Dispersion coefficients for second hyperpolarizabilities using coupled cluster cubic response theory

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Contents

1 Introduction **112**

2 Coupled Cluster response theory **114**

3 Dispersion coefficients for dynamic second hyperpolarizabilities **119**
3.1 Expansion of general hyperpolarizabilities components . . 119
3.2 Special expansions for $\gamma_{||}$, $\gamma_{\perp}$ and γ_K 125

4 Dispersion coefficients for the second hyperpolarizability of methane **130**
4.1 Convergence with the order of the expansion 131
4.2 Convergence with the basis set 134
4.3 The effect of electron correlation on the dispersion coefficients 137

5 Conclusions **141**

A Formulas for the sixth- through tenth-order dispersion coefficients for $\gamma_{||}$ and γ_{ms} **143**

1 Introduction

Linear response function approaches were introduced into the chemistry literature about thirty years ago Ref. [1, 2]. At that time they were referred to as Green functions or propagator approaches. Soon after the introduction it became apparent that they offered a viable and attractive alternative to the state specific approaches for obtaining molecular properties as excitation energies, transition moments and second order molecular properties.

The response function approaches have since developed into a useful tool, not only for calculating molecular properties related to the linear response but also for calculations of non-linear response molecular properties. For the most common electronic structure wave function models linear and non-linear response functions have been developed and have served as a useful tool for the calibration and interpretation of molecular properties. To give a specific example consider the history of the electric field induced second harmonic generation (ESHG) experiments of the second hyperpolarizability of the Ne atom. Based on a sequence of ESHG measurements using lasers of different frequencies Shelton found that the dispersion of the ESHG hyperpolarizability of Ne was anomalous [3, 4], in contrast to the positive dispersion found in a previous experiment [5] and in an early multiconfiguration self consistent field (MCSCF) calculation [6]. Based on an empirical calculation Bishop could demonstrate [7] that the anomalous dispersion obtained in the ESHG experiment [3, 4] can not be reproduced by theory. Accurate large-scale MCSCF response function calculations were then carried out and showed that the dispersion was not anomalous [8]. Subsequently this was confirmed by new experimental ESHG data [9]. Recently accurate coupled cluster singles and doubles (CCSD) response function calculations have been carried out and have challenged the accuracy of one of the new ESHG data points [10]. An experimental reinvestigation has not yet been performed for this point. The above example demonstrates clearly the enourmous development that has taken place since response functions were introduced. It also shows how important it is that the development in theory and experiment goes hand in hand.

In this paper we discuss how more direct approaches may be developed for calculating directly the dispersion of cubic response functions using coupled cluster theory. Power series expansions of frequency-dependent hyperpolarizabilities have in recent years become a widely-used tool for comparison of experimentally obtained and *ab initio* calculated hyperpolarizabilities for different optical proccesses, in particular for second hyperpolarizabilities where for many molecules experimental data is available for more than one optical process and often covers a wide range of frequencies [4, 11–14]. The most commonly used ansatz to expand the frequency-dependence of hyperpolarizabilities in the normal dispersion region [4, 9, 13–17] are even power series in the frequency arguments. The usefulness of this ansatz is emphasized by the fact that for the isotropic average of the second hyperpolarizability $\gamma_{||}$ a single, process-independent coefficient is sufficient to express the frequeny-dependence up to second-order in the frequencies [18, 19]:

$$\gamma_{||}(\omega_0;\omega_1,\omega_3,\omega_3) \;=\; \gamma_{||}(0)\Big(1 + A(\omega_0^2+\omega_1^2+\omega_2^2+\omega_3^2) + \mathcal{O}(\omega_i^4)\Big). \quad (1)$$

A sum-over-states expression for the coefficient A for the expansion of the diagonal components $\gamma_{\alpha\alpha\alpha\alpha}$ was derived by Bishop and De Kee [20] and calculations were reported for the atoms H and He. However, the usual approach to calculate dispersion coefficients for many-electron systems by means of *ab initio* response methods is still to extract these coefficients from a polynomial fit to pointwise calculated frequency-dependent hyperpolarizabilities. Despite the inefficiency and the numerical difficulties of such an approach [16, 21], no *ab initio* implementation has yet been reported for analytic dispersion coefficients for frequency-dependent second hyperpolarizabilities which is applicable to many-electron systems.

In a recent publication [22] we reported the implementation of dispersion coefficients for first hyperpolarizabilities based on the coupled cluster quadratic response approach. In the present publication we extend the work of Refs. [22–24] to the analytic calculation of dispersion coefficients for cubic response properties, i.e. second hyperpolarizabilities. We define the dispersion coefficients by a Taylor expansion of the cubic response function in its frequency arguments. Hence, this approach is

applicable to all hyperpolarizability components and the coefficients are independent of specific nonlinear optical proccesses.

The generality of a simple power series ansatz and an open-ended formulation of the dispersion formulas facilitate an alternative approach to the calculation of dispersion curves for hyperpolarizabilities complementary to the point-wise calculation of the frequency-dependent property. In particular, if dispersion curves are needed over a wide range of frequencies and for several optical proccesses, the calculation of the dispersion coefficients can provide a cost-efficient alternative to repeated calculations for different optical proccesses and different frequencies. The open-ended formulation allows to investigate the convergence of the dispersion expansion and to reduce the truncation error to what is considered tolerable.

In the next section we derive the Taylor expansion of the coupled cluster cubic response function in its frequency arguments and the equations for the required expansions of the cluster amplitude and Lagrangian multiplier responses. For the experimentally important isotropic averages $\gamma_{||}$, $\gamma_{\perp}$ and γ_K we give explicit expressions for the A and higher-order coefficients in terms of the coefficients of the Taylor series. In Sec. 4 we present an application of the developed approach to the second hyperpolarizability of the methane molecule. We test the convergence of the hyperpolarizabilities with respect to the order of the expansion and investigate the sensitivity of the coefficients to basis sets and correlation treatment. The results are compared with dispersion coefficients derived by least square fits to experimental hyperpolarizability data or to pointwise calculated hyperpolarizabilities of other *ab inito* studies.

2 Coupled Cluster response theory

In the derivation of response functions one considers a molecule or an atom described by the time-independent Hamiltonian $\hat{H}^{(0)}$ which is perturbed by an external one-electron perturbation $\hat{V}(t,\epsilon)$.

$$\hat{H}(t,\epsilon) \;=\; \hat{H}^{(0)} + \hat{V}(t,\epsilon) \tag{2}$$

We assume that the perturbation operator $\hat{V}(t,\epsilon)$ can be expanded in a sum over Fourier components as

$$\hat{V}(t,\epsilon) \;=\; \sum_j \hat{H}^{X_j}\epsilon_j(\omega_j)e^{(-i\omega_j t)} \quad , \tag{3}$$

where $\hat{H}^{X_j}$ are hermitian time- and field-independent one-electron operators and $\epsilon_j(\omega_j)$ are associated field strengths for frequencies ω_j. The letter ϵ without index is in the following used as abbreviation for the complete set $\{\epsilon_j\}$ of field strengths included in $\hat{V}$. The time-dependent ground-state coupled cluster wavefunction for such a system is conveniently parametrized in a form, where the oscillating phase factor caused by the so-called level-shift or time-dependent quasienergy $\mathcal{W}(t,\epsilon)$ is explicitly isolated [25–28]:

$$\Big|CC(t,\epsilon)\Big\rangle \;=\; \exp\left(-i\int_{t_0}^{t}\mathcal{W}(t',\epsilon)dt'\right)\exp\Big(\hat{T}(t,\epsilon)\Big)\Big|\mathrm{HF}\Big\rangle \tag{4}$$

The field- and time-dependent cluster operator is defined as $\hat{T}(t,\epsilon) = \sum_\mu t_\mu(t,\epsilon)\hat{\tau}_\mu$ and $|\mathrm{HF}\rangle$ is the SCF wavefunction of the unperturbed molecule. By keeping the Hartree-Fock reference fixed in the presence of the external perturbation, a two step approach, which would introduce into the coupled cluster wavefunction an artificial pole structure form the response of the Hartree Fock orbitals, is circumvented. The quasienergy $\mathcal{W}$ and the time-dependent coupled cluster equations are determined by projecting the time-dependent Schrödinger equation onto the Hartree-Fock reference and onto the bra states $\langle\mathrm{HF}|\hat{\tau}_\mu^\dagger\exp(-\hat{T})$:

$$\mathcal{W}(\epsilon,t) \;=\; \Big\langle\mathrm{HF}\Big|\hat{H}(\epsilon,t)\exp(\hat{T})\Big|\mathrm{HF}\Big\rangle. \tag{5}$$

$$\Big\langle\mathrm{HF}\Big|\hat{\tau}_\mu^\dagger\exp\Big(-\hat{T}(t,\epsilon)\Big)\hat{H}(t,\epsilon)\exp\Big(\hat{T}(t,\epsilon)\Big)\Big|\mathrm{HF}\Big\rangle - i\frac{d}{dt}t_\mu(t,\epsilon) \;=\; 0 \tag{6}$$

