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Dispersion coefficients for polarizabilities and first and second hyperpolarizabilities using full configuration interaction theory

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Abstract

Dispersion coefficients for frequency-dependent properties can efficiently be calculated from the derivatives of the properties with respect to their frequency arguments. We have derived and implemented analytic expressions for the second-order dispersion coefficients of second-, third-, and fourth-order properties in full configuration interaction (FCI) linear, quadratic, and cubic response theory. The accuracy of the second-order dispersion expansion is investigated for BH and Ne for CCSD and FCI. Padé approximants improve the results. The deviation from the analytic results is, in most cases, less than that between CCSD and FCI. The sensitivity of the dispersion coefficients to the choice of wavefunction model and basis set is found to be significant. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Many recent studies that compare experimental or theoretical calculations of molecular electric properties for different optical processes have made use of expansions in even powers of the frequencies for the dynamic electric properties [1–9]. The expansions have been used for interpolation of dispersion curves, to extrapolate measured frequency-dependent molecular properties to the static limit, and to compare dispersion curves calculated with different ab initio methods. For the components of the polarizability, $\alpha_{\mu\nu}$, the all-diagonal hyperpolarizability components $\beta_{\mu\mu\mu}$ and $\gamma_{\mu\mu\mu\mu}$, and for the averages $\overline{\alpha}$, $\beta_{\parallel}$ and $\gamma_{\parallel}$, the expansions contain only a single second-order dispersion coefficient [10–12]. Thus $\overline{\alpha}$, $\beta_{\parallel}$ and $\gamma_{\parallel}$ can be written in the form:

$$\overline{\alpha}(\omega_1;\omega_2) = \overline{\alpha}(0)\left[1 + A_{\alpha}\left(\omega_1^2 + \omega_2^2\right) + \mathscr{O}\left(\omega_i^4\right)\right], \tag{1}$$

$$\beta_{\parallel}(\omega_1;\omega_2,\omega_3) = \beta_{\parallel}(0)\left[1 + A_{\beta}\left(\omega_1^2 + \omega_2^2 + \omega_3^2\right) + \mathscr{O}\left(\omega_i^4\right)\right], \tag{2}$$

$$\gamma_{\parallel}(\omega_1;\omega_2,\omega_3,\omega_4) = \gamma_{\parallel}(0)\left[1 + A_{\gamma}\left(\omega_1^2 + \omega_2^2 + \omega_3^2 + \omega_4^2\right) + \mathscr{O}\left(\omega_i^4\right)\right]. \tag{3}$$

The second-order dispersion coefficients for different optical processes as, for example, second harmonic generation or the dc-Pockels effect are thus equivalent [10–12]. These coefficients therefore provide a way of expressing the dispersion of frequency-de-

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pendent properties that is transferable between the different optical processes.

The usual approach in theoretical studies of dispersion coefficients has been to calculate frequency-dependent molecular electric properties for a suitable number of frequencies and then to extract the coefficients from a polynomial fit [8,13]. Although this approach is inefficient and has numerical difficulties it was only recently that the first ab initio implementations have been reported for the analytic hyperpolarizability dispersion coefficients by Bishop and De Kee [14,15] for explicitly correlated wavefunctions based on a sum-over-states approach and by Hättig and Jørgensen [5–7] for quadratic and cubic response functions employing the CCS, CC2, and CCSD models and a derivative approach.

Although the expressions for the second-order dispersion coefficients for the first and second hyperpolarizabilities are known in a sum-over-states form since a number of years [10,14–16], a matrix formulation, which is a necessary prerequisite for an efficient implementation for many-electron systems, has until now not been given in the literature. We derive in the following analytic expressions for second-order dispersion coefficients in the full configuration interaction (FCI) method, based on the matrix formulation of response theory by Olsen and Jørgensen [17,18]. We calculate second-order FCI dispersion coefficients for the polarizability, and the first and second hyperpolarizabilities of BH as well as for α and γ of Ne. For BH we use a hierarchy of basis sets, and in both cases we compare with the coupled-cluster wavefunctions CCS, CC2, and CCSD to investigate the sensitivity of the coefficients to basis sets and correlation treatment. The CCSD and FCI results are compared with an explicit evaluation of the frequency-dependent property to examine the extent to which the second-order expansion is converged. To improve the accuracy of the frequency expansion we calculate diagonal Padé approximants [19].

BH was chosen because it has few electrons and thus makes FCI calculations in physical reasonable basis sets possible. However, it has low excitation energies, and thus the dispersion expansion will only converge for small frequencies, for example for $\gamma^{\mathrm{THG}}(\omega)$ the usual experimental frequency range of 0.04–0.1 a.u. is outside this region. Ne, on the other hand, has a high first excitation energy and the expansion converges fast for the experimental frequency range. However, because of the large number of electrons FCI calculations for Ne are only possible with small basis sets.

