Dispersion relations and sum rules in nonlinear optics

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We prove that dispersion relations similar to the Kramers-Kronig equations of linear optics can be obtained for the nonlinear-response function to all orders in the electric field. When energy dissipation is involved the dispersion relations obtained here concern the case in which nonlinearity on a probe beam is produced by external radiaton beams of any given frequency. Using the superconvergence theorem, we find a set of nonlinear sum rules. Some of them imply that the already known sum rules of linear optics—in particular, the Thomas-Reiche-Kuhn and the Alatarelli-Dexter-Nussenzweig-Smith sum rule—are true to all orders because all the nonlinear contributions vanish. Others do not have a linear counterpart and are specific to nonlinear optics. Implications of these results and possibilities of anomalous emission effects are dicussed.

I. INTRODUCTION

The Kramers-Kronig dispersion relations between the real and the imaginary parts of the linear-response functions have a fundamental importance in many aspects of physics, in elementary particle physics and scattering theory[1] as well as in optics, where they had been originally introduced.[2]

In the study of the optical properties of solids the dispersion relations are of particular value because they allow a determination of the optical absorption at any frequency from the measurements of the reflectivity only on the entire spectrum.[3] Another important application is due to the fact that a large number of sum rules can be obtained from the dispersion relations,[4] the most important being the Thomas-Reiche-Kuhn (TRK) sum rule for the absorption coefficient[5] and the Altarelli-Dexter-Nussenzweig-Smith (ADNS) sum rule for the refractive index.[6,7] These important applications have been confined to linear optics, though some general results on dispersion relations of the nonlinear optical response functions have been obtained by Kogan,[8] Caspers,[9] Price,[10] and Ridener and Good.[11,12] A set of some rules has also been derived by Peiponen for the nonlinear dielectric function in the model of the anharmonic oscillator.[13–15]

In this paper we address the problem of finding appropriate dispersion relations and sum rules applicable to nonlinear optics, where several photons are involved. We prove that general dispersion relations can be obtained for the nonlinear optical response functions to all orders in the electric fields by choosing an appropriate integration line in the n-dimensional frequency space. We concentrate in particular on the problem of the optical response of a medium in the presence of external intense radiation beams and prove that from the dispersion relations important sum rules can be obtained for the nonlinear optical functions. We extend to nonlinear optics, not only the well-known TRK sum rule, but also the ADNS sum rule $\int_0^\infty [n(\omega)-1]d\omega=0$. We also introduce sum rules for the nonlinear contribution to the optical constants considering their product by the square and the cube of the frequency. All the above sum rules are derived from the general properties of the short-time behavior of the Green's function and do not depend on any specific model.

The paper is organized as follows. In Sec. II we present the general properties of the response functions and their connection with optical processes, using only the causality principle. In Sec. III we show how dispersion relations can be derived for the nonlinear response functions and for the related optical constants to all orders. In Sec. IV we derive a set of sum rules. A discussion of their implications is given in Sec. V.

II. GENERAL PROPERTIES OF THE RESPONSE FUNCTION

We consider the general response of a system to external electric fields under the condition that the polarization $P(t)$ at time t depends on the fields $E(t')$ only at preceding times $t'\leq t$ (causality condition). We can write to all orders in the electric fields:

$$P(t)=\int_0^\infty dt_1 G^{(1)}(t_1)E(t-t_1)+\int_0^\infty dt_1\int_0^\infty dt_2 G^{(2)}(t_1,t_2)E(t-t_1)E(t-t_2)+\cdots$$
$$+\int_0^\infty dt_1\cdots\int_0^\infty dt_n G^{(n)}(t_1,\ldots,t_n)E(t-t_1)\cdots E(t-t_n)+\cdots\;, \quad (1)$$

with $G^{(n)}(t_1,\ldots,t_n)$ real symmetric functions that verify the causality condition

$$G^{(n)}(t_1,\ldots,t_i,\ldots,t_n)=0 \quad \text{if } t_i<0\ . \tag{2}$$

We Fourier transform the response function and the electric fields and obtain for the frequency component of the response function to all orders

$$P^{(n)}(\omega) = \frac{1}{(2\pi)^{n-1}}\int d\omega_1\cdots\int d\omega_n g^{(n)}(\omega_1,\ldots,\omega_n) \times E(\omega_1)\cdots E(\omega_n) \times\delta(\omega-(\omega_1+\cdots+\omega_n))\ , \tag{3}$$

where $E(\omega)$ is the Fourier transform of $E(t)$ and the nth-order susceptibility is

$$g^{(n)}(\omega_1,\omega_2,\ldots,\omega_n) = \int_0^\infty dt_1\int_0^\infty dt_2\cdots\int_0^\infty dt_n e^{i(\omega_1t_1+\omega_2t_2+\cdots+\omega_nt_n)} \times G^{(n)}(t_1,t_2,\ldots,t_n)\ . \tag{4}$$

