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Sum rules for arbitrary-order harmonic generation susceptibilities

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Abstract. Dispersion theory for harmonic generation susceptibilities is considered with the aid of complex analysis. New sum rules are obtained for the powers of arbitrary-order harmonic generation susceptibilities. The theory is based on the holomorphic properties and asymptotic behaviour of nonlinear susceptibilities. The present sum rules are reportedly important in nonlinear optical spectra analysis.

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1 Introduction

The Kramers-Kronig (K-K) relations, which relate the real and imaginary parts of linear optical susceptibility [1,2], are one of the most powerful tools of the optical spectroscopy that conventionally allow one to calculate the refractive index of a medium from the measured absorption spectrum and *vice versa*. The universal character of the K-K relations reflects the fact that they arise from causality, one of the most fundamental principle of physics stating the direction of the time arrow. Causality, in particular, ensures the holomorphicity of the linear response functions in the upper half of the complex angular frequency plane where they obey the Cauchy-Riemann equations [3]. This holomorphicity, in particular, allows one to derive useful constraints on the response functions that are referred to as the sum rules [4] and – along with microscopic theories – gives new insight on the theory of linear and nonlinear optical response. Physically, sum rules can be considered as restatements of causality and sum rules allow one to check the consistency of experimental data and theoretical models of the optical properties of the medium [5,6].

Recent advances in laser technology and the rapid development of nonlinear optical spectroscopy have stimulated search for analog K-K relations (called also dispersion relations) for nonlinear optical susceptibilities [7–9]. It has been shown [10] that a harmonic wave generation is described by the nonlinear susceptibility, which is a holomorphic function in the upper half plane similar to the linear susceptibility. Holomorphic functions with proper asymptotic behaviour satisfy the dispersion relations, which have been experimentally demonstrated for third-harmonic generation in polysilanes [11]. Universal constraints for the third-order susceptibility have been derived by Rapapa and Bassani [12] that are in good agreement with experimental data from third harmonic generation experiments. The works of Peiponen [2,13,14] have stimulated the study of the relevant sum rules for nonlinear optical susceptibilities that have been derived *e.g.* for many-electron systems [15], atomic hydrogen [16], and the anharmonic oscillator [17]. Bassani and Lucarini [18] have derived general properties and sum rules for higher order harmonic generation susceptibilities. Fast convergence of the nonlinear susceptibilities at high frequencies is of crucial importance for experimental data analysis. Since the convergence rate increases with the order of the nonlinear process, potential applicability of the sum rules for testing of measured spectra increases with the order of the nonlinear process. Intensity of the signal itself usually decreases rapidly with the increase of the order of the nonlinear process. This makes it important to search for sum rules, which have faster convergence even at relatively low order of the nonlinear optical process.

Sum rules with low convergence require the knowledge of the spectrum over the complete spectral range. However, it should be pointed out that sum rules with faster convergence are more useful in experimental data analysis with an unavoidable finite spectrum. Hence, the errors of numerical calculations of sum rules caused by a finite spectrum can be reduced. For finite spectra, there are alternative and practical methods for data inversion. These include, for instance, multiply subtractive K-K relations (MSKK) [19–21] and the maximum entropy method (MEM) [22]. Sum rules presented in this paper can then be used to check the consistency of the inverted data obtained using either MSKK or MEM. Vartiainen *et al.* [23] showed the applicability of sum rules in nonlinear optical spectroscopy by testing experimental data in order to determine the background susceptibility of coherent

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anti-Stokes Raman scattering of the nitrogen Q-branch measured over a finite spectral range.

In this theoretical study we derive dispersion relations and sum rules for the powers of nonlinear susceptibilities by generalizing the results of King [24] and Bassani and Lucarini [18]. The paper is organized as follows. Section 2 deals with the asymptotic behaviour of the arbitrary-order harmonic frequency generation susceptibilities. In Section 3 we present an extension of King's method for nonlinear susceptibilities and derive, as far as we know, new sum rules for harmonic generation susceptibilities that are not based on the K-K analysis. In Section 4 we give generalized results for K-K type dispersion relations and sum rules for the powers of arbitrary-order harmonic generation susceptibilities. In Section 5 we summarize our results. Finally, in Appendices A and B we present the mathematical background for the derivation of sum rules.