2. Theory

In response theory as formulated by Olsen and Jørgensen [17,18] the linear, quadratic, and cubic response functions as derived for FCI wavefunctions have the computational forms

$$\langle\langle A;B\rangle\rangle_{\omega_B} = -\hat{P}(A,B)\,A^{[1]\dagger}\left(\mathbf{E}^{[2]}-\omega_B\mathbf{1}\right)^{-1}B^{[1]}, \tag{4}$$

$$\langle\langle A;B,C\rangle\rangle_{\omega_B,\omega_C} = \hat{P}(A,B,C)\,A^{[1]\dagger}\left(\mathbf{E}^{[2]}+\omega_A\mathbf{1}\right)^{-1} \times\mathbf{B}^{[2]}\left(\mathbf{E}^{[2]}-\omega_C\mathbf{1}\right)^{-1}C^{[1]}, \tag{5}$$

$$\begin{aligned}\langle\langle A;B,C,D\rangle\rangle_{\omega_B,\omega_C,\omega_D} &= \hat{P}(A,B,C,D)\Big[-A^{[1]\dagger}\left(\mathbf{E}^{[2]}+\omega_A\mathbf{1}\right)^{-1}\mathbf{B}^{[2]}\left(\mathbf{E}^{[2]}\right.\\ &\quad\left.-(\omega_C+\omega_D)\mathbf{1}\right)^{-1}\mathbf{C}^{[2]}\left(\mathbf{E}^{[2]}-\omega_D\mathbf{1}\right)^{-1}D^{[1]}\\ &\quad+\left(A^{[1]\dagger}\left(\mathbf{E}^{[2]}+\omega_A\mathbf{1}\right)^{-1}\left(\mathbf{E}^{[2]}-\omega_B\mathbf{1}\right)^{-1}B^{[1]}\right)\\ &\quad\times\left(C^{[1]\dagger}\left(\mathbf{E}^{[2]}-\omega_D\mathbf{1}\right)^{-1}D^{[1]}\right)\Big],\end{aligned} \tag{6}$$

where $A^{[1]}$, $B^{[1]}$, and $C^{[1]}$ are gradient-type vectors associated with the applied perturbations and $\mathbf{E}^{[2]}$ is the electronic Hessian. The $A^{[2]}$, $B^{[2]}$, and $C^{[2]}$ matrices are similar to the vectors mentioned before but represent one higher derivative in the electronic variational parameters. We refer to Ref. [17,18] for the exact definitions of the vectors and matrices. $\hat{P}(A,B,C)$ and $\hat{P}(A,B,C,D)$ symmetrizes with respect to permutations of the perturbation indices A, B, C, and D.

If the operators A, B, C, and D in the respective matrices are equal to the components of the dipole operator, the linear, quadratic, and cubic response functions are equal to minus the respective components of the polarizability $\alpha_{AB}(\omega_A,\omega_B)$, first hyperpolarizability $\beta_{ABC}(\omega_A,\omega_B,\omega_C)$, and second hyperpolarizability $\gamma_{ABCD}(\omega_A,\omega_B,\omega_C,\omega_D)$.

For a molecular or atomic system in its electronic ground state the response functions are analytic in

their frequency arguments with the exception of the poles that occur when a frequency or a sum of frequencies becomes equal to an excitation energy. In the normal dispersion region below the first pole, response functions can thus be expanded in power series in their frequency arguments:

$$\alpha_{AB}(-\omega_B;\omega_B) = \sum_{n=0}^{\infty} \omega_B^{2n} D_{AB}(2n), \tag{7}$$

$$\beta_{ABC}(\omega_A;\omega_B,\omega_C) = \sum_{m,n=0}^{\infty} \omega_B^m \omega_C^n D_{ABC}(m,n), \tag{8}$$

$$\gamma_{ABCD}(\omega_A;\omega_B,\omega_C,\omega_D) = \sum_{l,m,n=0}^{\infty} \omega_B^l \omega_C^m \omega_D^n D_{ABCD}(l,m,n). \tag{9}$$

It should be noted that all odd-order dispersion coefficients vanish. This stems from the fact that α, β, and γ are symmetric in their frequency arguments, for instance $\beta(-2\omega;\omega,\omega) = \beta(2\omega;-\omega,-\omega)$. The coefficients $D_{AB}(n)$ are usually denoted the Cauchy moments, and are written in the form $S_{AB}(-2n-2)$. The polarizabilities/hyperpolarizabilities are functions of one independent frequency variable less than there are operator arguments of the response function because of the matching conditions $\omega_A + \omega_B = 0$, $\omega_A + \omega_B + \omega_C = 0$, and $\omega_A + \omega_B + \omega_C + \omega_D = 0$ for α, β and γ, respectively.

