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Dispersion formulas for the second hyperpolarizability components $\gamma_{\|}$, $\gamma_{\perp}$ and γ_K

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Abstract

The frequency-dependence of the isotropic parallel average $\gamma_{\|}$ of the second hyperpolarizability can be expanded in a compact way using dispersion coefficients, which are independent of the optical process, if three effective frequencies are introduced. We propose similar expansions for the second hyperpolarizability components $\gamma_{\perp}$ and γ_K and give explicit expressions for the hyperpolarizability dispersion coefficients in terms of the derivatives of the hyperpolarizabilities with respect to their frequency arguments. The relation of the hyperpolarizability dispersion coefficients to the Cauchy moments of linear response theory is discussed and comparison is made with previously proposed dispersion formulas. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Frequency-dependent electric or magnetic multipole hyperpolarizabilities can generally be expressed in terms of irreducible tensor components which transform according to an irreducible representation of the rotation group SO(3) and also according to an irreducible representation of the symmetric group S_n composed of the permutations of the operator indices independent of the accompanied frequency arguments [1–3]. The quantities measured in hyperpolarizability experiments are usually such irreducible tensor components, for example the isotropic parallel average of the second hyperpolarizability $\gamma_{\|}$, or simple linear combinations thereof, such as $\gamma_{\perp}$ and γ_K, which can be decomposed into $\gamma_{\perp} = \frac{1}{3}\gamma_{\|} + \frac{2}{3}\gamma_{\mathrm{ms}}$ and $\gamma_K = \gamma_{\|} - \gamma_{\mathrm{ms}}$, where γ_{ms} is an isotropic component which transforms according to the degenerated mixed-symmetry class of S_4. The symmetry of the hyperpolarizability components with respect to the permutation of the frequency arguments is of particular importance for the construction of dispersion formulas for non-linear optical properties [4]. For $\gamma_{\|}$ Shelton suggested [5], more than a decade ago, expanding the frequency-dependence in terms of the effective frequency $\omega_L^2 = \omega_0^2 + \omega_1^2 + \omega_2^2 + \omega_3^2$ which is symmetric in the four original frequency arguments:

$$\gamma_{\|}(\omega_0;\omega_1,\omega_2,\omega_3) = \gamma_{\|}(0)\left(1 + A\omega_L^2 + B\omega_L^4 + \cdots\right). \quad (1)$$

It was proven by Bishop that the coefficient A in Eq. (1) is the same for all optical processes and that

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B is the same for the dc-Kerr effect and for the electric-field induced second harmonic generation, but that different B coefficients are obtained for the third harmonic generation or other third-order optical processes [6]. The dispersion formula (1) was later extended for the vector average $\beta_{\|}$ of the first hyperpolarizability [7,8]. For $\gamma_{\perp}$ Bishop proposed the expansion [6]

$$\gamma_{\perp}(\omega_0;\omega_1,\omega_2,\omega_3) = \gamma_{\perp}(0)\left(1+\tilde{A}\omega_L^2+\tilde{B}\omega_L^4+\cdots\right) \quad (2)$$

with $\tilde{A}=p+qa$, where a is defined as $a=-(\omega_0\omega_3+\omega_1\omega_2)/\omega_L^2$ and p, q are frequency-independent. The dispersion of the ratio $\gamma_{\|}/\gamma_{\perp}$ can be expanded up to second order as [6]:

$$\frac{\gamma_{\|}}{3\gamma_{\perp}} = 1 + C\omega_L^2 + \cdots \quad (3)$$

with $C=r(1-6a)$ and r is frequency-independent.

In the last decade, the dispersion formula Eq. (1) has proven to be an important tool for comparing and assessing experimentally or theoretically determined frequency-dependent hyperpolarizabilities [9–14]. Eq. (1) is also the most frequently used ansatz for extrapolating experimental data from optical frequencies to the static limit [9,10]. However, despite the appealing features of such compact dispersion expansions with process-independent coefficients, an extension of Eq. (1) to a form with the fourth- and higher-order coefficients also strictly process-independent was not proposed until recently [4] and no such extension is known for $\gamma_{\perp}$. Apart from allowing a more detailed comparison between the dispersion curves obtained from different optical processes, such expansions with process-independent dispersion coefficients are also likely to be useful for implementation in ab initio quantum chemistry programs since it is expected that they can be used to reduce the computational costs for the calculation of hyperpolarizability dispersion curves [15].

