho &= \rho_0 + \rho_1(t) + \cdots, &t > t_1;\end{aligned}\tag{3}$$

[1] P. Franken, A. E. Hill, C. W. Peters, and G. Weinreich, Phys. Rev. Letters **7**, 118 (1961).

[2] W. C. Henneberger (unpublished); Zoltan Fried and W. M. Frank (to be published). J. A. Armstrong, N. Bloembergen, J. Ducuing, and P. S. Pershan, Phys. Rev. **127**, 1918 (1962); R. Loudon, Proc. Phys. Soc. (London) **80**, 952 (1962); P. S. Pershan, Tech. Rept. No. 393, Cruft Laboratory, Harvard University, 1962 (unpublished); P. N. Butcher and T. P. McLean, Proc. Phys. Soc. (London) **81**, 219 (1963).

[3] E. Adler (to be published).

[4] Sh. M. Kogan, Zhur. Eksperim. i Teor. Fiz. **43**, 304 (1962) [translation: Soviet Phys.—JETP **16**, 217 (1963)]; P. L. Kelley (to be published).

[5] R. Kubo, J. Phys. Soc. Japan **12**, 570 (1957); *Lectures in Theoretical Physics* (Interscience Publishers, Inc., New York, 1959), p. 120.

[6] V. L. Bonch-Bruevich and S. V. Tyablikov, *The Green Function Method in Statistical Mechanics* (North-Holland Publishing Company, Amsterdam, 1962).

where ρ_1 is to be proportional to h_1. Then

$$\rho_1 = [h_1|t_1 - t), \rho_0]\tag{4}$$

where, for any operator A,

$$A|s) \equiv \exp(iH_0s/\hbar)A\exp(-iH_0s/\hbar).\tag{5}$$

We will use the notation

$$\langle G\rangle_n \equiv \mathrm{Tr}(\rho_n G).\tag{6}$$

Then from (4), (5), and the fact that $\rho_0 = \rho_0(H_0)$, it follows that

$$\langle G\rangle_1 = \langle[G, h_1|-s_1)]\rangle_0, \quad s_1 \equiv t - t_1.\tag{7}$$

If G is the physical variable (polarization, current) whose response to the perturbation h_1 we are calculating, then

$$G(s|h_1) \equiv G_1(s) \equiv \langle[G, h_1|-s)]\rangle_0 = \langle[G|s), h_1]\rangle_0\tag{8}$$

is the effective "Green's function" for the linear response.[6] The relation

$$A(s|B) = -B(-s|A),\tag{9}$$

which follows from (8), gives the Onsager relation corresponding to A and B as driving force and response.[5]

The conventional susceptibility is the linear response to a harmonically varying disturbance, not to an impulse; so it is the Fourier transform of (8). Corresponding to s_1 positive in (7), we must take

$$G(\omega - |h_1) \equiv T_{\omega-}G(s|h_1),\tag{10}$$

$$T_{\omega-}f(s) \equiv \lim_{\lambda \to 0+}\int_0^\infty e^{-(i\omega+\lambda)s}f(s)ds.\tag{11}$$

If the limit $\lambda \to 0$ be written as a sum over poles,

$$f(\omega) \equiv T_\omega f(s) = \sum_n \frac{R_n}{\omega - \omega_n},\tag{12}$$

then we have to make the substitution

$$f(\omega) \to f(\omega-) \approx \mathcal{P}f(\omega) + i\pi\sum_n R_n\delta(\omega - \omega_n)\tag{13}$$

in order that integrals over ω, or over a continuum in place of $\sum_n$, should give the right answer. One such

integral is in the Kramers-Kronig relations[7]:

$$\pi i f(\omega-) = \mathcal{P} \int_{-\infty}^{\infty} \frac{f(\Omega-)d\Omega}{\omega-\Omega}. \qquad (14)$$

The "sum rule" expansion, of the Fourier transform, introduced by Kubo[5] is obtained as follows: Integration by parts gives

$$T_{\omega-}G_1(s) = (i\omega-)^{-1}[G_1(0) + T_{\omega-}(dG_1(s)/ds)]. \qquad (15)$$

Therefore,

$$T_{\omega-}G_1(s) = \sum_{n=0}^{p} (i\omega-)^{-(n+1)}G_1^{(n)}(0)$$
$$+ (i\omega-)^{-(p+1)}T_{\omega-}G_1^{(p+1)}(s), \qquad (16)$$

where

$$G_1^{(n)}(s) \equiv d^n G_1(s)/ds^n, \quad G_1^{(0)}(s) = G_1(s). \qquad (17)$$