To derive expressions for the dispersion coefficients we need power expansions of expressions of the form:

$$N(\omega) = (\mathbf{E}^{[2]} + \omega\mathbf{1})^{-1} A^{[1]} = \sum_{n=0}^{\infty} (-1)^n \omega^n C_A^{(n)}, \tag{10}$$

$$N(-\omega) = (\mathbf{E}^{[2]} - \omega\mathbf{1})^{-1} A^{[1]} = \sum_{n=0}^{\infty} \omega^n C_A^{(n)}, \tag{11}$$

where we have introduced the Cauchy vectors

$$C_A^{(n)} = (\mathbf{E}^{[2]-1})^{n+1} A^{[1]}. \tag{12}$$

The Cauchy vectors for $n \geqslant 0$ are obtained by solution of recursively defined sets of linear equations

$$\mathbf{E}^{[2]} C_A^{(n)} = C_A^{(n-1)}, \tag{13}$$

starting with the zeroth order Cauchy vector $C_A^{(0)} = \mathbf{E}^{[2]-1} A^{[1]}$, which is equal to the static limit of $N(\omega)$ and $N(-\omega)$. Solving the linear equations is the computational most demanding step (in terms of CPU time) in the computation of dispersion coefficients. Expanding the expressions for α, β, and γ to second order, we obtain:

$$D_{AB}(2) = 2A^{[1]\dagger}\mathbf{E}^{[2]-3}B^{[1]} = 2C_A^{(1)\dagger}C_B^{(0)}, \tag{14}$$

$$D_{ABC}(1,1) = 2\big[d_{ABC}(0,1,1) - d_{ABC}(1,0,1) - d_{ABC}(1,1,0) + 2d_{ABC}(2,0,0)\big], \tag{15}$$

$$D_{ABC}(2,0) = 2\big[d_{ABC}(0,2,0) - d_{ABC}(1,1,0) + d_{ABC}(2,0,0)\big], \tag{16}$$

$$D_{ABCD}(2,0,0) = 6d_{ABCD}(0,2,0,0) - 4d_{ABCD}(1,1,0,0) + 6d_{ABCD}(2,0,0,0)\big], \tag{17}$$

$$D_{ABCD}(1,1,0) = 4d_{ABCD}(0,1,1,0) - 4d_{ABCD}(1,1,0,0) - 4d_{ABCD}(1,0,1,0) + 12d_{ABCD}(2,0,0,0). \tag{18}$$

The intermediate coefficients $d_{ABC}(i,j,k)$, and $d_{ABCD}(i,j,k,l)$ are given by:

$$d_{ABC}(0,1,1) = \tfrac{1}{2}\hat{P}(B,C)\big[C^{[1]\dagger}\mathbf{E}^{[2]-2}\mathbf{A}^{[2]}\mathbf{E}^{[2]-2}B^{[1]}\big] = \tfrac{1}{2}\hat{P}(B,C)\big[C_C^{(1)\dagger}\mathbf{A}^{[2]}C_B^{(1)}\big], \tag{19}$$

$$d_{ABC}(0,2,0) = -\hat{P}(A,C)B^{[1]\dagger}\mathbf{E}^{[2]-3}\mathbf{A}^{[2]}\mathbf{E}^{[2]-1}C^{[1]} = -\hat{P}(A,C)C_B^{(2)\dagger}\mathbf{A}^{[2]}C_C^{(0)}, \tag{20}$$

$$\begin{aligned} d_{ABCD}(0,2,0,0) = {} & \tfrac{1}{6}P(A,C,D)\big[2C_B^{(2)\dagger}\mathbf{A}^{[2]}\mathbf{E}^{[2]-1}\mathbf{C}^{[2]}C_D^{(0)} \\ & + C_C^{(0)\dagger}\mathbf{A}^{[2]}\mathbf{E}^{[2]-3}\mathbf{B}^{[2]}C_D^{(0)} \\ & + C_D^{(0)\dagger}\mathbf{A}^{[2]}\mathbf{E}^{[2]-3}\mathbf{C}^{[2]}C_B^{(0)} \\ & + C_B^{(1)\dagger}\mathbf{C}^{[2]}\mathbf{E}^{[2]-2}\mathbf{A}^{[2]}C_D^{(0)} \\ & - 2\big(C_B^{(1)\dagger}C_A^{(1)}\big)\big(C^{[1]\dagger}C_D^{(0)}\big) \\ & - \big(C_D^{(0)\dagger}C_A^{(0)}\big)\big(C_C^{(1)\dagger}C_B^{(0)}\big)\big], \end{aligned} \tag{21}$$