The latter equation may be written in the shorthand form

$$e_\mu(t,\epsilon) - i\tfrac{d}{dt}t_\mu(t,\epsilon) \;=\; 0 \quad . \tag{7}$$

Frequency-dependent higher-order properties can now by obtained as derivatives of the time-average of the quasienergy $\{\mathcal{W}\}_T$ with respect

to the field strengths of the external perturbations. To derive computational efficient expressions for the derivatives of the coupled cluster quasienergy we use a variational formulation which is obtained by combining the quasienergy and the time-dependent coupled cluster equations to a quasienergy Lagrangian:

$$L(t,\epsilon) \;=\; \mathcal{W}(t,\epsilon) + \sum_{\mu} \bar{t}_{\mu} \left(e_{\mu}(t,\epsilon) - i\tfrac{d}{dt} t_{\mu}) \right) \tag{8}$$

The time-average of the quasienergy Lagrangian

$$\{L(t,\epsilon)\}_T \;=\; \lim_{t_0 \to \infty} \frac{1}{2t_0} \int_{-t_0}^{+t_0} L(t,\epsilon) dt \quad , \tag{9}$$

may now be required to be stationary with respect to the Fourier components of the cluster amplitudes and the Lagrangian multipliers [23–25, 28].

$$\delta\{L(t,\epsilon)\}_T \;=\; 0 \tag{10}$$

Inserting the perturbation and Fourier expansion of the cluster amplitudes and the Lagrangian multipliers,

$$\begin{aligned} t_{\mu}(t,\epsilon) \;&=\; t_{\mu}^{(0)} + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{j_1} \cdots \sum_{j_n} t^{X_{j_1} \cdots X_{j_n}}(\omega_{j_1}, \ldots, \omega_{j_n}) \\ &\qquad \times \prod_{m=1}^{n} \epsilon_{j_m}(\omega_{j_m}) e^{-i\omega_{j_m} t} \end{aligned} \tag{11}$$

$$\begin{aligned} \bar{t}_{\mu}(t,\epsilon) \;&=\; \bar{t}_{\mu}^{(0)} + \sum_{n=1}^{\infty} \frac{1}{n!} \sum_{j_1} \cdots \sum_{j_n} \bar{t}^{X_{j_1} \cdots X_{j_n}}(\omega_{j_1}, \ldots, \omega_{j_n}) \\ &\qquad \times \prod_{m=1}^{n} \epsilon_{j_m}(\omega_{j_m}) e^{-i\omega_{j_m} t} \end{aligned} \tag{12}$$

the variational condition for the time-averaged quasienergy (10) becomes a set of response equations for the individual expansion coefficients of $t_{\mu}(t,\epsilon)$ and $\bar{t}_{\mu}(t,\epsilon)$. In zeroth-order one obtains the usual coupled cluster equations, $e^{(0)} = 0$, and the equations for the zeroth-order Lagrangian multipliers,

$$\eta^{(0)} + \bar{t}^{(0)} \mathbf{A} \;=\; 0 \quad , \tag{13}$$

where the vector $\eta^{(0)}$ and the Jacobian matrix $\mathbf{A}$ are defined as partial derivatives of the quasienergy and the Lagrangian with respect to cluster amplitudes and Lagrangian multipliers:

$$\eta_\nu^{(0)} = \left(\frac{\partial \mathcal{W}}{\partial t_\nu}\right)_0 \quad , \tag{14}$$

$$A_{\mu\nu} = \left(\frac{\partial^2 L}{\partial \bar{t}_\mu \partial t_\nu}\right)_0 \quad . \tag{15}$$

The index 0 indicates that the derivatives are taken for zero perturbation strengths. The equations for the first-order amplitudes and multipliers are obtained as:

$$\Big(\mathbf{A} - \omega\mathbf{1}\Big) t^A(\omega) = -\xi^A \quad , \tag{16}$$

$$\bar{t}^A(\omega)\Big(\mathbf{A} + \omega\mathbf{1}\Big) = -\Big(\eta^A + \mathbf{F}t^A(\omega)\Big) \quad , \tag{17}$$

with ξ^A, η^A, and $\mathbf{F}$ defined as:

$$\xi_\mu^A = \left(\frac{\partial^2 L}{\partial \epsilon_A(0) \partial \bar{t}_\mu}\right)_0 \quad , \tag{18}$$

$$\eta_\mu^A = \left(\frac{\partial^2 L}{\partial \epsilon_A(0) \partial t_\mu}\right)_0 \quad , \tag{19}$$

$$F_{\mu\nu} = \left(\frac{\partial^2 L}{\partial t_\mu \partial t_\nu}\right)_0 \quad . \tag{20}$$

The second-order response equations for the cluster amplitudes and the Lagrangian multipliers are:

$$\Big(\mathbf{A} - (\omega_A + \omega_B)\mathbf{1}\Big) t^{AB}(\omega_A, \omega_B) = -\xi^{AB}(\omega_A, \omega_B) \quad , \tag{21}$$

$$\bar{t}^{AB}(\omega_A, \omega_B)\Big(\mathbf{A} + (\omega_A + \omega_B)\mathbf{1}\Big) = -\bar{\xi}^{AB}(\omega_A, \omega_B) \quad , \tag{22}$$

with the right hand side vectors defined as:

$$\xi^{AB}(\omega_A, \omega_B) = \hat{P}^{AB}\Big(\tfrac{1}{2}\mathbf{B}t^A(\omega_A)t^B(\omega_B) + \mathbf{A}^B t^A(\omega_A)\Big) \quad , \tag{23}$$

$$\bar{\xi}^{AB}(\omega_A,\omega_B) = \mathbf{F}t^{AB}(\omega_A,\omega_B) + \hat{P}^{AB}\Big(\tfrac{1}{2}\mathbf{G}t^A(\omega_A)t^B(\omega_B) + \mathbf{F}^A t^B(\omega_B) + \bar{T}^B(\omega_B)\mathbf{B}t^A(\omega_A) + \bar{T}^B(\omega_B)\mathbf{A}^A\Big) \quad . \tag{24}$$

The matrices $\mathbf{B}$, $\mathbf{G}$ and $\mathbf{F}^X$ are defined as partial third derivatives of the Lagrangian:

$$G_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial t_\mu \partial t_\nu \partial t_\gamma}\right)_0 \quad . \tag{25}$$

$$B_{\gamma\mu\nu} = \left(\frac{\partial^3 L}{\partial \bar{t}_\gamma \partial t_\mu \partial t_\nu}\right)_0 \quad . \tag{26}$$

$$F^X_{\mu\nu} = \left(\frac{\partial^2 L}{\partial t_\mu \partial t_\nu \partial \epsilon_X(0)}\right)_0 \quad . \tag{27}$$

$$A^X_{\mu\nu} = \left(\frac{\partial^2 L}{\partial \bar{t}_\mu \partial t_\nu \partial \epsilon_X(0)}\right)_0 \quad . \tag{28}$$

The response functions are obtained as derivatives of the real part of the time-averaged quasienergy Lagrangian:

$$\langle\langle X_1; X_2 \ldots, X_n\rangle\rangle_{\omega_2,\ldots,\omega_n} = \left(\frac{d^n\left\{\frac{1}{2}L(t,\epsilon) + \frac{1}{2}L(t,\epsilon)^*\right\}_T}{d\epsilon_1(\omega_1)\ldots d\epsilon_n(\omega_n)}\right)_0 \tag{29}$$

As a consequence of the time-averaging of the quasienergy Lagrangian, the derivative in the last equation gives only a nonvanishing result if the frequencies of the external fields fulfill the matching condition $\sum_i \omega_i = 0$. In fourth order Eq. (29) gives the cubic response function:

$$\begin{aligned}\langle\langle A; B, C, D\rangle\rangle_{\omega_B,\omega_C,\omega_D} = \\ &\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABCD}\Big\{\tfrac{1}{24}\,\mathbf{H}\,t^A(\omega_A)\,t^B(\omega_B)\,t^C(\omega_C)\,t^D(\omega_D) \\ &+ \tfrac{1}{4}\Big(\eta^{CD}(\omega_C,\omega_D) + \tfrac{1}{2}\mathbf{F}t^{CD}(\omega_C,\omega_D)\Big)t^{AB}(\omega_A,\omega_B) \\ &+ \tfrac{1}{6}\,\bar{t}^A(\omega_A)\,\mathbf{C}\,t^B(\omega_B)\,t^C(\omega_C)\,t^D(\omega_D) \\ &+ \tfrac{1}{2}\bar{t}^A(\omega_A)\,\mathbf{B}^B\,t^C(\omega_C)\,t^D(\omega_D)\Big\},\end{aligned} \tag{30}$$

with $\omega_A = -(\omega_B + \omega_C + \omega_D)$ and the vector η^{CD} defined as

$$\eta^{CD}(\omega_C, \omega_D) = \bar{\xi}^{CD}(\omega_C, \omega_D) - \mathbf{F}t^{CD}(\omega_C, \omega_D) \quad . \tag{31}$$

The operator $\hat{P}^{ABCD}$ symmetrizes with respect to permutations of the perturbation indices A, B, C and D and the accompanied frequencies and $\hat{C}^{\pm\omega}$ symmetrizes with respect to an inversion of the signs of all frequencies and simultaneous complex conjugation. The three matrices $\mathbf{H}$, $\mathbf{C}$ and $\mathbf{B}^X$ are defined as:

$$H_{\mu\nu\gamma\delta} = \left(\frac{\partial^3 L}{\partial t_\mu \, \partial t_\nu \, \partial t_\gamma \, \partial t_\delta}\right)_0 , \tag{32}$$

$$B^X_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial \bar{t}_\mu \, \partial t_\nu \, \partial t_\gamma \, \partial \epsilon_X(0)}\right)_0 , \tag{33}$$

$$C_{\mu\nu\gamma\delta} = \left(\frac{\partial^3 L}{\partial \bar{t}_\mu \, \partial t_\nu \, \partial t_\gamma \, \partial t_\delta}\right)_0 . \tag{34}$$

An implementation of the cubic response function Eq. (30) for the coupled cluster model hierachy CCS, CC2 and CCSD was reported in Ref. [24].