The symmetry in the times implies the symmetry of $g^{(n)}(\omega_1,\omega_2,\ldots,\omega_n)$ for the interchange of the frequencies. The reality of $G(t_1,\ldots,t_n)$ furthermore implies

$$g^{(n)}(-\omega_1,-\omega_2,\ldots,-\omega_n)=g^{(n)*}(\omega_1,\omega_2,\ldots,\omega_n)\ . \tag{5}$$

The above-defined susceptibility $g^{(n)}(\omega_1,\omega_2,\ldots)$ contains all the optical properties of the medium to all orders, in the presence of a number of radiation beams. When the external beams have definite frequencies $E(\omega_1),\ldots,E(\omega_n)$, we obtain in the nth-order polarization a contribution from all the possible sums of n terms, where in each term the frequency can have positive or negative sign, and a given frequency can be repeated up to n times.

We will concentrate our attention on the case that two radiation beams of frequency ω_1 and ω_2 act on the sample. We obtain the usual first-order response function at the two frequencies ω_1 and ω_2. We also obtain a second-order response function at the frequencies $2\omega_1$, $2\omega_2$, 0, $\omega_1+\omega_2$, $|\omega_2-\omega_1|$. They correspond to the phenomena of harmonic generation, optical rectification (nonlinear static polarization), and sum and difference frequency generation, respectively. In second order no energy dissipation is possible because the energy dissipation is the time average

$$-\left\langle \frac{dP}{dt}(t)E(t)\right\rangle\ , \tag{6}$$

which vanishes when the two contributions dP/dt and $E(t)$ have different frequencies

The third-order response function contains eight contributions whose frequencies are ω_1, ω_2, $3\omega_1$, $3\omega_2$, $|2\omega_1\pm\omega_2|$, and $|2\omega_2\pm\omega_1|$. The contributions of frequencies ω_1 and ω_2 contain a dissipative term proportional to the imaginary part of $P(\omega)$ which gives a contribution to (6) because dP/dt is in phase with the field $E(t)$. The dissipation is ten proportional to the imaginary part of $g^{(3)}(\omega_1,\omega_1,-\omega_1)$ or $g^{(3)}(\omega_1,\omega_2,-\omega_2)$ for the first beam, and $g^{(3)}(\omega_2,\omega_2,-\omega_2)$ or $g^{(3)}(\omega_2,\omega_1,-\omega_1)$ for the second beam.

A similar analysis can be carried out for the higher-order terms to obtain higher-order harmonic generation terms and dissipative higher-order contributions.

Our goal is to derive dispersion relations between the real and the imaginary part of the response functions similar to the Kramers-Kronig relations of linear optics. In the cases when a dissipative term is present such dispersion relations will connect the dissipative and the dispersive contribution to the polarization to all orders. This is expected to be very useful in nonlinear optics as it is in the linear case and will be shown to generate nonlinear sum rules.

III. NONLINEAR DISPERSION RELATIONS

A dispersion relation involves the integration of the susceptibility in the frequency space $\mathbb{R}^n$. In the case of the nonlinear susceptibility $g^{(n)}(\omega_1,\ldots,\omega_n)$, which is defined in $\mathbb{R}^n$, the domain of integration is chosen to be, for simplicity, a straight line of $\mathbb{R}^n$. We describe a general line of $\mathbb{R}^n$ in the parametric form

$$\omega_k(s)=v_ks+w_k \quad \text{with } k=1,2,\ldots,n\ . \tag{7}$$

where s is a real parameter which varies from $-\infty$ to $+\infty$ and v_k are the components of a vector that identifies the direction of the line. Substituting expression (7) into the definition (4) of $g^{(n)}$, we obtain

$$g^{(n)}(s)=g^{(n)}(\omega_1(s),\omega_2(s),\ldots,\omega_n(s)) = \int_0^\infty dt_1\int_0^\infty dt_2\cdots\int_0^\infty dt_n e^{i(v_1t_1+v_2t_2+\cdots+v_nt_n)s}G^{(n)}(t_1,t_2,\ldots,t_n)e^{i(w_1t_1+w_2t_2+\cdots+w_nt_n)}\ . \tag{8}$$

We can easily show from the above expression that the time-dependent Fourier transform of $g^{(n)}(s), g^{(n)}(\tau)$ vanishes for negative values of τ because of the causality condition (2), provided we impose the condition

$$v_k\geq 0 \quad \text{for } k=1,2,\ldots,n\ . \tag{9}$$

Then we can invoke Titchmarsh's theorem[16,17] to prove that the function $g^{(n)}(s)$ is holomorphic in the upper half-plane of the complex space $s+i\eta$ and that it vanishes at infinity in all directions of the half-plane. Consequently the following Kramers-Kronig dispersion relations hold:

$$\mathrm{Re}[g^{(n)}(s)]=\frac{1}{\pi}\mathrm{P}\int ds'\frac{\mathrm{Im}[g^{(n)}(s')]}{s'-s}\,, \tag{10}$$

$$\mathrm{Im}[g^{(n)}(s)]=-\frac{1}{\pi}\mathrm{P}\int ds'\frac{\mathrm{Re}[g^{(n)}(s')]}{s'-s}\,, \tag{11}$$

where P denotes the principal part of the integral, and the integral extends from $-\infty$ to $+\infty$. These relations were previously found by Caspers[9] for the second-order susceptibility, and by Ridener and Good[12] for the nth-order susceptibility, but only for the case of $v_k=1$. Expressions (10) and (11) extend the previous results to all orders and to all possible integration paths.

