Kramers-Kronig relations and sum rules for the second-harmonic susceptibility

S. Scandolo
International School for Advanced Studies, Via Beirut 4, I-34014 Trieste, Italy

F. Bassani
Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56126 Pisa, Italy

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A set of Kramers-Kronig relations are obtained for the second-harmonic generation susceptibility $\chi^{(2)}(\omega,\omega)$. Together with the asymptotic behavior in the frequency variable they give a set of sum rules up to the fifth moment of the susceptibility.

I. INTRODUCTION

The tight connection between causality, the Kramers-Kronig (KK) relations, and sum rules has been pointed out in many fields of physics.[1] In linear optics, in particular, these concepts have played a fundamental role.[2] This has not been the case yet in the study of nonlinear optical phenomena, mainly because of the experimental difficulties in performing phase-amplitude measurements of the complex nonlinear susceptibilities. Very recently, however, a direct experimental verification of the nonlinear KK relations has been reported for the photoinduced modification of the complex refractive index[3] and for the third-harmonic generation susceptibility,[4] in agreement with the theoretical predictions.[5]

Kramers-Kronig relations follow directly from the causality principle, and have therefore been the subject of much theoretical study, especially in the case of nonlinear response.[6,7] Recent experiments[8] have proved that it is possible to carry out phase-amplitude measurements of third-order susceptibilities in a wide frequency range, and to verify the relevant KK relations.

The existence of sum rules for the nonlinear optical functions has been recently pointed out,[6] using the dynamical short-time response of the system. In particular, it has been shown that the nonlinear modification of the absorption coefficient has a vanishing average when integrated over the frequency of the probe beam, in agreement with experimental findings.[9] Other sum rules, up to the third moment of the susceptibility, have been found.

We now concentrate our attention on the particular case of the second-harmonic generation susceptibility $\chi^{(2)}(\omega,\omega)$ with the purpose of obtaining all the appropriate KK relations and the relevant sum rules. We will first derive the high frequency limit and show that it vanishes as ω^{-6}. Then we will prove that this implies the existence of three types of KK relations and of a set of sum rules, up to the fifth moment of the susceptibility.

In Sec. II we derive the asymptotic limit for $\chi^{(2)}(\omega,\omega)$ and the KK relations. In Sec. III we give the relevant sum rules. Conclusions are presented in Sec. IV.

II. ASYMPTOTIC BEHAVIOR AND KRAMERS-KRONIG RELATIONS

The second-order contribution to the nonlinear polarizability $\mathbf{P}(t)$ in terms of the electric field $\mathbf{E}(t)$ is

$$P_i^{(2)}(t)=\int_0^\infty dt_1\int_0^\infty dt_2 G_{ijk}^{(2)}(t_1,t_2)\times E_j(t-t_1)E_k(t-t_2)\quad, \tag{1}$$

where the Kubo response function[10] in second order, with Cartesian indices i,j,k, is

$$G_{ijk}^{(2)}(t_1,t_2)=-\frac{e^3}{V\hbar^2}(1+P)\theta(t_1)\theta(t_2-t_1)\times\mathrm{Tr}\left\{\left[x_k(-t_2),[x_j(-t_1),x_i]\right]\rho_0\right\}\quad, \tag{2}$$

V being the total volume, P a permutation of the pairs (t_1,j) and (t_2,k), θ the Heaviside function, $\mathbf{x}$ denoting the total position operator $\sum_\alpha \mathbf{x}^{(\alpha)}$ ($\alpha=1,\ldots,N$ number of electrons), and ρ_0 a stationary density matrix (such that $[\rho_0,H_0]=0$). The total position operator evolves according to the unperturbed Hamiltonian $H_0=\sum_\alpha p_\alpha^2/2m+V(\mathbf{r}_1,\ldots,\mathbf{r}_N)$.

The phenomenon of second-harmonic generation can be obtained with monochromatic fields by performing the integrals in (1), and considering the contribution at frequency 2ω. We obtain

$$P_i^{(2)}(t)_{2\omega}=\chi_{ijk}^{(2)}(\omega,\omega)E_j(t)_\omega E_k(t)_\omega\quad, \tag{3}$$

where $\chi^{(2)}(\omega,\omega)$ is the Fourier transform of $G^{(2)}(t_1,t_2)$ with $\omega_1=\omega_2$. Defining $\tau^+=t_1+t_2$ and $\tau^-=(t_1-t_2)/2$, we have

$$\chi_{ijk}^{(2)}(\omega,\omega)=\int d\tau^+\int d\tau^- G_{ijk}^{(2)}(t_1,t_2)e^{i\omega\tau^+}\quad. \tag{4}$$

The asymptotic behavior of Eq. (4) as $\omega\to\infty$ can be obtained by integrating by parts on τ^+ and assuming that $G^{(2)}$ and all its derivatives vanish at infinite times. We obtain

$$\chi^{(2)}(\omega,\omega) = -\sum_m \frac{\left[\int d\tau^- \frac{\partial^m}{\partial\tau^{+m}} G^{(2)}(t_1,t_2)\right]_{\tau^+\to 0^+}}{(-i\omega)^{m+1}} \ . \quad (5)$$

