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Dispersion formulas for hyperpolarizability averages

By CHRISTOF HÄTTIG
Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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The frequency-dependence of experimentally-derived or point-wise *ab initio* calculated hyperpolarizability averages is often expanded up to fourth order in the frequencies using the dispersion formula $X_{\parallel}^{(n)}(\omega_1;\ldots,\omega_n) = X_{\parallel}^{(n)}(0)(1 + A\omega_L^2 + B\omega_L^4 + O(\omega_L^6))$ with $\omega_L^2 = \sum_i \omega_i^2$, where the coefficient A is independent of the optical process. We derive an extension of this dispersion formula which is open ended in the powers of the frequencies, uses only process-independent coefficients, and involves a minimal number of terms per order. It is shown that the dispersion formula can be cast into a form where dispersion coefficients drop out in a systematic manner for optical processes involving static electric fields. We discuss how the concept of these dispersion formulas can be generalized to other hyperpolarizability components and exemplify this approach at the experimentally important components $\beta_\perp$ and β_K of the first hyperpolarizability.

1. Introduction

Dispersion formulas have in the last decade been proven to be invaluable tools for comparing and assessing experimentally or theoretically determined frequency-dependent hyperpolarizabilities. Their usefulness is caused by the compact way in which they allow one to represent frequency-dependent properties, which makes them an ideal basis for interpolation or extrapolation to frequencies where the original data is not available. An important application is, e.g. the extrapolation of experimental data for frequency-dependent hyperpolarizabilities to the static limit.

Different kinds of dispersion formulas have been proposed in recent years for nonlinear optical properties [1–4]. The most successful and widely used one is a formula first suggested by Shelton [1] for the isotropic components of the second hyperpolarizability:

$$\gamma_{||}(\omega_1;\omega_2,\omega_3,\omega_4) = \gamma_{||}(0)(1 + A\omega_L^2 + B\omega_L^4 + C\omega_L^6 + \cdots), \quad (1)$$

with $\omega_L^2 = \omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2$. It was proven by Bishop that the coefficient A in equation (1) is the same for all processes and that B is the same for dc-Kerr effect and electric field induced second harmonic generation hyperpolarizabilities, $\gamma_{||}(-\omega;0,0,\omega)$ and $\gamma_{||}(-2\omega,\omega,\omega,0)$, respectively, but that other fourth-order powers of the frequencies than ω_L^4 are needed to represent the frequency-dependence of isotropic second hyperpolarizabilities with process-independent dispersion coefficients. The ansatz of equation (1) has also been used to fit the dispersion curve for the vector average of first hyperpolarizabilities [5].

Bishop and De Kee [3, 4] have recently shown that the all-diagonal components of hyperpolarizabilities of general order can be expanded up to fourth-order in the frequencies with process independent coefficients as:

$$X_{\alpha\alpha\ldots\alpha}^{(n)}(\omega_1;\omega_2,\ldots,\omega_n) = X_{\alpha\alpha\ldots\alpha}^{(n)}(0)(1 + AW_2 + BW_2^2 + B'W_4 + \cdots), \quad (2)$$

where the symmetrized frequency powers W_2 and W_4 are defined as $\sum_i \omega_i^2$ and $W_4 = \sum_i \omega_i^4$, respectively.

In the present article we show how the symmetry of irreducible hyperpolarizability tensors with respect to permutations of the operator and frequency indices can be utilized to derive open-ended dispersion formulas with a minimal number of terms per order.

In section 2 we derive such a dispersion formula for the all-parallel hyperpolarizabilities $X_{||}^{(n)}$. This dispersion formula has in second and fourth order a similar structure as (2) and can also be used to expand the all-diagonal components $X_{\alpha\alpha\ldots\alpha}^{(n)}$, however, its usefulness in practice will mainly arise from its applicability to the averages $X_{||}^{(n)}$ which are the measured quantities in many experiments. In section 3 we propose an alternative expansion in terms of symmetrized frequency products which has the advantage that for optical processes involving static electric fields certain classes of dispersion coefficients drop out. This formulation makes it most apparent which dispersion coefficients may be obtained from a certain nonlinear optical process or, alternatively, which dispersion coefficients are needed to calculate the hyperpolarizability for a specific optical process. In section 24 we demonstrate with an example of the first hyperpolarizability components $\beta_\perp$ and β^K,

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the orthogonal vector component in electric field induced second harmonic generation (ESHG) experiments and the Kerr hyperpolarizability, how the developed approach can be extended to other more general components.