In a recent publication [4] we devised a general approach for obtaining the frequency-dependence of irreducible hyperpolarizabilities compact dispersion expansions with coefficients which are strictly independent of optical processes. Using this approach, we derived in Ref. [4] an extension of Eq. (1) to higher orders in the frequency arguments and to the isotropic all-parallel averages of higher-order hyperpolarizabilities. In this Letter, we apply the approach in Ref. [4] to derive a compact dispersion expansion for the isotropic mixed-symmetry component γ_{ms}. We thereby obtain a dispersion expansion for the experimentally important component γ_K and an extension of Eq. (2) to higher orders in the frequencies.

2. Expansion of irreducible hyperpolarizability tensors in symmetrized frequency powers

The key idea of the approach devised in Ref. [4] can be summarized as follows: if the hyperpolarizability tensor $X^{(n)}_{l,(\mu)}$ transforms according to the irreducible representation μ of the symmetric group S_n constituted by the permutations of the operator indices, then $X^{(n)}_{l,(\mu)}$ is an eigenfunction of a projection operator $\hat{\mathscr{E}}_{l,(\mu)}=\sum_{\mathscr{P}\in S_n} c^{\mathscr{P}}_{l,(\mu)}\hat{\mathscr{P}}$ which projects onto the subspace of the representation μ, where l is an index for the degenerated components of μ. Since hyperpolarizabilities are invariant with respect to simultaneous permutations of the operator indices together with their accompanied frequency arguments,

$$X^{(n)}_{\xi_0\xi_1\ldots\xi_{n-1}}(\omega_0;\omega_1,\ldots,\omega_{n-1}) = X^{(n)}_{\xi_{p(0)}\xi_{p(1)}\ldots\xi_{(n-1)}}(\omega_{p(0)};\omega_{p(1)},\ldots,\omega_{p(n-1)}), \quad (4)$$

and the projection operators $\hat{\mathscr{E}}_{l,(\mu)}$ are idempotent, it follows [4] that a Taylor expansion of $X^{(n)}_{l,(\mu)}(\omega_0;\omega_1,\ldots,\omega_{n-1})$ in its frequency arguments can be written in terms of the symmetry-adapted frequency products $\sum_{\mathscr{P}\in S_n} c^{\mathscr{P}}_{l,(\mu)}\hat{\mathscr{P}}^{-1}\omega_0^{m_0}\omega_1^{m_1}\cdots\omega_{n-1}^{m_{n-1}}$.

The isotropic parallel average $\gamma_{\|}$, defined as [16]:

$$\gamma_{\|}=\tfrac{1}{15}\sum_{\xi\eta}\{\gamma_{\xi\eta\eta\xi}+\gamma_{\xi\eta\xi\eta}+\gamma_{\xi\xi\eta\eta}\}, \quad \xi,\eta=x,y,z, \quad (5)$$

is invariant, i.e. totally symmetric, with respect to independent permutations of the operator and frequency arguments. Thus the frequency-dependence

of $\gamma_{\|}$ can be expanded in terms of the symmetric frequency products,

$$\hat{\mathscr{S}}\omega_0^{m_0}\omega_1^{m_1}\omega_2^{m_2}\omega_3^{m_3} = \sum_{i_0}\sum_{i_1\neq i_0}\sum_{i_2\neq i_0,i_1}\sum_{i_3\neq i_0,i_1,i_2}\omega_{i_0}^{m_0}\omega_{i_1}^{m_1}\omega_{i_2}^{m_2}\omega_{i_3}^{m_3} \quad (6)$$

with $i_0,i_1,i_2,i_3 = 0,1,2,3$. The frequency-products in Eq. (6) can be rewritten in terms of the three basic products ω_{L2}^2, ω_{L3}^3 and ω_{L4}^4 defined as: [4]

$$\omega_{L2}^2 = -\sum_{i_0}\sum_{i_1\neq i_0}\omega_{i_0}\omega_{i_1} = \sum_i \omega_i^2 = \omega_L^2\,, \quad (7)$$