2 Holomorphicity and asymptotic behaviour of harmonic generation susceptibilities

Let us consider the polarization of an insulating medium. In this paper the spatial dispersion is not taken into account. The most general way to express the polarization of the medium $\mathbf{P}(t)$ is

$$P_i(t) = \int_0^\infty G_{ij}^{(1)}(t_1)E_j(t-t_1)\mathrm{d}t_1 + \iint_0^\infty G_{ijk}^{(2)}(t_1,t_2)E_j(t-t_1)E_k(t-t_1-t_2)\mathrm{d}t_2\mathrm{d}t_1 + \iiint_0^\infty G_{ijkl}^{(3)}(t_1,t_2,t_3)E_j(t-t_1)E_k(t-t_1-t_2) \times E_l(t-t_1-t_2-t_3)\mathrm{d}t_3\mathrm{d}t_2\mathrm{d}t_1 + \cdots . \quad (1)$$

Here $G^{(1)}(t_1)$ is a linear response function and $G^{(2)}(t_1,t_2)$ and $G^{(3)}(t_1,t_2,t_3)$ are higher order response functions with subscripts labelling the Cartesian coordinates x, y and z. A Fourier transform of the linear response function $G_{ij}^{(1)}(t)$ gives the linear susceptibility in the frequency domain

$$\chi_{ij}^{(1)}(\omega) = \int_0^\infty G_{ij}^{(1)}(t)\exp(\mathrm{i}\omega t)\mathrm{d}t, \quad (2)$$

where ω is the angular frequency and $G_{ij}^{(1)}(t)$ depends on the dielectric properties of an insulating medium. For the sake of simplicity, we drop the subscripts from the notation. The lower bound of the integration follows from the principle of causality since the response of the system cannot precede the interference that causes it [20]. Hence, $G^{(1)}(t)$ is a real function and we obtain that for purely imaginary angular frequencies $\chi^{(1)}(\mathrm{i}\omega)$ is a real function.

For monochromatic plane waves with frequency ω we have the nonlinear contribution with angular frequency $n\omega$ as follows [12]:

$$P^{(n)}(n\omega) = \varepsilon_0\chi^{(n)}(n\omega)E(\omega)E(\omega)\cdots E(\omega), \quad (3)$$

where $\chi^{(n)}(n\omega) = \chi^{(n)}(n\omega;\omega,\cdots,\omega)$ is the nth order harmonic generation susceptibility describing the nth order harmonic frequency generation in the medium. The arbitrary-order harmonic generation susceptibility $\chi^{(n)}(n\omega)$ is a Fourier transform of a general response function $G^{(n)}(t_1,\cdots,t_n)$. Defining $\tau = t_1+t_2+\cdots+t_n$ and $\tau_i = t_i - t_{i+1}$, we have

$$\chi^{(n)}(n\omega) = \int_0^\infty\cdots\int_0^\infty G^{(n)}(t_1,t_2,\cdots,t_n)\exp(\mathrm{i}\omega\tau) \times \exp(\mathrm{i}\omega\tau_1)\cdots\exp(\mathrm{i}\omega\tau_{n-1})\mathrm{d}\tau_{n-1}\cdots\mathrm{d}\tau. \quad (4)$$

The arbitrary-order susceptibility obtained from equation (4) is a holomorphic function in the upper half of the complex angular frequency plane [10,25].

