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Dispersion coefficients for first hyperpolarizabilities using coupled cluster quadratic response theory*

Christof Hättig, Poul Jørgensen

Department of Chemistry, University of Aarhus, DK-8000 Aarhus C, Denmark

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Abstract. The frequency dependence of third-order properties can in the normal dispersion region be expanded in a Taylor series in the frequency arguments. The dispersion coefficients thus obtained provide an efficient way of expressing the dispersion of frequency-dependent properties and are transferable between different optical processes. We derive analytic expressions for the dispersion coefficients of third-order properties in coupled cluster quadratic response theory and report an implementation for the three coupled cluster models CCS, CC2, and CCSD. Calculations are performed for the first hyperpolarizability of the NH_3 molecule. The convergence of the dispersion expansion with the order of the coefficients is examined and we find good convergence up to about half the frequency at which the first pole in the hyperpolarizability occurs. Padé approximants improve the convergence dramatically and extend the application range of the dispersion expansion to frequencies close to the first pole. The sensitivity of the dispersion coefficients on the dynamic correlation treatment and on the choice of the one-electron basis set is investigated. The results demonstrate that, contrary to presumptions in the literature, the dispersion coefficients are sensitive to basis set effects and correlation treatment similar to the static hyperpolarizabilities.

Key words: Coupled cluster response theory – Hyperpolarizabilities – Frequency-dependence – Ammonia – Dispersion coefficients

1 Introduction

Power series expansions of frequency-dependent hyperpolarizabilities have in recent years become a widely used tool for comparison of experimental or ab initio calculated hyperpolarizabilities for different optical proccesses [1–5]. The most commonly used ansatz for interpolation of dispersion curves and for the extrapolation of measured frequency-dependent hyperpolarizabilities to the static limit [1–7] are even power series in the frequencies. Such expansions have also been used to compare dispersion curves calculated with different ab initio methods [8]. The usefulness of the dispersion expansions is emphasized by the fact that a single, process-independent [9] second-order coefficient is obtained for the diagonal components of the hyperpolarizability $\beta_{\alpha\alpha\alpha}$ and for the vector component parallel to the molecular dipole moment $\beta_{\|}$ [10]:

$$\beta_{\|}(\omega_1;\omega_2,\omega_3) = \beta_{\|}(0)\bigl(1 + A(\omega_1^2+\omega_2^2+\omega_3^2) + \mathcal{O}(\omega_i^4)\bigr) \tag{1}$$

A sum-over-states expression for the coefficient A for the expansion of the diagonal components $\beta_{\alpha\alpha\alpha}$ was derived by Bishop and Kee [11], but an implementation has not been reported. The usual approach in ab initio calculations of dispersion coefficients has been to extract the coefficients from a polynomial fit to pointwise calculated frequency-dependent hyperpolarizabilities. Despite the inefficiency and the numerical difficulties of such an approach [6, 8], no ab initio implementation has yet been reported for analytic dispersion coefficients for frequency-dependent first hyperpolarizabilities.

Recently, we have reported the implementation of the quadratic response functions for the coupled cluster model hierarchy CCS, CC2, and CCSD [12]. The implementation is based on the calculation of frequency-dependent properties as derivatives of a variational quasienergy Lagrangian. The $2n+1$ and $2n+2$ rules [13, 14] are employed to calculate first hyperpolarizabilities without solving higher than first-order response equations. In the present publication we extend this work [12] to the analytic calculation of dispersion coefficients for quadratic response properties. We define the dispersion coefficients by a Taylor expansion of the quadratic response function in its frequency arguments. Hence, this approach is applicable to all hyperpolarizability components and the coefficients are independent of specific

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*Dedicated to Prof. Dr. Wilfried Meyer on the occasion of his 60th birthday

Correspondence to: C. Hättig
e-mail: haettig@kemi.aau.dk

nonlinear optical processes. For the experimentally important vector components $\beta_{\|}$, $\beta_{\perp}$, and β_{K} we calculate, from the coefficients of the Taylor expansion, coefficients for more compact dispersion formulas similar to Eq. (1).

The generality of the power series expansion and the open-ended formulation of the dispersion formulas facilitate an alternative approach to the calculation of dispersion curves for hyperpolarizabilities complementary to the pointwise calculation of the frequency-dependent property. In particular, if dispersion curves are needed over a wide range of frequencies and for different optical processes, the calculation of the dispersion coefficients can be a cost-efficient alternative to repeated calculations for different optical processes and different frequencies. The explicit calculation of dispersion coefficients also introduces a flexibility in the accuracy with which the dispersion contribution is determined by the order in the optical frequencies through which the dispersion coefficients are calculated.

In the next section we derive a Taylor expansion of the coupled cluster quadratic response function in its frequency arguments. For the experimentally important vector components $\beta_{\|}$, $\beta_{\perp}$, and β_{K} we give explicit expressions for the A and higher-order coefficients in terms of the coefficients of the Taylor series. In Sect. 3 we apply the dispersion expansion to the calculation of first hyperpolarizabilities for the ammonia molecule. We test the convergence of the hyperpolarizabilities with respect to the order of the dispersion coefficients and investigate the sensitivity of the coefficients to basis sets and correlation treatment. The last section contains some concluding remarks.

2 Theory

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

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

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

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

where $\hat{H}^{X_j}$ are hermitian time- and field-independent one-electron operators and $\epsilon_j(\omega_j)$ are the associated field strengths for frequencies ω_j. The letter ϵ without index is in the following used as a shorthand notation for the set $\{\epsilon_j\}$ of field strengths. 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 quasi-energy $\mathscr{W}(t,\epsilon)$ is explicitly isolated [15, 16]:

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

$\hat{T}(t,\epsilon)$ is the field- and time-dependent cluster operator $\hat{T}(t,\epsilon) = \sum_\mu t_\mu(t,\epsilon)\hat{\tau}_\mu$ 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 RPA pole structure, is circumvented.

The cluster amplitudes $t_\mu(t,\epsilon)$ are expanded in the Fourier components of the applied perturbations and in orders of the perturbation strengths as:

$$t_\mu(t,\epsilon) = t_\mu^{(0)} + \sum_{n=1}^{\infty}\frac{1}{n!}\sum_{j_1}\cdots\sum_{j_n} t^{X_{j_1}\cdots X_{j_n}}(\omega_{j_1},\ldots,\omega_{j_n}) \times \prod_{m=1}^{n}\epsilon_{j_m}(\omega_{j_m})\mathrm{e}^{-\mathrm{i}\omega_{j_m}t} \tag{5}$$

The quasi-energy $\mathscr{W}$ and the time-dependent coupled cluster equations are determined by projecting the time-dependent Schrödinger equation

$$\left(\hat{H} - i\frac{d}{dt}\right)\left|\mathrm{CC}(t,\epsilon)\right\rangle = 0 \tag{6}$$

onto the Hartree-Fock reference $\langle\mathrm{HF}|$ and onto the bra states $\langle\mathrm{HF}|\hat{\tau}_\mu^\dagger\exp(-\hat{T})$:

$$\mathscr{W}(\epsilon,t) = \left\langle\mathrm{HF}\middle|\hat{H}(\epsilon,t)\exp(\hat{T})\middle|\mathrm{HF}\right\rangle \tag{7}$$

$$\left\langle\mathrm{HF}\middle|\hat{\tau}_\mu^\dagger\exp\big(-\hat{T}(t,\epsilon)\big)\hat{H}(t,\epsilon)\exp\big(\hat{T}(t,\epsilon)\big)\middle|\mathrm{HF}\right\rangle - i\frac{d}{dt}t_\mu(t,\epsilon) = 0 \tag{8}$$