3 Dispersion coefficients for dynamic second hyperpolarizabilities

3.1 Expansion of general hyperpolarizabilities components

In the normal dispersion region below the first pole, response functions can be expanded in power series in their frequency arguments. The four frequencies, associated with the operator arguments of the cubic response function are related by the matching condition $\omega_A + \omega_B + \omega_C + \omega_D = 0$. Thus second hyperpolarizabilities or in general cubic response properties are functions of only three independent frequency variables, which may be chosen as ω_B, ω_C and ω_D:

$$\gamma_{ABCD}(-\omega_B - \omega_C - \omega_D; \omega_B, \omega_C, \omega_D) = \sum_{l,m,n=0}^{\infty} \omega_B^l \omega_C^m \omega_D^n D_{ABCD}(l, m, n) \tag{35}$$

with the coefficients $D_{ABCD}(l,m,n)$ defined as:

$$D_{ABCD}(l,m,n) \;=\; \frac{l!m!n!}{(l+m+n)!}\left(\frac{d^{l+m+n}\,\gamma_{ABCD}}{d\omega_B^l\,d\omega_C^m\,d\omega_D^n}\right)_{\omega_i=0} \tag{36}$$

To derive working expressions for the dispersion coefficients D_{ABCD} we need the power series expansion of the first-order and second-order responses of the cluster amplitudes and the Lagrangian multipliers in their frequency arguments. In Refs. [22, 29] we have introduced the coupled cluster Cauchy vectors:

$$t^A(\omega_A) \;=\; \sum_{n=0}^{\infty}\omega_A^n C^A(n) \quad , \tag{37}$$

$$C^A(n) \;=\; \frac{1}{n!}\left(\frac{d^n t^A(\omega_A)}{d\omega_A^n}\right)_{\omega_A=0} \;=\; -\,\mathbf{A}^{-n-1}\xi^A \quad , \tag{38}$$

and the corresponding expansion for the first-order Lagrange multipliers:

$$\bar{t}^A(\omega_A) \;=\; \sum_{n=0}^{\infty}\omega_A^n \bar{C}^A(n) \quad . \tag{39}$$

$$\bar{C}^A(n) \;=\; \frac{1}{n!}\left(\frac{d^n \bar{t}^A(\omega_A)}{d\omega_A^n}\right)_{\omega_A=0} \quad , \tag{40}$$

$$\;=\; \sum_{m=0}^{n}(-1)^{m+1}\Big(\mathbf{F}C^A(n-m)+\delta_{m,n}\eta^A\Big)\mathbf{A}^{-m-1} \quad , \tag{41}$$

The Cauchy vectors for $n \geq 0$ are obtained by solution of the recursive set of linear equations,

$$\mathbf{A}C^A(n) \;=\; C^A(n-1) \quad , \tag{42}$$

starting with the zeroth-order Cauchy vector which is equal to the static limit of the first-order cluster amplitude response: $C^A(0) = t^A(0)$. The $\bar{C}^A(n)$ vectors for $n \geq 0$ are obtained from the recurrence relation:

$$\bar{C}^A(n)\mathbf{A} \;=\; -\Big[\mathbf{F}C^X(n)+\bar{C}^A(n-1)\Big] \quad , \tag{43}$$

starting with $\bar{C}^A(0) = \bar{t}^A(0)$. The second-order response of the cluster amplitudes can be expanded in their two frequency arguments as:

$$t^{AB}(\omega_A, \omega_B) = \sum_{m,n=0}^{\infty} \omega_A^m \omega_B^n C^{AB}(m,n) \tag{44}$$

$$\begin{aligned} C^{AB}(m,n) &= \frac{1}{m!n!} \left(\frac{d^{m+n} t^{AB}(\omega_A, \omega_B)}{d\omega_A^m \, d\omega_B^n} \right)_{\omega_A=\omega_B=0} && (45) \\ &= -\sum_{p=0}^{m} \sum_{q=0}^{n} \binom{m-p+n-q}{m-p} \mathbf{A}^{-m+p-n+q-1} \, {}^c\xi^{AB}(p,q) \quad , \end{aligned}$$

with

$$\begin{aligned} {}^c\xi^{AB}(m,n) &= \frac{1}{m!n!} \left(\frac{d^{m+n} \xi^{AB}(\omega_A, \omega_B)}{d\omega_A^m \, d\omega_B^n} \right)_{\omega_A=\omega_B=0} && (46) \\ &= \hat{P}_{mn}^{AB} \left(\tfrac{1}{2} \mathbf{B} C^A(m) C^B(n) + \delta_{n,0} \mathbf{A}^B C^A(m) \right) && (47) \end{aligned}$$

The operator $\hat{P}_{mn}^{AB}$ symmetrizes with respect to permutation of the operators A and B together with the accompanied "Cauchy" orders m, n; δ is the Kronecker symbol. Similar as for the first-order Cauchy vectors the second-order Cauchy vectors are obtained as solutions of a recursive set of equations:

$$\mathbf{A} C^{AB}(m,0) = -\left({}^c\xi^{AB}(m,0) - C^{AB}(m-1,0) \right) \quad , \tag{48}$$

$$\mathbf{A} C^{AB}(0,n) = -\left({}^c\xi^{AB}(0,n) - C^{AB}(0,n-1) \right) \quad , \tag{49}$$

$$\begin{aligned} \mathbf{A} C^{AB}(m,n) = -\Big(& {}^c\xi^{AB}(m,n) - C^{AB}(m-1,n) \\ & - C^{AB}(m,n-1) \Big) \quad , \end{aligned} \tag{50}$$

starting with $C^{AB}(0,0) = t^{AB}(0,0)$. For the second-order response of the Larangian multipliers one finds the following expansion in the frequency argmuments:

$$\bar{t}^{AB}(\omega_A, \omega_B) = \sum_{m,n=0}^{\infty} \omega_A^m \omega_B^n \bar{C}^{AB}(m,n) \tag{51}$$

$$\bar{C}^{AB}(m,n) = \frac{1}{m!n!}\left(\frac{d^{m+n}\bar{t}^{AB}(\omega_A,\omega_B)}{d\omega_A^m\, d\omega_B^n}\right)_{\omega_A=\omega_B=0} \tag{52}$$

$$= -\sum_{p=0}^{m}\sum_{q=0}^{n}(-1)^{m-p+n-q}\binom{m-p+n-q}{m-p} \times {}^{c}\bar{\xi}^{AB}(p,q)\mathbf{A}^{-m+p-n+q-1} \tag{53}$$

with

$${}^{c}\bar{\xi}^{AB}(m,n) = \frac{1}{m!n!}\left(\frac{d^{m+n}\bar{\xi}^{AB}(\omega_A,\omega_B)}{d\omega_A^m\, d\omega_B^n}\right)_{\omega_A=\omega_B=0} \tag{54}$$

$$= \mathbf{F}C^{AB}(m,n) + \hat{P}_{mn}^{AB}\Big(\tfrac{1}{2}\mathbf{G}C^{A}(m)C^{B}(n) + \delta_{m,0}\mathbf{F}^{A}C^{B}(n) + \bar{C}^{B}(n)\mathbf{B}C^{A}(m) + \delta_{m,0}\bar{C}^{B}(n)\mathbf{A}^{A}\Big) \ .$$

The $\bar{C}^{AB}(m,n)$ vectors are calculated using the equations:

$$\bar{C}^{AB}(m,0)\mathbf{A} = -\Big({}^{c}\bar{\xi}^{AB}(m,0) + \bar{C}^{AB}(m-1,0)\Big) \ , \tag{55}$$

$$\bar{C}^{AB}(0,n)\mathbf{A} = -\Big({}^{c}\bar{\xi}^{AB}(0,n) + \bar{C}^{AB}(0,n-1)\Big) \ , \tag{56}$$

$$\bar{C}^{AB}(m,n)\mathbf{A} = -\Big({}^{c}\bar{\xi}^{AB}(m,n) + \bar{C}^{AB}(m-1,n) + \bar{C}^{AB}(m,n-1)\Big) \ , \tag{57}$$

The matrices $\mathbf{F}$, $\mathbf{G}$, $\mathbf{F}^X$, $\mathbf{H}$, $\mathbf{A}^X$, $\mathbf{B}$, and $\mathbf{C}$ which appear in the expression for the second hyperpolarizability in Eq. (30) are defined as partial derivatives of the quasienergy Lagrangian taken at zero field strengths and hence are frequency-independent.