$$\omega_{L3}^3 = \tfrac{1}{2}\sum_{i_0}\sum_{i_1\neq i_0}\sum_{i_2\neq i_0,i_1}\omega_{i_0}\omega_{i_1}\omega_{i_2} = \sum_i \omega_i^3\,, \quad (8)$$

$$\omega_{L4}^4 = -\tfrac{1}{6}\sum_{i_0}\sum_{i_1\neq i_0}\sum_{i_2\neq i_0,i_1}\sum_{i_3\neq i_0,i_1,i_2}\omega_{i_0}\omega_{i_1}\omega_{i_2}\omega_{i_3} = -4\omega_0\omega_1\omega_2\omega_3 = \Big(\sum_i \omega_i^4\Big) - \tfrac{1}{2}\omega_{L2}^2\,. \quad (9)$$

(Note that in Ref. [4] a different notation was used which denoted ω_{L2}^2, ω_{L3}^3, ω_{L4}^4 as Q_2, Q_3, Q_4.) Using these three effective frequencies ω_{L2}^2, ω_{L3}^3 and ω_{L4}^4 as expansion variables, we obtain for $\gamma_{\|}$ a compact dispersion formula with a minimal number of strictly process-independent coefficients which, up to sixth order in the frequencies can be written in the form (cmp. Eq. (16) in Ref. [4]):

$$\gamma_{\|}(\omega_0;\omega_1,\omega_2,\omega_3) = \gamma_{\|}(0)\big(1 + A\omega_{L2}^2 + B\omega_{L2}^4 + B'\omega_{L4}^4 + C\omega_{L2}^6 + C'\omega_{L3}^6 + C''\omega_{L2}^2\omega_{L4}^4\cdots\big)\,. \quad (10)$$

We note that ω_{L4}^4 vanishes, if one of the frequency arguments of $\gamma_{\|}$ becomes zero; and that ω_{L3}^3 vanishes, if two of the frequency arguments become zero. Thus for optical processes with one or more static electric fields, the dispersion formula (10) reduces in a simple way to an expansion with a smaller number of coefficients.

The isotropic second hyperpolarizability measured in ESHG experiments with the optical field polarized perpendicular to the static field,

$$\gamma_{\perp} = \tfrac{1}{15}\sum_{\xi\eta}\big(2\gamma_{\xi\eta\eta\xi} - 3\gamma_{\xi\eta\xi\eta} + 2\gamma_{\xi\xi\eta\eta}\big), \quad \xi,\eta = x,y,z\,, \quad (11)$$

and the isotropic component measured in dc-Kerr experiments, $\gamma_K = \frac{3}{2}(\gamma_{\|} - \gamma_{\perp})$, can be decomposed into the irreducible tensor components $\gamma_{\|}$ and γ_{ms} as $\gamma_{\perp} = \frac{1}{3}\gamma_{\|} + \frac{2}{3}\gamma_{\mathrm{ms}}$ and $\gamma_K = \gamma_{\|} - \gamma_{\mathrm{ms}}$. The irreducible second hyperpolarizability γ_{ms}, defined as

$$\gamma_{\mathrm{ms}} = \tfrac{1}{6}\sum_{\xi\eta}\big(\gamma_{\xi\eta\eta\xi} - 2\gamma_{\xi\eta\xi\eta} + \gamma_{\xi\xi\eta\eta}\big) \quad (12)$$

is an eigenfunction of the projector

$$\hat{\mathscr{E}}_{\mathrm{ms}} = \tfrac{1}{3}\{E + (13) + (24) + (13)(24)\} \times\{E - (12) - (34) + (12)(34)\} \times\{E + (13) - (12) - (123)\} \quad (13)$$

where E is the identity operation and (12), (13), (123), etc. denote permutations of the operator indices in the cartesian hyperpolarizability components that contribute to γ_{ms}. Thus its frequency-dependence can be expanded in the symmetry-adapted frequency products according to the arguments discussed above:

$$T_{k,l,m,n}^{ms} = \tfrac{1}{4}\{E + (31) - (21) - (321)\} \times\{E - (21) - (43) + (43)(21)\} \times\{E + (31) + (42) + (42)(31)\} \times\omega_0^k\omega_1^l\omega_2^m\omega_3^n \quad (14)$$