Similarly defining

$$h_1^{(n)} \equiv (d^n h_1|s)/ds^n)_{s=0}, \qquad (18)$$

we have

$$G_1^{(n)}(0) = \langle [G^{(n)}, h_1] \rangle_0 = (-)^n \langle [G, h_1^{(n)}] \rangle_0. \qquad (19)$$

The usefulness of this expansion is that in practice the first few terms (say, $n=0, \cdots p-1$) of (16) turn out to be identically zero (irrespective of the details of the system), and the high-frequency limit has the simple form

$$T_\omega G_1(s) \approx (i\omega)^{-(p+1)} \langle [G^{(p)}, h_1] \rangle_0. \qquad (20)$$

Of course, one has, exactly,

$$T_{\omega-}G_1(s) = (i\omega-)^{-p} T_{\omega-} \langle [G^{(p)}, h_1|-s)] \rangle_0$$
$$\equiv [-i(\omega-)]^{-p} T_{\omega-}G(s|h_1^{(p)})$$
$$\equiv [-i(\omega-)]^{-p} G(\omega-|h_1^{(p)}). \qquad (21)$$

The foregoing results may be illustrated by the electric polarizability of an atom or molecule. We have

$$G = q\mathbf{x}, \quad h_1 = -q\mathbf{x} \cdot \mathbf{E}. \qquad (22)$$

If the stationary states of the unperturbed system have energies $\hbar\omega_n$, and $\omega_l - \omega_n \equiv \omega_{ln}$, then

$$[G|s), h_1]_{nn} = (2q^2/\hbar)\sum_l(\mathbf{x}_{nl}\mathbf{x}_{ln}) \cdot \mathbf{E} \sin(\omega_{ln}s). \qquad (23)$$

The polarizability is defined by

$$\mathbf{E} = \mathbf{E}_\omega e^{i\omega t}, \quad q\langle\mathbf{x}\rangle_1 = \alpha(\omega) \cdot \mathbf{E}_\omega e^{i\omega t}. \qquad (24)$$

[7] See, for example, *Quantum Theory*, edited by D. R. Bates (Academic Press Inc., New York, 1961), Vol. 1, 372, 373; J. R. Macdonald and M. K. Brachman, Rev. Mod. Phys. **28**, 393 (1956). Strictly speaking, the Kramers-Kronig relations will not hold if λ^2 is allowed to tend to zero as in the right-hand form of Eq. (13); due care must be had in summing over the levels of the system, for example at a sharp "absorption edge." These remarks apply also, of course, to the discussion following Eq. (62). Not letting λ^2 become zero means, physically, that we have perturbations of slowly increasing, rather than constant, amplitude.

TABLE I. Derivation of the terms of the sum-rule series for linear polarizability.

m	$G^{(m)}$	n	$h_1^{(n)}$	$[G^{(m)}, h_1^{(n)}]$
0	x_α	0	x_β	0
0		1	$(1/m)p_\beta$	$(1/m)\delta_{\alpha,\beta}$
0		2	$-(1/m)dV/dx_\beta$	0
1	$(1/m)p_\alpha$	2		$(1/m^2)d^2V/dx_\alpha dx_\beta$
2	$-(1/m)dV/dx_\alpha$	2		0

Therefore,

$$\alpha(\omega) = \frac{2q^2}{\hbar} \sum_l \sum_n \rho_n \mathbf{x}_{nl}\mathbf{x}_{ln} \left(\frac{\omega_{ln}}{\omega_{ln}^2 - \omega^2}\right)$$

$$\equiv -\frac{q^2}{m} \sum_\nu \frac{\mathbf{f}_\nu}{\omega^2 - \omega_\nu^2} \qquad (25)$$

where $\rho_n \equiv \rho_0(\hbar\omega_n)$. By (13),

$$\alpha(\omega-) = -\frac{q^2}{\hbar} \sum_l \sum_n \rho_n \mathbf{x}_{nl}\mathbf{x}_{ln} \left\{ 2\mathcal{P}\frac{\omega_{ln}}{\omega^2 - \omega_{ln}^2} \right.$$
$$\left. + \pi i \delta(\omega - \omega_{ln}) + \pi i \delta(\omega + \omega_{ln}) \right\}. \qquad (26)$$