To find the power series expansion of Eq. (30) in ω_B, ω_C, ω_D we can thus replace the first-order responses of the cluster amplitudes and Lagrangian multipliers and the second-order responses of the cluster amplitudes by the expansions in Eqs. (37), (39) and (44) and express ω_A as $-\omega_B - \omega_C - \omega_D$. However, doing so starting from Eq. (30) leads to expressions which involve an unneccessary large number of second-order Cauchy vectors $C^{AB}(m,n)$. To keep the number of second-order

equations for the intermediates $C^{AB}(m,n)$ and $\bar{C}^{AB}(m,n)$ minimal, we use Eqs. (22) – (24) and (31) to rewrite the first term in Eq. (30) in the alternative forms:

$$\begin{aligned}\hat{P}^{ABCD}\ \tfrac{1}{4}\Big(\eta^{CD}(\omega_C,\omega_D)+\tfrac{1}{2}\mathbf{F}t^{CD}(\omega_C,\omega_D)\Big)t^{AB}(\omega_A,\omega_B) \qquad (58)\\ =\hat{C}^{BCD}\Big\{\eta^{AB}(\omega_A,\omega_B)t^{CD}(\omega_C,\omega_D)+\bar{\xi}^{CD}(\omega_C,\omega_D)t^{AB}(\omega_A,\omega_B)\Big\}\\ =\hat{C}^{BCD}\Big\{\eta^{AB}(\omega_A,\omega_B)t^{CD}(\omega_C,\omega_D)+\bar{t}^{CD}(\omega_C,\omega_D)\xi^{AB}(\omega_A,\omega_B)\Big\}\end{aligned}$$

where $\hat{C}^{BCD}$ is a permutation operator which generates the three cyclic permuations of B, C, and D: $\hat{C}^{BCD}(BCD) = (BCD) + (CDB) + (DBC)$. To obtain an efficient expression for the power series expansion of the cubic response function in the frequency arguments, we introduce the intermediates $P_{AB,CD}(i,j;k,l)$ defined for $i+j > k+l$ as

$$P_{AB,CD}(i,j;k,l) \;=\; {}^{c}\eta^{AB}(i,j)\ C^{CD}(k,l) + \bar{C}^{CD}(k,l)\ {}^{c}\xi^{AB}(i,j) \quad (59)$$

for $i+j < k+l$ as

$$P_{AB,CD}(i,j;k,l) \;=\; {}^{c}\eta^{CD}(k,l)\ C^{AB}(i,j) + \bar{C}^{AB}(i,j)\ {}^{c}\xi^{CD}(k,l) \quad (60)$$

and for $i+j = k+l$ as

$$\begin{aligned}P_{AB,CD}(i,j;k,l) \;=\; &\mathbf{F}C^{AB}(i,j)C^{CD}(k,l) \qquad (61)\\ &+\Big({}^{c}\eta^{AB}(i,j)+\bar{C}^{AB}(i-1,j)+\bar{C}^{AB}(i,j-1)\Big)C^{CD}(k,l)\\ &+\Big({}^{c}\eta^{CD}(k,l)+\bar{C}^{CD}(k-1,l)+\bar{C}^{CD}(k,l-1)\Big)C^{AB}(i,j)\ ,\end{aligned}$$

where ${}^{c}\eta^{AB}(i,j) = {}^{c}\bar{\xi}^{AB}(i,j) - \mathbf{F}C^{AB}(i,j)$. If we consider $i+j+k+l$ as the order of $P_{AB,CD}(i;j,k,l)$ in the frequencies and $i+j$ as order of the vectors $C^{XY}(i,j)$, $\bar{C}^{XY}(i,j)$ we obtain $2n+1$ and $2n+2$ rules [30] for the second-order Cauchy C^{XY} vectors and their Lagrangian multiplier counterparts $\bar{C}^{XY}$: second-order Cauchy vectors C^{XY} up to order n are sufficient to calculate the $P_{AB,CD}(i,j;k,l)$ up to order $2n+1$ and from the vectors $\bar{C}^{XY}$ up to order n the $P_{AB,CD}(i,j;k,l)$ intermediates can be calculated up to order $2n+2$.

The coupled cluster expression for frequency-dependent second hyperpolarizability, Eq. (30), can now be expanded in a Taylor series in its frequency arguments around its static limit as:

$$\gamma_{ABCD}(\omega_A;\omega_B,\omega_C,\omega_D) \tag{62}$$
$$= -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{i,j,k,l=0}^{\infty}\omega_A^i\,\omega_B^j\,\omega_C^k\,\omega_D^l\,d_{ABCD}(i,j,k,l)\quad,$$

with the coefficients $d_{ABCD}(i,j,k,l)$ defined as

$$\begin{aligned} d_{ABCD}(i,j,k,l) &= \hat{C}^{BCD}P_{AB,CD}(i,j;k,l) \\ &\quad +\hat{P}^{ABCD}\Big\{\tfrac{1}{24}\,\mathbf{H}\,C^A(i)\,C^B(j)\,C^C(k)\,C^D(l) \\ &\qquad +\tfrac{1}{6}\,\bar{C}^A(i)\,\mathbf{C}\,C^B(j)\,C^C(k)\,C^D(l) \\ &\qquad +\delta_{j,0}\tfrac{1}{2}\bar{C}^A(i)\,\mathbf{B}^B\,C^C(k)\,C^D(l)\Big\}\quad. \end{aligned} \tag{63}$$

Rewriting the redundant frequency ω_A as $-\omega_B-\omega_C-\omega_D$, we find:

$$\gamma_{ABCD}(\omega_A;\omega_B,\omega_C,\omega_D)$$
$$= -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{pqr=0}^{\infty}\sum_{lmn=0}^{\infty}(-1)^{p+q+r}\,\frac{(p+q+r)!}{p!\,q!\,r!} \tag{64}$$
$$\times\omega_B^{p+l}\,\omega_C^{q+m}\,\omega_D^{r+n}d_{ABCD}(p+q+r,l,m,n)\quad,$$

$$= -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{lmn=0}^{\infty}\omega_B^l\omega_C^m\omega_D^n\sum_{p=0}^{l}\sum_{q=0}^{m}\sum_{r=0}^{n}(-1)^{p+q+r} \tag{65}$$
$$\times\frac{(p+q+r)}{p!\,q!\,r!}d_{ABCD}(p+q+r,l-p,m-q,n-r)\quad.$$

From Eq. (65) we identify for the dispersion coefficients $D_{ABCD}(l,m,n)$ defined in Eq. (35) the expression

$$D_{ABCD}(l,m,n) = -\sum_{p=0}^{l}\sum_{q=0}^{m}\sum_{r=0}^{n}(-1)^{p+q+r}\frac{(p+q+r)!}{p!q!r!} \tag{66}$$

$$\times\frac{1}{2}\Big(d_{ABCD}(p+q+r,l-p,m-q,n-r) + (-1)^{l+m+n}d_{ABCD}(p+q+r,l-p,m-q,n-r)^*\Big) \quad .$$

Thus coefficients with an even total order $l+m+n$ are real and coefficients with an odd total order $l+m+n$ are pure imaginary. In the following we consider only dipole hyperpolarizabilities. In this case the four operators A, B, C and D are cartesian components of the dipole operator and the odd dispersion coefficients vanish.

3.2 Special expansions for $\gamma_{||}$, $\gamma_\perp$ and γ_K

For optical processes which can be parametrized in terms of a single laser frequency like third harmonic generation (THG), electric field induced second harmonic generation (ESHG), the dc-Kerr effect, and degenerate four wave mixing (DFWM), specialized versions of Eq. (35) can be derived, with dispersion coefficients that depend only on one order parameter. For example the third harmonic generation hyperpolarizability $\gamma^{THG}_{ABCD}(\omega) = \gamma_{ABCD}(-3\omega;\omega,\omega,\omega)$ can be expanded as:

$$\gamma^{THG}_{ABCD}(\omega) = \sum_{n=0}^{\infty} \omega^{2n} D^{THG}_{ABCD}(2n) \quad , \tag{67}$$

with

$$D^{THG}_{ABCD}(n) = \sum_{m=0}^{n}\sum_{l=0}^{m} D_{ABCD}(n-m,m-l,l) \quad . \tag{68}$$

The analogous dispersion coefficients for the ESHG hyperpolarizability $\gamma^{ESHG}_{ABCD}(\omega) = \gamma_{ABCD}(-2\omega;\omega,\omega,0)$, the dc-Kerr effect $\gamma^{dc-Kerr}_{ABCD}(\omega) = \gamma_{ABCD}(-\omega;0,0,\omega)$ and DFWM $\gamma^{DFWM}_{ABCD}(\omega) = \gamma_{ABCD}(-\omega;\omega,\omega,-\omega)$ are found as:

$$D^{ESHG}_{ABCD}(n) = \sum_{m=0}^{n} D_{ABCD}(n-m,m,0) \tag{69}$$

$$D^{dc-Kerr}_{ABCD}(n) = D_{ABCD}(0,0,n) \tag{70}$$

$$D^{DFWM}_{ABCD}(n) = \sum_{m=0}^{n}\sum_{l=0}^{m}(-1)^l D_{ABCD}(n-m,m-l,l) \tag{71}$$

An alternative compact expansion with coefficients which are independent of the optical process can be derived for the isotropic parallel average of the second hyperpolarizability $\gamma_{||}$ defined as [13]

$$\gamma_{||} \;=\; \tfrac{1}{15}\sum_{\xi\eta}\Big\{\gamma_{\xi\eta\eta\xi}+\gamma_{\xi\eta\xi\eta}+\gamma_{\xi\xi\eta\eta}\Big\}, \qquad\qquad \xi,\eta = x,y,z, \qquad (72)$$

which is the tensor component probed in the majority of hyperpolarizability measurements. It was first suggested by Shelton [18] based on a single resonance model that $\gamma_{||}$ can be expanded in low orders in terms of the effective frequency $\omega_L^2 = \omega_0^2+\omega_1^2+\omega_2^2+\omega_3^2$ as

$$\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3) \;=\; \gamma_0\left(1+A\omega_L^2+\ldots\right) \quad . \qquad (73)$$