$$= \big(\omega_0^k\omega_1^l - \omega_0^l\omega_1^k\big)\big(\omega_2^m\omega_3^n - \omega_2^n\omega_3^m\big) + \big(\omega_0^k\omega_3^l - \omega_0^l\omega_3^k\big)\big(\omega_2^m\omega_1^n - \omega_2^n\omega_1^m\big) + \big(\omega_2^k\omega_1^l - \omega_2^l\omega_1^k\big)\big(\omega_0^m\omega_3^n - \omega_0^n\omega_3^m\big) + \big(\omega_2^k\omega_3^l - \omega_2^l\omega_3^k\big)\big(\omega_0^m\omega_1^n - \omega_0^n\omega_1^m\big)\,. \quad (15)$$

The mixed-symmetry frequency products $T_{k,l,m,n}^{ms}$ are antisymmetric in the first and last two indices and symmetric under the exchange of the index pairs k, l and m, n:

$$T_{k,l,m,n}^{ms} = -T_{l,k,m,n}^{ms} = -T_{k,l,n,m}^{ms} = T_{m,n,k,l}^{ms}\,. \quad (16)$$

From Eq. (16) it follows that $T_{k,l,m,n}^{ms}$ can only be nonvanishing if $k\neq l$ and $m\neq n$. Therefore, $T_{0,0,0,0}^{ms} = 0$ and the mixed-symmetry hyperpolarizability γ_{ms} vanishes in the static limit. Using the relations

$$\big(\omega_0^p\omega_1^p\omega_2^p\omega_3^p\big)T_{k,l,m,n}^{ms} = T_{k+p,l+p,m+p,n+p}^{ms} \quad (17)$$

$$\big(\omega_0^p + \omega_1^p + \omega_2^p + \omega_3^p\big)T_{k,l,m,n}^{ms} = T_{k+p,l,m,n}^{ms} + T_{k,l+p,m,n}^{ms} + T_{k,l,m+p,n}^{ms} + T_{k,l,m,n+p}^{ms} \quad (18)$$

the mixed-symmetry frequency products can be expanded in a smaller number of effective frequencies, similarly as the total symmetric frequency products in Eq. (6). In order to obtain an expansion for $\gamma_{\rm ms}$ with a minimal number of process-independent coefficients and a form which, when one of the frequency arguments becomes zero, reduces to the expansion of $\beta_{\rm ms} = \beta_{(23)}$ as proposed in Refs. [4,15], we introduce the two mixed-symmetry effective frequencies

$$\begin{aligned}\omega_{M2}^2 &= \tfrac{1}{2} T_{1,0,1,0}^{ms} \\ &= (\omega_0 - \omega_1)(\omega_2 - \omega_3) \\ &\quad + (\omega_0 - \omega_3)(\omega_2 - \omega_1) \end{aligned} \tag{19}$$

and

$$\begin{aligned}\omega_{M4}^4 &= -3 T_{2,1,1,0}^{ms} \\ &= -3\big[(\omega_0^2\omega_1 - \omega_1^2\omega_0)(\omega_2 - \omega_3) \\ &\quad + (\omega_0 - \omega_1)(\omega_2^2\omega_3 - \omega_3^2\omega_2) \\ &\quad + (\omega_0^2\omega_3 - \omega_3^2\omega_0)(\omega_2 - \omega_1) \\ &\quad + (\omega_0 - \omega_3)(\omega_2^2\omega_1 - \omega_1^2\omega_2)\big]. \end{aligned} \tag{20}$$

Using ω_{M2}^2 and ω_{M4}^4 and products of these with the symmetric effective frequencies ω_{L2}^2 and ω_{L4}^4 the irreducible hyperpolarizability $\gamma_{\rm ms}$ can be expanded, up to sixth order in the frequency arguments, as:

$$\begin{aligned}&\gamma_{\rm ms}(\omega_0;\omega_1,\omega_2,\omega_3) \\ &\quad = \gamma_{\|}(0)\big(A_{\rm ms}\omega_{M2}^2 + B_{\rm ms}\omega_{M2}^2\omega_{L2}^2 + B'_{\rm ms}\omega_{M4}^4 \\ &\qquad + C_{\rm ms}\omega_{M2}^2\omega_{L2}^4 + C'_{\rm ms}\omega_{M4}^4\omega_{L2}^2 \\ &\qquad + C''_{\rm ms}\omega_{M2}^2\omega_{L4}^4 + \cdots\big). \end{aligned} \tag{21}$$