The "sum rule" series (16) is developed as follows: If the Hamiltonian of the system is

$$H_0 = (1/2m)p^2 + V(\mathbf{x}), \qquad (27)$$

the variables to be substituted in the series (leaving out the constants multiplying them) are as given in Table I. The Green's function for α is $-q^2\mathbf{x}(s|\mathbf{x})$, in the notation of Eq. (8), and so we obtain from (16)

$$\alpha(\omega) = -q^2 \left\{ \frac{1}{m\omega^2}1 + \frac{1}{m^2\omega^4}\langle\nabla\nabla V\rangle_0 + \mathbf{R}_4 \right\}, \qquad (28)$$

where

$$\mathbf{R}_4(\omega) = \frac{1}{m^2\omega^4}\frac{2}{\hbar} \sum_l \sum_n \rho_n (\nabla V)_{nl}(\nabla V)_{ln}\left(\frac{\omega_{ln}}{\omega^2 - \omega_{ln}^2}\right)$$

$$= O(\omega^{-6}). \qquad (29)$$

The reason for calling (16) the "sum rule" series is illustrated by this case. Writing the summand on the right of (25) as

$$\mathbf{f}_\nu \left[\frac{1}{\omega^2} + \frac{\omega_\nu^2}{\omega^4} + \frac{\omega_\nu^4}{\omega^4(\omega^2 - \omega_\nu^2)} \right],$$

and comparing the resulting three sums with the three terms of (28), one obtains the formulas $\sum_\nu \mathbf{f}_\nu = 1$ (the familiar one), $m \sum_\nu \mathbf{f}_\nu \omega_\nu^2 = \langle\nabla\nabla V\rangle_0$.

The example represented by Eqs. (22) to (29) was for a single active particle with charge q. For many particles, one would replace the first term of (27), $\mathbf{x}$, and ∇ by sums over particles, and $V(\mathbf{x})$ by the many-particle potential. It is an interesting fact that central forces between the particles make no contribution to the

quantity which then replaces $\langle \nabla^2 V \rangle_0$ (the trace of $\langle \nabla\nabla V \rangle_0$, which gives the sum rule for cubic symmetry). In fact, for an atom or molecule with fixed nuclei the many-electron result has $\mathrm{Tr}\langle \nabla\nabla V \rangle_0 \to 4\pi e^2 \sum_i Z_i n(\mathbf{X}_i)$, where the sum is over the nuclei, at positions $\mathbf{X}_i$ with charges $Z_i e$, and where $n(\mathbf{x})$ is the electron density.

2. THE QUADRATIC THEORY

We replace (2) by

$$H(t) = H_0 + h_1 \delta(t - t_1) + h_2 \delta(t - t_2), \quad (30)$$

and (3) by

$$
\begin{aligned}
\rho(t) &= \rho_0(H_0), & t &< t_1, t_2; \\
&\simeq \rho_0 + \rho_1(t), & t_1 &< t < t_2; \\
&\simeq \rho_0 + \rho_2(t), & t_2 &< t < t_1; \\
&\simeq \rho_0 + \rho_1 + \rho_2 + \rho_{21}(t), & t_1 &< t_2 < t; \\
&\simeq \rho_0 + \rho_1 + \rho_2 + \rho_{12}(t), & t_2 &< t_1 < t.
\end{aligned} \quad (31)
$$

Then the quadratic effect linear in h_1 and in h_2 is given by

$$\rho_{21}(t) = [h_2 | t_2 - t), [h_1 | t_1 - t), \rho_0]], \quad (32)$$

$$\langle G \rangle_{21} = \langle [[G, h_2 | -s_2)], h_1 | -s_1)] \rangle_0, \quad (33)$$

where $s_1 \equiv t - t_1$, $s_2 \equiv t - t_2$. In analogy with (8), we may use the notation

$$\langle G \rangle_{21} \equiv G_{21}(s_2, s_1) \equiv G(s_2, s_1 | h_2, h_1). \quad (34)$$

One should remember that the right-hand symbols (s_1 and h_1 in this case) represent the earlier time ($t_1 < t_2$, or $s_1 > s_2$).

The Fourier transform is

$$
\begin{aligned}
G(\omega_1-, \omega_2- \,|\, h_1, h_2) \\
= T_{\omega_1-}(s_1) T_{\omega_2-}(s_2)(G_{12}(s_1 < s_2) + G_{21}(s_2 < s_1)). \quad (35)
\end{aligned}
$$

[On the left-hand side of (35), the order of factors merely signifies that ω_1 goes with h_1 and ω_2 with h_2; both $\omega_1 > \omega_2$ and $\omega_2 > \omega_1$ are permissible, of course.] The transformed function $(G_{12} + G_{21})$ has discontinuous derivatives at $s_1 = s_2$. One may, however, remove this feature by writing

$$
\begin{aligned}
G(\omega_1-, \omega_2- \,|\, h_1, h_2) \\
= T_{(\omega_1 + \omega_2)-}(s) \{ T_{\omega_1-}(s') G(s, s+s' | h_2, h_1) \\
+ T_{\omega_2-}(s') G(s, s+s' | h_1, h_2) \}. \quad (36)
\end{aligned}
$$