As was proven later by Bishop [19], the coefficient A in the expansion (73) is the same for all optical processes. If the expansion (73) is extended to fourth-order [4, 19] by adding the term $B\omega_L^4$ the coefficient B is the same for the dc-Kerr effect and for electric field induced second-harmonic generation, but other fourth powers of the frequencies than ω_L^4 are in general needed to represent the frequency-dependence of $\gamma_{||}$ with process-independent dispersion coefficients [19]. Bishop and De Kee [20] proposed recently for the all-diagonal components $\gamma_{\alpha\alpha\alpha\alpha}$ the expansion

$$\gamma_{\alpha\alpha\alpha\alpha}(\omega_0;\omega_1,\omega_2,\omega_3) \;=\; \gamma_0 + AW_2 + BW_2^2 + B'W_4 + \ldots \quad , \qquad (74)$$

with $W_n = \sum_i \omega_i^n$ and B and B' process-independent. Employing the invariance of $\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3)$ with respect to permutations of the frequency arguments, we have prooved [31] that the expansion (74) is valid also for the isotropic parallel average $\gamma_{||}$ and that it can be generalized to arbitrarly high orders in the frequency arguments, using only process-independent dispersion coefficients.However, the ansatz in Eq. (74) has the disadvantage that simplifications which occur if one or more of the external fields are static are not reflected in the effective frequencies W_n: Already for the dc-Kerr effect and also for the electric field induced second harmonic generation both fourth-order coefficients, B and B', enter the description of the dispersion. In Ref. [31] we proposed therefore for

$\gamma_{||}$ the alternative open-ended expansion:

$$\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3) \;=\; \gamma_0 \left(1+\sum_{n=1}^{\infty}\sum_{2k+3k+4m=2n} A_{k,l,m}\,\omega_{L2}^{2k}\,\omega_{L3}^{3l}\,\omega_{L4}^{4m}\right) \quad , \tag{75}$$

where the coefficients $A_{k,l,m}$ are strictly process-independent and the effective frequencies ω_{L2}^2, ω_{L3}^3 and ω_{L4}^4 are defined as: [32]

$$\omega_{L2}^2 \;=\; \sum_i \omega_i^2 \;=\; \omega_L^2, \tag{76}$$

$$\omega_{L3}^3 \;=\; \sum_i \omega_i^3 \;=\; 3\Big(\omega_0\omega_1\omega_2+\omega_0\omega_1\omega_3+\omega_0\omega_2\omega_3+\omega_1\omega_2\omega_3\Big) \tag{77}$$

$$\omega_{L4}^4 \;=\; \sum_i \Big(\omega_i^4-\frac{1}{2}\omega_i^2\Big) \;=\; -\,4\omega_0\omega_1\omega_2\omega_3 \tag{78}$$

These effective frequencies are chosen such that ω_{L3}^3 contributes only for optical processes with at least three non-zero frequency arguments, while ω_{L4}^4 is only non-zero if all four frequency arguments are non-zero. During the implementation it was also found that this choice for the effective frequencies leads to the most compact expressions for the coefficients $A_{k,l,m}$ in terms of $D(n,m,l)$. Using a similar notation as in Eq. (73), $\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3)$ can up to sixth order in the frequencies be expanded as

$$\begin{aligned}\gamma_{||}(\omega_0;\omega_1,\omega_2,\omega_3) \;=\; \gamma_0\Big(1 &+A\omega_{L2}^2+B\omega_{L2}^4+B'\omega_{L4}^4 \\ &+C\omega_{L2}^6+C'\omega_{L3}^6+C''\omega_{L2}^2\omega_{L4}^4\ldots\Big)\,.\end{aligned} \tag{79}$$

The hyperpolarizability dispersion coefficients A, B, B', C, C', C'' etc. can be calculated from the coefficients $D(l,m,n)$ of the Taylor expansion introduced in Eqs. (35) and (66). The required expressions are found by equating the coefficients for the individual frequency powers $\omega_1^l\omega_2^m\omega_3^n$ in the two expansions and were derived in Ref. [33]. In analogy to the parallel isotropic average of the hyperpolarizability, we introduce the

parallel isotropic averages of the dispersion coefficients,

$$D_{||}(l,m,n) \;=\; \frac{1}{15}\sum_{\xi\eta}\Big\{D_{\xi\eta\eta\xi}(l,m,n)+D_{\xi\eta\xi\eta}(l,m,n)+D_{\xi\xi\eta\eta}(l,m,n)\Big\}, \tag{80}$$

with $\xi,\eta = x,y,z$. With the $D_{||}(l,m,n)$ coefficients f.x. A, B, and B' can be calculated as:

$$A \;=\; \frac{1}{2\gamma_0}\,D_{||}(2,0,0) \quad , \tag{81}$$

$$B \;=\; \frac{1}{4\gamma_0}D_{||}(4,0,0) \quad , \tag{82}$$

$$B' \;=\; \frac{1}{4\gamma_0}\Big(D_{||}(2,1,1)-4D_{||}(4,0,0)\Big) \quad . \tag{83}$$

Expressions for the sixth- through tenth-order coefficients are given in the Appendix. In ESHG experiments with the optical field polarized perpendicular to the static electric field, the measured second hyperpolarizability is: [13]

$$\gamma_\perp \;=\; \frac{1}{15}\sum_{\xi\eta}\Big\{2\gamma_{\eta\xi\xi\eta}-3\gamma_{\xi\eta\xi\eta}+2\gamma_{\xi\xi\eta\eta}\Big\}, \qquad\qquad \xi,\eta = x,y,z. \tag{84}$$

The component $\gamma_\perp$ is also related to the second hyperpolarizability measured in dc-Kerr experiments

$$\gamma_K \;=\; \frac{3}{2}\Big(\gamma_{||}-\gamma_\perp\Big) \tag{85}$$

To obtain for $\gamma_\perp$ and γ_K compact dispersion formulas similar as Eq. (79) for $\gamma_{||}$, these hyperpolarizability components must be written as sums of tensor components which are irreducibel with respect to the permutational symmetry of the operator indices and frequency arguments:

$$\gamma_\perp \;=\; \frac{1}{3}\gamma_{||}+\frac{2}{3}\gamma_{ms} \quad , \tag{86}$$

$$\gamma_K \;=\; \gamma_{||}-\gamma_{ms} \quad , \tag{87}$$

with

$$\gamma_{ms} = \frac{1}{6}\sum_{\xi\eta}\Big\{\gamma_{\eta\xi\xi\eta} - 2\gamma_{\xi\eta\xi\eta} + \gamma_{\xi\xi\eta\eta}\Big\}, \qquad \xi,\eta = x,y,z. \quad (88)$$

The index ms indicates that γ_{ms} transforms according to the mixed symmetry representation of the symmetric Group S_4 [33]. γ_{ms} is an irreducible tensor component which describes a deviation from Kleinman symmetry [34]. It vanishs in the static limit and for third harmonic generation ($\omega_1 = \omega_2 = \omega_3$). Up to sixth order in the frequency arguments it can be expanded as [33]:

$$\begin{aligned}\gamma_{ms}(\omega_0;\omega_1,\omega_2,\omega_3) &= \gamma_{||}(0)\Big(A_{ms}\omega_{M2}^2 + B_{ms}\omega_{M2}^2\omega_{L2}^2 + B'_{ms}\omega_{M4}^4 \quad (89)\\ &\quad + C_{ms}\omega_{M2}^2\omega_{L2}^4 + C'_{ms}\omega_{M4}^4\omega_{L2}^2 + C''_{ms}\omega_{M2}^2\omega_{L4}^4 + \ldots\Big)\ ,\end{aligned}$$

with the mixed-symmetry effective frequencies ω_{M2}^2 and ω_{M4}^4 defined as:

$$\omega_{M2}^2 = (\omega_0-\omega_1)(\omega_2-\omega_3) + (\omega_0-\omega_3)(\omega_2-\omega_1) \quad (90)$$

$$\begin{aligned}\omega_{M4}^4 &= -3\Big[(\omega_0^2\omega_1 - \omega_1^2\omega_0)(\omega_2-\omega_3) + (\omega_0-\omega_1)(\omega_2^2\omega_3 - \omega_3^2\omega_2) \quad (91)\\ &\quad + (\omega_0^2\omega_3 - \omega_3^2\omega_0)(\omega_2-\omega_1) + (\omega_0-\omega_3)(\omega_2^2\omega_1 - \omega_1^2\omega_2)\Big]\end{aligned}$$

We note that ω_{M4}^4 vanishs if two of the four the frequency arguments ω_0, ω_1, ω_2, ω_3 become zero. For the case that three frequency arguments are equal (third harmonic generation) both mixed-symmetry effective frequencies ω_{M2}^2 and ω_{M4}^4 vanish. The coefficients A_{ms}, B_{ms}, B'_{ms}, etc. can again be calculated from the coefficients $D(l,m,n)$ of the Taylor expansion in ω_1, ω_2, ω_3. Explicite expressions for the dispersion coefficients up to sixth order were derived in Ref. [33] and are listed in the Appendix. The approach outlined in Eqs. (35) – (89) has been implemented for the calculation of dispersion coefficients for cubic response functions for the coupled cluster model hierachy CCS, CC2 and CCSD into the coupled cluster response code described in Refs. [22–24, 29, 35–41].