We note that if $\omega_3 = 0$ then the effective frequency ω_{M2}^2 reduces to $2\omega_1^2 - \omega_0^2 - \omega_2^2$, which is the mixed-symmetry effective frequency (second-order in ω_i) introduced in Refs. [4,15] to expand $\beta_{\rm ms}$, and ω_{M4}^4 reduces to $(2\omega_1 - \omega_0 - \omega_2)\omega_{L3}^3$, where $2\omega_1 - \omega_0 - \omega_2$ is equal to the mixed-symmetry frequency (first-order in ω_i) used to expand $\beta_{\rm ms}$. The term $C''\omega_{M2}^2\omega_{L4}^4$ vanishes if one of the frequency arguments is zero. If two of the frequency arguments of $\gamma_{\rm ms}$ are zero then the terms proportional to ω_{M4}^4 also drop out.

3. Explicit expressions of the process-independent dispersion coefficients for $\gamma_{\|}$ and $\gamma_{\rm ms}$

If the dispersion expansions in Eqs. (10) and (21) are to be useful not only for fits to given frequency-dependent hyperpolarizability results but also for implementation in ab initio quantum chemistry codes, then explicit expressions are needed for the dispersion coefficients A, B, B', etc. and $A_{\rm ms}$, $B_{\rm ms}$, $B'_{\rm ms}$, etc. in terms of intermediates which are suitable for computations that use standard ab initio wavefunction ansatzes. Response theory codes usually have available the first- and second-order responses of the wavefunction parameters with respect to the cartesian components of a frequency-dependent dipole perturbation and the cartesian tensor components of the frequency-dependent second hyperpolarizability γ_{ijkl} with $i,j,k,l = x,y,z$. Using the approach introduced in Ref. [15] to compute dispersion coefficients for first hyperpolarizabilities within the coupled cluster quadratic response approach, these intermediates can be generalized straightforwardly to compute derivatives of the wavefunction responses and of the hyperpolarizability components with respect to the frequencies of the perturbing fields, evaluated in the static limit. The latter derivatives are dispersion coefficients defined by a simple Taylor expansion of $\gamma_{ijkl}(\omega_0;\omega_1,\omega_2,\omega_3)$ in the independent frequency arguments ω_1, ω_2, and ω_3:

$$\begin{aligned}&\gamma_{ijkl}(\omega_0;\omega_1,\omega_1,\omega_3) \\ &\quad = \sum_{l,m,n=0}^{\infty} \omega_1^l \omega_2^m \omega_3^n D_{ijkl}(l,m,n), \end{aligned} \tag{22}$$

$$\begin{aligned}&D_{jkl}(l,m,n) \\ &\quad = \frac{l!m!n!}{(l+m+n)!} \\ &\qquad \times \left(\frac{d^{l+m+n}\gamma_{ijkl}(\omega_0;\omega_1,\omega_2,\omega_3)}{d\omega_1^l\, d\omega_2^m\, d\omega_3^n} \right)_{\omega_i = 0} \end{aligned} \tag{23}$$

The derivatives $D_{ijkl}(l,m,n)$ provide efficient access to the coefficients of the dispersion expansions in

Eqs. (10) and (21). In order to obtain more compact expressions, we introduce (by analogy to the irreducible hyperpolarizabilities $\gamma_{||}$ and $\gamma_{\rm ms}$) the irreducible linear combinations of the derivatives D_{ijkl}:

$$D_{||}(l,m,n) = \tfrac{1}{15}\sum_{\xi\eta}\left\{D_{\xi\eta\eta\xi}(l,m,n) + D_{\xi\eta\xi\eta}(l,m,n) + D_{\xi\xi\eta\eta}(l,m,n)\right\}, \quad (24)$$

$$D_{\rm ms}(l,m,n) = \tfrac{1}{6}\sum_{\xi\eta}\left\{D_{\xi\eta\eta\xi}(l,m,n) - 2D_{\xi\eta\xi\eta}(l,m,n) + D_{\xi\xi\eta\eta}(l,m,n)\right\}, \quad (25)$$