2. Expansion of hyperpolarizability averages in symmetrized frequency powers

Usual gas- and liquid-phase experiments measure only the lowest rank scalar and vector components of the hyperpolarizability tensors. In the case that all applied fields have parallel polarizations, which is the most common situation in electric field induced second harmornic generation (ESHG), third harmonic generation (THG), and other high harmonic generation experiments, the measurable quantities are the all-parallel isotropic averages of even-order hyperpolarizabilities,

$$X_{\parallel}^{(2n)}(\omega_1;\omega_2,\ldots,\omega_{2n}) = \frac{1}{N_{2n}} \sum_{\hat{P}\in\mathfrak{S}_{2n}} \hat{P} X^{(2n)}_{\xi\xi\xi\xi\ldots\xi\xi}(\omega_1;\omega_2,\ldots,\omega_{2n}), \quad (3)$$

and the all-parallel vector averages parallel to the molecular dipole moment of odd-order hyperpolarizabilities,

$$X_{\parallel}^{(2n+1)}(\omega_1;\omega_2,\ldots,\omega_{2n+1}) = \frac{1}{N_{2n+1}} \sum_{\hat{P}\in\mathfrak{S}_{2n+1}} \hat{P} X^{(2n+1)}_{\xi\xi\xi\xi\ldots\xi\xi z}(\omega_1;\omega_2,\ldots,\omega_{2n+1}), \quad (4)$$

where the z axis is defined parallel to the permanent molecular dipole moment and summation over $\xi = x,y,z$ is assumed. Thus the components $X_{\parallel}^{(n)}$ are traces of the hyperpolarizabilities symmetrized with respect to the indices of which the traces were taken. N_n are normalization constants which for the isotropic averages are chosen such that for atoms they become identical to the diagonal components. The sum over $\hat{P}$ in equations (3) and (4) is over all permutations of the operator indices of the hyperpolarizability, or, expressing it in group theoretical terms: the hyperpolarizability components $X_{\parallel}^{(n)}$ are irreducible tensor components which transform according to the total symmetric representation of the symmetric group S_n, i.e. they are eigenfunctions of the symmetrizers $\hat{S} = \sum_{\hat{P}\in\mathfrak{S}_n} \hat{P}$. Because all hyperpolarizability components are invariant with respect to simultaneous permutations of operator indices *together* with their accompanied frequency arguments,

$$X^{(n)}_{\xi\xi\ldots\xi}(\omega_1;\omega_2,\ldots,\omega_n) = X^{(n)}_{\xi(1)\xi(2)\ldots\xi(n)}(\omega_{p(1)};\omega_{p(2)},\ldots,\omega_{p(n)}), \quad (5)$$

the hyperpolarizability averages $X_{\parallel}^{(n)}$ are invariant with respect to permutations of the frequency arguments *independent* of the operators indices and vice versa.

Dynamic hyperpolarizabilities are, with the exception of the poles, analytic functions of their frequency arguments. It follows, that below the first pole they may be expanded in a Taylor series in the frequencies. However, for the all-parallel components $X_{\parallel}^{(n)}$, which are totally symmetric with respect to permutations of their frequency arguments, a general Taylor expansion would introduce an unneccessary large number of expansion coefficients. In a Taylor series the hyperpolarizabilities would be expanded in terms of powers of the individual frequencies ω_i^k and products of ω_i^k. From group theory it follows that to the expansion of $X_{\parallel}^{(n)}$ only linear combinations of frequency products can contribute which are totally symmetric with respect to permutations of the frequency indices. These linear combinations can most generally be written as

$$T^{(n)}_{m_1,m_2,\ldots,m_n} = \hat{S}\,\omega_1^{m_1}\omega_2^{m_2}\cdots\omega_n^{m_n} = \sum_{i_1}\sum_{i_2\neq i_1}\cdots\sum_{i_n\neq i_1,i_2,\ldots}\omega_{i_1}^{m_1}\omega_{i_2}^{m_2}\cdots\omega_{i_n}^{m_n}, \quad (6)$$