4 Dispersion coefficients for the second hyperpolarizability of methane

The expressions (62) – (89) have been applied to calculate dispersion coefficients for the isotropic components of the second hyperpolarizability of methane using the three coupled cluster models CCS, CC2 and CCSD and five different basis sets taken from the series of correlation consistent basis sets developed by Dunning and coworkers [42]. The calculations were performed at the experimental equilibrium distance $r_{\mathrm{CH}} = 2.052$ a.u. [43, 44] For all three coupled cluster models we employed the d-aug-cc-pVDZ, t-aug-cc-pVDZ and d-aug-cc-pVTZ basis sets, which were selected to obtain basis set saturation to different levels of accuracy. The d-aug-cc-pVDZ and t-aug-cc-pVDZ basis sets do not contain f functions at the C atom and no d functions for H, but the t-aug-cc-pVDZ basis contains many diffuse functions. The d-aug-cc-pVTZ basis contains such polarization functions with higher angular momenta and the exponents of its most diffusest functions are intermediate between those in the d-aug-cc-pVDZ and t-aug-cc-pVDZ basis. This basis is therefore expected to provide a balanced compromise between diffusenes and polarization level. For the CCSD calculations we included in addition the t-aug-cc-pVTZ and the d-aug-cc-pVQZ basis sets to test saturation towards an improved description of the valence and diffuse region. The d-aug-cc-pVQZ basis comprises for methane 353 contracted functions and includes 3 g functions for the C atom and 3 f functions for H. We expect this basis to give results of benchmark quality near to the one-particle basis set limit. In a recent investigation of the second hyperpolarizabilities of Ne, Ar, N_2 and CH_4 [45] the d-aug-cc-pVQZ basis was employed to caculate the static hyperpolarizability of CH_4, which was then combined with dispersion curves for four different optical processes calculated pointwise at 6 frequencies using the t-aug-cc-pVTZ basis. Due to the large computational costs, a pointwise calculation of dispersion curves with the d-aug-cc-pVQZ basis was not feasible. The analytic calculation of the dispersion coefficients reduces the computational costs significantly if the dispersion expansion can be truncated in low order. The A and B coefficients for example can be calculated with approximately the same

order	THG	ESHG	DFWM	Kerr
0	2.3782(3)	2.3782(3)	2.3782(3)	2.3782(3)
2	2.1486(5)	1.0743(5)	7.1619(4)	3.5810(4)
4	1.4148(7)	3.5673(6)	1.6258(6)	3.9637(5)
6	8.4389(8)	1.0639(8)	3.4110(7)	3.8291(6)
8	4.8816(10)	3.0270(9)	7.0106(8)	3.4179(7)
10	2.8113(12)	8.4138(10)	1.4398(10)	2.8965(8)

Table 1: Coefficients for $\gamma_{||}(\omega)$ for third harmonic generation (THG), degenerate four wave mixing (DFWM), electric field induced second harmonic generation (ESHG), and Kerr effect in methane at the experimental geometry $r_{\mathrm{CH}} = 2.052$ a.u. A CCSD wavefunction and the t-aug-cc-pVDZ basis were used. (Results given in atomic units, the number in parentheses indicate powers of ten.)

computational costs as for one frequency-dependent calculation for the electric field induced second harmonic generation (ESHG) process. This made it possible to calculate Taylor and Padé approximations to the d-aug-cc-pVQZ dispersion curves which are correct through fourth order in the optical frequencies.

4.1 Convergence with the order of the expansion

First, we examine for a fixed basis set and a fixed wavefunction model the convergence of truncated Taylor expansions and Padé approximants with the order of the dispersion coefficients. In Table 1 we compiled for the t-aug-cc-pVDZ basis set and a CCSD wavefunction the coefficients up to tenth order for the parallel isotropic average $\gamma_{||}$ for THG, ESHG, DFWM and dc-Kerr effect. From the tabulated coefficients we calculated the Taylor approximations of order 2 through 10 for two wavelength, 671.5 nm and 476.5 nm. The first wavelength has been chosen intermediate between the typical experimental wavelengths 632.8 and 694.3 nm, used in many dc-Kerr, THG and ESHG experiments. The second wavelength

is the shortest which has been used in ESHG measurements for methane and has been chosen as representative for the high-frequency limit of the usual experimental frequency range. The results are listed in Table 2 together with the results obtained with diagonal Padé approximants [46] which are correct through the same order in the frequency arguments and the series limits which were calculated using the implementation for the frequency-dependent response functions.

The convergence rate of the Taylor expansion and the series of diagonal Padé approximants is in the normal dispersion region determined by how close the frequency argument is to the first pole in the hyperpolarizability. For the dc-Kerr effect this occurs when ω equals the first dipole-allowed transition energy $\Delta\varepsilon_{01}$; for ESHG and THG the first pole occurs at $\omega = \Delta\varepsilon_{01}/2$ and $\omega = \Delta\varepsilon_{01}/3$, respectively. For degenerate four wave mixing the first pole occurs usually when ω equals half the transition energy for the first two-photon dipole-allowed transition.

The differences in the positions for the first poles are distinctly reflected by the different convergence rates for the four non-linear optical processes: For both frequencies $\gamma_{||}$ for the dc-Kerr effect converges very fast. Already the second-order Taylor approximations obtained from only γ_0 and A are within 1% (671.5 nm) and 1.5% (476.5 nm) of the series limit. The error is reduced by about a factor of two if instead the [0,1] Padé approximant is used, which is also calculated using only γ_0 and A. With the [1,1] Padé approximant, calculated from γ_0 and the A and B coefficients, the error is reduced to less than 0.1%. For degenerate four wave mixing already a fourth-order Taylor approximation is needed to get $\gamma_{||}^{DFWM}(\omega)$ at the two frequencies correct within 1%. Again the errors are drastically reduced if instead a [1,1] Padé approximant is used, which can be obtained from the same dispersion coeffcients. The convergence is again somewhat slower for the ESHG process: at the higher of the two frequencies (476.5 nm) already a sixth-order Taylor expansion would be needed to get the hyperpolarizability correct within 1%, alternatively this accuracy can be obtained using the [1,1] Padé approximant which requires only the dispersion coefficients up to fourth order, i. e. the A and B coefficients.

	$\gamma_{\|\|}$ at 671.5 nm (0.0678531 a.u.)							
	Kerr		DFWM		ESHG		THG	
order/approximant	Taylor	Padé	Taylor	Padé	Taylor	Padé	Taylor	Padé
2 / [0,1]	2543.08	2555.36	2707.95	2761.02	2872.82	3002.69	3367.42	4071.93
4 / [1,1]	2551.48	2551.93	2742.41	2746.43	2948.43	2962.08	3667.33	3797.81
6 / [1,2]	2551.85	2551.87	2745.74	2746.08	2958.82	2960.37	3749.69	3778.96
8 / [2,2]	2551.87	2551.87	2746.05	2746.09	2960.18	2960.38	3771.62	3779.46
10 / [2,3]	2551.87	2551.87	2746.08	2746.09	2960.35	2960.38	3777.44	3779.55
∞	2551.87		2746.09		2960.38		3779.56	

	$\gamma_{\|\|}$ at 476.5 nm (0.0956209 a.u.)							
	Kerr		DFWM		ESHG		THG	
order/approximant	Taylor	Padé	Taylor	Padé	Taylor	Padé	Taylor	Padé
2 / [0,1]	2705.63	2757.90	3033.05	3281.87	3360.47	4051.64	4342.73	13672.1
4 / [1,1]	2738.76	2742.50	3168.97	3204.57	3658.70	3788.73	5525.55	7315.26
6 / [1,2]	2741.69	2741.95	3195.04	3201.01	3740.03	3768.23	6170.61	6861.30
8 / [2,2]	2741.93	2741.95	3199.94	3201.07	3761.18	3768.36	6511.79	6884.80
10 / [2,3]	2741.95	2741.95	3200.86	3201.08	3766.56	3768.36	6691.45	6894.48
∞	2741.95		3201.08		3768.36		6896.81	

Table 2: Convergence of the Taylor series and the series of diagonal Padé approximants (CCSD response, t-aug-cc-pVDZ basis). The "inifinite" order results were calculated using the implementation for the frequency-dependent response function.

A similar convergence is found for the third harmonic generation process at the lower of the two frequencies, 671.5 nm. At the higher frequency, 476.5 nm, the Taylor approximations for the third harmonic generation hyperpolarizability converge only very slowly, even with a tenth-order Taylor approximation a one-percent accuracy is not obtained. This accuracy, however, is still achieved with a [1,2] Padé approximant calculated from the dispersion coefficients up to sixth order.

The much better performance of the diagonal Padé approximants compared to the Taylor expansion is not unexpected since similar convergence trends were found previously for the expansion of the first hyperpolarizabilities $\beta_{||}^{SHG}(\omega)$ and $\beta_{||}^{EOPE}(\omega)$ of ammonia. The good performance of Padé approximants for the approximation of dispersion curves for frequency-dependent properties is also well known from linear polarizabilities [47]. The present results are promising for further applications to other molecules. A truncation error of 1% in the electronic hyperpolarizability will be acceptable for most pratical applications. To achieve an overall accuracy of 1% in *ab initio* calculations would require very large basis sets, the inclusion of connected triples and a very accurate treatment of vibrational effects — a challenging task no yet met for polyatomic systems. Also, only for the most accurate ESHG and dc-Kerr measurements [4, 9, 11–14] the uncertainities are less than 1%; for THG, DFWM, ac-Kerr and CARS measurements the uncertainities are often larger than 10% [13, 48, 49].