The general form of the dispersion relations here obtained allows us to derive integral equations connecting the real and the imaginary parts of the susceptibility to all orders for the cases of interest. This is done by choosing an appropriate integration line through the choice of the parameters v_k and w_k in (7). Considering two beams, for instance, we obtain in second order the same results first obtained by Kogan.[8]

For the second-harmonic generation we must consider $g^{(2)}(\omega_1,\omega_1)$ and consequently we must choose $v_1=1$, $v_2=1$ and $w_1=0$, $w_2=0$ in Eq. (7), and use Eqs. (10) and (11) to obtain

$$\mathrm{Re}[g^{(2)}(\omega_1,\omega_1)]=\frac{2}{\pi}\mathrm{P}\int_0^\infty d\omega_1'\frac{\omega_1'\mathrm{Im}[g^{(2)}(\omega_1',\omega_1')]}{\omega_1'^2-\omega_1^2}\,, \tag{12}$$

$$\mathrm{Im}[g^{(2)}(\omega_1,\omega_1)]=-\frac{2\omega_1}{\pi}\mathrm{P}\int_0^\infty d\omega_1'\frac{\mathrm{Re}[g^{(2)}(\omega_1',\omega_1')]}{\omega_1'^2-\omega_1^2}\,. \tag{13}$$

For the sum and difference frequency generation we can fix ω_2 and vary ω_1 ($v_1=1$, $v_2=0$, $w_1=0$, $w_2=w_2$), and obtain a dispersion relation by performing the integral on ω_1 which mixes real and imaginary parts of the difference and sum frequency generation susceptibility, as given by Caspers.[9] The above expressions are, however, of limited use in optics because they connect phase and amplitude of the response function, and only the amplitude is generally considered.

In higher order, however, the real and imaginary part of the function $P^{(n)}(\omega)$ at the frequencies ω_1 and ω_2 can give dispersive and dissipative effects, respectively. In particular, the expression of $P^{(n)}(\omega_1)$ that contains dissipation is given by a sum of contributions proportional to

$$g^{(2p+2q+1)}(\omega_1,\omega_1,-\omega_1,\ldots,\omega_2,-\omega_2,\ldots)\,, \tag{14}$$

where $p=0,1,\ldots$ give the number of pairs ω_1, $-\omega_1$, q the number of pairs $\omega_2,-\omega_2$, and $2p+2q+1=n$. The expression for $P^{(n)}(\omega_2)$ can be obtained by interchanging ω_1 and ω_2 in (14). Dispersive-dissipative effects can thus be observed, with two monochromatic beams, in the two-dimensional subset of $\mathbb{R}^n$ given by (14), and dispersion relations of type (10) and (11) can be derived for any line of type (7) included in this subset and satisfying condition (9). Since we consider the beam of frequency ω_1 as a probe in the presence of a second beam ω_2, such lines exist for any ω_2 to all orders only in correspondence to the parameters

$$v_k=(1,0,0,\ldots)\ \text{and}\ w_k=(0,\omega_2,-\omega_2,\ldots)\,. \tag{15}$$

We can therefore conclude that the only Kramers-Kronig dispersion relations involving dispersive-dissipative effects are obtained for the odd response functions and are the following:

$$\mathrm{Re}[g^{(2q+1)}(\omega_1,\omega_2,-\omega_2,\ldots)]=\frac{2}{\pi}\mathrm{P}\int_0^\infty d\omega_1'\frac{\omega_1'\mathrm{Im}[g^{(2q+1)}(\omega_1,\omega_2,-\omega_2,\ldots)]}{\omega_1'^2-\omega_1^2}\,, \tag{16}$$

$$\mathrm{Im}[g^{(2q+1)}(\omega_1,\omega_2,-\omega_2,\ldots)]=-\frac{2\omega_1}{\pi}\mathrm{P}\int_0^\infty d\omega_1'\frac{\mathrm{Re}[g^{(2q+1)}(\omega_1,\omega_2,-\omega_2,\ldots)]}{\omega_1'^2-\omega_1^2}\,, \tag{17}$$

where we have limited the domain of integration to positive frequencies by means of the symmetry properties of $g^{(n)}$, expressed by Eqs. (4) and (5).

The dispersion relations (16) and (17) are the main result of our analysis and have an important physical significance. They extend to the nonlinear case the usual Kramers-Kronig relations when the nonlinearity in the dielectric function is produced by an additional external beam. Dissipative and dispersive components are then connected to all orders.