The asymptotic behaviour of the harmonic generation susceptibilities have been studied in literature [12,18,25]. The convergence of the arbitrary-order harmonic generation susceptibility was obtained from the Kubo response function formalism, which is of the form [25]

$$\chi^{(n)}(n\omega) = \frac{\psi}{\omega^{2n+2}} + O(\omega^{-(2n+2)}), \quad \text{with} \quad n = 2,3,\cdots \quad (5)$$

where ψ depends on the model used to describe the medium and $O(\omega^{-(2n+2)})$ denotes terms that converge strictly faster than $\omega^{-(2n+2)}$. In particular, for the basic classical anharmonic oscillator model we have

$$\chi^{(n)}(n\omega) = \psi D(n\omega)[D(\omega)]^n, \quad (6)$$

where

$$D(\omega) = (\omega_0^2 - \omega^2 - \mathrm{i}\Gamma\omega)^{-1}. \quad (7)$$

Here ω_0 is the resonance angular frequency of the medium and Γ is the oscillator dephasing time. $D(\omega)$ has two poles, which are located in the lower half plane and are explicitly given by $\omega_{1,2} = \pm\sqrt{\omega_0^2 - \Gamma^2/4} - \mathrm{i}\Gamma/2$. This ensures the holomorphicity of $\chi^{(n)}(n\omega)$.

3 Extension of King's method for harmonic generation susceptibilities

In order to obtain sum rules for linear susceptibility King [24] suggested to consider complex functions

$$f_1(\hat\omega) = \frac{\chi^{(1)}(\hat\omega)}{\hat\omega + \mathrm{i}\omega'}; \quad f_2(\hat\omega) = \frac{\chi^{(1)}(\hat\omega)}{\hat\omega - \mathrm{i}\omega'} \quad (8)$$

where $\hat\omega$ is the complex angular frequency and ω' is a real positive frequency. The integration is carried out around a closed semi-circle contour C containing the real axis and the upper half of the complex angular frequency plane, as presented in Figure 1a. There is one pole at the imaginary axis with function $f_2(\hat\omega)$ and the pole is enclosed by the

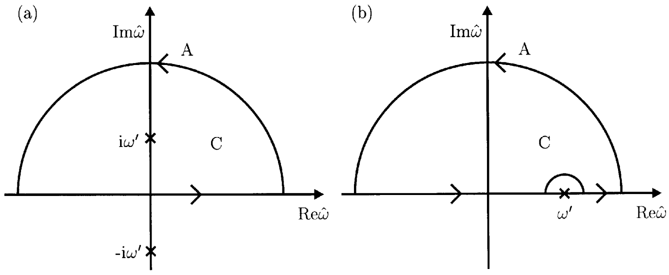

Fig. 1. Contour for derivation of (a) King's and (b) Kramers-Kronig type dispersion relations and sum rules (×=pole).

integration path. The contour integration can be split into two parts as follows:

$$\lim_{|\hat{\omega}|\to\infty}\oint_{\mathrm{C}} f(\hat{\omega})\mathrm{d}\hat{\omega} = \int_{-\infty}^{\infty} f(\omega)\mathrm{d}\omega + \lim_{|\hat{\omega}|\to\infty}\int_{\mathrm{A}} f(\hat{\omega})\mathrm{d}\hat{\omega}. \quad (9)$$

The integral along the arc A tends to zero when the radius (=frequency) of the circle approaches infinity, which is guaranteed by the asymptotic fall-off of the linear susceptibility that is proportional to ω^{-2}. Since $\mathrm{Im}\{\chi^{(1)}(\mathrm{i}\omega)\}$ is zero for all real frequencies ω, we obtain a sum rule given by King [24] for linear susceptibility

$$\int_0^{\infty} \frac{\omega \mathrm{Im}\{\chi^{(1)}(\omega)\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \omega' \int_0^{\infty} \frac{\mathrm{Re}\{\chi^{(1)}(\omega)\}}{\omega^2+\omega'^2}\mathrm{d}\omega. \quad (10)$$

In the derivation of equation (10) we have used a symmetry property, which can be expanded for the complex angular frequencies and for nonlinear susceptibilities as follows [26]:

$$\chi^{(n)}(-n\hat{\omega}^*) = \left[\chi^{(n)}(n\hat{\omega})\right]^*, \quad (11)$$

where (*) denotes the complex conjugate. equation (11) shows that for real angular frequencies the real part of the arbitrary-order susceptibility is an even function and the imaginary part an odd function.