where the summations run over all n frequency arguments. Alternatively, the hyperpolarizability components $X_{\parallel}^{(n)}$ can be expanded in the symmetrized frequency powers $W_k = \sum_i \omega_i^k$ and products of them, which follows from the fact, that $T^{(n)}_{m_1,m_2,\ldots,m_n}$ can be expanded in this way using the recurrence relation:

$$T^{(n)}_{m_1,m_2,\ldots,m_n} = \sum_{i_1}\sum_{i_2\neq i_1}\cdots\sum_{i_{n-1}\neq i_1,i_2,\ldots}\omega_{i_1}^{m_1}\omega_{i_2}^{m_2}\cdots\omega_{i_{n-1}}^{m_{n-1}} \times (W_{m_n} - \omega_{i_1}^{m_n} - \omega_{i_2}^{m_n}\cdots\omega_{i_{n-1}}^{m_n}) \quad (7)$$

$$= W_{m_n} T^{(n-1)}_{m_1,m_2,\ldots m_{n-1}} - \sum_{i=1}^{n-1} T^{(n-1)}_{m_1,\ldots,m_i+m_n,\ldots,m_{n-1}}. \quad (8)$$

An expansion in products of the symmetrized frequency powers W_k, which would be a straightforward extension of equation (2), still involves dispersion coefficients which are redundant in the sense that they can be expressed as linear combinations of other coefficients.

In the following, we show that in fact the first n symmetrized frequency powers W_k are sufficient to expand exactly $X_{\parallel}^{(n)}$. We note at this point that W_1 vanishes because the frequency arguments of hyperpolarizabilities are subject to the restriction $\sum_i \omega_i = 0$. Moreover, the hyperpolarizabilities are symmetric with respect to an overall inversion of the frequency signs and therefore a power series expansion can be restricted to terms of even order in the frequencies. Thus, we obtain the open-ended dispersion formula:

$$X_{\parallel}^{(n)}(\omega_1;\omega_2,\ldots,\omega_n) = X_{\parallel}^{(n)}(0)\Bigg(1 + \sum_{m=1}^{\infty} \sum_{2*k_2+3*k_3\cdots+n*k_n=2m} \times A_{k_2k_3\cdots k_n} W_2^{k_2} W_3^{k_3} \cdots W_n^{k_n}\Bigg). \quad (9)$$

To prove that indeed the W_k for $k = 2,3,\ldots,n$ are sufficient to expanded $X_{\parallel}^{(n)}$ exactly, we need to find an equation that relates the W_k for $k > n$ to the W_k's for $k \le n$. To derive the required equation, we show that symmetrized frequency products of the form

$$Q_m = \frac{(-1)^{m-1}}{(m-1)!} \sum_{i_1} \sum_{i_2 \neq i_1} \cdots \sum_{i_m \neq i_1, i_2, \ldots} \omega_1 \omega_2 \cdots \omega_m, \quad m \ge 1, \quad (10)$$

where the summations run over all frequency arguments $\omega_1,\ldots,\omega_n$, can be written in terms of the sums W_k with $k \le m$. To relate the products Q_m to the frequency sums W_k we use the recurrence relation

$$\begin{aligned}
&\frac{(-1)^{m-1}}{(m-1)!} \sum_{i_1} \sum_{i_2 \neq i_1} \cdots \sum_{i_m \neq i_1, i_2, \ldots} \omega_1 \omega_2 \cdots \omega_m^p \\
&\quad = \frac{(-1)^{m-1}}{(m-1)!} \sum_{i_1} \sum_{i_2 \neq i_1} \cdots \sum_{i_{m-1} \neq i_1, i_2, \ldots} \omega_1 \omega_2 \cdots \omega_{m-1} \\
&\qquad \times \Big(\sum_{i_m} \omega_{i_m}^p - \omega_{i_1}^p - \omega_{i_2}^p \cdots - \omega_{i_{m-1}}^p \Big) \\
&\quad = -\frac{Q_{m-1}}{m-1} W_p + \frac{(-1)^{m-2}}{(m-2)!} \\
&\qquad \times \sum_{i_1} \sum_{i_2 \neq i_1} \cdots \sum_{i_{m-1} \neq i_1, i_2, \ldots} \omega_1 \omega_2 \cdots \omega_{m-1}^{p+1}. \quad (11)
\end{aligned}$$

Applying this relation $(m-1)$ times to equation (10) leads to the expression:

$$Q_m = -\sum_{k=1}^{m-1} W_k \frac{Q_{m-k}}{m-k} + \sum_{i_1} \omega_{i_1}^m. \quad (12)$$

Using $W_1 = Q_1 = 0$, the last equation can be written as:

$$Q_m = W_m - \sum_{k=2}^{m-2} W_k \frac{Q_{m-k}}{m-k}. \quad (13)$$

From equation (13) we obtain immediately that $Q_2 = W_2$ and $Q_3 = W_3$. Therefore it follows from induction that the products Q_m can generally be written in terms of the sums W_k with $k \le m$.