Equations (35) and (36) give the Fourier component, $\langle G \rangle_{\omega_1 + \omega_2}$, resulting from a "perturbed part of the Hamiltonian" $h_1 \exp(i\omega_1 t) + h_2 \exp(i\omega_2 t)$, the addition of the other terms from $h_1^\dagger$ and $h_2^\dagger$ being understood. Since

$$G(s, s+s' | h_1, h_2) = \langle [[G | s), h_1], h_2 | -s')] \rangle_0, \quad (37)$$

we have

$$
\begin{aligned}
G(\omega_1-, \omega_2- \,|\, h_1, h_2) \\
= T_{(\omega_1 + \omega_2)-}(s) \{ T_{\omega_1-}(s') \langle [[G | s), h_2], h_1 | -s')] \rangle_0 \\
+ T_{\omega_2-}(s') \langle [[G | s), h_1], h_2 | -s')] \rangle_0 \}. \quad (38)
\end{aligned}
$$

Results equivalent to the foregoing have been given by Kubo,[5] by Kogan[4] and by Kelley[4] (see also Butcher and McLean, reference 2).

The sum rule expansion has to be derived from (36) rather than (35), because of the discontinuity in the integrand of (35). The general formula corresponding to (16) looks complicated, because one may expand the integral over one variable to an arbitrary number of terms, with their remainder, and then expand each term, as an integral over the other variable, to an arbitrary number of terms. Formulas like (21) rather than (20) may be obtained if required, for example, Eq. (43) below. The infinite series is[8]

$$
\begin{aligned}
& G(\omega_1, \omega_2 | h_1, h_2) \\
& = - \sum_{l=0}^{\infty} \sum_{n=0}^{\infty} \frac{i^{(n-l)}}{(\omega_1 + \omega_2)^{l+1}} \\
& \quad \times \left\{ \frac{1}{\omega_1^{n+1}} G_{21}^{(l,0,n)} + \frac{1}{\omega_2^{n+1}} G_{12}^{(l,0,n)} \right\}, \quad (39)
\end{aligned}
$$

where

$$G_{21}^{(l,m,n)} \equiv \langle [[G^{(l)}, h_2^{(m)}], h_1^{(n)}] \rangle_0 \quad (40)$$

and $G^{(l)}$, etc., are given by (18).

3. APPLICATION OF THE SUM-RULE EXPANSION

The nonlinear polarizability first observed was in quartz, a crystal lacking inversion symmetry. One can think of this polarization as proportional to the local value of $\mathbf{E}_1 \mathbf{E}_2$. A model for the effect[3] is a localized electron with Hamiltonian (27) and perturbation $-q\mathbf{x} \cdot \mathbf{E}(t)$. If the potential $V(\mathbf{x})$ lacks a center of symmetry, a polarization proportional to E^2 results. With $G = \mathbf{x}$, $h_1 = \mathbf{x}$, $h_2 = \mathbf{x}$, one finds that $G^{(l,0,n)} = 0$ for $l + n < 4$. The two nonzero ones with $l + n = 4$ are

$$G_{12}^{(3,0,1)} = -\frac{1}{m^3} \nabla\nabla\nabla V,$$

$$(41)$$

$$G_{12}^{(4,0,0)} = +\frac{2}{m^3} \nabla\nabla\nabla V.$$

Combining the resulting terms as in (39) gives

$$\langle \mathbf{x} \rangle_{\omega_1 + \omega_2} \approx \frac{q^2}{m^3} \langle \nabla\nabla\nabla V \rangle_0 : \mathbf{E}_{\omega_1} \mathbf{E}_{\omega_2} \left(\frac{1}{(\omega_1 + \omega_2)\omega_1 \omega_2} \right)^2, \quad (42)$$

where $\mathbf{E}_\omega$ is a Fourier component of $\mathbf{E}(t)$. Equation (42) agrees with the result for the "anharmonic oscillator," with potential $ax^2 + bx^3$; but it is, of course, more

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[8] Such series are evidently asymptotic; they need not be convergent, in applications.

general. The result derived from (16) is

$$\langle \mathbf{x}\rangle_{\omega_1+\omega_2}=\frac{q^2}{m^3}(\mathbf{E}_{\omega_1}\mathbf{E}_{\omega_2}:)\frac{T_{\omega_1+\omega_2}(s)}{(\omega_1+\omega_2)^3}\left\{\left(\frac{T_{\omega_1}(s')}{\omega_1}+\frac{T_{\omega_2}(s')}{\omega_2}\right)\right.$$

$$\times\langle[[\{(\nabla\nabla V)\cdot\mathbf{p}\}|s),\mathbf{x}],\mathbf{p}|-s')]\rangle_0$$