4.2 Convergence with the basis set

In Table 3 we have listed the results of a basis set and correlation study for the hyperpolarizability dispersion coefficients. In a previous investigation of the basis set effects on the dispersion coefficients for the first hyperpolarizability β of ammonia [22] we found quite different trends for the static hyperpolarizability and for the dispersion coefficients. While the static hyperpolarizability was very sensitive to the inclusion of diffuse functions, the dispersion coefficients remained almost unchanged on augmentation of the basis set with additional diffuse functions, but the results obtained with the CC2 and CCSD models, which include dynamic electron correlation, showed large changes with an increase of the

polarization level from double zeta to triple zeta basis sets. This basis set trend for the hyperpolarizability dispersion coefficients is corroborated by the CC2 and CCSD results for the second hyperpolarizability of methane, although the effects are less exaggerated than for $\beta_{||}$ of ammonia. For methane also the static hyperpolarizability is sensitive to the polarization level of the basis set.

The dispersion coefficients for the mixed-symmetry component γ_{ms} which describes the deviation from Kleinman symmetry are for methane more than an order of magnitude smaller than coefficients of the same order in the frequencies for $\gamma_{||}$. Their varations with basis sets and wavefunction models are, however, of comparable absolute size and give rise to very large relative changes for the mixed-symmetry dispersion coefficients.

From a basis set study at the CCSD level for the static hyperpolarizability we concluded in Ref. [45] that the d-aug-cc-pVQZ results for γ_0 is converged within $1-2\%$ to the CCSD basis set limit. The small variations for the A, B and B' coefficients between the two triple zeta basis sets and the d-aug-cc-pVQZ basis, listed in Table 4, indicate that also for the first dispersion coefficients the remaining basis set error in d-aug-cc-pVQZ basis is only of the order of $1-2\%$. This corroborates that the results for the frequency-dependent hyperpolarizabilities obtained in Ref. [45] by a combination of the static d-aug-cc-pVQZ hyperpolarizability with dispersion curves calculated using the smaller t-aug-cc-pVTZ basis set are close to the CCSD basis set limit.

	CCS			CC2			CCSD		
	daD	taD	daT	daD	taD	daT	daD	taD	daT
γ_0[a]	2132.9	2174.7	2227.2	2526.1	2580.5	2555.5	2327.6	2378.2	2363.5
A	6.6855	6.6706	6.6614	7.7064	7.6795	7.5063	7.5573	7.5287	7.3776
B	33.521	33.349	32.985	43.532	43.232	41.048	41.976	41.667	39.754
B'	−2.4211	−2.4097	−2.4183	−4.8706	−4.7963	−4.3894	−4.3070	−4.2404	−3.8940
C	148.05	146.85	143.78	214.46	212.31	195.93	203.41	201.26	187.06
C'	25.768	25.472	24.542	37.662	37.141	33.708	35.624	35.112	32.090
C''	−57.356	−56.599	−54.989	−103.92	−101.98	−91.363	−93.170	−91.386	−82.401
D	606.59	600.10	582.33	975.58	963.29	865.45	910.20	898.24	814.60
D'	−570.96	−561.66	−542.10	−1080.1	−1057.7	−930.69	−958.13	−937.87	−832.83
D''	197.62	195.13	186.71	333.75	308.48	288.92	305.80	300.87	267.12
D'''	337.41	332.87	319.97	549.57	540.80	480.52	511.61	503.18	451.30
A_{ms}	−0.2320	−0.1763	0.0077	−0.2320	−0.3919	−0.1550	−0.4436	−0.3696	−0.1307
B_{ms}	0.1123	0.4387	1.3481	0.1123	−1.1510	0.1251	−1.3517	−0.8670	0.4147
B'_{ms}	−0.8197	−0.7818	−0.6555	−0.8197	−1.1717	−0.9662	−1.1536	−1.1061	−0.9097
C_{ms}	11.814	13.008	15.632	11.814	7.2571	10.919	6.8975	8.9250	12.687
C'_{ms}	−8.5246	−8.1038	−6.8990	−8.5243	−13.753	−11.271	−13.263	−12.672	−10.375
C''_{ms}	0.2520	0.1024	−0.3894	0.2520	−1.5512	−2.0347	−0.8649	−1.0837	−1.5779

Table 3: Comparison of the dispersion coefficients for $\gamma_{||}$ and γ_{ms} for different basis sets and coupled cluster models.

4.3 The effect of electron correlation on the dispersion coefficients

If we compare results obtained with the same basis sets with the three coupled cluster models CCS, CC2 and CCSD, we find similar trends as observed in Refs. [22, 45]: The CCS model underestimates strongly the static hyperpolarizabilities and their dispersion. The results are usually of similar quality as those obtained with SCF. For methane, the CCS static hyperpolarizabilities are intermediate between the SCF and the CCSD values obtained in the same basis set. In Ref. [45] the CCS percentage dispersion contribution to the third harmonic generation (THG) hyperpolarizability of methane was found to be slightly smaller than for SCF, both underestimating significantly the dispersion obtained with the correlated coupled cluster models CC2 and CCSD. Accordingly the CCS dispersion coefficients listed in Table 3 are substantially smaller than the respective CCSD results obtained in the same basis sets.

The CC2 model performes very different for static hyperpolarizabilities and for their dispersion. For methane, CC2 overestimates γ_0 by a similar amount as it is underestimated by CCS, thus giving no improvement in accuracy relative to the uncorrelated methods CCS and SCF. In contrast to this, the CC2 dispersion coefficients listed in Table 3 are by a factor of 3 – 8 closer to the CCSD values than the respective CCS results. The dispersion coefficients should be sensitive to the lowest dipole-allowed excitation energy, which determines the position of the first pole in the dispersion curve. The substantial improvements in accuracy for the dispersion coefficients are thus consistent with the good performance of CC2 for excitation energies [35, 37, 50].

The CCSD model gives for static and frequency-dependent hyperpolarizabilities usually results close to the experimental values, provided that the effects of vibrational averaging and the pure vibrational contributions have been accounted for. Zero point vibrational corrections for the static and the electric field induced second harmonic generation (ESHG) hyperpolarizability of methane have recently been calculated by Bishop and Sauer using SCF and MCSCF wavefunctions [51].

	$\gamma_0^e(R_e)$ [a]	$\bar{\gamma}_0{}^e$ [b]	A [c]	B [c]	B' [c]	A_{ms}	B_{ms}	B'_{ms}
CCS d-aug-cc-pVTZ	2227	2512	6.661	32.99	−2.42	−0.01	1.35	−0.66
CC2 d-aug-cc-pVTZ	2555	2840	7.506	41.05	−4.39	−0.16	0.13	−0.97
CCSD d-aug-cc-pVTZ	2364	2649	7.378 (7.9)	39.75 (43)	−3.89	−0.13	0.41	−0.91
CCSD t-aug-cc-pVTZ	2365	2650	7.378 (7.9)	39.75 (43)	−3.90	−0.13	0.43	−0.91
CCSD d-aug-cc-pVQZ	2330	2615	7.338 (7.9)	39.30 (44)	−3.84	−0.06	0.46	−1.34
SCF [d]	1882	2186	7.049 (7.73)	36.68 (44.94)				
MCSCF [d]	2152	2438	7.057 (7.61)	36.85 (43.81)				
Experiment Ref. [14]		2607[e]	(7.38)[e]	(100.6)[e]		(-0.16 ± 0.014)[e]		
Experiment Ref. [53]		2590[f]	(7.46)[f]	(95.08)[f]				

Table 4: Comparison of various *ab initio* results and experimental estimates for the dispersion coefficients of the electronic hyperpolarizabilities $\gamma^e_{||}$ and γ^e_{ms} of methane. (All results in atomic units. Results for the dispersion coefficients refer to single point calculations at the equilibrium geometry. Where available, dispersion coefficients for the vibrational average are given in parentheses.)

Combining [52] the zero point vibrational corrections of Ref. [51] with the CCSD results obtained in the t-aug-cc-pVTZ and d-aug-cc-pVQZ basis sets we obtained the estimates for the ZPV corrected γ_0, A and B coefficients listed in Table 4. An experimental estimate for γ_0, A, and B has been derived by Shelton by fitting the results of ESHG measurements to the expresssion $\gamma(\omega_{L2}^2) = \gamma_0(1 + A\omega_{L2}^2 + B\omega_{L2}^4)$. This fit was later repeated by Bishop and Pipin [53] after subtraction of *ab initio* calculated results for the pure vibrational contribution to the hyperpolarizability from the orignal experimental values. These fits did not include higher powers of ω_{L2} than ω_{L2}^4. The results, in particular the B coefficient, obtained in this way are affected by higher-order terms. The contributions from the C and higher-order coefficients to the ESHG hyperpolarizability are substantial for wavelengths shorter than 671.5 nm ($\omega_{L2}^2 > 0.03$ a.u.), when a polynomial (Taylor) expansion is used, as follows from the discussion of the convergence of the dispersion expansion. The increasing importance of the sixth- and higher-order terms with increasing frequency can also be seen from the difference between the fourth-order Taylor approximation and the [1,1] Padé approximant for the CCSD hyperpolarizability in the d-aug-cc-pVQZ basis, which are both plotted in Figure 1. The dispersion coefficients obtained from the two fits to the experimental ESHG data are thus not strictly comparable with analytically calculated dispersion coefficients, as have been calculated in the present work, or with results obtained by least square fits to higher polynomials in ω_{L2} as done by Bishop and Sauer in Ref. [51] for the SCF and MCSCF results included in Table 4. Nevertheless, the *ab initio* calculated A coefficients agree with the values deduced from the experimental ESHG data within $\approx 10\%$. The B coefficients derived by Shelton and by Bishop and Pipin from their fits to the experimental ESHG data are about a factor of $2 - 2.5$ larger than the *ab initio* calculated values, which is likely an effect of the inclusion of higher-order terms in the "experimental" estimates for B, since the variations of B with basis set, *ab initio* method and zero point vibrational correction are only small. This is also corroborated by the closeness (within $1 - 3\%$) of the CCSD dispersion curves to the results of the ESHG experiments of Refs. [4, 54] and to the dispersion curve fitted to this data (see Fig.