where the summation is over ξ, $\eta = x, y, z$. Using the coefficients $D_{||}$ and $D_{\rm ms}$ the irreducible hyperpolarizabilities $\gamma_{||}$ and $\gamma_{\rm ms}$ may formally be expanded in simple Taylor expansions as in Eq. (22) which, however, have large redundancies in the coefficients $D_{||}(l,m,n)$ and $D_{\rm ms}(l,m,n)$. In order to obtain explicit expressions for the coefficients A, $A_{\rm ms}$, B, $B_{\rm ms}$, etc. of the compact expansions in Eqs. (10) and (21) we insert the definition of the effective frequencies, Eqs. (7)–(9), (19) and (20), into the dispersion formulas Eqs. (10) and (21) and express ω_0 as $-\omega_1-\omega_2-\omega_3$. Equating the coefficients of the individual frequency products $\omega_1^l\omega_2^m\omega_3^n$ in the dispersion expansion with the coefficients of the Taylor expansion, an overdetermined set of equations is obtained for the dispersion coefficients in Eqs. (10) and (21). These equations have, however, a unique solution; the redundancies in the equations reflect the redundancy in the coefficients of the Taylor expansion, which are a consequence of the symmetry of the irreducible hyperpolarizabilities in their frequency arguments. For the dispersion coefficients for $\gamma_{||}$ one obtains the simple expressions:

$$A = \frac{1}{2\gamma_{||}(0)} D_{||}(2,0,0), \quad (26)$$

$$B = \frac{1}{4\gamma_{||}(0)} D_{||}(4,0,0), \quad (27)$$

$$B' = \frac{1}{4\gamma_{||}(0)}\left(D_{||}(2,1,1) - 4D_{||}(4,0,0)\right), \quad (28)$$

$$C = \frac{1}{8\gamma_{||}(0)} D_{||}(6,0,0), \quad (29)$$

$$C' = \frac{1}{9\gamma_{||}(0)}\left(D_{||}(4,2,0) - 6D_{||}(6,0,0)\right), \quad (30)$$

$$C'' = \frac{1}{8\gamma_{||}(0)} \times \left(D_{||}(4,1,1) - 2D_{||}(4,2,0) + 3D_{||}(6,0,0)\right) \quad (31)$$

and for the dispersion coefficients for $\gamma_{\rm ms}$ one finds:

$$A_{\rm ms} = \frac{1}{\gamma_{||}(0)} D_{\rm ms}(2,0,0), \quad (32)$$

$$B_{\rm ms} = \frac{1}{2\gamma_{||}(0)} D_{\rm ms}(4,0,0), \quad (33)$$

$$B'_{\rm ms} = -\frac{1}{9\gamma_{||}(0)}\left(D_{\rm ms}(3,1,0) + D_{\rm ms}(4,0,0)\right), \quad (34)$$

$$C_{\rm ms} = \frac{1}{4\gamma_{||}(0)} D_{\rm ms}(6,0,0), \quad (35)$$

$$C'_{\rm ms} = -\frac{1}{18\gamma_{||}(0)} D_{\rm ms}(5,1,0), \quad (36)$$

$$C''_{\rm ms} = \frac{1}{24\gamma_{||}(0)}\left(3D_{\rm ms}(3,2,1) - 2D_{\rm ms}(5,1,0)\right). \quad (37)$$

Thus, once the derivatives of second hyperpolarizabilities with respect to their frequency arguments are implemented, the coefficients of the dispersion formulas, Eqs. (10) and (21), can be computed easily using Eqs. (24)–(37). Work in this direction is in progress and will be subject of a forthcoming publication [17].