$$+\left(\frac{T_{\omega_1}(s')+T_{\omega_2}(s')}{\omega_1+\omega_2}\right)\langle[[(m(\nabla\nabla V)\cdot(\nabla V)$$

$$\left.-\{\{(\nabla\nabla V)\cdot\mathbf{p}\}\cdot\mathbf{p}\})|s),\mathbf{x}],\mathbf{x}|-s')]\rangle_0\right\},\quad(43)$$

the scalar products $(\mathbf{E}_1\mathbf{E}_2:)$ being taken in the order $T_1[[\ ,\cdot\mathbf{E}_2],\cdot\mathbf{E}_1]$ and $T_2[[\ ,\cdot\mathbf{E}_1],\cdot\mathbf{E}_2]$. The next integrations by parts give the leading term (42).

If the system has inversion symmetry, there remains an effect $\sim 10^{-3}$ smaller which can be represented as the sum of "Faraday" and "quadrupole" contributions. These have been calculated by Adler[3] (for a model of the dielectric in which it is divided into a periodic lattice of separate localized systems) by taking into account the "plane wave" dependence, on position, of the perturbing fields and the component of polarization which is calculated. One obtains contributions to the polarization, additional to the "anharmonic" part to which (42) and (43) apply, which are not zero when the system has inversion symmetry. The sum rule series may be applied to these. However, it will be applied below to a somewhat different formulation of nonlinear polarization.

An appropriate Hamiltonian for an electron in the dielectric is[9]

$$H=\frac{1}{2m}\left|\mathbf{p}-\frac{q}{c}\mathbf{A}\right|^2+V(\mathbf{x}).\quad(44)$$

In this gauge, in which its scalar potential is zero, the laser electric field is[9a]

$$\mathbf{E}(\mathbf{x},t)=-(1/c)\partial\mathbf{A}/\partial t=-(1/c)\sum_\nu i\omega_\nu A_{-\kappa_\nu}$$
$$\times\exp(i\omega_\nu t-i\kappa_\nu\cdot\mathbf{x}).\quad(45)$$

(It is convenient to label components by wave vector κ rather than angular frequency ω, so long as one remembers to pair these correctly in sums.) The component of the current density with wave vector $-\kappa$ is the expectation of

$$\mathbf{J}^\kappa\equiv\frac{q}{m}\left(\mathbf{p}^\kappa-\frac{q}{c}\mathbf{A}^\kappa\right)\quad(46)$$

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[9] We are leaving out the spin term here, and the corresponding term (Ref. 3) in Eq. (46). It is shown by Adler, (Ref. 3) for his model and neglecting spin-orbit coupling, that if the system has zero spin polarization in its unperturbed state then the contribution from spin terms to the quadratic polarizability is negligible.

[9a] The superscript and subscript κ, λ, μ occurring throughout the rest of this section should be read as vectors.

TABLE II. The contributions to the "sum frequency" quadratic-polarization current, due to the field given by Eq. (45), in the notation of Eqs. (8) and (33). $\kappa=\kappa_1+\kappa_2$.

Term	A	B	C
$\mathbf{p}^\kappa$	G		G
$(q/c)A_{-\kappa}\exp[i(\kappa-\kappa_\nu)\cdot\mathbf{x}]$		$G(\nu=1\text{ or }2)$	
$-(q/mc)\mathbf{p}^{-\kappa_\nu}\cdot A_{-\kappa_\nu}$		h_2 or h_1	h_1 and h_2
$(q^2/mc^2)A_{-\kappa_1}\cdot A_{-\kappa_2}\exp(-\kappa\cdot\mathbf{x})$	h		

where, for any quantum operator U,

$$U^\kappa\equiv\{U,\exp(i\kappa\cdot\mathbf{x})\}.\quad(47)$$

The linear polarization is usually calculated, from (44) and (46), letting $\kappa\to 0$. One may, of course, expand the linear polarization in ascending powers of κ. However, the second term (proportional to κ) vanishes if the system has inversion symmetry. Otherwise, its order of magnitude relative to the first term is (lattice constant)/(optical wavelength), so it should not become important until x-ray frequencies are reached. For the quadratic polarization, we may make the same expansion in the wave vectors κ_1, κ_2; but the parity situation is now reversed. The first term (independent of the κ's) vanishes if the system has inversion symmetry, but the term proportional to the κ's doesn't. [Again, its estimated order of magnitude is smaller than that of the (nonvanishing) first term by the factor (lattice constant)/(optical wavelength).] As with the linear case, the polarization proportional to the κ's is out of phase with the polarization independent of the κ's by $\pi/2$. It has recently been detected, in a crystal with inversion symmetry.[10]