$$\begin{aligned} d_{ABCD}(0,1,1,0) = {} & \tfrac{1}{4}\hat{P}(A,D)\hat{P}(B,C)\big[2C_A^{(0)\dagger}\mathbf{D}^{[2]}\mathbf{E}^{[2]-3}\mathbf{C}^{[2]}C_B^{(0)} \\ & - C_C^{(1)\dagger}\mathbf{D}^{[2]}\mathbf{E}^{[2]-1}\mathbf{A}^{[2]}C_B^{(1)} \\ & - C_C^{(1)\dagger}\mathbf{A}^{[2]}\mathbf{E}^{[2]-2}\mathbf{B}^{[2]}C_D^{(0)} \\ & - C_C^{(1)\dagger}\mathbf{D}^{[2]}\mathbf{E}^{[2]-2}\mathbf{A}^{[2]}C_B^{(0)} \\ & + C_B^{(1)\dagger}\mathbf{C}^{[2]}\mathbf{E}^{[2]-2}\mathbf{D}^{[2]}C_A^{(0)} \\ & + \big(C_C^{(1)\dagger}C_B^{(1)}\big)\big(A^{[1]}C_D^{(0)}\big)\big] \end{aligned} \tag{22}$$

and corresponding expressions where the indices A, B, C, and D are permuted.

The Cauchy vectors are all linear in the perturbation. Thus for α and β only equations that are linear in the perturbation need to be solved in order to obtain the dispersion coefficients. To obtain the dispersion coefficients for γ it is necessary to solve equations of the form:

$$X_{\mathrm{PR}}(l,k) = E^{[2]-l} P^{[2]} E^{[2]-k} R^{[1]}, \tag{23}$$

which are quadratic in the external perturbations, with P and R corresponding to one of the operators A, B, C, or D. No higher order equations need to be solved. This is in agreement with standard knowledge of derivative theory. To find the second and third energy derivates only equations that are linear in the perturbation need to be solved whereas to find the fourth derivative of the energy, equations that are quadratic in the perturbations need to be solved. This is an example of the $2n+1$ rule that says that the response of a wavefunction to nth order is sufficient to determine the energy derivatives to order $2n+1$.

3. Computational details

The calculations on the BH molecule were carried out for the ground state $^1\Sigma^+$ at the experimental internuclear distance 2.3289 a_0 [20]. The correlation consistent basis sets of Dunning and coworkers [21–23] were used for both molecules. For BH we used varying cardinal numbers X and augmentation levels x while for Ne only the basis sets aug-cc-pVDZ and d-aug-cc-pVDZ were employed. In both cases the 1s orbital was kept frozen. The CC calculations were carried out using a local version of the DALTON program. The derivation of the formulas for the CC dispersion coefficients is described in Refs. [5–7]. The FCI calculations were carried out using the LUCIA program [1] From both programs we obtained the Cartesian tensor components. In most experiments, all applied fields have parallel polarization. The measured quantities are the scalar components of the tensors α and γ given by the isotropic average, and the vector component of β in the direction of the permanent dipole moment μ which defines the molecular z axis:

$$\overline{\alpha} = \tfrac{1}{3}\sum_{\eta} \alpha_{\eta\eta}, \quad \eta = x,y,z, \tag{24}$$

$$\beta_{\parallel} = \tfrac{1}{5}\sum_{\eta} \{\beta_{z\eta\eta} + \beta_{\eta z\eta} + \beta_{\eta\eta z}\}, \quad \eta = x,y,z, \tag{25}$$

$$\gamma_{\parallel} = \tfrac{1}{15}\sum_{\eta\xi} \{\gamma_{\xi\eta\eta\xi} + \gamma_{\xi\eta\xi\eta} + \gamma_{\xi\xi\eta\eta}\}, \quad \eta,\xi = x,y,z. \tag{26}$$

For atoms the formulas are neatly reduced to $\overline{\alpha} = \alpha_{zz} = \alpha$ for the polarizability and employing $\gamma_{xxzz} + \gamma_{xzzx} + \gamma_{xzxz} = \gamma_{zzzz}$ to $\gamma_{\parallel} = \gamma_{zzzz} = \gamma$ for the second hyperpolarizability which is significantly reducing the computational cost. For linear molecules we have $\overline{\alpha} = \frac{1}{3}(2\alpha_{xx} + \alpha_{zz})$ for the polarizability. For the first and second hyperpolarizabilities, we calculated $\beta^{\mathrm{SHG}}_{\mu\nu\eta}(-2\omega;\omega,\omega)$ and $\gamma^{\mathrm{THG}}_{\mu\nu\eta\xi}(-3\omega;\omega,\omega,\omega)$, respectively. β^{SHG} is symmetric with respect to permutation of the second and third index, ν and η, whereas γ^{THG} is symmetric with respect to permutation of the second, third, and fourth index, ν, η, and ξ, which can be used to simplify the equations. For γ we furthermore use that for a linear molecule $\gamma_{xxyy} + \gamma_{xyyx} + \gamma_{xyxy} = \gamma_{xxxx}$, and we obtain

$$\beta^{\mathrm{SHG}}_{\parallel} = \tfrac{1}{5}\{3\beta_{zzz} + 2\beta_{zxx} + 4\beta_{xxz}\}, \tag{27}$$

$$\gamma^{\mathrm{THG}}_{\parallel} = \tfrac{1}{15}\{3\gamma_{zzzz} + 8\gamma_{xxxx} + 6\gamma_{zzxx} + 6\gamma_{xxzz}\}. \tag{28}$$