4. Comparison with other dispersion formulas

The most widely accepted and used dispersion formula for frequency-dependent properties is propably the Cauchy expansion of the frequency-dependent polarizability,

$$\alpha_{\xi\eta}(-\omega;\omega) = \sum_{k=0}^{\infty} \omega^{2k} S_{\xi\eta}(-2k-2)\,. \tag{38}$$

The expansion coefficients of Eq. (38), the so-called Cauchy moments, are for diagonal polarizabilities $\alpha_{\xi\xi}$ and for the isotropic average $\bar{\alpha}$ moments over non-negative distributions which permits the application of a number of useful theorems of moment theory to the expansions of these polarizability components [18,19]. It is therefore interesting to investigate how the hyperpolarizability dispersion coefficients are related to the Cauchy moments of linear response theory. The even Cauchy moments $S(-2k-2)$ with $k>0$ are derivatives of the frequency-dependent polarizability with respect to the frequency, evaluated in the static limit:

$$S_{\xi\eta}(-2k-2) = \frac{1}{(2k)!}\left(\frac{\mathrm{d}^{2k}\alpha_{\xi\eta}(-\omega;\omega)}{\mathrm{d}\,\omega^{2k}}\right)_{\omega=0}. \tag{39}$$

In this respect the coefficients $D_{ijkl}(l,m,n)$ defined in Eqs. (22) and (23) and the analogous derivatives of the first hyperpolarizabilities [15],

$$D_{ijk}(l,m) = \frac{1}{l!m!}\left(\frac{\mathrm{d}^{l+m}\beta_{ijk}(-\omega_1-\omega_2;\omega_1,\omega_2)}{\mathrm{d}\,\omega_1^{l}\,\mathrm{d}\,\omega_2^{m}}\right)_{\omega_i=0} \tag{40}$$

are straightforward generalizations of the Cauchy moments to frequency-dependend third- and fourth-order properties. A direct relation between the Cauchy moments and the coefficients $D_{ijk}(l,m)$ and $D_{ijkl}(l,m,n)$ is obtained if only one of the order parameters has a non-zero value. These coefficients are first and second derivatives of the Cauchy moments with respect to the field strengths ϵ_μ, ϵ_ν of static electric fields:

$$D_{\xi\eta\mu}(l,0) = \left(\frac{\mathrm{d}S_{\xi\eta}(l-2)}{\mathrm{d}\,\epsilon_\mu}\right)_0, \tag{41}$$

$$D_{\xi\eta\mu\nu}(l,0,0) = \left(\frac{\mathrm{d}^2 S_{\xi\eta}(l-2)}{\mathrm{d}\,\epsilon_\mu \mathrm{d}\,\epsilon_\nu}\right)_0. \tag{42}$$

The effective frequencies for the expansion of $\gamma_{\|}$ and γ_{ms} were chosen such that a hierarchical structure is obtained where only one dispersion coefficient per order contributes to the hyperpolarizabilities with only two non-zero frequency arguments and the full number of dispersion coefficients contributes only if all frequency arguments take non-zero values. As a consequence of this structure the dispersion coefficients A, B, C and A_{ms}, B_{ms}, C_{ms}, which contribute to the expansion of the dc-Kerr hyperpolarizabilities ($\omega_1=\omega_2=0$), can be calculated from the derivatives $D_{ijkl}(l,0,0)$ with two of the order parameters zero. These dispersion coefficients can therefore be expressed as sums over the second derivatives of Cauchy moments with respect to the field strengths of static electric fields. The coefficient A, for example, is related to the $S(-4)$ Cauchy moments by:

$$A = \frac{1}{15\gamma_{\|}(0)} \sum_{\xi\eta} \left\{ \left(\frac{\mathrm{d}^2 S_{\xi\eta}(-4)}{\mathrm{d}\,\epsilon_\eta \mathrm{d}\,\epsilon_\xi}\right)_0 + \frac{1}{2}\left(\frac{\mathrm{d}^2 S_{\xi\xi}(-4)}{\mathrm{d}\,\epsilon_\eta^2}\right)_0 \right\}. \tag{43}$$

Relations similar to the Cauchy moments can be established for the derivatives $D_{\xi\eta\mu}(l,m)$ of the first hyperpolarizabilities, since the coefficients $D_{\xi\eta\mu\nu}(l,m,0)$ with one zero argument are the first derivatives of the $D_{\xi\eta\mu}(l,m)$coefficients with respect to a static electric field:

$$D_{\xi\eta\mu\nu}(l,m,0) = \left(\frac{\mathrm{d}D_{\xi\eta\nu}(l,m)}{\mathrm{d}\,\epsilon_\nu}\right)_0. \tag{44}$$

As mentioned in the introduction, from the combination of the dispersion formulas for the irreducible hyperpolarizabilities $\gamma_{\|}$ and γ_{ms} we obtain dispersion expansions for the hyperpolarizabilities