The latter equation may be written in the shorthand form

$$e_\mu(t,\epsilon) - i\frac{d}{dt}t_\mu(t,\epsilon) = 0 \tag{9}$$

Frequency-dependent higher-order properties can be obtained either by expansion of expectation values or as derivatives of the quasi-energy with respect to the field strengths of the external perturbations. For nonvariational ab initio methods which do not satisfy the Hellman-Feynman theorem, the latter route is preferable, because it conserves the symmetry of the response functions with respect to permutations of the operators X_i together with the accompanied frequencies ω_i. To derive expressions for the derivatives of the coupled cluster quasi-energy we use a variational formulation which is obtained by combining the quasi-energy and the time-dependent coupled cluster equations to a quasi-energy Lagrangian:

$$L(t,\epsilon) = \mathscr{W}(t,\epsilon) + \sum_\mu \bar{t}_\mu\left(e_\mu(t,\epsilon) - i\frac{d}{dt}t_\mu\right) \tag{10}$$

The time-average of the quasi-energy Lagrangian

$$\{L(t,\epsilon)\}_T = \lim_{t_0\to\infty}\frac{1}{2t_0}\int_{-t_0}^{+t_0} L(t,\epsilon)\,dt \tag{11}$$

may now be required to be stationary with respect to the Fourier components of the cluster amplitudes and the Lagrangian multipliers [12, 16–18]:

$$\delta\{L(t,\epsilon)\}_T = 0 \tag{12}$$

Inserting the perturbation and Fourier expansion of the cluster amplitudes (5) and an analogous expansion of the Lagrangian multipliers into Eq. (12), this becomes a variational condition for the individual expansion coefficients. In zeroth-order one obtains the usual coupled cluster equations, $e^{(0)} = 0$, and the equations for the zeroth-order Lagrangian multipliers:

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

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

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

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

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

$$\xi^A + \left(\mathbf{A} - \omega\mathbf{1}\right)t^A(\omega) = 0 \tag{16}$$

$$\left(\eta^A + \mathbf{F}t^A(\omega)\right) + \bar{t}^A(\omega)\left(\mathbf{A} + \omega\mathbf{1}\right) = 0 \tag{17}$$

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

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

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

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

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

$$\langle\langle X_1; X_2, \ldots, X_n\rangle\rangle_{\omega_2,\ldots,\omega_n} = \left(\frac{d^n\{\frac{1}{2}L(t,\epsilon) + \frac{1}{2}L(t,\epsilon)^*\}_T}{d\epsilon_1(\omega_1)\cdots d\epsilon_n(\omega_n)}\right)_0 \tag{21}$$

As a consequence of the time-averaging of the quasi-energy 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 third order, Eq. (21) gives the quadratic response function:

$$\begin{aligned}\langle\langle A; B, C\rangle\rangle_{\omega_B,\omega_C} &= \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABC}\Big\{\tfrac{1}{6}\mathbf{G}t^A(\omega_A)t^B(\omega_B)t^C(\omega_C) \\ &\quad + \tfrac{1}{2}\bar{t}^A(\omega_A)\mathbf{B}t^B(\omega_B)t^C(\omega_C) \\ &\quad + \tfrac{1}{2}\mathbf{F}^A t^B(\omega_B)t^C(\omega_C) + \bar{t}^A(\omega_A)\mathbf{A}^B t^C(\omega_C)\Big\}\end{aligned} \tag{22}$$

with $\omega_A = -(\omega_B + \omega_C)$. The operator $\hat{P}^{ABC}$ symmetrizes with respect to permutations of the perturbation indices A, B, and C 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 four matrices $\mathbf{G}$, $\mathbf{B}$, $\mathbf{F}^X$, and $\mathbf{A}^X$ are defined as:

$$G_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial t_\mu \partial t_\nu \partial t_\gamma}\right)_0 \tag{23}$$

$$B_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial \bar{t}_\mu \partial t_\nu \partial t_\gamma}\right)_0 \tag{24}$$

$$F_{\mu\nu}^X = \left(\frac{\partial^3 L}{\partial \epsilon_X \partial t_\mu \partial t_\nu}\right)_0 \tag{25}$$

$$A_{\mu\nu}^X = \left(\frac{\partial^3 L}{\partial \epsilon_X \partial \bar{t}_\mu \partial t_\nu}\right)_0 \tag{26}$$

If the operators A, B, and C are components of the dipole operator, the quadratic response function is equal to minus the respective component of the first hyperpolarizability $\beta_{ABC}(\omega_A;\omega_B,\omega_C)$. An implementation of Eq. (22) for the coupled cluster model hierachy CCS, CC2, and CCSD has been reported in [12].

For a finite molecular or atomic system in its electronic ground state, the response function is analytic in its frequency arguments with the exceptions of the poles that occur when a frequency or a sum of frequencies becomes equal to an excitation energy. Hence, for frequencies below the first pole, quadratic response functions can be expanded in a power series in the frequency arguments. Because the frequencies ω_A, ω_B, and ω_C are related by the matching condition $\omega_A + \omega_B + \omega_C = 0$, first hyperpolarizabilities, or quadratic response properties in general, are functions of only two independent frequency variables, which may be chosen as ω_B and ω_C:

$$\beta_{ABC}(-\omega_B - \omega_C;\omega_B,\omega_C) = \sum_{n,m=0}^{\infty} \omega_B^n \omega_C^m D_{ABC}(n,m) \tag{27}$$

To derive computational tractable expressions for the dispersion coefficients $D_{ABC}(n,m)$ we need the power series expansion of the first-order responses of the cluster amplitudes and the Lagrangian multipliers in the frequencies. In [19] we have introduced the coupled cluster Cauchy vectors:

$$C^X(n) = \frac{1}{n!}\left(\frac{d^n t^X(\omega_X)}{d\omega_X^n}\right)_{\omega_X=0} = -\mathbf{A}^{-n-1}\xi^X \tag{28}$$

$$t^X(\omega_X) = \sum_{n=0}^{\infty} \omega_X^n C^X(n) \tag{29}$$

The Cauchy vectors for $n \geq 0$ are obtained by solution of a recursive set of linear equations, starting with the zeroth-order Cauchy vector $C^X(0)$ which is equal to the static limit of the first-order cluster amplitude response:

$$C^X(0) = t^X(0) \tag{30}$$

$$C^X(n) = \mathbf{A}^{-1}C^X(n-1) \tag{31}$$

The corresponding expansion for the first-order Lagrange multipliers is found as:

$$\bar{C}^X(n) = \frac{1}{n!}\left(\frac{d^n\bar{t}^X(\omega_X)}{d\omega_X}\right)_{\omega_X=0} \tag{32}$$

$$= (-1)^{n+1}\eta^X\mathbf{A}^{-n-1} + \sum_{m=0}^{n}(-1)^{m+1}\left(\mathbf{F}C^X(n-m)\right)\mathbf{A}^{-m-1} \tag{33}$$

$$\bar{t}^X(\omega_X) = \sum_{n=0}^{\infty}\omega_X^n\bar{C}^X(n) \tag{34}$$

As can be proven by induction, the $\bar{C}^X(n)$ vectors for $n \geq 0$ can be calculated by the recurrence relations:

$$\bar{C}^X(0) = \bar{t}^X(0) \tag{35}$$

$$\bar{C}^X(n) = -\left[\mathbf{F}C^X(n) + \bar{C}^X(n-1)\right]\mathbf{A}^{-1} \tag{36}$$

The matrices $\mathbf{G}$, $\mathbf{B}$, $\mathbf{F}^X$, and $\mathbf{A}^X$ were defined in Eqs. (23)–(26) as partial derivatives of the quasi-energy Lagrangian taken at zero field strengths, $\epsilon = 0$, and hence are frequency independent. To find the power series expansion of Eq. (22) in ω_B and ω_C we have thus to replace the first-order cluster amplitudes and Lagrangian multipliers by the expansions in Eqs. (29) and (34) and must express ω_A as $-\omega_B - \omega_C$. For the first step it is convenient to introduce the intermediates

$$d_{ABC}(j,k,l) = \hat{P}^{ABC}_{jkl}\Big\{\tfrac{1}{6}\mathbf{G}C^A(j)C^B(k)C^C(l) + \tfrac{1}{2}\bar{C}^A(j)\mathbf{B}C^B(k)C^C(l) + \tfrac{1}{2}\delta_{j0}\mathbf{F}^A C^B(k)C^C(l) + \delta_{k0}\bar{C}^A(j)\mathbf{A}^B C^C(l)\Big\} \tag{37}$$