The evaluation of (5) is performed using (2) and carrying out the derivatives analytically. It is convenient to split $G^{(2)}$ into a product of a causal function $f = \theta(t_1)\theta(t_2 - t_1)$ and a dynamical contribution

$$g(t_1,t_2) = \left\langle \left[x_k(-t_2),[x_j(-t_1),x_i]\right]\right\rangle_0 , \quad (6)$$

where, in order to simplify the notation, we have replaced the trace on the density matrix by the average on the occupied states $\langle\cdots\rangle_0$. The mth-order derivative then reads

$$\frac{\partial^m}{\partial\tau^{+m}} G^{(2)}(t_1,t_2) = -\frac{e^3}{V\hbar^2}(1+P)\sum_{n=0}^{m}\frac{m!}{n!(m-n)!} \times \frac{\partial^{m-n}}{\partial\tau^{+m-n}} f(t_1,t_2)\frac{\partial^n}{\partial\tau^{+n}} g(t_1,t_2) \ . \quad (7)$$

We first consider the derivatives of the dynamical contribution (6); these can be written in terms of derivatives on the times t_1 and t_2 as

$$\frac{\partial^n}{\partial\tau^{+n}} g(t_1,t_2) = \sum_{p=0}^{n}\frac{n!}{p!(n-p)!}\frac{\partial^p}{\partial t_1^p}\frac{\partial^{n-p}}{\partial t_2^{n-p}} g(t_1,t_2) \ . \quad (8)$$

The derivatives in (8) can easily be performed using the following expressions for the time derivatives of the position operator:

$$\frac{d}{dt}x_i(-t) = -\frac{p_i}{m} ,$$
$$\frac{d^2}{dt^2}x_i(-t) = -\frac{1}{m}\frac{\partial V}{\partial x_i} ,$$
$$\frac{d^3}{dt^3}x_i(-t) = \frac{1}{m^2}\left[\frac{\partial^2 V}{\partial x_i \partial x_j}p_j - i\hbar\frac{\partial^3 V}{\partial x_i\partial x_j\partial x_j}\right] ,$$
$$\frac{d^4}{dt^4}x_i(-t) = -\frac{1}{m^3}\left[\frac{\partial^3 V}{\partial x_i\partial x_j\partial x_k}p_j p_k - 2i\hbar\frac{\partial^4 V}{\partial x_i\partial x_j\partial x_k^2}p_j - \hbar^2\frac{\partial^5 V}{\partial x_i\partial x_j^2\partial x_k^2} - m\frac{\partial^2 V}{\partial x_i\partial x_j}\frac{\partial V}{\partial x_j}\right] \ . \quad (9)$$

As can be seen from the second derivative, which represents the *total* force acting on the system, only the *external* potential appears, since the internal electron-electron contributions cancel out. Using (9) in expressions (8) and (7) one can show, after some algebra, that the first nonvanishing contributions to (8) are those with $n = 4$ (and $p = 3,4$). Specifically,

$$\frac{\partial^4 g}{\partial t_1^4} = -2\frac{\hbar^2}{m^3}\left\langle\frac{\partial^3 V}{\partial x_i\partial x_j\partial x_k}\right\rangle_0 , \quad (10)$$

and

$$\frac{\partial^4 g}{\partial t_1^3\partial t_2} = \frac{\hbar^2}{m^3}\left\langle\frac{\partial^3 V}{\partial x_i\partial x_j\partial x_k}\right\rangle_0 \ . \quad (11)$$

We then consider the derivative of the causal function f and can confine ourselves to the first one, which gives a nonzero contribution in lowest order. We have

$$\frac{\partial f}{\partial\tau^+} = \delta(t_1)\theta(t_2-t_1) \ . \quad (12)$$

By inserting (12), (10), and (11) into (8) we obtain that the first nonvanishing derivative in expression (7) is

$$\frac{\partial^5}{\partial\tau^{+5}}G^{(2)}_{ijk}(t_1,t_2) = \frac{\pi e^3 N}{32m^3}\left\langle\frac{\partial^3 V}{\partial x_i\partial x_j\partial x_k}\right\rangle_0 \times[\delta(t_1)\theta(t_2-t_1)+\delta(t_2)\theta(t_1-t_2)] \ . \quad (13)$$

Using (13), performing the integral on τ^-, and taking the limit $\tau^+ \to 0^+$, we immediately obtain the asymptotic behavior

$$\chi^{(2)}_{ijk}(\omega,\omega) = \frac{\frac{Ne^3}{8m^3}\left\langle\frac{\partial^3 V}{\partial x_i\partial x_k\partial x_k}\right\rangle_0}{\omega^6} + o(\omega^{-6}) \ . \quad (14)$$