For dynamic properties depending on n frequency arguments, the symmetrized products Q_m vanish for $m > n$ and equation (15) becomes a $(n-1)$-term recurrence relation for the frequency sums W_m:

$$W_m = \sum_{k=2}^{n} \frac{1}{k} Q_k W_{m-k}, \quad m > n. \quad (14)$$

Because the non-vanishing Q_k can be expressed in terms of the first $n-1$ frequency sums $W_2,\ldots,W_n$, it follows from equation (14) that the frequency sums W_m with $m > n$ can be expressed in terms of the $W_2,\ldots,W_n$. Thus, we have proven that the frequency-dependence of the isotropic averages of even hyperpolarizabilities and the vector averages of odd hyperpolarizabilities can be expanded exactly in the form of equation (9).

Adopting a notation similar to the one used by Shelton and Rice [6] and Bishop and De Kee [3, 4], equation (9) can for the first and second hyperpolarizabilities up to terms of eight order in the frequencies be written in the form:

$$\begin{aligned}
\beta_{\parallel}(\omega_1;\omega_2,\omega_3) = \beta_{\parallel}(0)(1 &+ A W_2 \\
&+ B W_2^2 + C W_3^2 + C' W_3^2 \\
&+ D W_2^4 + D' W_2 W_3^2 + \cdots), \quad (15)
\end{aligned}$$

$$\begin{aligned}
\gamma_{\parallel}(\omega_1;\omega_2,\omega_3,\omega_4) = \gamma_{\parallel}(0)(1 &+ A W_2 + B W_2^2 \\
&+ B' W_4 + C W_3^2 + C' W_3^2 \\
&+ C'' W_2 W_4 + D W_2^4 \\
&+ D' W_2 W_3^2 + D' W_2^2 W_4 \\
&+ D''' W_4^2 + \cdots). \quad (16)
\end{aligned}$$

According to equation (15), one fourth-order coefficient (B) is sufficient to expand the vector average $\beta_{\parallel}$ and diagonal components $\beta_{\alpha\alpha\alpha}$ of first hyperpolarizabilities, which differs from the two coefficients proposed by Bishop and De Kee [4].

The dispersion formula equation (2) may in principle also be applied to linear polarizabilities. In this case it reduces, as a general dispersion formula should, to a form which is closely related to the well known Cauchy expansion:

$$\alpha(-\omega;\omega) = \alpha(0)\Big(1 + \sum_{k}^{\infty} A_k W_2^k\Big), \quad (17)$$

with $W_2 = 2\omega^2$ and $A_k = 2^{-k} S(-2k)/\alpha(0)$.

3. Expansion of hyperpolarizability averages in symmetrized frequency products

For hyperpolarizabilities which describe nonlinear optical effects that involve static electric fields, the dispersion formula equation (9) can be simplified: for each zero frequency argument one of the symmetrized frequency powers W_k used in the original expansion can be expressed in terms of $W_{k'}$ with $k' < k$. For example can the second hyperpolarizability $\gamma_{\parallel}$ with one zero fre-

quency argument be expanded using only W_2 and W_3. W_4 becomes in this case $\frac{1}{2}W_2^2$.

$$\gamma_{\parallel}(\omega_1;\omega_2,\omega_3,0) = \gamma_{\parallel}(0)(1 + A W_2 + (B + \tfrac{1}{2}B')W_2^2 + \mathcal{O}(\omega^6)). \tag{18}$$

A special case of this is the well known fact that $\gamma_{\parallel}$ for the dc-Kerr effect (two static fields) and for electric field induced second harmonic generation (one static field) can be expanded using one common, process-independent, fourth-order coefficient [6, 7]. (For the same reason, only one process-independent fourth-order coefficient is needed to expand $\beta_{\parallel}(\omega_1;\omega_2,\omega_3)$.) It is a disadvantage of the dispersion expansion (9) that these simplifications enter in an indirect way via additional relations that exist in such cases between the symmetrized frequency powers W_k. A reduction of the dispersion formula to the form of the next lower order property is only obtained after a reordering of terms, which in higher order becomes tedious.