The sum rule of equation (10) is now extended for higher-order susceptibilities, which describe the arbitrary-order harmonic wave generation, by considering complex functions:

$$g_1(\hat{\omega}) = \frac{\hat{\omega}^j[\chi^{(n)}(n\hat{\omega})]^k}{\hat{\omega}+\mathrm{i}\omega'}; \quad g_2(\hat{\omega}) = \frac{\hat{\omega}^j[\chi^{(n)}(n\hat{\omega})]^k}{\hat{\omega}-\mathrm{i}\omega'}, \quad (12)$$

where indices j and k are integers and ω' is a real positive frequency. In the case of $g_2(\hat{\omega})$, there is one pole at $\hat{\omega} = \mathrm{i}\omega'$ in the upper half plane. The pole induces a residue term when integrating along the contour presented in Figure 1a. In the general case, we must have a convergent integral, which can be ensured with proper choice of indices j and k. Then we can express sum rules for the arbitrary-order harmonic generation susceptibility, analogous to the linear case of equation (10) as follows (for a more detailed derivation see Appendix A):

$$\omega' \int_0^{\infty} \frac{\omega^j \mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \int_0^{\infty} \frac{\omega^{j+1} \mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega \qquad j=0,2,4,\ldots \quad (13)$$

$$\int_0^{\infty} \frac{\omega^{j+1} \mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = -\omega' \int_0^{\infty} \frac{\omega^{j} \mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega \qquad j=1,3,5,\ldots \quad (14)$$

Herein, as an example, we present a new sum rule which is analogous to the linear case and is of the form

$$\int_0^{\infty} \frac{\omega \mathrm{Im}\{\chi^{(3)}(3\omega)\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \omega' \int_0^{\infty} \frac{\mathrm{Re}\{\chi^{(3)}(3\omega)\}}{\omega^2+\omega'^2}\mathrm{d}\omega. \quad (15)$$

Sum rules presented above are extensions of King's sum rules but for the nonlinear susceptibility.

4 Kramers-Kronig type relations and sum rules

Causality guarantees the holomorphicity of harmonic generation susceptibility in the upper half of the complex angular frequency plane [10]. Convergence of nonlinear dispersion relations follows from the asymtotic fall-off of the susceptibility as shown in Section 2. In order to derive dispersion relations for $[\chi^{(n)}(n\omega)]^k$, we consider the following function:

$$f(\hat{\omega}) = \frac{\hat{\omega}^{2\alpha}\left[\chi^{(n)}(n\hat{\omega})\right]^k}{\hat{\omega}-\omega'}, \quad (16)$$

where α, n, and k are integers and ω' is a real positive frequency. The contour for the derivation of K-K type relations is presented in Figure 1b and the integration can be split into two parts according to equation (9). Due to a pole at a positive real frequency axis, we have to replace the integral over the real frequency axis in equation (9) with a Cauchy principal value integral. The convergence of the integral along the arc obeys equation (5) and allows us to derive $k(2n+2)$ K-K type relations. Only the formulas that contain even powers of $\hat{\omega}$ are relevant since both even and odd powers reduce to the same set of sum rules. The higher powers of the harmonic generation susceptibilities converge very rapidly. For the value $\alpha = k(n+1)$ the integral along the arc converges to a certain purely imaginary value that depends on the model used to describe the susceptibility. For even powers, the K-K type relations can be expressed as follows:

$$\omega'^{2\alpha-1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\} = -\frac{2}{\pi} \times \mathrm{P}\int_0^\infty \frac{\omega^{2\alpha}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \text{with } 0 \le \alpha \le k(n+1) \quad (17)$$

$$\omega'^{2\alpha}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\} = \frac{2}{\pi} \times \mathrm{P}\int_0^\infty \frac{\omega^{2\alpha+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \text{with } 0 \le \alpha \le k(n+1)-1 \quad (18)$$

$$\omega'^{2\alpha}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\} = \frac{2}{\pi} \times \mathrm{P}\int_0^\infty \frac{\omega^{2\alpha+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega + \psi^k, \text{with } \alpha = k(n+1) \quad (19)$$

where P denotes the Cauchy principal value. Note that in equations (17–19) the integrals are divergent if $\alpha > k(n+1)$. As far as we know, a detailed derivation of the constrains of the convergence of equations (17–19) has not been presented in the literature before. Therefore, we present a detailed calculation of the condition of the convergence of dispersion relations involving the function $f(\hat{\omega})$ in Appendix B. Dispersion relations presented above are general and not model dependent excluding equation (19). Sum rules can be obtained from dispersion relations above. As an example, see Appendix B as concerns the derivation of a sum rule equation (20).