It is to be noticed that the asymptotic behavior in (14) is different from that of the susceptibility in a pump-and-probe experiment. This implies different KK relations, because in this case we can consider all types of analytical functions which vanish sufficiently fast at infinity, $\omega^n\chi^{(2)}$ with $n \le 4$. Therefore we obtain the first set of KK relations similar to those of the linear case:

$$\mathrm{Re}\chi^{(2)}(\omega,\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega'\mathrm{Im}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' ,$$

$$\mathrm{Im}\chi^{(2)}(\omega,\omega) = -\frac{2\omega}{\pi}\int_0^\infty \frac{\mathrm{Re}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' , \quad (15)$$

and two additional sets of independent KK relations:

$$\mathrm{Re}\chi^{(2)}(\omega,\omega) = \frac{2}{\pi\omega^2}\int_0^\infty \frac{\omega'^3\mathrm{Im}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' ,$$

$$\mathrm{Im}\chi^{(2)}(\omega,\omega) = -\frac{2}{\pi\omega}\int_0^\infty \frac{\omega'^2\mathrm{Re}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' , \quad (16)$$

and

$$\mathrm{Re}\chi^{(2)}(\omega,\omega) = \frac{2}{\pi\omega^4}\int_0^\infty \frac{\omega'^5\mathrm{Im}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' ,$$

$$\mathrm{Im}\chi^{(2)}(\omega,\omega) = -\frac{2}{\pi\omega^3}\int_0^\infty \frac{\omega'^4\mathrm{Re}\chi^{(2)}(\omega',\omega')}{\omega'^2-\omega^2}d\omega' \ . \quad (17)$$

We have not specified the tensorial indices because the above KK relations are the same for all of them.

While dispersion relations (15) were already given by Kogan,[11] discussed by Price[12] and Caspers,[13] and have been employed by Sipe and co-workers[14] to simplify their calculation of $\chi^{(2)}$, the dispersion relations (16) and (17) are different and must also be satisfied by the second-order susceptibility. They may find direct application in analyzing and interpreting the experimental data.

III. SUM RULES

As in the analogous case of pump-and-probe experiments,[6] the derived KK relations and the knowledge of the asymptotic behavior give the sum rules which the susceptibility must obey. In the present case, by considering $\omega = 0$ in (15), we obtain the following property of the static limit:

$$\chi^{(2)}(0,0) = \frac{2}{\pi}\int_0^\infty \frac{\mathrm{Im}\chi^{(2)}(\omega',\omega')}{\omega'}d\omega' \ . \qquad (18)$$

We also obtain, considering the limit $\omega = 0$ in the KK relations (16) and (17), the following sum rules:

$$\int_0^\infty \omega \mathrm{Im}\chi^{(2)}(\omega,\omega)d\omega = 0 \ , \qquad (19)$$

$$\int_0^\infty \mathrm{Re}\chi^{(2)}(\omega,\omega)d\omega = 0 \ , \qquad (20)$$

$$\int_0^\infty \omega^3 \mathrm{Im}\chi^{(2)}(\omega,\omega)d\omega = 0 \ , \qquad (21)$$

$$\int_0^\infty \omega^2 \mathrm{Re}\chi^{(2)}(\omega,\omega)d\omega = 0 \ . \qquad (22)$$

We next use the superconvergence theorem[15] on the KK relations (17), and compare the asymptotic behavior thus obtained with the asymptotic behavior independently derived in expression (14). This gives the two additional sum rules

$$\int_0^\infty \omega^4 \mathrm{Re}\chi^{(2)}(\omega,\omega)d\omega = 0 \ , \qquad (23)$$

and

$$\int_0^\infty \omega^5 \mathrm{Im}\chi^{(2)}_{ijk}(\omega,\omega)d\omega = -\frac{\pi}{16}\frac{Ne^3}{m^3}\left\langle \frac{\partial^3 V}{\partial x_i \partial x_j \partial x_k}\right\rangle_0 . \qquad (24)$$

In the last expression we have specified the tensorial indices because the value of the constant depends on them, while the preceding sum rules are independent of them.

Both the real and the imaginary parts of the nonlinear susceptibilities display a strong dispersive behavior, as shown by the set of vanishing sum rules. On the other hand, the finite-value sum rule (24) may be taken as an indication of the overall strength of second-harmonic generation in a given system. We wish to note that the above sum rules are completely general and have not been found previously to our knowledge, except for the sum rules (19) and (20) which were previously given by Peiponen[16] for the specific case of the anharmonic oscillator. We have also verified that the anharmonic oscillator, as expected, obeys all the sum rules here derived.

IV. CONCLUSIONS

The main result of this paper is to have given the general asymptotic behavior of the second-harmonic susceptibility $\chi^{(2)}(\omega,\omega)$. From this, three sets of KK dispersion relations are obtained, and in turn seven sum rules are found.

Apart from the relevance *per se* of the KK relations and sum rules here given, we wish to emphasize that they can be of great help in analyzing available experiments, to connect the phase and amplitude of the susceptibilities, and to establish if other contributions exist outside a given frequency range. They can also be very valuable in assessing the validity of computational methods, since in general exact calculations are not possible.

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