The operator $\hat{P}^{ABC}_{jkl}$ used in Eq. (37) symmetrizes with respect to permutation of the operators A, B, C together with the accompanied "Cauchy" orders j, k, l; δ is the Kronecker symbol. Using the intermediates $d_{ABC}(j,k,l)$, the hyperpolarizability can be expanded around its static limit as:

$$\beta_{ABC}(\omega_A;\omega_B,\omega_C) = -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{j,k,l=0}^{\infty}\omega_A^j\omega_B^k\omega_C^l d_{ABC}(j,k,l) \tag{38}$$

$$= -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{pq=0}^{\infty}\sum_{kl=0}^{\infty}(-1)^{p+q}\binom{p+q}{p}\omega_B^{p+k}\omega_C^{q+l} \times d_{ABC}(p+q,k,l) \tag{39}$$

$$= -\tfrac{1}{2}\hat{C}^{\pm\omega}\sum_{mn=0}^{\infty}\omega_B^n\omega_C^m\sum_{p=0}^{n}\sum_{q=0}^{m}(-1)^{p+q}\binom{p+q}{p} \times d_{ABC}(p+q,n-p,m-q) \tag{40}$$

and the dispersion coefficients $D_{ABC}(n,m)$ are found as

$$D_{ABC}(n,m) = -\sum_{p=0}^{n}\sum_{q=0}^{m}(-1)^{p+q}\binom{p+q}{p} \times \tfrac{1}{2}\left(d_{ABC}(p+q,n-p,m-q) + (-1)^{m+n} \times d_{ABC}(p+q,n-p,m-q)^*\right) \tag{41}$$

From the last equation it follows that all coefficients with even total order $m+n$ are real

$$D_{ABC}(n,m) = -\sum_{p=0}^{n}\sum_{q=0}^{m}(-1)^{p+q}\binom{p+q}{p} \times \mathrm{Re}\left(d_{ABC}(p+q,n-p,m-q)\right) \tag{42}$$

while coefficients with odd $m+n$ are pure imaginary:

$$D_{ABC}(n,m) = -\sum_{p=0}^{n}\sum_{q=0}^{m}(-1)^{p+q}\binom{p+q}{p} \times \mathrm{Im}\left(d_{ABC}(p+q,n-p,m-q)\right) \tag{43}$$

For electric hyperpolarizabilities, all three operators A, B, and C are real and for these properties the odd dispersion coefficients vanish.

As mentioned in the Introduction, the direct ab initio calculation of the dispersion coefficients opens an alternative route to the calculation of dispersion curves for frequency-dependent properties which is complementary to the conventional approach of a pointwise calculation of the frequency-dependent property for a certain number of frequencies between which the dispersion curve is interpolated using a polynomial or rational function. For both approaches the computational most demanding steps (in terms of CPU time) are the solution of linear equations. The pointwise calculation of a general frequency-dependent third-order property requires at each frequency point the solution of four sets of linear equations [$t^X(\omega_X)$, $t^X(-\omega_X)$, $\bar{t}^X(\omega_X)$, $\bar{t}^X(-\omega_X)$]. In comparison, the calculation of the dispersion coefficients requires for each additional even order $2k = n+m$ the solution of the four sets of linear equations for the vectors $C^X(2k-1)$, $C^X(2k)$, $\bar{C}^X(2k-1)$, $\bar{C}^X(2k)$.

For optical processes which can be parametrized in terms of a single laser frequency like the electro-optical or dc Pockels effect (EOPE), second harmonic generation (SHG), and optical rectification (OR), specialized versions of Eq. (27) can be derived. For the electro-optical Pockels effect one obtains:

$$\beta^{\mathrm{EOPE}}_{ABC}(\omega) = \beta_{ABC}(-\omega;\omega,0) = \sum_{n=0}^{\infty}\omega^{2n}D^{\mathrm{EOPE}}_{ABC}(n) \tag{44}$$

with

$$D^{\mathrm{EOPE}}_{ABC}(n) = D_{ABC}(n,0) \tag{45}$$

and for the second harmonic generation the dispersion formula is:

$$\beta^{\mathrm{SHG}}_{ABC}(\omega) = \beta_{ABC}(-2\omega;\omega,\omega) = \sum_{n=0}^{\infty}\omega^{2n}D^{\mathrm{SHG}}_{ABC}(n) \tag{46}$$

with

$$D^{\mathrm{SHG}}_{ABC}(n) = \sum_{m=0}^{n}D_{ABC}(n-m,m) \tag{47}$$

The hyperpolarizability describing the electro-optical Pockels effect is related to the optical rectification hyperpolarizability by $\beta^{\mathrm{OR}}_{CBA}(\omega) = \beta^{\mathrm{EOPE}}_{ABC}(\omega)$. Accordingly, the dispersion coefficients are related by $D_{CBA}^{\mathrm{OR}}(n) = D_{ABC}^{\mathrm{EOPE}}(n)$.

For the vector component of the first hyperpolarizability in the direction of the permanent dipole moment, which is defined as

$$\beta_{\|} = \frac{1}{5}\sum_{\xi}\left\{\beta_{z\xi\xi} + \beta_{\xi z\xi} + \beta_{\xi\xi z}\right\} \quad \xi = x,y,z \tag{48}$$

with the z axis chosen parallel to the molecular dipole moment, an alternative, more compact, expansion can be used [20]:

$$\beta_{\|}(\omega_0;\omega_1,\omega_2) = \beta_{\|}(0)\left(1 + \sum_{n=1}^{\infty}\sum_{m=0}^{n/3} A_{2n-6m,6m}\,\omega_{L2}^{2n-6m}\omega_{L3}^{6m}\right) \tag{49}$$

with $\omega_{L2}^2 = \omega_0^2 + \omega_1^2 + \omega_2^2$ and $\omega_{L3}^3 = \omega_0^3 + \omega_1^3 + \omega_2^3 = 3\omega_0\omega_1\omega_2$ [20, 21]. Adopting a notation commonly used for dispersion formulas for the isotropic second hyperpolarizability $\gamma_{\|}$ [4], Eq. (49) can up to sixth order in the frequencies be written as

$$\beta_{\|}(\omega_0;\omega_1,\omega_2) = \beta_{\|}(0)\left(1 + A\omega_{L2}^2 + B\omega_{L2}^4 + C\omega_{L2}^6 + C'\omega_{L3}^6 + \cdots\right) \tag{50}$$

The coefficients A, B, C, C' etc. are related to the dispersion coefficients $D(n,m)$ introduced in Eqs. (27) and (41). The necessary expressions are found by equating the coefficients for the frequency products $\omega_1^n\omega_2^m$ in Eq. (49) with the coefficients of the Taylor expansion of $\beta_{\|}(\omega_0;\omega_1,\omega_2)$ in ω_1 and ω_2 as in Eq. (27). Introducing, by analogy to the averaged hyperpolarizability, the averaged dispersion coefficients

$$D_{\|}(n,m) = \frac{1}{5}\sum_{\xi}\left\{D_{z\xi\xi}(n,m) + D_{\xi z\xi}(n,m) + D_{\xi\xi z}(n,m)\right\} \quad \xi = x,y,z \tag{51}$$

the A and B coefficients, for example, can be calculated as:

$$A = \frac{1}{2\beta_{\|}(0)}\,D_{\|}(2,0) \tag{52}$$

$$B = \frac{1}{4\beta_{\|}(0)}\,D_{\|}(4,0) \tag{53}$$

Expressions for the sixth- through tenth-order coefficients are given in the Appendix. Another important hyperpolarizability component is [4]:

$$\beta_{\perp} = \frac{1}{5}\sum_{\xi}\left\{2\beta_{z\xi\xi} - 3\beta_{\xi z\xi} + 2\beta_{\xi\xi z}\right\} \quad \xi = x,y,z \tag{54}$$

which is related to the measured quantity in electro-optical Pockels and dc Kerr experiments β_K as [4]:

$$\beta_K = \frac{3}{2}(\beta_{\|} - \beta_{\perp}) \tag{55}$$

To obtain a similar dispersion formula for $\beta_{\perp}$, this hyperpolarizability component must be written as a sum of two tensor components which are irreducible with respect to the permutational symmetry of the operator indices and frequency arguments [22]:

$$\beta_{\perp} = \tfrac{1}{3}\beta_{\|} + \tfrac{2}{3}\beta_{\mathrm{ms}} \tag{56}$$

$$\beta_{\mathrm{ms}} = \sum_{\xi}\left\{\tfrac{1}{2}\beta_{z\xi\xi} - \beta_{\xi z\xi} + \tfrac{1}{2}\beta_{\xi\xi z}\right\} \quad \xi = x,y,z \tag{57}$$