The third-order dissipative contribution will include two-photon absorption, stimulated Raman effect, and corrections to the nonlinear absorption due to two-step processes at intermediate-state resonance frequencies. The related dispersive term gives the correction to the real part of the dielectric function due to the external beam.

The dispersion relations (10) and (11), and those which can be obtained from them [such as (12) and (13) or (16) and (17)], allow the derivation of dispersion relations among all optical constants. The case of the dielectric function is obvious because of its connection with the susceptibility. A nonlinear contribution to the complex dielectric function

$$\tilde{\epsilon}^{\mathrm{NL}}(\omega_1,\omega_2,E_2)=\epsilon_1^{\mathrm{NL}}(\omega_1,\omega_2,E_2)+i\epsilon_2^{\mathrm{NL}}(\omega_1,\omega_2,E_2) \tag{18}$$

is immediately obtained for the radiation probe beam of frequency ω_1 in the presence of an external beam ω_2. In those cases where dissipation is present we obtain

$$\tilde{\epsilon}^{\mathrm{NL}}(\omega_1,\omega_2,E_2)=4\pi\sum_{n\ \mathrm{odd}>1}a_n g^{(n)}(\omega_1,\omega_2,-\omega_2,\ldots)E_2^{n-1}\,, \tag{19}$$

with $n=2q+1$ in expression (14), and

$$a_n=\frac{1}{2^{n-1}}\frac{(n-1)!}{\left[\frac{n-1}{2}\right]!\left[\frac{n-1}{2}\right]!}\,. \tag{20}$$

It can be observed that the nonlinear dielectric function depends on the intensity of the external light beam as well as on its frequency. The linear limit is also expression (19) with $n=1$ and addition of 1.

The case of the conductivity σ is also obvious since it is related to the dielectric function by

$$\tilde{\sigma}(\omega_1,\omega_2,E_2)=-i\omega_1\frac{\tilde{\epsilon}(\omega_1,\omega_2,E_2)}{4\pi} . \quad (21)$$

The conductivity is therefore holomorphic in the upper half-plane of the complex space if the dielectric function is holomorphic. In the case of the complex refractive index, the holomorphic properties in the complex plane do not follow from those of the susceptibility because of the branching points introduced by the squared root. We can, however, follow the same procedure as Nussenzweig,[17] and prove that real and imaginary parts of the refractive index $\tilde{n}=n+i\kappa$ are related by dispersion relations also in the nonlinear case, when the nonlinearity is due to the presence of an external light beam. In that case the refractive index depends on the intensity and on the frequency ω_2 of the external beam and can be written

$$\tilde{n}(\omega_1,\omega_2,E_2)=\tilde{n}_0(\omega_1)+\tilde{n}^{\,\mathrm{NL}}(\omega_1,\omega_2,E_2)$$
$$=\tilde{n}_0+\tilde{n}_1E_2^2+\tilde{n}_2E_2^4+\cdots , \quad (22)$$

where E_2 is the electric field of the external beam of frequency ω_2. The theorem of Nussenzweig[17] shows that $\tilde{n}$ is a holomorphic function of ω_1 (in the upper half complex plane), and we show in the Appendix that its asymptotic behavior is determined by the linear term $\tilde{n}_0$. Consequently we obtain for the refractive index the following dispersion relations to all orders:

$$n(\omega_1,\omega_2,E_2)-1=\frac{2}{\pi}\mathrm{P}\int d\omega_1'\frac{\omega_1'\kappa(\omega_1',\omega_2,E_2)}{\omega_1'^2-\omega_1^2} , \quad (23)$$

$$\kappa(\omega_1,\omega_2,E_2)=-\frac{2\omega_1}{\pi}\mathrm{P}\int d\omega_1'\frac{n(\omega_1',\omega_2,E_2)}{\omega_1'^2-\omega_1^2} , \quad (24)$$

where n and κ denote the real and imaginary parts, respectively.

IV. NONLINEAR SUM RULES

We can now show that a number of sum rules are contained in the above dispersion relations, as in the case of linear optics. Some of them are immediately evident. Others are obtained by making use of the superconvergence theorem to obtain the asymptotic behavior from the dispersion relations, and then comparing it with the asymptotic behavior of the optical functions when this is known to the desired order.[4,6]

In the first category is the static dielectric function sum rule, which is immediately obtained by setting $\omega_1=0$ in Eq. (16) and using (19). We obtain a nonlinear correction to the static dielectric function due to the nonlinear optical transitions,

$$\epsilon_1^{\mathrm{NL}}(0,\omega_2,E_2)=\frac{2}{\pi}\int_0^\infty\frac{\epsilon_2^{\mathrm{NL}}(\omega_1,\omega_2,E_2)}{\omega_1}d\omega_1 . \quad (25)$$

This may be a relevant effect in semiconductors since it modifies the screening of all electrostatic charges.