For the dispersion coefficients we adapt a similar notation such that the second-order dispersion coefficients of α, β, and γ can be expressed as:

$$\overline{D}^{\alpha}(2n) = \tfrac{1}{3}\sum_{\eta} D_{\eta\eta}(2n), \quad \eta = x,y,z, \tag{29}$$

$$D^{\beta}_{\parallel}(n,m) = \tfrac{1}{5}\sum_{\eta} D_{z\eta\eta}(n,m) + D_{\eta z\eta}(n,m) + D_{\eta\eta z}(n,m), \quad \eta = x,y,z, \tag{30}$$

$$D^{\gamma}_{\parallel}(l,m,n) = \tfrac{1}{15}\sum_{\eta\xi} D_{\xi\eta\eta\xi}(l,m,n) + D_{\xi\eta\xi\eta}(l,m,n) + D_{\xi\xi\eta\eta}(l,m,n), \quad \eta,\xi = x,y,z. \tag{31}$$

[1] LUCIA, a full restricted active-space CI program by J. Olsen, Lund, with contributions from H. Larsen.

By comparison of Eqs. (1) and (3) with, respectively, Eqs. (7) and (9), equations for the coefficients A_α, A_β, and A_γ are found as:

$$A_\alpha = \frac{1}{2\bar{\alpha}(0)}\bar{D}(2)\,, \tag{32}$$

$$A_\beta = \frac{1}{2\beta_\parallel(0)}D_\parallel(2,0)\,, \tag{33}$$

$$A_\gamma = \frac{1}{2\gamma_\parallel(0)}D_\parallel(2,0,0)\,. \tag{34}$$

4. Results and discussion

In Tables 1–3 we have given the second-order coefficients, A_α, A_β, and A_γ, of BH for different basis sets, and the wavefunction models CCS, CC2, CCSD, and FCI in order to investigate the sensitivity of the dispersion coefficients to the basis set and the wavefunction model. It has previously been stated that the dispersion coefficients are less dependent on the number of basis functions and the wave function model than the static hyperpolarizabilities [1–3]. However, recent studies of Hättig and Jørgensen [5,6] have shown that this is not the case – at least for the molecules they investigated. They found that the dispersion coefficients are as sensitive to both the number of basis functions and to the wavefunction model as the static properties. The variations, however, were found to be different from those observed for static polarizabilities and hyperpolarizabilities.

For both A_α, A_β, and A_γ the convergence in the hierarchy CCS–CC2–CCSD–FCI is nearly independent of the basis set. In particular for A_β a small change in the relative and absolute errors is seen when changing the cardinal number whereas the errors are constant when only changing the augmentation level. For A_α the CCS and CC2 values are nearly equal. The relative error between CC2 and CCSD is about 19% whereas there is an excellent agreement between CCSD and FCI with a relative deviation of about 0.1%. The dispersion coefficient of $\beta_\parallel(\omega)$, A_β, is not very well described by either of the approximate theories. For most basis sets both the CCS and CC2 models even fail to predict the correct sign. CCSD provides the correct sign, but underestimates the FCI second-order dispersion coefficient by about 16% for the TZ basis sets. The difficulties in describing A_β are not surprising. We have previously seen that large deviations from FCI for $\beta_\parallel(0)$ are due to an intricate cancellation of large contributions [24], and for $\beta_{xxz}(\omega)$ CCS and CC2 did not always give the correct sign [25]. Furthermore BH is indeed a very challenging system because of the low-lying excited states. Inspection of the Cartesian components of the second-order dispersion coefficient also shows that it is only for D_{xxz}

Table 1
Second-order coefficients, A_α, for $\bar{\alpha}(\omega)$ of BH in a.u. as a function of basis set and wavefunction model

	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	13.847	13.357	11.191	11.176
d-aug-cc-pVDZ	13.870	13.383	11.241	11.227
t-aug-cc-pVDZ	13.879	13.390	11.247	11.233
q-aug-cc-pVDZ	13.879	13.391	11.247	11.233
aug-cc-pVTZ	13.790	13.673	11.582	11.577
d-aug-cc-pVTZ	13.830	13.715	11.622	11.617
t-aug-cc-pVTZ	13.833	13.718	11.625	11.620