The index ms indicates that β_{ms} transforms according to the mixed-symmetry representation of the symmetric group S_3. This irreducible tensor component vanishes in the static limit and also if Kleinman symmetry [4, 23] is assumed, which is a frequently used approximation in the calculation of dynamic hyperpolarizabilities. The value of β_{ms} is thus a measure for the deviation from Kleinman symmetry. The hyperpolarizability measured in Kerr effect experiments β_{K}, Eq. (54), may be expressed as the difference between $\beta_{\|}$ and β_{ms}:

$$\beta_{\mathrm{K}} = \beta_{\|} - \beta_{\mathrm{ms}} \tag{58}$$

The irreducible tensor component β_{ms} can be expanded in powers of the optical frequencies as [20, 21]:

$$\beta_{\mathrm{ms}}(\omega_0;\omega_1,\omega_2) = \beta_{\|}(0)\left(\sum_{n=0}^{\infty}\sum_{m=0}^{n/3} A_{1,2n-6m,6m+3}\,\omega_{M1}\omega_{L2}^{2n-6m}\omega_{L3}^{6m+3} + \sum_{n=0}^{\infty}\sum_{m=0}^{n/3} A_{2,2n-6m,6m}\,\omega_{M2}^2\omega_{L2}^{2n-6m}\omega_{L3}^{6m}\right) \tag{59}$$

with $\omega_{M1} = 2\omega_1 - \omega_2 - \omega_0$ and $\omega_{M2}^2 = 2\omega_1^2 - \omega_2^2 - \omega_0^2$. Using a similar notation as in Eq. (50) the dispersion expansion for β_{ms} can up to fourth order be written as:

$$\beta_{\mathrm{ms}}(\omega_0;\omega_1,\omega_2) = \beta_{\|}(0)\left(A_{\mathrm{ms}}\omega_{M2}^2 + B_{\mathrm{ms}}\omega_{M2}^2\omega_{L2}^2 + B'_{\mathrm{ms}}\omega_{M1}\omega_{L3}^3 + \cdots\right) \tag{60}$$

The coefficients of the dispersion formula for β_{ms} can again be calculated from the dispersion coefficients $D(n,m)$ for the cartesian components of β. Expressions for the coefficients up to tenth order are given in the Appendix.

For the dc Pockels effect $[\beta(-\omega;\omega,0)]$ and for the optical rectification process $[\beta(0;-\omega,\omega)]$, where one of the frequency arguments is zero, the effective frequency ω_{L3}^3 vanishes and the expansions in Eqs. (49) and (59) reduce to:

$$\beta_{\|}(-\omega;\omega,0) = \beta_{\|}(0;\omega,-\omega) = \beta_{\|}(0)\left(1 + \sum_{n=1}^{\infty} 2^{2n}A_{2n,0}\,\omega^{2n}\right) \tag{61}$$

and

$$\beta_{\mathrm{ms}}(-\omega;\omega,0) = \beta_{\mathrm{ms}}(0;\omega,-\omega) = \beta_{\|}(0)\left(0 + \sum_{n=0}^{\infty} 2^{2n}A_{2,2n,0}\,\omega^{2n+2}\right) \tag{62}$$

Inserting Eqs. (49) and (59) into Eqs. (56) and (58) we obtain dispersion formulas for the experimentally important hyperpolarizability components $\beta_\perp$ and β_K. Up to fourth order they read:

$$\begin{aligned}\beta_\perp(\omega_0;\omega_1,\omega_2) = \frac{\beta_\parallel(0)}{3}\Bigg(1 &+ \left(A + 2A_{\mathrm{ms}}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^2 \\ &+ \left(B + 2B_{\mathrm{ms}}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^4 \\ &+ 2B'_{\mathrm{ms}}\omega_{M1}\omega_{L3}^3 + \cdots\Bigg)\end{aligned} \tag{63}$$

$$\begin{aligned}\beta_K(\omega_0;\omega_1,\omega_2) = \beta_\parallel(0)\Bigg(1 &+ \left(A - A_{\mathrm{ms}}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^2 \\ &+ \left(B - B_{\mathrm{ms}}\frac{\omega_{M2}^2}{\omega_{L2}^2}\right)\omega_{L2}^4 \\ &- B'_{\mathrm{ms}}\omega_{M1}\omega_{L3}^3 + \cdots\Bigg)\end{aligned} \tag{64}$$

For the second hyperpolarizability the deviation of the ratio $\gamma_\parallel/\gamma_\perp$ from 3 is sometimes used as a measure for the deviation from Kleinman symmetry [1]. Bishop [24] showed that this ratio can be expanded up to second order in frequency arguments as:

$$\begin{aligned}&\frac{\gamma_\parallel(\omega_0;\omega_1,\omega_2,\omega_3)}{\gamma_\perp(\omega_0;\omega_1,\omega_2,\omega_3)} \\ &\quad = 3\big(1 + r(\omega_L^2 + 6\omega_0\omega_3 + 6\omega_1\omega_2) + \cdots\big)\end{aligned} \tag{65}$$

where r is frequency independent. Using Eqs. (50) and (60) we can expand the analogous ratio for the first hyperpolarizabilty up to second order as:

$$\frac{\beta_\parallel}{\beta_\perp} = \frac{3\beta_\parallel}{\beta_\parallel + 2\beta_{\mathrm{ms}}} = 3\big(1 - 2A_{\mathrm{ms}}\omega_{M2}^2 + \cdots\big) \tag{66}$$

Using the approach outlined in Eqs. (27)–(60) we have implemented the calculation of dispersion coefficients for quadratic response functions for the coupled cluster model hierarchy CCS, CC2, and CCSD into the coupled cluster response code described in [12, 18, 19, 25–31].

3 Dispersion coefficients for the first hyperpolarizability of ammonia

To investigate the convergence of the dispersion expansion and the sensitivity of the coefficients to basis set and correlation treatment, we calculated the dispersion coefficients for ammonia, NH_3, up to tenth order with three different basis sets and the three coupled cluster models CCS, CC2, and CCSD. The calculations were carried out at the experimental geometry $R_{\mathrm{NH}} = 1.012$ Å and $\angle_{\mathrm{HNH}} = 106.7^\circ$ [32] and we used three basis sets taken from the series of correlation consistent basis sets developed by Dunning and coworkers [33–35], namely t-aug-cc-pVDZ, aug-cc-pVTZ, and t-aug-cc-pVTZ. These basis sets were selected to obtain basis set saturation to different levels of accuracy. The t-aug-cc-pVDZ does not contain f functions at the N atom and no d functions for H, but many diffuse functions, while the aug-cc-pVTZ basis contains these higher angular momentum functions but only a few diffuse functions. The t-aug-cc-pVTZ basis set is expected to give results near the basis set limit as it contains higher angular momentum functions and a sufficient number of diffuse functions. The CCSD results for the frequency-dependent first hyperpolarizabilities of ammonia obtained in the t-aug-cc-pVTZ basis set are in reasonable agreement with the experimental result from Ward and Miller [36], who measured at the ruby laser frequency the second harmonic generation hyperpolarizability of ammonia $\beta_\parallel^{\mathrm{SHG}}(694.3\,\mathrm{nm}) = -48.4 \pm 1.2$ au [37]. The CCSD response result in the t-aug-cc-pVTZ basis at the equilibrium geometry is for this frequency -51.2 au. The zero-point vibrational correction was calculated by Spirko et al. [38] at the MCSCF level and was found to increase the absolute value of $\beta_\parallel^{\mathrm{SHG}}$ by about 6%. The pure vibrational contribution was estimated by Bishop et al. [39] as ≈ -0.18 au. Adding these corrections to the CCSD response result for the t-aug-cc-pVTZ basis we obtain ≈ -54.5 au, which compares reasonable well with the experimental result if one takes into account that we have not included the effects of connected triples.