In the second category we find a large number of sum rules by studying the asymptotic behavior of $\tilde{\epsilon}^{\,\mathrm{NL}}(\omega_1,\omega_2,E_2)$. Once the asymptotic behavior is established, we can verify if the superconvergence theorem is applicable to the appropriate dispersion relations and by comparison obtain relevant sum rules as was done by Altarelli and co-workers[6,7] for the linear case. From relations (16) and (17), and similar expressions of related holomorphic functions, we obtain the values of integrals of the type

$$\int\omega_1^q g^{(n)}(\omega_1,\omega_2,-\omega_2,\ldots)d\omega_1$$

with all values of q, from 0 to that which gives the correct asymptotic behavior. Similarly, for the refractive index we use the superconvergence theorem and relations (23) and (24) to obtain the asymptotic behavior and we then compare it with the asymptotic behavior of the refractive index when this is known.

We show in the Appendix that the asymptotic behavior of ϵ^{NL} is of the type ω^{-4}. Then we immediately obtain, by the superconvergence theorem, the following sum rules for the real and imaginary parts of the nonlinear dielectric function to all orders:

$$\int_0^\infty\omega_1\epsilon_2^{\mathrm{NL}}(\omega_1,\omega_2,E_2)d\omega_1=0 , \quad (26)$$

$$\int_0^\infty\epsilon_1^{\mathrm{NL}}(\omega_1,\omega_2,E_2)d\omega_1=0 . \quad (27)$$

The first is the extension to nonlinear optics of the f-sum rule (TRK). Both sum rules (26) and (27) have been previously obtained by Peiponen[14] for the case of the anharmonic oscillator. Our analysis shows that they are valid in general, and proves that the basic sum rules of linear optics are valid to all orders since the nonlinear contribution vanishes.

The validity to all orders of the absorption coefficient sum rule and of the ADNS sum rule can also be proved in a similar way considering that $\tilde{n}^{\,\mathrm{NL}}$ has the same asymptotic behavior as $\tilde{\epsilon}^{\,\mathrm{NL}}$, as shown in the Appendix. We obtain the nonlinear sum rules

$$\int_0^\infty\omega_1\kappa^{\mathrm{NL}}(\omega_1,\omega_2,E_2)d\omega_1=0 , \quad (28)$$

$$\int_0^\infty n^{\mathrm{NL}}(\omega_1,\omega_2,E_2)d\omega_1=0 . \quad (29)$$

The first sum rule (28) shows that the absorption coefficient sum rule of linear optics is valid to all orders since the nonlinear contribution vanishes. The second (29) analogously shows that the ADNS sum rule $\int_0^\infty(n-1)d\omega=0$ is also valid to all orders.

New sum rules can also be obtained for all the products of the nonlinear optical functions by ω_1^2 and ω_1^3, always making use of the superconvergence theorem. We consider the function $\omega_1^2\tilde{\epsilon}^{\,\mathrm{NL}}(\omega_1,\omega_2,E_2)$, which is holomorphic and goes to infinity as ω_1^{-2}, as shown in the appendix. The dispersion relation leads to the asymptotic behavior

$$-\frac{c(\omega_2,E_2)}{\omega^4}=-\frac{2}{\pi}\frac{1}{\omega^4}\int_0^\infty\omega_1^3\epsilon_2(\omega_1,\omega_2,E_2)d\omega_1 ,$$

which gives the following sum rules:

$$\int_0^\infty \omega_1^2 \epsilon_1^{\rm NL}(\omega_1,\omega_2,E_2)d\omega_1=0 \ , \quad (30)$$

$$\int_0^\infty \omega_1^3 \epsilon_2^{\rm NL}(\omega_1,\omega_2,E_2)d\omega_1=\frac{\pi}{2}c(\omega_2,E_2) \ . \quad (31)$$

A similar analysis on the refractive index gives

$$\int_0^\infty \omega_1^2 n^{\rm NL}(\omega_1,\omega_2,E_2)d\omega_1=0 \ , \quad (32)$$

$$\int_0^\infty \omega_1^3 \kappa^{\rm NL}(\omega_1,\omega_2,E_2)d\omega_1=\frac{\pi}{4}c(\omega_2,E_2) \ . \quad (33)$$

In the sum rules (31) and (33), the quantity c depends on the nonlinear properties of the medium and on the external beams. Its value can be computed for each individual case as shown in the Appendix.

Similar sum rules can be obtained in the same way from the dispersion relations (10) and (11) also in those cases, such as $n=2$, when no dissipation is present. As an example we report the sum rule for second-harmonic generation:

$$\int_0^\infty {\rm Re}[g^{(2)}(\omega_1,\omega_1)]d\omega_1=0 \ , \quad (34)$$

$$\int_0^\infty \omega_1 {\rm Im}[g^{(2)}(\omega_1,\omega_1)]d\omega_1=0 \ . \quad (35)$$

The results reported above do not exhaust the possibilities for sum rules. Many others can be obtained by various mathematical manipulations, as described in Ref. 4 for the linear case, or by considering other types of response functions, such as σ or $(1/\epsilon)$. Using the prescriptions we have given, and the appropriate dispersion relations, sum rules can be derived for all problems of specific interest.