Figure 1: The ESHG hyperpolarizability of CH_4.

1). Compared with the CCSD results, the MCSCF values for γ_0, A and B obtained in Ref. [51] are close the uncorrelated SCF results in the same basis set. Both underestimate the static hyperpolarizability and the dispersion (cmp. Fig. 1).

A crude experimental estimate for the A_{ms} coefficient is obtained from Sheltons fit of ESHG measurements for the hyperpolarizability ratio $\gamma_{||}/\gamma_{\perp}$ to the expression $3(1+A^*\omega_{L2}^2)$. Using the dispersion expansions (79) and (89), we obtain for the ratio $\gamma_{||}/\gamma_{\perp}$ up to second order in the frequencies the expansion

$$\frac{\gamma_{||}}{\gamma_{\perp}} \;=\; 3(1-2A_{ms}\omega_{M2}^2+\ldots) \quad . \tag{92}$$

For ESHG the effective frequency ω_{M2}^2 is $-3\omega^2 = \omega_{L2}^2/2$, thus $A^{*,\mathrm{ESHG}} = A_{ms}$. Since the fit made by Shelton did not include higher than second powers of ω_{L2}^2, the experimental estimate for A_{ms} is similar as the B

coefficient affected by higher-order terms. Nevertheless, this estimate agrees in sign and in the order of magnitude with the CCSD results in the best basis sets. The agreement is as good as can be expected taking into account the smallness of A_{ms} and its sensitivity to basis variations and correlation treatment. To our knowledge this is the first *ab intio* calculation for the frequency-dependence of the hyperpolarizability ratio $\gamma_{||}/\gamma_{\perp}$ for a many-electron system. The only other *ab intio* calculation for $\gamma_{||}/\gamma_{\perp}$, we are aware of, are CI-Hylleraas calculations for helium, H_2 and D_2 by Bishop and Pipin [55] and Bishop et al. [56].

5 Conclusions

We have derived and implemented analytic dispersion coefficients for second hyperpolarizabilities for the coupled cluster models CCS, CC2 and CCSD. The dispersion coefficients are defined through a power series expansion of the cubic response function in its frequency arguments and are thus applicable to general frequency-dependent fourth-order properties and are independent of the non-linear optical process. For the irreducible tensor components of the second hyperpolarizability γ, the dispersion can be expressed in a compact form using permutation symmetry-adapted linear combinations of the optical frequencies. In an application to the second hyperpolarizability of methane we find good convergence of the Taylor expansion in the typical experimental frequency range for the dc-Kerr effect, DFWM and ESHG. For third harmonic generation a good convergence of the Taylor expansion is only found for small frequencies. With Padé approximants the convergence of the dispersion expansion is improved significantly for all four investigated optical processes and the application range of the dispersion expansion is considerably extended to higher frequencies. For many molecules, in particular such with the first transition frequencies lying as high as in methane, the first two dispersion coefficients will be sufficient to obtain the dispersion curves within a one percent accuracy in the usual experimental frequency range, provided that the dispersion curve is calculated using a [1,1] Padé approximant.

A comparison of the dispersion coefficients obtained with different

basis sets and the coupled cluster models CCS, CC2 and CCSD shows that the dispersion coefficients are as sensitive to the choice of the basis set and the correlation treatment as are the static hyperpolarizabilities. Similar as in a previous study on the dispersion coefficients for the first hyperpolarizability of ammonia, we find that the CC2 model performs considerably better for dispersion coefficients than it does for static hyperpolarizabilities.

Our results indicate that dispersion coefficients obtained from fits of pointwise given frequency-dependent hyperpolarizabilities to low order polynomials can be strongly affected by the inclusion of high-order terms. A and B coefficients derived from a least square fit of experimental frequency-dependent hyperpolarizibility data to a quadratic function in ω_i^2 are therefore not strictly comparable to dispersion coefficients calculated by analytical differentiation or from fits to higher-order polynomials. *Ab initio* calculated dispersion curves should therefore be compared with the original frequency-dependent experimental data.

The present study demonstrates that the analytic calculation of hyperpolarizability dispersion coefficients provides an efficient alternative to the pointwise calculation of dispersion curves. The dispersion coefficients provide additional insight into non-linear optical properties and are transferable between the various optical processes, also to processes not investigated here as for example the ac-Kerr effect or coherent anti-Stokes Raman scattering (CARS), which depend on two independent laser frequencies and would be expensive to study with calculations explictly frequency-dependent calculations.

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A Formulas for the sixth- through tenth-order dispersion coefficients for $\gamma_{||}$ and γ_{ms}

The coefficients for the sixth- through tenth-order terms of the dispersion expansion Eq. (75) for $\gamma_{||}$ are found as:

$$C = A_{3,0,0} = \frac{1}{8\gamma_{||}(0)} D_{||}(6,0,0) \tag{93}$$

$$C' = A_{0,2,0} = \frac{1}{9\gamma_{||}(0)} \Big(D_{||}(4,2,0) - 6D_{||}(6,0,0) \Big) \tag{94}$$

$$C'' = A_{1,0,1} = \frac{1}{8\gamma_{||}(0)} \Big(D_{||}(4,1,1) - 2D_{||}(4,2,0) + 3D_{||}(6,0,0) \Big) \tag{95}$$

$$D = A_{4,0,0} = \frac{1}{16\gamma_{||}(0)} D_{||}(8,0,0) \tag{96}$$

$$D' = A_{2,0,1} = \frac{1}{16\gamma_{||}(0)} \Big(D_{||}(6,1,1) - 2D_{||}(6,2,0) + D_{||}(7,1,0) \Big) \tag{97}$$

$$D'' = A_{0,0,2} = \frac{1}{16\gamma_{||}(0)} \Big(D_{||}(4,2,2) - D_{||}(4,3,1) - D_{||}(5,2,1) + 4D_{||}(7,1,0) \Big) \tag{98}$$

$$D''' = A_{1,2,0} = \frac{1}{18\gamma_{||}(0)} \Big(D_{||}(6,2,0) - 10D_{||}(8,0,0) \Big) \tag{99}$$

$$E = A_{5,0,0} = \frac{1}{32\gamma_{||}(0)} D_{||}(10,0,0) \tag{100}$$

$$E' = A_{3,0,1} = \frac{1}{32\gamma_{||}(0)} \Big(D_{||}(8,1,1) - 2D_{||}(10,2,0) + D_{||}(9,1,0) \Big) \tag{101}$$

$$E'' = A_{1,0,2} = \frac{1}{32\gamma_{||}(0)} \Big(D_{||}(6,2,2) - 2D_{||}(6,3,1) + 3D_{||}(8,1,1) + 10D_{||}(8,2,0) - 29D_{||}(9,1,0) \Big) \tag{102}$$

$$E''' = A_{2,2,0} = \frac{1}{36\gamma_{||}(0)}\Big(D_{||}(8,2,0) - 15D_{||}(10,0,0)\Big) \tag{103}$$

$$E'''' = A_{0,2,1} = \frac{1}{36\gamma_{||}(0)}\Big(D_{||}(6,3,1) - 9D_{||}(8,1,1) - 14D_{||}(8,2,0) + 61D_{||}(9,1,0)\Big) \tag{104}$$

The dispersion coefficients for γ_{ms} are obtained as:

$$A_{ms} = \frac{1}{\gamma_{||}(0)} D_{ms}(2,0,0) \quad , \tag{105}$$

$$B_{ms} = \frac{1}{2\gamma_{||}(0)} D_{ms}(4,0,0) \quad , \tag{106}$$

$$B'_{ms} = -\frac{1}{9\gamma_{||}(0)}\Big(D_{ms}(3,1,0) + D_{ms}(4,0,0)\Big) \quad , \tag{107}$$

$$C_{ms} = \frac{1}{4\gamma_{||}(0)} D_{ms}(6,0,0) \quad , \tag{108}$$

$$C'_{ms} = -\frac{1}{18\gamma_{||}(0)} D_{ms}(5,1,0) \quad , \tag{109}$$

$$C''_{ms} = \frac{1}{24\gamma_{||}(0)}\Big(3D_{||}(3,2,1) - 2D_{||}(5,1,0)\Big) \quad , \tag{110}$$

with the intermediates $D_{ms}(l,m,n)$ defined as:

$$D_{ms}(l,m,n) = \frac{1}{6}\sum_{\xi\eta}\Big\{D_{\eta\xi\xi\eta}(l,m,n) - 2D_{\xi\eta\xi\eta}(l,m,n) + D_{\xi\xi\eta\eta}(l,m,n)\Big\}, \tag{111}$$

where the summation is over $\xi, \eta = x, y, z$.

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