First, we examine the convergence of truncated expansions with the order of the dispersion coefficients. In Table 1 we have listed the coefficients for the parallel hyperpolarizability component $\beta_\parallel$ for SHG and for the EOPE, $D_\parallel^{\mathrm{SHG}}(n)$ (Eq. 47) and $D_\parallel^{\mathrm{EOPE}}(n)$ (Eq. 45), for the aug-cc-pVTZ basis, and a CCSD wavefunction. From these coefficients we calculated for three different frequencies, which cover the usual experimental range of 0.04–0.1 au, the Taylor approximations of order 2 through 10 and the diagonal Padé approximants [40] which are correct through the same order in the frequency arguments. The results are compiled in Table 2 and displayed for selected orders in Fig. 1 together with the hyperpolarizabilities obtained from response function calculations without expansion for the frequency dependence. For the EOPE we find a fast convergence of the dispersion expansion. Already the fourth-order Taylor approximation gives results which up to $\omega = 0.1$ au are within 2% of the nonexpanded hyperpolarizabilities. Using the [1, 1] Padé approximant, which is constructed from the same dispersion coefficients and is also correct up to $\mathcal{O}(\omega^4)$, decreases the error by about an order of magnitude. With this accuracy, the error in the dispersion expansion is already smaller than the remaining basis set effects, vibrational effects, or the contribution of connected triple excitations. Thus, the

Table 1. Coefficients for $\beta_\parallel(\omega)$ for second harmonic generation (SHG) and electro-optical Pockels effect (EOPE) of ammonia at the experimental geometry. A CCSD wavefunction and the aug-cc-pVTZ basis were used. Results are given in atomic units; the numbers in parentheses indicate powers of ten

Order	SHG	EOPE
0	−2.79248(1)	−2.79248(1)
2	−2.37315(3)	−7.91105(2)
4	−1.75122(5)	−1.94579(4)
6	−1.23489(7)	−4.39681(5)
8	−8.49697(8)	−9.33439(6)
10	−5.77775(10)	−1.89759(8)

Table 2. Convergence of the Taylor series and the series of diagonal Padé approximants for $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ and $\beta_{\parallel}^{\mathrm{OR}}(\omega)$ (CCSD, aug-cc-pVTZ basis). The "inifinite" order results were calculated using the implementation for the frequency-dependent response function

Order/ approximant	$\beta_{\parallel}^{\mathrm{OR}}(\omega)$ (au)					
	$\omega = 0.0428286$ au ($\lambda = 1064$ nm)		$\omega = 0.0656249$ au ($\lambda = 694.3$ nm)		$\omega = 0.1$ au ($\lambda = 455.6$ nm)	
	Taylor	Padé	Taylor	Padé	Taylor	Padé
2/[0, 1]	−29.3755	−29.4549	−31.3316	−31.8050	−35.8354	−38.9619
4/[1, 1]	−29.4409	−29.4440	−31.6925	−31.7353	−37.7812	−38.4159
6/[1, 2]	−29.4436	−29.4437	−31.7276	−31.7311	−38.2208	−38.3376
8/[2, 2]	−29.4437	−29.4437	−31.7308	−31.7311	−38.3142	−38.3374
10/[2, 3]	−29.4437	−29.4437	−31.7311	−31.7311	−38.3332	−38.3375
∞	−29.4437		−31.7311		−38.3378	
	$\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ (au)					
2/[0, 1]	−32.2767	−33.0801	−38.1451	−44.0450	−51.6564	−185.962
4/[1, 1]	−32.8656	−32.9577	−41.3931	−42.9061	−69.1685	−118.478
6/[1, 2]	−32.9417	−32.9528	−42.3795	−42.7983	−81.5174	−108.943
8/[2, 2]	−32.9513	−32.9527	−42.6718	−42.7919	−90.0144	−107.446
10/[2, 3]	−32.9525	−32.9527	−42.7574	−42.7924	−95.7922	−107.706
∞	−32.9527		−42.7926		−107.883	

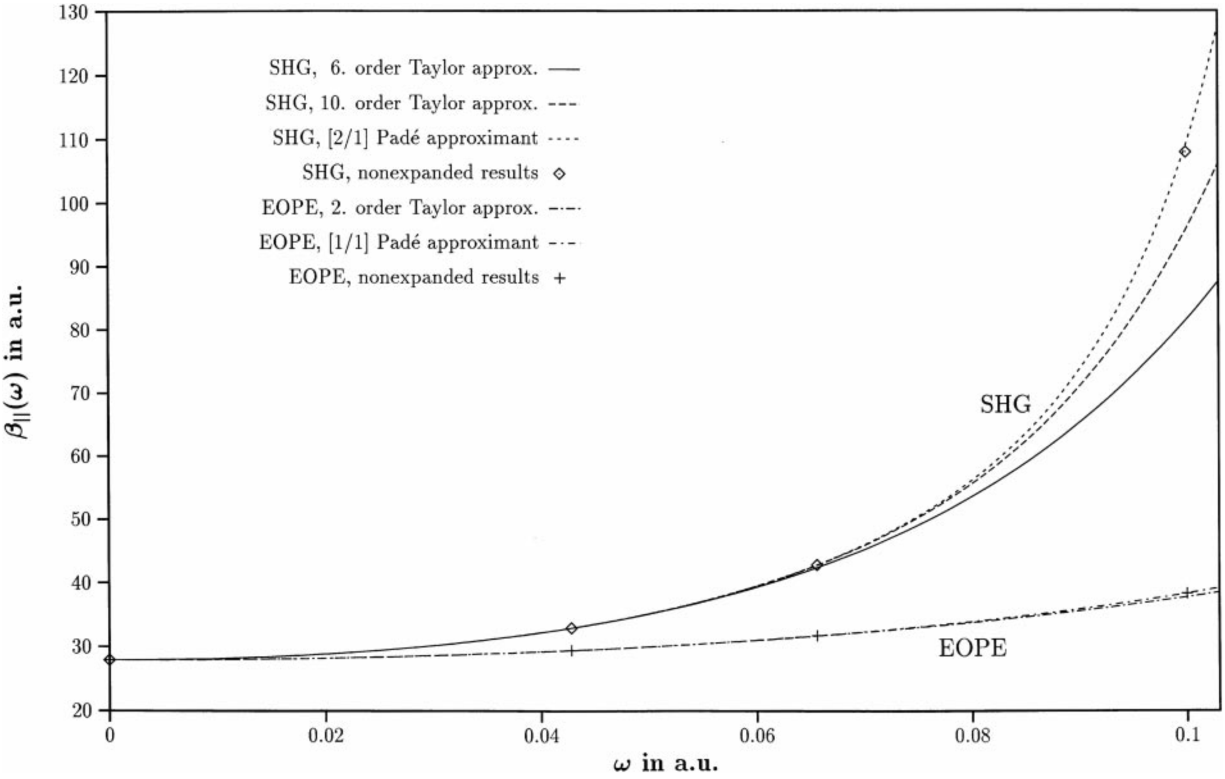

Fig. 1. Convergence of $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ and $\beta_{\parallel}^{\mathrm{EOPE}}(\omega)$ with the order of the Taylor and Padé approximants (dispersion coefficients calculated with a CCSD wavefunction and the aug-cc-pVTZ basis)

inclusion of the sixth-order coefficient will in this case hardly affect a comparison with experiment.