V. DISCUSSION AND PRELIMINARY APPLICATIONS

The results we have obtained are of general physical interest and can also be used to explain specific experimental phenomena in nonlinear optics.

First of all, nonlinear dissipative processes like two-photon absorption and stimulated Raman processes produce modification of the dispersive properties, which can be computed from Eqs. (16) and (17). This leads, for instance, to an anomalous dispersion near the resonance condition for excitation from the ground-state energy E_0 to the energy state E_i [when $\omega_1+\omega_2=(E_i-E_0)/\hbar$ or $|\omega_1-\omega_2|=(E_i-E_0)/\hbar$], similar to that of linear optics.

The nonlinear sum rules that we have obtained contain interesting information. For instance, the sum rule (26) implies that the nonlinear $\tilde{\epsilon}_2^{\rm NL}(\omega_1,\omega_2,E_2)$ must have negative contributions corresponding to emission in such a way as to compensate the dissipation due to two-photon and Raman transition processes. The sum rule (28) implies that the nonlinear positive absorption coefficient must be compensated by nonlinear amplification processes.

The verification of all the derived sum rules may be of interest. Predictions on higher-frequency nonlinear processes may be obtained by computing the relevant integrals up to a given value of the frequency. They may be experimentally verified by using synchrotron radiation over a very large frequency domain as the probe beam and laser radiation as the external beam.

The nonlinear anomalous emission processes have a resonant behavior at the steplike resonant processes, so that they may compensate the linear absorption under appropriate conditions. This can be tested in atomic physics experiments on a three-level system. Results like those first obtained by Alzetta *et al.*[19] can then find an explanation in the sum-rule conditions, which of course are automatically present in calculations with the density-matrix formalism.[20]

Analogous results were obtained experimentally by Fröhlich *et al.*[22] in an investigation of the dynamical Stark effect in semiconductors. The nonlinear contribution was explained by making use of the density-matrix calculation of the nonlinear susceptibility in the three-level system approximation,[23] and its integral was shown to vanish. We have now proved that this is a particular case of the general sum rules obeyed by any physical system.

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APPENDIX

The mathematical tool for obtaining sum rules from the dispersion relations is the so-called superconvergence property, which states that if a function $g(x)$ is defined by

$$g(x)=\int_0^\infty \frac{f(y)}{y^2-x^2}dy \ , \quad (A1)$$

and $f(y)$ dies off at large y faster than $(y\ \ln y)^{-1}$, then for large x the following expansion holds:

$$g(x)=\frac{-1}{x^2}\int_0^\infty f(y)dy+o(x^{-2}) \ . \quad (A2)$$

where $o(x^{-2})$ denotes terms dying off faster than x^{-2}.

If the above superconvergence property holds, then it can be applied to the dispersion relations involving the optical functions with an appropriate choice of the function $f(y)$. If in addition the asymptotic behavior of such expressions can be independently obtained, then by comparing the two results, a large number of sum rules can be obtained, as summarized in the review paper by Bassani and Altarelli for the linear optical functions.[18]

We now derive the asymptotic behavior of the dielectric function and prove that the superconvergence property can be applied also to the nonlinear dispersion equations, so that sum rules can be obtained.

We make use of the properties of the time-dependent Green's functions with a procedure similar to the one adopted by Altarelli and Smith[7] for the linear-response function.

The time-dependent dielectric function is

$$\tilde{\epsilon}=\tilde{\epsilon}^{L}(\tau)+\tilde{\epsilon}^{\mathrm{NL}}(\tau,\omega_2,E_2)$$
$$=1+\sum_{n\ \mathrm{odd}}2a_nE_2^{n-1}\int g^{(n)}(\omega_1,\omega_2,-\omega_2,\ldots)e^{-i\omega_1\tau}d\omega_1\ , \qquad \text{(A3)}$$

where we separate the linear and the nonlinear contribution. The coefficients a_n are given by expression (20). This can be expressed in terms of the time-dependent Green's function as

$$\tilde{\epsilon}(\tau,\omega_2,E_2)=1+\sum_{n\ \mathrm{odd}}4\pi a_nE_2^{n-1}\times\int_0^\infty dt_2\cdots dt_n\,G^{(n)}(\tau,t_2,\ldots,t_n)\times e^{-i(\omega_2t_2-\omega_2t_3+\omega_2t_4-\cdots)}\ . \qquad \text{(A4)}$$

To obtain the asymptotic behavior as a function of ω_1 we consider the expression of the inverse Fourier transform

$$\tilde{\epsilon}(\omega_1,\omega_2,E_2)-1=\int_0^\infty[\tilde{\epsilon}(\tau,\omega_2E_2)-1]e^{i\omega_1\tau}d\tau\ , \qquad \text{(A5)}$$

and perform the above time integral by parts to obtain

$$\tilde{\epsilon}(\omega_1,\omega_2,E_2)-1=-\frac{[\epsilon(\tau,\omega_2,E_2)-1]_{\tau=0^+}}{i\omega_1}-\frac{[(\partial/\partial\tau)\epsilon(\tau,\omega_2,E_2)]_{\tau=0^+}}{\omega_1^2}-\frac{[\partial^2\epsilon(\tau,\omega_2,E_2)/\partial\tau^2]_{\tau=0^+}}{i\omega_1^3}+\frac{[\partial^3\epsilon(\tau,\omega_2,E_2)/\partial\tau^3]_{\tau=0^+}}{\omega_1^4}+\cdots\ , \qquad \text{(A6)}$$

where we have used the fact that the Green's function and all its derivatives vanish for $\tau\rightarrow\infty$, as they represent the response to an instantaneous (δ-like) excitation after an infinite time [Eq. (1)].