$$\int_0^\infty \omega^{2\alpha}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega = 0, \quad \text{with } 0 \le \alpha \le k(n+1)-1. \quad (20)$$

$$\int_0^\infty \omega^{2\alpha+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega = 0, \quad \text{with } 0 \le \alpha \le k(n+1)-2. \quad (21)$$

$$\int_0^\infty \omega^{2\alpha+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega = -\frac{\pi}{2}\psi^k, \quad \text{with } \alpha = k(n+1)-1. \quad (22)$$

The sum rules, equations (21–22), can be derived in a similar manner as the sum rule equation (20). Note that the generalized sum rules above reduce to the formulas given by Bassani and Lucarini [18] in the special case $k = 1$.

5 Conclusions

In this paper we investigated the holomorphic properties of the arbitrary-order harmonic generation susceptibilities $\chi^{(n)}(n\omega)$, which are responsible for the nth harmonic generation processes, and obtained a new set of sum rules for $[\chi^{(n)}(n\omega)]^k$. We showed that the asymptotic behaviour of nonlinear susceptibilities allowed us to introduce the K-K type dispersion relations for $[\chi^{(n)}(n\omega)]^k$. With the aid of the complex analysis, we generalized the sum rules given by King [24] and Bassani and Lucarini [18]. The high convergence of $[\chi^{(n)}(n\omega)]^k$ is believed to make these sum rules an important tool in nonlinear optical spectroscopy. As a potential application of the present sum rules, we mention, for instance, sum rule tests of spectra related to enhanced harmonic wave generation from layered nanocomposites [27,28].

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Appendix A: Derivation of extended King's method

The derivation of extended King's method is based on the complex integration along the contour presented in Figure 1a. Let us consider functions given by equation (12). In the case of $g_1(\hat{\omega})$, the function is holomorphic in the upper half plane and we obtain

$$\int_0^\infty \frac{\omega^{j+1}\mathrm{Im}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega - \omega'\int_0^\infty \frac{\omega^{j}\mathrm{Re}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega = 0, \quad \text{with } j\text{=even}. \quad (A.1)$$

$$\int_0^\infty \frac{\omega^{j+1}\mathrm{Re}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega + \omega'\int_0^\infty \frac{\omega^{j}\mathrm{Im}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega = 0, \quad \text{with } j\text{=odd}. \quad (A.2)$$

In turn, $g_2(\hat{\omega})$ has one pole at the positive imaginary axis, which induces a residue term to dispersion relations as follows:

$$\int_0^\infty \frac{\omega^{j+1}\mathrm{Im}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega + \omega'\int_0^\infty \frac{\omega^{j}\mathrm{Re}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega = \pi\mathrm{Res}_{\hat{\omega}=\mathrm{i}\omega'}[g_2(\hat{\omega})], \quad \text{with } j\text{=even}. \quad (A.3)$$

$$\int_0^\infty \frac{\omega^{j+1}\mathrm{Re}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega - \omega'\int_0^\infty \frac{\omega^{j}\mathrm{Im}\left\{\chi^{(n)}(n\omega)^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega = \pi\mathrm{i}\mathrm{Res}_{\hat{\omega}=\mathrm{i}\omega'}[g_2(\hat{\omega})], \quad \text{with } j\text{=odd}. \quad (A.4)$$