The convergence rate of the Taylor expansion and the series of diagonal Padé approximants is determined by the position of the first pole in the hyperpolarizability. For $\beta_{\parallel}^{\mathrm{OR}}(\omega)$ this occurs when ω equals the first dipole-allowed transition energy. In the example we used here (CCSD, aug-cc-pVTZ basis), this is the case for $\omega = 0.243$ au or $\lambda = 187$ nm, which is much larger than the frequencies we considered. For the SHG hyperpolarizability $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ the situation is different, because in $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ the first pole occurs already when ω equals half the excitation energy of the transition. Thus the first pole for $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ occurs already at $\omega = 0.122$ au, i.e. slightly above the largest frequency considered in Table 2. Consequently, the convergence of the SHG hyperpolarizability is not so favorable as for $\beta_{\parallel}^{\mathrm{EOPE}}(\omega)$. However, a sixth-order Taylor approximation is still for frequencies up to that of the ruby laser ($\lambda = 694.5$ nm) within 1% of the nonexpanded hyperpolarizabilities. Again, the

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

	CCS			CC2			CCSD		
	taD	*aT*	*taT*	*taD*	*aT*	*taT*	*taD*	*aT*	*taT*
$\beta_{\|}(0)$[a]	−1.973(1)	−1.905(1)	−2.107(1)	−4.680(1)	−3.853(1)	−4.666(1)	−3.306(1)	−2.792(1)	−3.302(1)
A	1.097(1)	9.693(0)	1.042(1)	1.724(1)	1.503(1)	1.564(1)	1.640(1)	1.416(1)	1.477(1)
B	1.072(2)	9.324(1)	9.904(1)	2.331(2)	1.940(2)	1.979(2)	2.111(2)	1.742(2)	1.774(2)
C	9.503(2)	8.447(2)	8.669(2)	2.846(3)	2.313(3)	2.290(3)	2.435(3)	1.968(3)	1.938(3)
C'	2.429(2)	2.079(2)	2.212(2)	7.206(2)	5.672(2)	5.733(2)	6.124(2)	4.750(2)	4.817(2)
D	7.893(3)	7.192(3)	7.156(3)	3.286(4)	2.602(4)	2.514(4)	2.644(4)	2.089(4)	2.000(4)
D'	6.210(3)	5.274(3)	5.601(3)	2.627(4)	1.970(4)	1.989(4)	2.097(4)	1.552(4)	1.568(4)
E	6.286(4)	5.838(4)	5.675(4)	3.664(5)	2.811(5)	2.669(5)	2.766(5)	2.124(5)	1.991(5)
E'	1.011(5)	8.609(4)	9.064(4)	6.054(5)	4.353(5)	4.366(5)	4.534(5)	3.223(5)	3.228(5)
A_{ms}	−0.810(0)	−0.380(0)	−0.570(0)	−2.494(0)	−2.080(0)	−1.895(0)	−2.147(0)	−1.579(0)	−1.580(0)
B_{ms}	−2.494(1)	−2.535(1)	−2.205(1)	−5.377(1)	−5.291(1)	−4.335(1)	−4.758(1)	−4.545(1)	−3.836(1)
B'_{ms}	−3.159(0)	−2.495(0)	−3.028(0)	−1.072(1)	−0.906(1)	−0.902(1)	−8.758(0)	−7.274(1)	−7.301(1)
C_{ms}	−3.155(2)	−3.479(2)	−2.868(2)	−7.753(2)	−7.758(2)	−6.180(2)	−6.671(2)	−6.603(2)	−5.349(2)
C'_{ms}	−1.018(2)	−8.846(1)	−9.453(2)	−3.546(2)	−2.951(2)	−2.831(2)	−2.866(2)	−2.364(2)	−2.279(2)
D_{ms}	−3.017(3)	−3.370(3)	−2.756(3)	−9.424(3)	−9.143(3)	−7.271(4)	−7.725(3)	−7.465(3)	−6.008(3)
D'_{ms}	−1.733(3)	−1.597(3)	−1.591(3)	−7.237(3)	−5.986(3)	−5.526(3)	−5.655(3)	−4.659(3)	−4.314(3)
D''_{ms}	−4.483(2)	−4.792(2)	−4.068(2)	−1.887(3)	−1.730(3)	−1.419(3)	−1.435(3)	−1.304(3)	−1.079(3)
E_{ms}	−2.524(4)	−2.799(4)	−2.303(4)	−1.046(5)	−0.967(5)	−0.775(5)	−8.094(4)	−7.481(4)	−6.052(4)
E'_{ms}	−2.213(4)	−2.115(4)	−2.018(4)	−1.180(5)	−0.962(5)	−0.863(5)	−8.805(4)	−7.165(4)	−6.445(5)
E''_{ms}	−1.402(4)	−1.496(4)	−1.275(4)	−7.485(4)	−6.578(4)	−5.430(4)	−5.464(4)	−4.779(4)	−3.971(4)
E'''_{ms}	−1.640(3)	−1.528(3)	−1.513(3)	−1.067(4)	−0.858(4)	−0.773(4)	−7.529(3)	−6.001(3)	−5.436(3)

[a] the SCF results in the three basis sets are: t-aug-cc-pVDZ, 14.35 au; aug-cc-pVTZ, 13.69 au; t-aug-cc-pVTZ, 15.50 au; other correlated ab initio results for $\beta_{\|}(0)$ are: MP2, CCSD, and CCSD(T) in a $[5s3p2d/3s2p1d] + (1s1p)$ basis: 32.5, 30.0, and 34.5 au [45]; MCSCF in a $[8s5p3d1f/4s2p1d]$ basis: 27.77 au [38]; MCSCF in a d-aug-cc-pVDZ basis: 28.24 au [8]

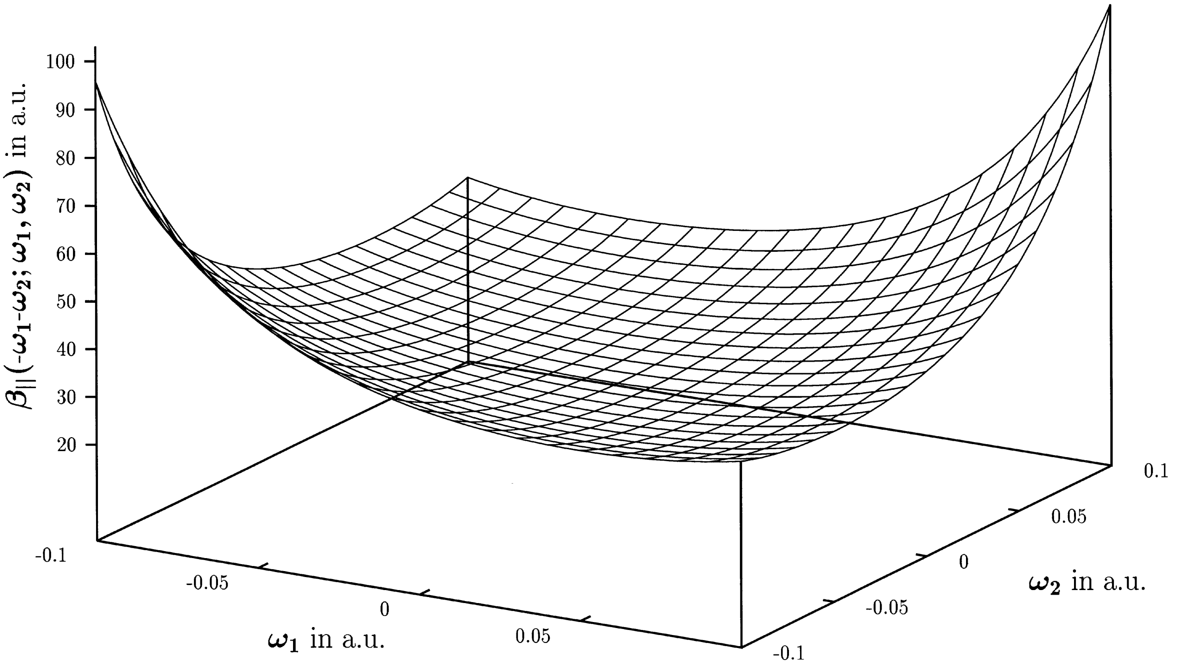

Fig. 2. The parallel vector component $\beta_{\|}(-\omega_1 - \omega_2; \omega_2, \omega_3)$ of the first hyperpolarizability of ammonia as a function of the frequencies ω_1 and ω_2, calculated from the dispersion coefficients through tenth order for a CCSD wavefunction and the aug-cc-pVTZ basis set (experimental equilibrium geometry)

use of Padé approximants improves the convergence dramatically. With the [1,2] approximant, calculated from the coefficients up to $D_{\|}^{\mathrm{SHG}}(6)$, one obtains for frequencies up to 0.1 au results within 1% of the nonexpanded hyperpolarizabilities. Such an accuracy is sufficient for many applications. Usually, the uncertainity of experimental measurements of $\beta_{\|}$ are significantly larger than this uncertainity, often of the order of 10% , and also for ab initio calculations a 1% accuracy for hyperpolarizabilities is a challenging task not met for polyatomic systems, in particular close to a pole.