By using expression (A4) and Kubo's formula for the time-dependent Green's function[21] we can now show that the first three terms on the right-hand side of Eq. (A6) vanish for the nonlinear part of the dielectric function. We observe that the first contribution in (A6) vanishes because $[\epsilon(\tau)-1]$ at zero time vanishes to all orders. The first time derivative, which contributes to the second term, can be expressed as follows:

$$\frac{\partial\epsilon}{\partial\tau}(\tau,\omega_2,E_2)=\sum_{n\ \mathrm{odd}}4\pi a_nE_2^{n-1}\int_0^\infty dt_2\cdots dt_n\frac{\partial}{\partial\tau}G^{(n)}(\tau,t_2,\ldots,t_n)e^{-i(\omega_2t_2-\omega_2t_3+\omega_2t_4-\omega_2t_5+\cdots)}\ , \qquad \text{(A7)}$$

with

$$G^{(n)}(\tau,t_2,\ldots,t_n)=\frac{1}{n\ (-i\hbar)^n}\sum_P\mathrm{Tr}\{\Theta(t_2-\tau)\Theta(t_3-t_2)\cdots\Theta(t_n-t_{n-1})[\mu(-\tau),[\mu(-t_2),\ldots,\mu(-t_n),\rho]]\mu\}\ , \qquad \text{(A8)}$$

where the sum is on all possible permutations of $\tau,t_2,\ldots,t_n$;Θ is the step function; μ is the dipole operator at zero time; $\mu(t)$ evolves with the unperturbed Hamiltonian $H_0=p^2/2m+V(x)$; ρ is a density matrix operator such that $[\rho,H_0]=0$.

Let us consider the first time derivative and use the condition $\tau<t_2,\ldots,t_n$, since we are interested only in the limit $\tau\rightarrow0$. We obtain

$$\lim_{\tau\rightarrow0}\frac{\partial}{\partial\tau}G^{(n)}(\tau,t_2,\ldots,t_n)=\frac{1}{n!(-i\hbar)^n}\lim_{\tau\rightarrow0}\frac{\partial}{\partial\tau}\mathrm{Tr}\left\{\left[\mu(-\tau),\sum_{P'}\Theta(t_3-t_2)\cdots\Theta(t_n-t_{n-1})[\mu(-t_2),[\cdots\mu(-t_n),\rho]]\right]\mu\right\}. \qquad \text{(A9)}$$

Using the Heisenberg expression for the time derivative of $\mu(\tau)$, Eq. (A9) becomes

$$\lim_{\tau\rightarrow0}\frac{\partial}{\partial\tau}G^{(n)}(\tau,t_2,\ldots,t_n)=\frac{1}{n!(-i\hbar)^{n+1}}\mathrm{Tr}\left\{\left[[\mu,H_0],\sum_{P'}\Theta(t_3-t_2)\cdots\Theta(t_n-t_{n-1})[\mu(-t_2),[\cdots\mu(-t_n)\rho]]\right]\mu\right\}. \qquad \text{(A10)}$$

Using the property

$$\mathrm{Tr}[A,B]C=\mathrm{Tr}[C,A]B \qquad \text{(A11)}$$

and the fact that

$$[\mu,H_0]=+i\hbar\frac{e}{m}p \ , \tag{A12}$$

we obtain

$$\lim_{\tau\to 0}\frac{\partial}{\partial\tau}G^{(n)}(\tau,t_2,\ldots,t_n)=\frac{-1}{n!(-i\hbar)^{n+1}}\frac{e^2\hbar^2}{m}\mathrm{Tr}\left\{\sum_{P'}\Theta(t_3-t_2)\cdots\Theta(t_n-t_{n-1})[\mu(-t_2),[\ldots\mu(-t_n)\rho]]\right\} . \tag{A13}$$

For the Green's function in first order the trace just gives the density ρ, so that we obtain

$$\lim_{\tau\to 0}\frac{\partial}{\partial\tau}G^{(1)}(\tau)=\frac{e^2}{m}\rho \tag{A14}$$

and expression (A6) in the linear approximation gives the asymptotic behavior

$$\tilde{\epsilon}(\omega_1)=1-\frac{\omega_p^2}{\omega_1^2} \ , \tag{A15}$$

from which all the linear sum rules are obtained. For all the higher-order Green's functions we obtain

$$\lim_{\tau\to 0}\frac{\partial}{\partial\tau}G^{(n)}(\tau,t_2,\ldots,t_n)=0 \ , \tag{A16}$$

since the trace of a commutator vanishes.