From equation (13) it follows that the symmetrized frequency products Q_k, $k = 2,\ldots,Q_n$ form a basis for the expansion of the hyperpolarizability averages which is formally equivalent to the W_k. Thus, we can alternatively expand $X_{\parallel}^{(n)}$ as:

$$X_{\parallel}^{(n)}(\omega_1;\omega_2,\ldots,\omega_n) = X_{\parallel}^{(n)}(0)\left(1 + \sum_{m=1}^{\infty} \sum_{2*k_2+3*k_3\cdots+n*k_n=2m} \times A_{k_2k_3\cdots k_n} Q_2^{k_2} Q_3^{k_3} \cdots Q_n^{k_n}\right). \tag{19}$$

For the first hyperpolarizability $\beta_{\parallel}$ the expansions in Q_k and W_k are identical as $Q_2 = W_2$ and $Q_3 = W_3$. For higher hyperpolarizabilities the expansion in the symmetrized products has, however, the advantage that terms proportional to Q_k vanish if not at least k frequency arguments have non-zero values. Thus, for optical processes involving one or more static electric fields, such a dispersion expansion reduces in a simple way to the form for lower order properties: if one frequency argument is zero all terms proportional to Q_n can be dropped, if two frequencies are zero also the terms proportional to Q_{n-1} can be dropped and so on.

Expanding the isotropic average of the second hyperpolarizibility in terms of the products Q_k, it becomes immediately apparent that one process-independent fourth-order coefficient is sufficient to expand $\gamma_{\parallel}$ for ESHG and the dc-Kerr effect:

$$\gamma_{\parallel}(\omega_1;\omega_2,\omega_3,\omega_4) = \gamma_{\parallel}(0)(1 + \tilde{A} Q_2 + \tilde{B} Q_2^2 + \tilde{B}' Q_4 + \mathcal{O}(\omega^6)), \tag{20}$$

$$\gamma_{\parallel}(\omega_1;\omega_2,\omega_3,0) = \gamma_{\parallel}(0)(1 + \tilde{A} Q_2 + \tilde{B} Q_2^2 + \mathcal{O}(\omega^6)). \tag{21}$$

Multipolar hyperpolarizabilities and in particular dipole hyperpolarizabilities can be expressed in terms of irreducible tensor components which are irreducible with respect to both, the rotation group $SO(3)$ and the permuation group of the operator and frequency indices S_n [8]. In the derivations of the last two sections we used only that the irreducible components $X_{\parallel}^{(n)}$ are totally symmetric with respect to independent permutations of the operator and frequency indices and the even symmetry of hyperpolarizabilities with respect to inversion of the frequency signs. Therefore, the dispersion formulas (9) and (19) can also be applied to expand other hyperpolarizability components which are totally symmetric with respect to permutations of the operator indices as, for example, the all-diagonal components $X_{\alpha\alpha\ldots\alpha}^{(n)}$, the irreducible octupolar anisotropies of the first hyperpolarizability β and a quadrupolar and a hexadecapolar anisotropy tensor of the second hyperpolarizability γ.

4. Dispersion expansion of the components $\beta_{\perp}$ and β_K of the first hyperpolarizability

The approach of the last two sections can be extended to irreducible hyperpolarizability components which transform according to other irreducible representations of the symmetric group. Such components describe deviations from Kleinman symmetry [9] and vanish in the static limit. Assume that $X_{l,(\mu)}^{(n)}$ transforms according to the irreducible representation μ of the symmetric group S_n constituted by the permutations of the operator indices. Then $X_{l,(\mu)}^{(n)}$ is an eigenfunction of a projection operator $\hat{\mathcal{Q}}_{l,(\mu)} = \sum_{\mathcal{P}\in S^n} c_{l,(\mu)}^{\mathcal{P}} \hat{\mathcal{P}}$ which projects onto the subspace of the representation μ. l is an index for the degenerated components of μ. From the invariance of hyperpolarizabilities with respect to simultaneous permutation of the operator indices together with their accompanied frequency arguments, equation (5), and from the idempotency of the projection operators $\mathcal{Q}_{l,(\mu)}$ it follows that a Taylor expansion of this component can be written in terms of the symmetry-adapted frequency products