In the literature it has been speculated that the A and higher-order hyperpolarizability dispersion coefficients

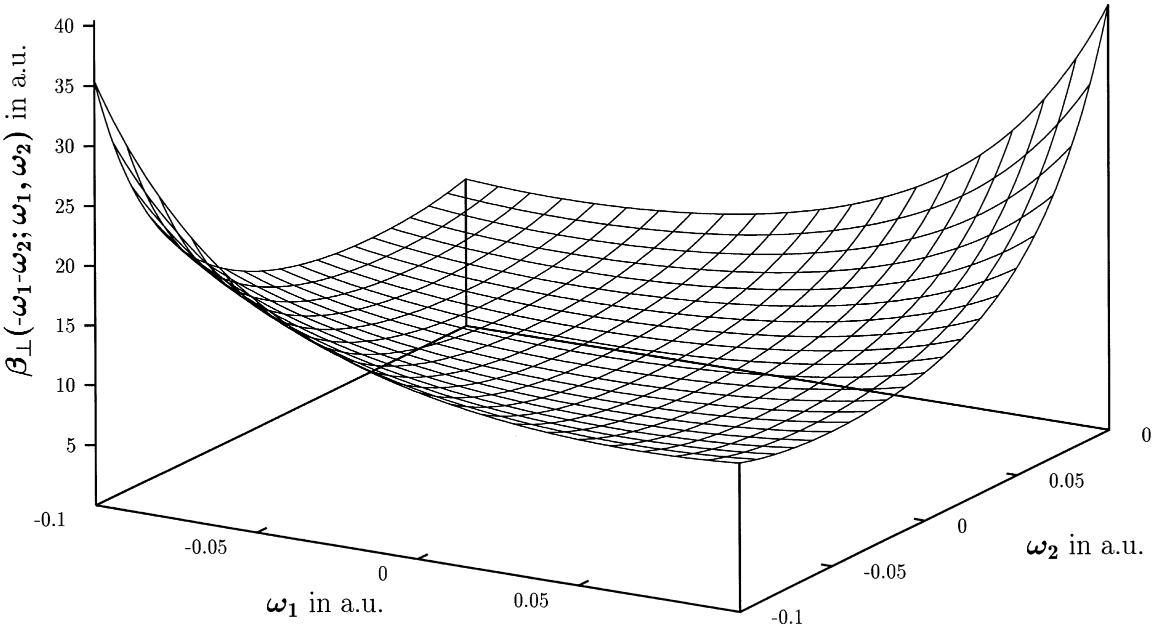

Fig. 3. The perpendicular vector component $\beta_\perp(-\omega_1-\omega_2;\omega_2,\omega_3)$ of the first hyperpolarizability of ammonia as a function of the frequencies ω_1 and ω_2, calculated from the dispersion coefficients through tenth order for a CCSD wavefunction and the aug-cc-pVTZ basis set (experimental equilibrium geometry)

are less dependent on the choice of basis set and ab initio method than static hyperpolarizabilities [2–4]. In particular, it was expected that the dispersion coefficients are less sensitive to the correlation treatment than the static hyperpolarizabilities. This expectation was based on the observation that the MP2 pseudo-energy derivative method developed by Rice and Handy [41] gave for some molecules similar A coefficients as were obtained in time-dependent Hatree-Fock (TDHF) calculations with the same basis sets [3, 4]. For theoretical reasons the A coefficient and higher-order coefficients should be sensitive to the lowest dipole-allowed excitation energy which determines the position of the first pole in the dispersion curve. Since in the MP2 pseudo-energy derivative method the positions of the poles are not correlated and thus are the same as in TDHF, it is not unexpected that both methods give similar A coefficients. In Table 3 we compiled the dispersion coefficients for $\beta_\|$ and β_{ms} for the three basis sets t-aug-cc-pVDZ, aug-cc-pVTZ, and t-aug-cc-pVTZ and the three coupled cluster models CCS, CC2, and CCSD. For ammonia, the dispersion coefficients for the Kleinman-forbidden mixed-symmetry vector component β_{ms} are about an order of magnitude smaller than the coefficient of the same order in the frequencies for $\beta_\|$. As a consequence, the difference between $\beta_\|$ and β_K is relatively small, as seen in Figs. 2 and 4. The perpendicular hyperpolarizability component $\beta_\perp$ is shown in Fig. 3. If we compare the results obtained for the static hyperpolarizability $\beta_\|(0)$ with CCS, CC2, and CCSD, we find that these methods behave similar to what we have observed in previous coupled cluster response calculations of polarizabilities and hyperpolarizabilities [12, 19, 42]: CCS gives results of similar quality as SCF and the CCSD results are usually close to the experimental results, while CC2 often overestimates the static hyperpolarizabilities by a similar amount as they are underestimated by CCS and HF. In many cases, CC2 is not an improvement relative to the uncorrelated methods CCS and SCF. This is in contrast to the good performance of CC2 for excitation energies, where usually the results improve systemtically in each step of the hierarchy CCS–CC2–CCSD [27, 43]. If we compare the dispersion coefficients for the three coupled cluster models listed in Table 3, we find a large increase of the dispersion coefficients from CCS to CCSD by a factor of 1.4–4.8. The inclusion of dynamic electron correlation increases significantly the dispersion of the hyperpolarizability. For all coefficients the CC2 results are about a factor 3 closer to the CCSD results than the CCS values. In particular, for the two leading coefficients for $\beta_\|$, A and B, the CC2 results differ only by 6% and 11% from the CCSD values.

If we compare the results for the three basis sets t-aug-cc-pVDZ, aug-cc-pVTZ, and t-aug-cc-pVTZ, we find large but quite different basis set effects for the static hyperpolarizabilties and for the dispersion coefficients. The static hyperpolarizabilties are very sensitive to the inclusion of diffuse functions, as also observed in many previous studies. The results for $\beta_\|$ in the t-aug-cc-pVDZ and t-aug-cc-pVTZ basis sets are thus similar and by about 10–15% larger than the aug-cc-pVTZ basis results. In contrast, the dispersion coefficients show large changes from the t-aug-cc-pVDZ basis to the triple zeta basis sets aug-cc-pVTZ and t-aug-cc-pVTZ, in particular for the correlated models CC2 and CCSD, but only small changes with an increasing number of diffuse functions.