The complex integration with the residue term of the first-order pole can be calculated as follows:

$$\oint_C g_2(\hat{\omega})\mathrm{d}\hat{\omega} = 2\pi \mathrm{i} g_2(\mathrm{i}\omega') = 2\pi\mathrm{i}(\mathrm{i}\omega')^j[\chi^{(n)}(n\mathrm{i}\omega')]^k$$
$$= \begin{cases} 2\pi\mathrm{i}\omega'^j[\chi^{(n)}(n\mathrm{i}\omega')]^k & \text{with } j=0,4,8,\cdots \\ -2\pi\omega'^j[\chi^{(n)}(n\mathrm{i}\omega')]^k & \text{with } j=1,5,9,\cdots \\ -2\pi\mathrm{i}\omega'^j[\chi^{(n)}(n\mathrm{i}\omega')]^k & \text{with } j=2,6,10,\cdots \\ 2\pi\omega'^j[\chi^{(n)}(n\mathrm{i}\omega')]^k & \text{with } j=3,7,11,\cdots \end{cases} \quad \text{(A.5)}$$

Now, we can combine the results for functions $g_1(\hat{\omega})$ and $g_2(\hat{\omega})$ and obtain

$$\int_0^\infty \frac{\omega^j \mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \begin{cases} \frac{\pi}{2\omega'}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=0 \\ -\frac{\pi\omega'^{j-1}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=2,6,10,\ldots \\ \frac{\pi\omega'^{j-1}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=4,8,12,\ldots \end{cases} \quad \text{(A.6)}$$

$$\int_0^\infty \frac{\omega^{j+1} \mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \begin{cases} -\frac{\pi\omega'^{j}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=1,5,9,\ldots \\ \frac{\pi\omega'^{j}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=3,7,11,\ldots \end{cases} \quad \text{(A.7)}$$

$$\int_0^\infty \frac{\omega^{j+1} \mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \begin{cases} \frac{\pi}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=0 \\ -\frac{\pi\omega'^{j}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=2,6,10,\ldots \\ \frac{\pi\omega'^{j}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=4,8,12,\ldots \end{cases} \quad \text{(A.8)}$$

$$\int_0^\infty \frac{\omega^{j} \mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2+\omega'^2}\mathrm{d}\omega = \begin{cases} \frac{\pi\omega'^{j-1}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=1,5,9,\ldots \\ -\frac{\pi\omega'^{j-1}}{2}\left[\chi^{(n)}(\mathrm{i}n\omega)\right]^k & j=3,7,11,\ldots \end{cases} \quad \text{(A.9)}$$

We can summarize our results by combining equations (A.6–A.9) into the form of equations (13, 14) presented in Section 3.

Appendix B: Convergence of K-K type relations

In this section we derive the convergence of dispersion relations and sum rules. As far as we know, a detailed derivation has not been presented in the literature before. The convergence of dispersion relations and sum rules are restricted by the integral along the arc A, presented in Figure 1b. Let us consider the function

$$f(\hat{\omega}) = \frac{\hat{\omega}^m\left[\chi^{(n)}(n\hat{\omega})\right]^k}{\hat{\omega}-\omega'}, \quad \text{(B.1)}$$

where m, n and k are integers and ω' is located at the positive real axis. We consider both even and odd powers of $\hat{\omega}$. Bassani and Lucarini [18] used only even powers of $\hat{\omega}$ since both even and odd powers reduce to the same set of sum rules. Nevertheless, different K-K type relations arise for even and odd powers. By the definition of the arbitrary-order harmonic frequency generation susceptibility, we know that at high frequencies, the convergence is proportional to $\psi\omega^{-(2n+2)}$. By expressing complex angular frequency in polar coordinates $\hat{\omega} = R\mathrm{e}^{\mathrm{i}\varphi}$ such that $\mathrm{d}\hat{\omega} = R\mathrm{i}\mathrm{e}^{\mathrm{i}\varphi}\mathrm{d}\varphi$, we have for the integral along the arc A

$$\int_A \frac{\hat{\omega}^m\left[\chi^{(n)}(n\hat{\omega})\right]^k}{\hat{\omega}-\omega'}\mathrm{d}\hat{\omega} = \int_0^\pi \frac{R^m\mathrm{e}^{\mathrm{i}m\varphi}\psi^k}{[R^{2n+2}\mathrm{e}^{\mathrm{i}(2n+2)\varphi}]^k(R\mathrm{e}^{\mathrm{i}\varphi}-\omega')}R\mathrm{i}\mathrm{e}^{\mathrm{i}\varphi}\mathrm{d}\varphi$$
$$= \mathrm{i}\psi^k R^{m-k(2n+2)}\int_0^\pi \frac{\mathrm{e}^{\mathrm{i}[m+1-k(2n+2)]\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\mathrm{d}\varphi \quad \text{(B.2)}$$