$$\sum_{\mathcal{P}\in S^n} c_{l,(\mu)}^{\mathcal{P}} \hat{\mathcal{P}}^{-1} \omega_1^{m_1} \omega_2^{m_2} \ldots \omega_n^{m_n} = \tilde{\mathcal{Q}}_{l,(\mu)} \omega_1^{m_1} \omega_2^{m_2} \ldots \omega_n^{m_n}.$$

Using recurrence relations analogous to those derived in section 2, such symmetry-adapted frequency products can be rewritten in a similar form as the terms appearing in the dispersion formulas (9) and (19). However, for irreducible representations other than the totally symmetric one the structure of the projection operators

depends much more on the actual group order and is difficult to generalize. We therefore exemplify this procedure in the following only for the experimentally important mixed-symmetry vector component of the first hyperpolarizability β. The orthogonal vector component $\beta_\perp$,

$$\beta_\perp = \tfrac{1}{5}\sum_\xi \{2\beta_{z\xi\xi\xi} - 3\beta_{\xi\xi\xi} + 2\beta_{\xi\xi\xi}\}, \quad \xi = x,y,z, \tag{22}$$

which can be measured in ESHG experiments with the optical field perpendicular to the static field [6], and the component β_K,

$$\beta_K = \tfrac{3}{2}\left(\beta_\parallel - \beta_\perp\right) \tag{23}$$

measured in dc-Kerr experiments, can be written as linear combinations of the irreducible tensors $\beta_\parallel$ and $\beta_{(23)}$,

$$\beta_\perp = \tfrac{1}{3}\beta_\parallel + \tfrac{2}{3}\beta_{(23)}, \tag{24}$$

$$\beta_K = \beta_\parallel - \beta_{(23)}, \tag{25}$$

where $\beta_{(23)}$ is defined as:

$$\beta_{(23)} = \sum_\xi \left\{\tfrac{1}{2}\beta_{z\xi\xi\xi} - \beta_{\xi\xi\xi} + \tfrac{1}{2}\beta_{\xi\xi\xi}\right\} \quad \xi = x,y,z. \tag{26}$$

The hyperpolarizability $\beta_{(23)}$ is an irreducible vector component which transforms according to the mixed-symmetry representation of S_3 and is an eigenfunction of the projector $\hat{\mathcal{Q}}_{1,(23)} = \tfrac{1}{2}\{E + (31) - (12) - (123)\}$ [8]. Consequently its dispersion can be expanded in the symmetry-adapted frequency products:

$${}^{(23)}T_{k,l,m} = \tfrac{1}{2}\left(\omega_1^k\omega_2^l\omega_3^m + \omega_1^m\omega_2^l\omega_3^k - \omega_1^l\omega_2^k\omega_3^m - \omega_1^m\omega_2^k\omega_3^l\right). \tag{27}$$

In analogy to the totally symmetric frequency powers W_k, we introduce the mixed-symmetry frequency powers $W_k^{(23)} = \tilde{\mathcal{Q}}_{1,(23)}\omega_1^k = \tfrac{1}{2}\omega_1^k - \omega_2^k + \tfrac{1}{2}\omega_3^k$. Similar to the totally symmetric products $T^{(n)}_{m_1,\ldots,m_n}$, defined in equation (6), the mixed-symmetry products ${}^{(23)}T_{k,l,m}$ can be rewritten as products of $W_i^{(23)}$ with symmetrized frequency powers W_j:

$$\begin{aligned}
{}^{(23)}T_{k,l,m} &= \tfrac{1}{2}\left(\omega_2^l\omega_1^k - \omega_2^k\omega_1^l\right)\omega_3^m + \tfrac{1}{2}\left(\omega_2^l\omega_3^k - \omega_2^k\omega_3^l\right)\omega_1^m \qquad (28)\\
&= \tfrac{1}{3}\left(W_k^{(23)}W_l - W_l^{(23)}W_k\right)W_m\\
&\quad + \tfrac{1}{2}\left(W_{k+m}\omega_2^l - W_{l+m}\omega_2^k\right.\\
&\quad \left. + W_k\omega_2^{l+m} - W_l\omega_2^{k+m}\right) \qquad (29)\\
&= \tfrac{1}{3}\left(W_k^{(23)}W_l - W_l^{(23)}W_k\right)W_m\\
&\quad + \tfrac{1}{3}\left(W_{k+m}W_l^{(23)} - W_{l+m}W_k^{(23)}\right.\\
&\quad \left. + W_kW_{l+m}^{(23)} - W_lW_{k+m}^{(23)}\right), \qquad (30)
\end{aligned}$$