Table 2
Second-order coefficients, A_β, for $\beta_\parallel(-2\omega,\omega,\omega)$ of BH in a.u. as a function of basis set and wavefunction model

	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	−23.951	1.7372	17.921	20.370
d-aug-cc-pVDZ	−18.342	3.7128	19.032	21.502
t-aug-cc-pVDZ	−19.989	2.9780	18.860	21.361
q-aug-cc-pVDZ	−20.062	2.9389	18.835	21.336
aug-cc-pVTZ	−19.757	−2.1354	16.912	19.959
d-aug-cc-pVTZ	−23.892	−4.3756	16.718	19.960
t-aug-cc-pVTZ	−23.503	−4.1745	16.752	19.983

Table 3
Second-order coefficients, A_γ, of $\gamma_\parallel(-3\omega;\omega,\omega,\omega)$ of BH in a.u. as a function of basis set and wavefunction model

	CCS	CC2	CCSD	FCI
aug-cc-pVDZ	31.057	32.125	28.992	29.366
d-aug-cc-pVDZ	30.393	30.181	28.121	28.413
t-aug-cc-pVDZ	30.201	29.979	27.917	28.206
q-aug-cc-pVDZ	29.850	29.629	27.561	27.853
aug-cc-pVTZ	29.763	29.355	26.286	27.935
d-aug-cc-pVTZ	28.862	28.407	26.683	27.009
t-aug-cc-pVTZ	28.837	28.383	26.670	26.996

that CCS and CC2 fail to predict the correct sign, and it is also this component where the largest deviation between CCSD and FCI is observed. For A_γ both CCS and CC2 overestimate the second-order dispersion coefficient. CC2 is slightly improving the CCS results. As for A_α a very good agreement between CCSD and FCI is obtained. At the t-aug-cc-pVDZ level that we will consider later the relative error is 1.0%. Thus both for A_α and A_γ we obtain the same relative errors that previously have been observed for static $\alpha(0)$ and $\gamma(0)$ whereas for A_β they are much larger [24]. In the papers of Hättig and Jørgensen it was found that for dispersion coefficients, the CC2 model clearly was an improvement upon CCS in accordance with the good performance of CC2 for excitation energies [26,27]. However, this is not observed for BH.

If we compare the changes of the dispersion coefficients with the static (hyper)polarizabilities we see that the effect of changing the cardinal number is somewhat larger than the effect of augmentation with an additional set of diffuse functions. This is in agreement with recent investigations of the dispersion coefficients for NH_3 and CH_4 [5,6] where it was found that the dispersion coefficients are more sensitive to the cardinal number than to the augmentation level. For NH_3 and CH_4 diffuse functions are not as important for the dispersion coefficients as for the static (hyper)polarizabilities. This is also observed for BH. However, going from aug-cc-pVXZ to d-aug-cc-pVXZ still a noticeable change is seen whereas continuing to the triple augmented level hardly has any effect.

In Tables 4 and 5 we have given the approximate values of $\bar{\alpha}(\omega)$, $\beta_\parallel^{\mathrm{SHG}}(\omega)$, and $\gamma_\parallel^{\mathrm{THG}}(\omega)$ for CCSD and FCI by truncating the Taylor expansion after second order. Furthermore we have given the diagonal [0,1] Padé approximants [19,28] which are correct through the same order in the frequency argument as the truncated Taylor expansions. We employ a relatively small basis set, t-aug-cc-pVDZ since the variation between the CCSD and FCI wavefunctions is not very sensitive to the basis set. The frequencies were chosen according to the location of the first pole. The lowest excitation energies are 0.2345 a.u. ($^1\Sigma^+$) and 0.1083 a.u. ($^1\Pi$) calculated using FCI and a t-aug-cc-pVDZ basis set. The first pole in $\alpha(\omega)$ thus corresponds to the excitation energy for $^1\Pi$. For the second harmonic generation and third harmonic generation hyperpolarizabilities, $\beta_\parallel^{\mathrm{SHG}}(\omega)$ and $\gamma_\parallel^{\mathrm{THG}}(\omega)$, the situation is different. The first pole occurs already when ω equals one-half and one-third of the

Table 4
Analytic values of $\bar{\alpha}(\omega)$, $\beta_\parallel^{\mathrm{SHG}}(\omega)$, and $\gamma_\parallel^{\mathrm{THG}}(\omega)$ for BH compared with the Taylor series to second- and fourth-order and the diagonal Padé approximants for CCSD. The basis set is t-aug-cc-pVDZ. All values are in a.u.