Table II indicates the different contributions to the quadratic polarization as calculated in terms of (44) and (46). The contributions A and B are given by the theory of Sec. 1; contribution C is to be calculated as in Sec. 2. The component of current represented in Table II is that at angular frequency $\omega_1+\omega_2$. In the Bloch scheme, contribution A is proportional to κ (plus higher powers, of course) because it is given by inter-band matrix elements of $\exp(-i\kappa\cdot\mathbf{x})$ and, hence, of $\kappa\cdot\mathbf{p}+O(\kappa^2)$. Similarly, the contributions B are proportional to κ_1 or to κ_2. (More generally, it is obvious that the contributions A and B are zero in the limit κ's $\to 0$.) The contribution from C consists of sums over triples of matrix elements $\langle n|\mathbf{p}^\kappa|m\rangle\langle m|\mathbf{p}^\lambda|l\rangle\langle l|\mathbf{p}^\mu|n\rangle$, with $\kappa+\lambda+\mu=0$. On expanding in the wave vectors, one has a part independent of the κ's (vanishing if the system has inversion symmetry) and a part proportional to the κ's. An expression for the former (the part of the polarization independent of the κ's) will be found in the forth-coming paper by Kelley.[4] From all the foregoing contributions, in the Bloch scheme one has a sum over the Brillouin zone of functions of interband matrix elements of $\mathbf{p}$. It should be noted that the triples of matrix

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[10] R. W. Terhune, P. D. Maker, and C. M. Savage, Phys. Rev. Letters 8, 404 (1962).

elements include matrix elements between occupied one-electron states as well as between unoccupied one-electron states.

The sum rule series is obtained by the procedure of Sec. 2, applied to the G's and h's of Table II, using the formulas

$$[f(\mathbf{x}), \mathbf{p}^\kappa] = (\nabla f)^\kappa, \tag{48}$$

$$[p_\alpha{}^\kappa, p_\beta{}^\lambda] = i(\kappa_\beta p_\alpha{}^{\kappa+\lambda} - \lambda_\alpha p_\beta{}^{\kappa+\lambda}). \tag{49}$$

It is useful to express the results in terms of $\mathbf{P}$ (polarization density) and the $\mathbf{E}$'s, rather than $\mathbf{J}$ and the $\mathbf{A}$'s. We find that the series begins

$$\mathbf{P} = \mathbf{P}^{(4,1)} + \mathbf{P}^{(6,0)} + \mathbf{P}^{(6,1)} + \cdots, \tag{50}$$

where $\mathbf{P}^{(m,n)}$ means the terms of order $\omega^{-m}\kappa^n$ (i.e., a sum of terms of this order in the ω's and κ's). There is no $(m=4, n=0)$ term, and no term with $m<4$. The first term of (50) comes from the A and B contributions in Table II; the second term comes from the C contribution; the third term comes from A, B, and C. The expressions for these are

$$\mathbf{P}_{\omega_1+\omega_2}{}^{(4,1)} = qn\frac{q^2}{m^2}\frac{i}{\omega_1\omega_2(\omega_1+\omega_2)}\left\{\frac{1}{2}\frac{\kappa_1+\kappa_2}{\omega_1+\omega_2}\mathbf{E}_1\cdot\mathbf{E}_2\right.$$
$$\left.+\frac{1}{\omega_1}\kappa_1\cdot\mathbf{E}_1\mathbf{E}_2+\frac{1}{\omega_2}\kappa_2\cdot\mathbf{E}_2\mathbf{E}_1\right\}, \tag{51}$$

$$\mathbf{P}_{\omega_1+\omega_2}{}^{(6,0)} = qn\frac{q^2}{m^3}\frac{1}{[\omega_1\omega_2(\omega_1+\omega_2)]^2}\langle\nabla\nabla\nabla V\rangle_0 : \mathbf{E}_1\mathbf{E}_2, \tag{52}$$

$$\mathbf{P}_{\omega_1+\omega_2}{}^{(6,1)} = qn\frac{q^2}{m^3}\frac{i}{\omega_1\omega_2(\omega_1+\omega_2)}$$
$$\times(\mathbf{S}:\langle\nabla\nabla V\rangle_0 + \mathbf{T}\cdot\langle\nabla\nabla V\rangle_0), \tag{53}$$

where

$$\mathbf{S} = \left(\frac{\kappa_1}{\omega_2{}^2}+\frac{\kappa_2}{\omega_1{}^2}\right)\frac{\mathbf{E}_1\mathbf{E}_2}{\omega_1+\omega_2}+\frac{\mathbf{E}_1\kappa_2\mathbf{E}_2+\mathbf{E}_2\kappa_1\mathbf{E}_1}{(\omega_1+\omega_2)^3}, \tag{53'}$$