The limit of the integral (B.2) at high frequencies defines the convergence of dispersion relations. For the convergent integral, the limit is finite when the radius $R = |\hat{\omega}|$ of the arc A approaches infinity. This restricts the highest power m. For values $m < 2k(n+1)$ the integral converges to zero

$$\lim_{R\to\infty}\left[\mathrm{i}\psi^k R^{m-k(2n+2)}\int_0^\pi \frac{\mathrm{e}^{\mathrm{i}[m+1-k(2n+2)]\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\mathrm{d}\varphi\right] = 0. \quad \text{(B.3)}$$

Higher powers than $m = 2k(n+1)$ are divergent. For the value $m = 2k(n+1)$, the integral along the arc converges to a certain purely imaginary value that depends on the model used to describe the medium as follows:

$$\lim_{|\hat{\omega}|\to\infty}\left[\int_A \frac{\hat{\omega}^m\left[\chi^{(n)}(n\hat{\omega})\right]^k}{\hat{\omega}-\omega'}\mathrm{d}\hat{\omega}\right] = \lim_{R\to\infty}\left[\mathrm{i}\psi^k\int_0^\pi \frac{\mathrm{e}^{\mathrm{i}\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\mathrm{d}\varphi\right]\cdot \quad \text{(B.4)}$$

Let R be large enough such that $R \geq 2\omega'$. Then, by Lebesgue's convergence theorem, the integral along the arc A has a converging majorant

$$\left|\frac{\mathrm{e}^{\mathrm{i}\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\right| \leq \frac{1}{1-|\omega'/R|} \leq \frac{1}{1-1/2} = 2, \quad \text{(B.5)}$$

which is a constant. In equation (B.4), we can change the order of the integration and the limiting process as follows:

$$\lim_{R\to\infty}\left[\mathrm{i}\psi^k\int_0^{\pi}\frac{\mathrm{e}^{\mathrm{i}\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\mathrm{d}\varphi\right]= \mathrm{i}\psi^k\int_0^{\pi}\left[\lim_{R\to\infty}\left(\frac{\mathrm{e}^{\mathrm{i}\varphi}}{\mathrm{e}^{\mathrm{i}\varphi}-\omega'/R}\right)\right]\mathrm{d}\varphi = \mathrm{i}\psi^k\int_0^{\pi}\mathrm{d}\varphi=\pi\mathrm{i}\psi^k. \quad (B.6)$$

Integration around the closed semi-circle presented in Figure 1b can be expressed as follows:

$$\lim_{|\hat\omega|\to\infty}\oint_{\mathrm{C}} f(\hat\omega)\mathrm{d}\hat\omega=\pi\mathrm{i}\mathrm{Res}_{\hat\omega=\omega'}f(\hat\omega) = \pi\mathrm{i}\omega'^m\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}-\pi\omega'^m\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}. \quad (B.7)$$

On the other hand, we have

$$\lim_{|\hat\omega|\to\infty}\oint_{\mathrm{C}} f(\hat\omega)\mathrm{d}\hat\omega=\mathrm{P}\int_{-\infty}^{\infty}f(\omega)\mathrm{d}\omega+\lim_{|\hat\omega|\to\infty}\int_{\mathrm{A}}f(\hat\omega)\mathrm{d}\hat\omega. \quad (B.8)$$