4 Conclusions

We have derived and implemented analytic dispersion coefficients for the quadratic response function of the coupled cluster models CCS, CC2, and CCSD. The

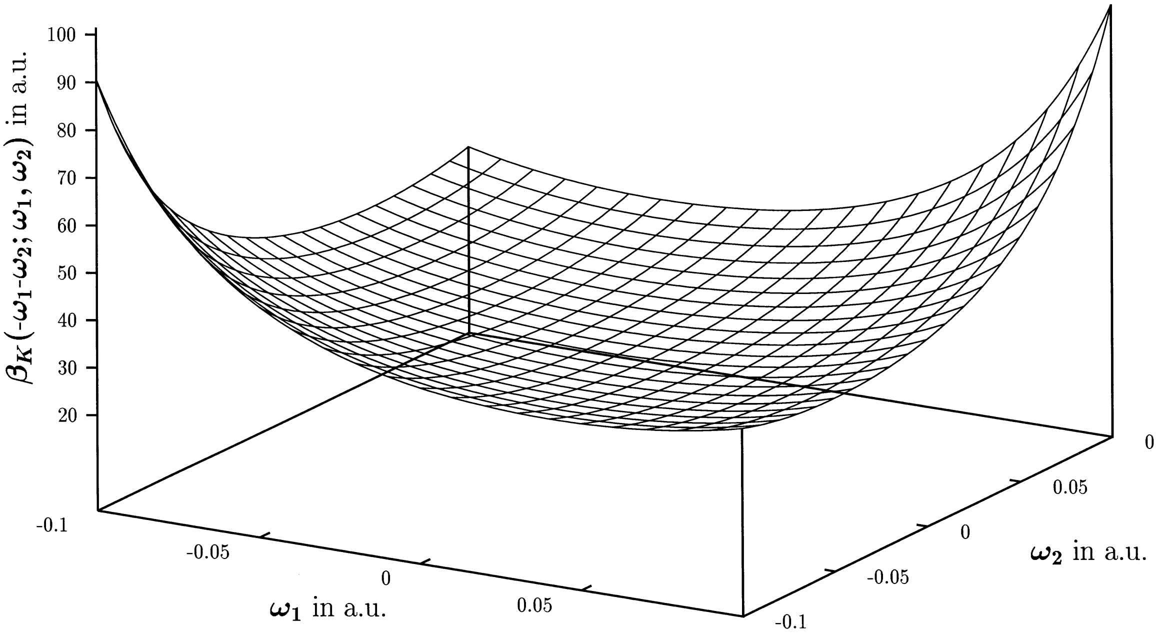

Fig. 4. The Kerr component $\beta_K(-\omega_1-\omega_2;\omega_2,\omega_3)$ of the first hyperpolarizability of ammonia as a function of the frequencies ω_1 and ω_2, calculated from the dispersion coefficients through tenth order for a CCSD wavefunction and the aug-cc-pVTZ basis set (experimental equilibrium geometry)

dispersion coefficients are defined through a power series expansion of the quadratic response function in its frequency arguments and are thus applicable to general frequency-dependent third-order properties and independent of the nonlinear optical process. For the irreducible tensor components the dispersion can be expressed in compact dispersion formulas using permutation symmetry-adapted linear combinations of the optical frequencies. In an application to the first hyperpolarizability of ammonia, we find fast convergence of the Taylor expansion up to frequencies of half the first pole. With Padé approximants the convergence of the dispersion expansion can be improved significantly and its application range is extended to frequencies near to the first pole. For many molecules, in particular such with high-lying first transition frequencies, the first two or three dispersion coefficients will be sufficient to obtain the dispersion curves within a 1% accuracy in the usual experimental frequency range. A comparison of the dispersion coefficients obtained with three different basis sets and the three coupled cluster models CCS, CC2, and CCSD shows that the dispersion coefficients are similarly sensitive to the choice of the basis set and the correlation treatment as the static hyperpolarizability, although the effects are different. While the static hyperpolarizability is very sensitive to the saturation of the basis set with diffuse functions, the dispersion coefficients are only affected a little by the number of diffuse functions. However, relatively large changes are found with respect to the zeta level of the valence basis. We also find that for the static hyperpolarizability and for the dispersion coefficients the performance of the coupled cluster model hierarchy CCS–CC2–CCSD is quite different: while the static CC2 hyperpolarizability is not improved compared to the CCS result, the CC2 dispersion coefficients are closer to the CCSD results by about a factor of three compared to the corresponding CCS values. The basis set effects on the dispersion coefficients and the performance of the coupled cluster hierarchy are consistent with the expectation that the dispersion coefficients are sensitive to the accuracy with which the lowest dipole-allowed excitations are described.

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Appendix A. Formulas for the sixth- through tenth-order dispersion coefficients for $\beta_\parallel$ and β_{ms}

The coefficients for the sixth- through tenth-order terms of the dispersion expansion of Eq. (49) for $\beta_\parallel$ are found as:

$$C = A_{3,0} = \frac{1}{8\beta_\parallel(0)} D_\parallel(6,0) \tag{A1}$$

$$C' = A_{0,2} = \frac{1}{9\beta_\parallel(0)} \left(D_\parallel(4,2) - 6D_\parallel(6,0)\right) \tag{A2}$$

$$D = A_{4,0} = \frac{1}{16\beta_\parallel(0)} D_\parallel(8,0) \tag{A3}$$

$$D' = A_{1,2} = \frac{1}{18\beta_\parallel(0)} \left(D_\parallel(6,2) - 10D_\parallel(8,0)\right) \tag{A4}$$

$$E = A_{5,0} = \frac{1}{32\beta_\parallel(0)} D_\parallel(10,0) \tag{A5}$$

$$E' = A_{2,2} = \frac{1}{36\beta_\parallel(0)} \left(D_\parallel(8,2) - 15D_\parallel(10,0)\right) \tag{A6}$$

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

$$A_{\mathrm{ms}} = A_{2,0,0} = \frac{1}{\beta_{\|}(0)} D_{\mathrm{ms}}(2,0) \tag{A7}$$

$$B_{\mathrm{ms}} = A_{2,1,0} = \frac{1}{2\beta_{\|}(0)} D_{\mathrm{ms}}(4,0) \tag{A8}$$

$$B'_{\mathrm{ms}} = A_{1,0,1} = -\frac{1}{9\beta_{\|}(0)} \big(D_{\mathrm{ms}}(3,1) + D_{\mathrm{ms}}(4,0)\big) \tag{A9}$$

$$C_{\mathrm{ms}} = A_{2,2,0} = \frac{1}{4\beta_{\|}(0)} D_{\mathrm{ms}}(6,0) \tag{A10}$$

$$C'_{\mathrm{ms}} = A_{1,1,1} = -\frac{1}{18\beta_{\|}(0)} D_{\mathrm{ms}}(5,1) \tag{A11}$$

$$D_{\mathrm{ms}} = A_{2,3,0} = \frac{1}{8\beta_{\|}(0)} D_{\mathrm{ms}}(8,0) \tag{A12}$$

$$D'_{\mathrm{ms}} = A_{1,2,1} = -\frac{1}{36\beta_{\|}(0)} \big(D_{\mathrm{ms}}(7,1) - D_{\mathrm{ms}}(8,0)\big) \tag{A13}$$

$$D''_{\mathrm{ms}} = A_{2,0,2} = \frac{1}{9\beta_{\|}(0)} \big(D_{\mathrm{ms}}(6,2) - 3D_{\mathrm{ms}}(7,1) + 5D_{\mathrm{ms}}(8,0)\big) \tag{A14}$$

$$E_{\mathrm{ms}} = A_{2,4,0} = \frac{1}{16\beta_{\|}(0)} D_{\mathrm{ms}}(10,0) \tag{A15}$$

$$E'_{\mathrm{ms}} = A_{1,3,1} = -\frac{1}{72\beta_{\|}(0)} \big(D_{\mathrm{ms}}(9,1) - 2D_{\mathrm{ms}}(10,0)\big) \tag{A16}$$

$$E''_{\mathrm{ms}} = A_{2,1,2} = \frac{1}{18\beta_{\|}(0)} \big(D_{\mathrm{ms}}(8,2) - 4D_{\mathrm{ms}}(9,1) + 8D_{\mathrm{ms}}(10,0)\big) \tag{A17}$$

$$E'''_{\mathrm{ms}} = A_{1,0,3} = -\frac{1}{81\beta_{\|}(0)} \big(D_{\mathrm{ms}}(7,3) - D_{\mathrm{ms}}(8,2) - 5D_{\mathrm{ms}}(9,1) + 22D_{\mathrm{ms}}(10,0)\big) \tag{A18}$$

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

$$\begin{aligned} D_{\mathrm{ms}}(n,m) &= \sum_{\xi} \left\{ \tfrac{1}{2} D_{z\xi\xi}(n,m) - D_{\xi z\xi}(n,m) + \tfrac{1}{2} D_{\xi\xi z}(n,m) \right\} \\ &\quad \xi = x,y,z \end{aligned} \tag{A19}$$

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