$$\mathbf{T} = \frac{1}{\omega_1\omega_2}\left(\frac{\kappa_1}{\omega_2}\cdot\mathbf{E}_1\mathbf{E}_2+\frac{\kappa_2}{\omega_1}\cdot\mathbf{E}_2\mathbf{E}_1\right)+\frac{1}{(\omega_1+\omega_2)^2}$$
$$\times\left(\frac{\omega_1+2\omega_2}{\omega_2{}^2}\kappa_2\cdot\mathbf{E}_1\mathbf{E}_2+\frac{\omega_2+2\omega_1}{\omega_1{}^2}\kappa_1\cdot\mathbf{E}_2\mathbf{E}_1\right)$$
$$+\frac{\mathbf{E}_1\cdot\mathbf{E}_2}{2(\omega_1+\omega_2)^3}(\kappa_1+\kappa_2). \tag{53''}$$

Here n is the electron density, and $\mathbf{E}_1$, $\mathbf{E}_2$ stand for $\mathbf{E}_{-\kappa_1}$ (i.e., E_{ω_1}) and $\mathbf{E}_{-\kappa_2}$. The quadratic polarization of free carriers is given by (51) alone. (In this case, $\kappa_1\cdot\mathbf{E}_1$ and $\kappa_2\cdot\mathbf{E}_2$ will of course be zero; we then require only the first term in the brace.) The coefficient of qn on the right of (52) is identical with the right-hand side of

(42), although the calculations were in quite different terms, as it should be.

The term given by (53) introduces the crystal field and symmetry into the part of $\mathbf{P}$ proportional to the κ's. It is evident from this term that the relation between the direction of $\mathbf{P}$ and the directions of the $\mathbf{E}$'s and κ's is not simple, even for a cubic crystal. For $\omega_1=\omega_2\equiv\omega$, and a cubic crystal, we have

$$\mathbf{P}_{2\omega}{}^{(6,1)} = qn\frac{q^2}{m^3}\frac{i}{(2\omega)^3\omega^3}\langle\nabla^2 V\rangle_0\{\kappa_1\cdot\mathbf{E}_2\mathbf{E}_1+\kappa_2\cdot\mathbf{E}_1\mathbf{E}_2$$
$$+\tfrac{3}{4}(\kappa_1+\kappa_2)\mathbf{E}_1\cdot\mathbf{E}_2\}. \tag{54}$$

The replacement of $\langle\nabla\nabla V\rangle_0$ and $\langle\nabla\nabla\nabla V\rangle_0$ by their many-body equivalents is on the same lines as explained at the end of Sec. 1.

4. DISPERSION RELATIONS

The Kramers-Kronig relations apply in a normal way to (35). That is,

$$\pi i G(\omega_1-, \omega_2-|h_1, h_2)$$
$$= \mathcal{P}\int_{-\infty}^{\infty} G(\Omega-, \omega_2-|h_1, h_2)\frac{d\Omega}{\omega_1-\Omega}, \tag{55}$$

and similarly for ω_2. However, the usefulness of (14), for the linear response function $G(\omega-)$, depends on the facts that it may be rewritten as two integral relations connecting the parts of G which are even and odd in ω, with the integrals going from 0 to ∞, and that these parts are separately of physical interest. With the quadratic response function, the parts of physical interest will be even or odd in ω_1 and ω_2 together, but not separately; and so the separation of (55) into integrals over even and odd parts does not have the same usefulness as for the linear case.

However, if we treat G as a function of

$$\omega^+\equiv\omega_1+\omega_2, \quad \omega^-\equiv\omega_1-\omega_2, \tag{56}$$

then the relation (14) will apply to the variable ω^+, *with ω^- held fixed.* Furthermore, we may define functions which are even, or odd, in ω^+ as follows: Let $C(\omega_1,\omega_2)$ be a quadratic response function or part of one, and let S_{12} be the operator which interchanges ω_1 and ω_2. Then

$$2C^s(\omega^+,\omega^-) \equiv (1+S_{12})C(\omega_1,\omega_2),$$
$$2C^a(\omega^+,\omega^-) \equiv (1-S_{12})C(\omega_1,\omega_2). \tag{57}$$