where we used,

$$\begin{aligned}
W_k^{(23)}W_l - W_l^{(23)}W_k &= \tfrac{3}{2}(\omega_2^lW_k - \omega_2^kW_l)\\
&= \tfrac{3}{2}(\omega_2^l\omega_1^k + \omega_2^l\omega_3^k - \omega_2^k\omega_1^l - \omega_2^k\omega_3^l).
\end{aligned} \tag{31}$$

Further, the $W_n^{(23)}$ are related by a recurrence relation similar to equation (14),

$$W_n^{(23)} = \tfrac{1}{2}\varrho_2W_{n-2}^{(23)} + \tfrac{1}{3}\varrho_3W_{n-3}^{(23)}, \qquad n > 2. \tag{32}$$

Because $\varrho_2 = W_2$ and $\varrho_3 = W_3$, the mixed-symmetry frequency powers $W_n^{(23)}$ for n larger than 2 and thereby also the symmetry-adapted frequency products ${}^{(23)}T_{k,l,m}$ can be written as linear combinations of products of $W_1^{(23)}$ and $W_2^{(23)}$ with powers of W_1 and W_2. For symmetry reasons $W_1^{(23)}$ and $W_2^{(23)}$ appear only linear in these terms. The Kleinman forbidden component $\beta_{(23)}$ vanishes for zero frequencies. Therefore one cannot use its static limit in the way $\chi_\parallel^{(n)}(0)$ was used to define relative dispersion coefficients. For convenience we use instead $\beta_\parallel(0)$ and expand the dispersion of $\beta_{(23)}$ in products of $W_1^{(23)}$ and $W_2^{(23)}$ with powers of W_1 and W_2 as:

$$\begin{aligned}
\beta_{(23)}(\omega_1;\omega_2,\omega_3) = \beta_\parallel(0)\Bigg(&\sum_{n=0}^{\infty}\sum_{m=0}^{n/3} A^{(23)}_{1,n-3m,2m+1}\\
&\times W_1^{(23)}W_2^{n-3m}W_3^{2m+1}\\
&+ \sum_{n=0}^{\infty}\sum_{m=0}^{n/3} A^{(23)}_{2,n-3m,2m}\\
&\times W_2^{(23)}W_2^{n-3m}W_3^{2m}\Bigg).
\end{aligned} \tag{33}$$

5. Summary

The number of dispersion coefficients needed to expand a hyperpolarizability component is determined by its permutational symmetry in the operator and frequency indices. We have derived two dispersion formulas for the all-parallel hyperpolarizability averages $\chi_\parallel^{(n)}$ which involve only process-independent dispersion coefficients, are open-ended in the powers of the frequencies and include only a minimal number of terms. The first dispersion formula, equation (9), which expands the hyperpolarizabilities in terms of symmetrized frequency powers (W_k), is up to fourth-order

terms equivalent to a dispersion formula proposed recently by Bishop and De Kee. The second dispersion formula, equation (19) expands the hyperpolarizabilities in terms of symmetrized frequency products (ϱ_k), which has the advantage that the expansion becomes simpler and more transparent for optical processes which involve static electric fields. We showed that for the expansion of the vector component of first hyperpolarizabilities $\beta_{\|}$ a single process-independent fourth-order coefficient is sufficient. To the best of our knowledge, this was not recognized before. The approach developed here can be applied to other hyperpolarizability components, if they are expressed in terms of irreducible tensor components. We demonstrated this for the experimentally important components $\beta_{\perp}$ and β_K of the first hyperpolarizability which are linear combinations of the irreducible components $\beta_{\|}$ and $\beta_{(23)}$. For $\beta_{(23)}$ a dispersion formula with a similar structure to that of the formula for $\beta_{\|}$ was derived.

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