Negative angular frequencies are not physically reasonable and we can reformulate the Cauchy principal value integration with the aid of the symmetry relation equation (11). For the even integer m it holds

$$\mathrm{P}\int_{-\infty}^{\infty}f(\omega)\mathrm{d}\omega=2\omega'\int_0^{\infty}\frac{\omega^m\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega + 2\mathrm{i}\int_0^{\infty}\frac{\omega^{m+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.9)$$

and for the odd m

$$\mathrm{P}\int_{-\infty}^{\infty}f(\omega)\mathrm{d}\omega=2\int_0^{\infty}\frac{\omega^{m+1}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega + 2\mathrm{i}\omega'\int_0^{\infty}\frac{\omega^{m}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega\cdot \quad (B.10)$$

In equations (B.7–B.10), we can separate the real- and imaginary parts. For values $m\le 2k(n+1)-1$ with even integer m, K-K type relations are of the form

$$\omega'^m\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= \frac{2}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{m+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.11)$$

$$\omega'^m\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= -\frac{2\omega'}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{m}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.12)$$

and for odd integers m, the corresponding equations are

$$\omega'^m\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= \frac{2\omega'}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{m}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.13)$$

$$\omega'^m\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= -\frac{2}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{m+1}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega. \quad (B.14)$$

For the value $m=2k(n+1)$, the imaginary part of left hand side of equation (B.8) contains an extra term, which is caused by the integration along the arc A and the dispersion relation (B.11) is transformed as follows:

$$\omega'^m\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= \frac{2}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{m+1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega+\psi^k. \quad (B.15)$$

Now we are able to derive sum rules for the arbitrary-order harmonic frequency generation susceptibilities. For example, the two highest convergent even powers of equation (B.12) are $m=2k(n+1)$ and $m=2k(n+1)-2$. By inserting these values into (B.12) we obtain

$$\omega'^{2k(n+1)}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= -\frac{2\omega'}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{2k(n+1)}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.16)$$

$$\omega'^{2k(n+1)-2}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\}= -\frac{2\omega'}{\pi}\mathrm{P}\int_0^{\infty}\frac{\omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega. \quad (B.17)$$

Equation (B.17) is multiplied by ω'^2, which is subtracted from equation (B.16) and we obtain

$$0=-\frac{2\omega'}{\pi}\mathrm{P}\int_0^{\infty}\frac{\left(\omega^2-\omega'^2\right)\omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2-\omega'^2}\mathrm{d}\omega, \quad (B.18)$$

which leads to the sum rule

$$\int_0^{\infty}\omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega=0. \quad (B.19)$$

In a similar manner, we obtain for the highest convergent odd powers $m = 2k(n+1) - 1$ and $m = 2k(n+1) - 3$ equations

$$\omega'^{2k(n+1)-1}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\} = -\frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{\omega^{2k(n+1)}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2 - \omega'^2}\mathrm{d}\omega, \quad \text{(B.20)}$$

$$\omega'^{2k(n+1)-3}\mathrm{Im}\left\{\left[\chi^{(n)}(n\omega')\right]^k\right\} = -\frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{\omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2 - \omega'^2}\mathrm{d}\omega. \quad \text{(B.21)}$$

Now, in turn, equation (B.21) is multiplied by ω'^2 and subtracted from equation (B.20) leading to

$$0 = -\frac{2}{\pi}\mathrm{P}\int_0^\infty \frac{(\omega^2 - \omega'^2)\omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}}{\omega^2 - \omega'^2}\mathrm{d}\omega, \quad \text{(B.22)}$$

which is of the form

$$\int_0^\infty \omega^{2k(n+1)-2}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega = 0. \quad \text{(B.23)}$$

We have shown that both even (B.19) and odd (B.23) powers reduce to the same sum rule but different K-K type dispersion relations. Sum rule given by equations (B.19, B.23) can be reduced to the form

$$\int_0^\infty \omega^{2\alpha}\mathrm{Re}\left\{\left[\chi^{(n)}(n\omega)\right]^k\right\}\mathrm{d}\omega = 0 \quad \text{(B.24)}$$

with $0 \le \alpha \le k(n+1) - 1$. The other sum rules given by equations (21, 22) are obtained from similar mathematical procedures to that above.

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