$\gamma_\perp$ and γ_K. These expansions can be written up to fourth order as:

$$\gamma_\perp(\omega_0;\omega_1,\omega_2,\omega_3) = \frac{\gamma_\parallel(0)}{3}\left(1+\left(A+2A_{\rm ms}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^2 + \left(B+2B_{\rm ms}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^4 + B'\omega_{L4}^4 + 2B'_{\rm ms}\omega_{M4}^4 + \cdots\right), \quad (45)$$

$$\gamma_K(\omega_0;\omega_1,\omega_2,\omega_3) = \gamma_\parallel(0)\left(1+\left(A-A_{\rm ms}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^2 + \left(B-B_{\rm ms}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^4 + B'\omega_{L4}^4 - B'_{\rm ms}\omega_{M4}^4 + \cdots\right). \quad (46)$$

The dispersion formula for $\gamma_\perp$, Eq. (45), can be compared with formula (2) derived by Bishop: For the dc-Kerr effect, electric field induced second harmonic generation, degenerate four wave mixing and third harmonic generation $\omega_1=\omega_2$. The ratio $\omega_{M2}^2/\omega_{L2}^2$ used in Eq. (45) can then be rewritten as $\frac{3}{2}a-\frac{1}{4}$, where a is the frequency ratio used in Eq. (2) to expand $\gamma_\perp$. We thus identify the frequency-independent constants p and q of Eq. (2) as $p=A-\frac{1}{2}A_{\rm ms}$ and $q=3A_{\rm ms}$.

The dispersion formulas (10) and (21) can also be used to obtain a dispersion expansion for the ratio $\gamma_\parallel/\gamma_\perp$. The deviation of this ratio from 3 is sometimes used as a measure for the deviation from Kleinman symmetry [16]. Up to second-order in the frequency arguments we obtain:

$$\frac{\gamma_\parallel}{\gamma_\perp}=\frac{3\gamma_\parallel}{\gamma_\parallel+2\gamma_{\rm ms}}=3\left(1-2A_{\rm ms}\,\omega_{M2}^2+\cdots\right). \quad (47)$$

We note that since the dispersion formulas for the first hyperpolarizabilities $\beta_\parallel$ and $\beta_\perp$ have the same structure up to second order as those for the second hyperpolarizabilities, a similar dispersion formula holds for the ratio $\beta_\parallel/\beta_\perp$. By substituting $(\frac{3}{2}a-\frac{1}{4})\omega_{L2}^2$ for ω_{M2}^2 in Eq. (47), we can identify the frequency-independent constant r in the dispersion formula derived by Bishop [6], Eq. (3), as $r=A_{\rm ms}/2$. Thus, the frequency-dependence of the hyperpolarizability components $\gamma_\parallel$, $\gamma_\perp$, γ_K and of the ratio $\gamma_\parallel/\gamma_\perp$ can be expressed in second-order using only two process-independent coefficients A and $A_{\rm ms}$. That the process-independent constants q and r used in previously proposed dispersion formulas for $\gamma_\perp$ and $\gamma_\parallel/\gamma_\perp$ are related simply by factor of 6 has not, to our knowledge, been noticed before.

5. Summary

We have proposed general dispersion formulas with strictly process-independent coefficients for the second hyperpolarizability components $\gamma_\parallel$, $\gamma_\perp$ and γ_K. The effective frequencies used as expansion variables are chosen such that a hierarchical structure is obtained where dispersion coefficients drop out in a systematic manner if some of the frequency arguments become zero. We have derived explicit expressions for all dispersion coefficients, up to sixth order, in terms of derivatives of cartesian hyperpolarizability components with respect to their frequency arguments, evaluated in the static limit. Such derivatives can be implemented straightforwardly in quantum chemical response codes. These expressions therefore provide a convenient basis for the implementation of the dispersion coefficients in ab initio response programs. We have discussed the relation between the hyperpolarizability dispersion coefficients and the Cauchy moments of linear response theory and shown that some of the dispersion coefficients are directly related to the second derivatives of the Cauchy moments with respect to the field strengths of static electric fields and to the first derivatives of the dispersion coefficients for first hyperpolarizabilities.

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