	$\omega = 0.0$ (4556 nm)	$\omega = 0.01$ (2278 nm)	$\omega = 0.02$ (1519 nm)	$\omega = 0.03$ (1064 nm)	$\omega = 0.0428286$ (694.3 nm)	$\omega = 0.0656249$ (488.0 nm)	$\omega = 0.093368$
$\bar{\alpha}(\omega)$	21.626	21.675	21.825	22.090	22.640	24.601	34.300
Taylor (2)	–	21.674	21.820	22.063	22.518	23.721	25.866
Padé [0,1]	–	21.674	21.822	22.073	22.556	23.945	26.901
Taylor (4)	–	21.675	21.825	22.088	22.622	24.292	27.073
Padé [1,1]	–	21.675	21.825	22.090	22.634	24.505	31.095
$\beta_\parallel^{\mathrm{SHG}}(\omega)$	70.382	71.184	73.648	77.896	85.005	–	–
Taylor (2)	–	71.178	73.568	77.550	84.991	–	–
Padé [0,1]	–	71.187	73.719	78.363	88.817	–	–
Taylor (4)	–	71.184	73.653	77.980	86.777	–	–
Padé [1,1]	–	71.1827	73.640	77.928	86.651	–	–
$\gamma_\parallel^{\mathrm{THG}}(\omega)$	11182	11573	13018	17941	–	–	–
Taylor (2)	–	11556	12680	14553	–	–	–
Padé [0,1]	–	11569	12912	16008	–	–	–
Taylor (4)	–	11572	12931	15821	–	–	–
Padé [1,1]	–	11581	13719	16636	–	–	–

Table 5
Analytic values of $\overline{\alpha}(\omega)$, $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$, and $\gamma_{\parallel}^{\mathrm{THG}}(\omega)$ for BH compared with the Taylor series to second-order and the [0,1] diagonal Padé approximants for FCI. The basis set is t-aug-cc-pVDZ. All values are in a.u.

	$\omega = 0.0$	$\omega = 0.01$ (4556 nm)	$\omega = 0.02$ (2278 nm)	$\omega = 0.03$ (1519 nm)	$\omega = 0.0428286$ (1064 nm)	$\omega = 0.0656249$ (694.3 nm)	$\omega = 0.093368$ (488.0 nm)
$\overline{\alpha}(\omega)$	21.634	21.683	21.833	22.098	22.648	24.621	34.721
Taylor	–	21.682	21.828	22.071	22.525	23.727	25.870
Padé	–	21.682	21.830	22.080	22.563	23.951	26.902
$\beta_{\parallel}^{\mathrm{SHG}}(\omega)$	74.462	75.426	78.449	83.955	96.068	–	–
Taylor	–	75.416	78.279	83.051	91.968	–	–
Padé	–	75.429	78.486	84.171	97.348	–	–
$\gamma_{\parallel}^{\mathrm{THG}}(\omega)$	11321	11722	13203	18349	–	–	–
Taylor	–	11704	12854	14770	–	–	–
Padé	–	11718	13094	16281	–	–	–

lowest excitation energy, respectively. Thus the first poles of $\beta_{\parallel}^{\mathrm{SHG}}(\omega)$ and $\gamma_{\parallel}^{\mathrm{THG}}(\omega)$ occur already at $\omega = 0.0542$ and $\omega = 0.0361$ a.u., respectively.

Since we are only considering the second-order dispersion coefficients we may only expect converged results for low frequencies. The [0,1] diagonal Padé approximant improves the convergence to some extent. For all three properties, we see that, as expected, the deviation from the analytic results increases with increasing frequency. For $\overline{\alpha}$ the deviations from the analytic results are for the first four frequencies below 0.5% which is also the case for the first three frequencies considered for $\beta_{\parallel}$. For the last frequency of $\beta_{\parallel}$ the error is 1.3% for FCI which should be compared to an error of 11.5% between the analytic results of CCSD and FCI. For $\gamma_{\parallel}$ the truncation error of the two lower frequencies is less than 1% which is acceptable for electronic hyperpolarizabilities.

Both for $\alpha(\omega)$ and $\gamma(\omega)$ the agreement between CCSD and FCI for the static case is maintained when increasing the frequency whereas for $\beta(\omega)$ this is not the case. This is due to the poor agreement between the second-order dispersion coefficients of $\beta(\omega)$. For CCSD we have also included the fourth-order dispersion coefficients. The results are not in all cases improved as expected. For $\omega = 0.0428286$ a.u. $\beta(\omega)$ and $\gamma(\omega)$ are overestimated. Inspection of the higher-order terms shows that both the sixth-, eight-, and tenth-order coefficients have a sign which is opposite to that of the second- and fourth-order coefficients. The good agreement for the second-order Taylor expansion with the analytic result for $\beta(\omega)$ at $\omega = 0.0428286$ a.u. is accidental. For $\beta(\omega)$ this is supported by the [0,1] Padé approximant which overestimates the result significantly. However, for $\beta(\omega)$ at $\omega = 0.0428286$ a.u. for FCI the second-order Taylor approximation underestimates the analytic result significantly whereas the [0,1] Padé approximant improves the result.