We now consider the second time derivative, for which we use twice the Heisenberg expression for the time derivative of the dipole moment and obtain

$$\lim_{\tau\to 0}\frac{\partial^2}{\partial\tau^2}G^{(n)}(\tau,t_2,\ldots,t_n)$$
$$=\frac{1}{n!(-i\hbar)^{n+2}}\mathrm{Tr}\left\{\left[[[\mu,H_0],H_0],\sum_{P'}\Theta(t_2-t_3)\cdots\Theta(t_n-t_{n-1})[\mu(-t_2),[\ldots\mu(-t_n),\rho]]\right]\mu\right\} . \tag{A17}$$

The above expression can be shown to vanish by noticing that the double commutator is a function of only μ because $d^2\mu/d\tau^2=F(x)$. By applying the property (A11) of the trace we observe that the commutator μ with a function of μ vanishes.

The third time derivative is different from zero, and its value can be computed from the expression

$$\lim_{\tau\to 0}\frac{\partial^3}{\partial\tau^3}G^{(n)}(\tau,t_2,\ldots,t_n)$$
$$=\frac{1}{(i\hbar)^{n+2}}\frac{e}{m}\mathrm{Tr}\left\{\left[[[p,H_0],H_0]\sum_{P'}\Theta(t_2-t_3)\cdots\Theta(t_{n-1}-t_n)[\mu(-t_2),[\ldots\mu(-t_n),\rho]]\right]\mu\right\} . \tag{A18}$$

We introduce the potential $V(x)$ in the expression

$$[[p,H_0],H_0]=\frac{-i\hbar^3}{2m}\left[2\frac{\partial^2 V}{\partial x^2}p+\frac{\partial^3 V}{\partial x^3}\right] , \tag{A19}$$

and again use expression (A11) for the trace of triple products to obtain

$$\lim_{\tau\to 0}\frac{\partial^3}{\partial\tau^3}G^{(n)}(\tau,t_2,\ldots,t_n)=\frac{e^2}{n!(-i\hbar)^{n-1}m^2}\mathrm{Tr}\left[\frac{\partial^2 V}{\partial x^2}\sum_{P'}\Theta(t_2-t_3)\cdots\Theta(t_{n-1}-t_n)[\mu(-t_2),[\ldots\mu(-t_n)\rho]]\right] . \tag{A20}$$

The above expression is different from zero and is the Green's function to order $n-1$ associated with the operator $\partial^2 V/\partial x^2$ instead of the operator dipole moment.

Substituting the time derivatives of $G^{(n)}(\tau,t_2,\ldots,t_n)$ into (A6), we find the following asymptotic expression for the nonlinear contribution:

$$\tilde{\epsilon}^{NL}(\omega_1,\omega_2,E_2)=\frac{c}{\omega_1^4}+o(\omega_1^{-4})$$
$$=\frac{1}{\omega_1^4}\sum_{n\ \mathrm{odd}>1}\frac{4\pi a_n e^2}{n!(-i\hbar)^{n-1}m^2}E_2^{n-1}\int_0^\infty\int_0^\infty dt_2\cdots dt_n e^{-i(\omega_2t_2-\omega_2t_3+\omega_2t_4-\omega_2t_5+\cdots)}$$
$$\times\mathrm{Tr}\sum_{P'}\left[\Theta(t_2-t_3)\cdots\Theta(t_{n-1}-t_n)\times[\mu(-t_2),[\ldots\mu(-t_n),\rho]]\frac{\partial^2V}{\partial x^2}\right]+o(\omega_1^{-4})\ . \tag{A21}$$

A similar expression holds for the index of refraction because of the connection $\tilde{n}=\sqrt{\tilde{\epsilon}}$, except that in this case the coefficient of the expansion is $c/2$, c being the numerator in expression (A21). The last term $o(\omega_1^{-4})$ means that the residual asymptotic contribution goes to zero faster than ω_1^{-4}. This is sufficient to prove all the sum rules reported in the text when the sum vanishes. The requirement that the optical functions go to zero at the order ω_1^{-4} requires the numerator in the expressions of type (A2) to vanish.

The sum rules (31) and (33) require that the imaginary part of ϵ^{NL} goes to zero as $\omega_1\rightarrow\infty$ faster than $\omega_1^{-4}\log^{-1}(\omega_1)$. This has to be proven mathematically for any physical system, but we can take this for granted since it is a general property of the dissipation to decrease faster than the dispersion for high frequency. Then, comparison of the asymptotic behavior (A21) with the expression $\omega_1^3\epsilon_2^{NL}(\omega_1,\omega_2)$ and $\omega_1^3\kappa^{NL}(\omega_1,\omega_2)$ gives the sum rules (31) and (33).

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