If R_1 is the operator changing ω_1 to $-\omega_1$, and similarly for R_2, and if R^+ changes ω^+ to $-\omega^+$ (but leaving ω^- unchanged), and similarly R^- changes ω^- to $-\omega^-$, we have

$$R^+C^s=R_1R_2C^s, \quad R^+C^a=-R_1R_2C^a, \tag{58}$$

and

$$R^-C^s=C^s, \quad R^-C^a=-C^a. \tag{59}$$

On account of (59), the relation (14) for ω^+ as variable, with ω^- fixed, holds for C^s and C^a separately. We then have four relations of the usual form, with integrals over ω^+ from 0 to ∞ : two connecting the even and odd (in ω^+) parts of C^s and two connecting the even and odd parts of C^a. By (58), these even and odd parts are given by the operations on the right of (57) applied to the two parts of C satisfying

$$R_1 R_2 C = \sigma C, \quad \sigma = \pm 1. \tag{60}$$

($\sigma = +1$ gives the even part of C^s and the odd part of C^a.) When (as in the next paragraph) $R_1 R_2 C = C^*$, we have

$$\pi i C^s(\omega^+, \omega^-)$$

$$= 2 \mathcal{P} \int_0^\infty (\omega^+ \operatorname{Re} + i\Omega \operatorname{Im}) C^s(\Omega, \omega^-) \frac{d\Omega}{(\omega^+)^2 - \Omega^2},$$

$$\pi i C^a(\omega^+, \omega^-) \tag{61}$$

$$= 2 \mathcal{P} \int_0^\infty (\Omega \operatorname{Re} + i\omega^+ \operatorname{Im}) C^a(\Omega, \omega^-) \frac{d\Omega}{(\omega^+)^2 - \Omega^2}.$$

[To avoid confusion the minus signs attached to the ω's in (55), etc., which indicate the "time sense" in (11) and correspond to the sign of the denominator in (14) and (55), are omitted in (61).]

For an illustration,[11] let C be the constant in the relation $P_{\omega_1 + \omega_2}{}^\alpha = C_{\alpha\beta\gamma} E_{\omega_1}{}^\beta E_{\omega_2}{}^\gamma$, for the "anharmonic" part of the polarization independent of the κ's. Of course,

$$S_{12} C_{\alpha\beta\gamma} = C_{\alpha\gamma\beta}; \tag{62}$$

so C^s and C^a are the symmetric and antisymmetric parts of the tensor whose β, γ component is $C_{\alpha\beta\gamma}$. Now, $C(\omega_1, \omega_2)$ may be expanded like Eq. (12), in a (double) series of poles, the terms having denominators of form

$$(\omega_1 - \omega_m)(\omega_2 - \omega_n), \quad (\omega_1 - \omega_m)(\omega_1 + \omega_2 - \omega_n),$$

$$\text{and} \quad (\omega_2 - \omega_m)(\omega_1 + \omega_2 - \omega_n).$$

[11] A more complete discussion, than is contained in these two final paragraphs, of the division of a response function into real and imaginary parts and into parts satisfying (60), on the basis of parity rules will be found in P. J. Price, in Proceedings of the Ohio State University Symposium on Lasers and Applications (Ohio State University Press, to be published).

When we make the substitution (13) for each pole, the products of principal values $[\mathcal{P}(\omega_1 - \omega_m)^{-1}\mathcal{P}(\omega_2 - \omega_n)^{-1}$, etc.], and the products of delta functions, will together give the real part of C, with $\sigma = +1$, in the present case (in the absence of a static magnetic field), while the products of principal values and delta functions $[\mathcal{P}(\omega_1 - \omega_n)^{-1}\delta(\omega_2 - \omega_n)$, etc.] will together give the imaginary part, with $\sigma = -1$. These two parts of C may appropriately be called the "reversible" and "irreversible" parts, respectively. Writing

$$C(\omega_1-, \omega_2-) = C_{\text{rev}}(\omega_1, \omega_2) + iC_{\text{irrev}}(\omega_1, \omega_2), \tag{63}$$

a representative dispersion relation is

$$\pi C^s{}_{\text{rev}}(\omega^+, \omega^-) = 2\mathcal{P} \int_0^\infty \Omega C^s{}_{\text{irrev}}(\Omega, \omega^-) \frac{d\Omega}{(\omega^+)^2 - \Omega^2}. \tag{64}$$

The relations, such as (64), for C^s are the analogs of those for the linear electric susceptibility. The relations for C^a have the roles of reversible and irreversible parts interchanged.

For the part of the quadratic polarizibility linear in the κ's, dispersion relations similar to (64), etc., will hold with κ_1 and κ_2 held constant and, hence, will hold for the coefficients of κ_1 and κ_2 separately or in any linear combination. (In this case the reversible part is imaginary and the irreversible part real, in the absence of a static magnetic field.) The relations with κ_1 taken as proportional to ω_1, κ_2 to ω_2, should also be valid, since (50) indicates that the response function will still fall off fast enough as $|\omega_1|$, $|\omega_2| \to \infty$. One may conjecture that the dispersion relations (55), etc., hold also for the complete quadratic polarizability, with the κ's on which it depends governed by the actual $\omega(\kappa)$ functions.

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