In Table 6 we have given the second-order dispersion coefficients of Ne, and in Table 7 we compare the analytic values of the CCSD and FCI wavefunction models with the truncated Taylor expansion. The basis sets are not good enough to compare with extrapolated values from the literature but we do note that there is a significant change in the dispersion coefficient when changing the basis set and the wavefunction model which is in contrast to previous statements that the dispersion coefficients of Ne were insensitive to basis set and wavefunction model [1]. For Ne the CC2 model overestimates the CCSD results but is much closer to CCSD than CCS. This is in accordance with what has been observed for excitation energies [26,27]. As mentioned in Section 1, Ne has higher excitation energies than BH, 0.7073

Table 6
Values of second-order coefficients for α and γ of Ne in a.u.

	aug-cc-pVDZ		d-aug-cc-pVDZ	
	D_{α}	D_{γ}	D_{α}	D_{γ}
CCS	0.33230	2.1584	0.42132	2.1640
CC2	0.44959	2.7292	0.57312	3.0349
CCSD	0.42716	2.6269	0.53878	2.8064
FCI	0.41737	2.5828	0.52703	–

Table 7
Analytic values of $\alpha(\omega)$ and $\gamma^{\mathrm{THG}}(\omega)$ of Ne compared with the Taylor series and the diagonal Padé approximant for CCSD and FCI. The basis set is aug-cc-pVDZ. All values are given in a.u.

	$\omega = 0.0$		$\omega = 0.0428286$ $\lambda = 1064$ nm		$\omega = 0.0656249$ $\lambda = 694.3$ nm		$\omega = 0.093368$ $\lambda = 488.0$ nm	
	CCSD	FCI	CCSD	FCI	CCSD	FCI	CCSD	FCI
$\alpha(\omega)$	2.0028	1.9811	2.0060	1.9842	2.0102	1.9883	2.0180	1.9958
Taylor (2)	–	–	2.0060	1.9842	2.0102	1.9883	2.0177	1.9956
Padé [0,1]	–	–	2.0060	1.9842	2.0102	1.9883	2.0178	1.9957
$\gamma^{\mathrm{THG}}(\omega)$	29.593	28.093	31.374	29.755	34.017	32.214	39.558	37.355
Taylor (2)	–	–	31.304	29.691	33.611	31.843	37.726	35.684
Padé [0,1]	–	–	31.409	29.787	34.242	32.421	40.808	38.494
Taylor (4)	–	–	31.372	–	33.983	–	39.250	–
Padé [1,1]	–	–	31.375	–	34.021	–	39.602	–

a.u. for the ^{1}P state (FCI, aug-cc-pVDZ). For the three frequencies included in Table 7, we obtain full convergence for $A_{\alpha(\mathrm{Ne})}$. For $A_{\gamma(\mathrm{Ne})}$ the deviations from the analytic results are between 0.1% and 3% which again should be compared to a deviation between the CCSD and FCI results of 7%.

Thus for both molecules we have truncation errors that are smaller than the errors between FCI and CCSD. For $\bar{\alpha}$ and $\gamma_{\parallel}^{\mathrm{THG}}(\omega)$ of Ne the frequencies even lie within the usual experimental range.

5. Conclusions

Analytic second-order dispersion coefficients have been derived and implemented for the second-, third-, and fourth-order properties in full configuration interaction linear, quadratic, and cubic response theory. The dispersion coefficients are defined through a power series expansion in their frequency arguments and are thus independent of the non-linear optical process. The computation of one dispersion coefficient costs approximately the same as one point for a frequency-dependent property. This provides an efficient and compact way of benchmarking the frequency-dependent properties.

In an application we found that the deviation between the second-order dispersion expansion and the analytic result is, in most cases, less than that between CCSD and FCI. Because of the expense of the FCI calculations, it is at the moment not possible to calculate the FCI values in large basis sets close to basis set saturation. However, in cases where the CCSD and FCI wavefunctions have similar convergence trends, and the difference between the two wavefunctions does not vary much with the basis sets it is possible to estimate the remaining error between the CCSD and the exact result from results obtained with smaller basis sets that are more suitable for FCI calculations. It is thus possible, in a relatively cheap way, to benchmark the dispersion, the only requirement being that the dispersion expansion can be truncated to low order. For that reason, the molecule should not have low excitation energies.

The dependency on basis set and wavefunction model was investigated and, contrary to previous statements, we found significant variations with the basis set and the wavefunction model employed.

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