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Frequency-dependent first hyperpolarizabilities using coupled cluster quadratic response theory

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Abstract

The first implementation of frequency-dependent hyperpolarizabilities is presented using coupled cluster quadratic response theory. The quadratic response functions are derived for the coupled cluster model hierarchy CCS, CC2 and CCSD and implemented for general frequency-dependent first hyperpolarizabilities. Calculations are performed on the second harmonic generation and the optical rectification hyperpolarizabilities of FH and the results are compared with experimental results and former theoretical investigations. © 1997 Elsevier Science B.V.

1. Introduction

During the last decade accurate ab initio calculations of static first and second hyperpolarizabilities for atoms and small molecules have become available through the use of accurate correlation methods combined with the finite field technique and reliable basis sets [1]. However, most of the experimental data on hyperpolarizabilities are obtained from experiments that use optical processes and are therefore related to the frequency-dependent hyperpolarizabilities at the particular frequencies used in the experiment. For hyperpolarizabilities the dispersion is often large, and the extrapolation from a limited set of experimentally determined frequency-dependent hyperpolarizabilities to the static zero frequency limit is a difficult task, if it is at all possible. This often hinders the direct comparison of the experimental data with theoretically determined static properties. The direct ab initio calculation of the frequency-dependent properties has only been routine for correlated wavefunctions at the MCSCF [2,3] level. Dynamical electron correlation effects are often crucially important for hyperpolarizabilities and MCSCF hyperpolarizabilities are therefore, with the exception of small systems, limited in accuracy.

It is well known that the effect of dynamical correlation in general is most efficiently dealt with using second-order Møller–Plesset perturbation theory or coupled cluster theory. The development of frequency-dependent response properties for these and other non-variational correlation methods have been hindered by the lack of a general theory for frequency-dependent response functions for non-variational correlation methods. These difficulties have recently been overcome through the introduction of time-dependent quasi-energy Lagrangians [4–6] and linear and non-linear response functions have been derived within this framework for a series of methods [4,7–11]. Implementations and applications of linear response functions derived from quasi-energy Lagrangians have been reported for dynamic polarizabilities at the MP2 level [8,9] and for excitation energies for a hierarchy of coupled cluster

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models CCS, CC2, CCSD and CC3 [10–12].

CCSD linear and quadratic response properties have been derived previously [13–15], and an implementation of the frequency-dependent polarizabilities has been presented in Ref. [16] in a form compatible with the $2n+1$ and $2n+2$ rule expressions [17,18] obtained directly from the quasi-energy Lagrangian. An implementation of analytical static hyperpolarizabilities has been presented int Ref. [19]. In addition to being limited to static hyperpolarizabilities, this implementation did not exploit the benefits of the $2n+1$ and $2n+2$ rules, hindering its use as an efficient tool for accurate hyperpolarizability calculations.

An important advantage of coupled cluster based methods relative to other non-variational correlation methods is that the pole structure is in accordance with the exact response function and that the positions of the poles are improved systematically within the hierarchy CCS, CC2, CCSD, CC3, and CCSDT. Such a systematic improvement of the pole structure will not be obtained for methods based on Møller–Plesset perturbation theory, while implementations based on truncated CI approaches will suffer from increased requirements for the configuration space to account for orbital relaxation effects [20,21].

In the present Letter we report an implementation of the general frequency-dependent quadratic response functions for the coupled cluster models CCS, CC2 and CCSD, using the $2n+1$ and $2n+2$ rule expressions. We present a first application of the coupled cluster quadratic response (CCQR) approach to the second harmonic generation (SHG) and the optical rectification (OR) hyperpolarizabilities of the FH molecule.

2. Coupled cluster quadratic response theory

To derive the quadratic response function in a form that is applicable to both non-approximated and approximated coupled cluster models we use the variational Lagrangian approach [18,22,23] based on the time-dependent coupled cluster quasi-energy [11]. We consider the case where a system described by $H^{(0)}$ is perturbed by an external one electron perturbation

$$H(\epsilon,t) = H^{(0)} + V(\epsilon,t), \tag{1}$$

and we assume that $V(\epsilon,t)$ can be written as a sum over Fourier components:

$$V(\epsilon,t) = \sum_X H^X \epsilon_X(\omega_X) \mathrm{e}^{-i\omega_X t}. \tag{2}$$

For time-dependent perturbations orbital relaxation is not treated explicitly but only approximately through the single excitation manifolds of the coupled cluster parameters as discussed previously [10]. The coupled cluster quasi-energy can then be written as

$$\begin{aligned}\mathcal{W}(\epsilon,t) &= \langle \mathrm{HF}| \left(H(\epsilon,t) - i\frac{\mathrm{d}}{\mathrm{d}t} \right) \exp(T) |\mathrm{HF}\rangle \\ &= \langle \mathrm{HF}| H(\epsilon,t) \exp(T) |\mathrm{HF}\rangle. \end{aligned} \tag{3}$$

Based on an expansion of $T(\epsilon,t)$ in $V(\epsilon,t)$,

$$\begin{aligned} T(\epsilon,t) &= \sum_\mu t_\mu(\epsilon,t)\tau_\mu \\ &= \sum_\mu (t_\mu^{(0)} + t_\mu^{(1)}(\epsilon,t) + t_\mu^{(2)}(\epsilon,t) + \ldots)\tau_\mu, \end{aligned} \tag{4}$$

the cluster amplitudes can in each order be written as a sum over Fourier components, as for example for the linear response

$$t_\mu^{(1)}(\epsilon,t) = \sum_X t^X(\omega_X)\epsilon_X(\omega_X)\mathrm{e}^{-i\omega_X t}. \tag{5}$$

For the coupled cluster models we consider here, the time-dependent amplitudes are determined by a set of equations that can be written in the form

$$e_\mu(\epsilon,t) - i\frac{\mathrm{d}t_\mu}{\mathrm{d}t} = 0, \tag{6}$$

where the expression $e_\mu(\epsilon,t)$ does not contain derivatives with respect to time. (See Table 1 of Ref. [10] for explicit expressions for the amplitude equations for CCS, CC2, CCSD, CC3 and CCSDT.) The coupled cluster quasi-energy Lagrangian then becomes

$$L(\epsilon,t) = \mathcal{W}(\epsilon,t) + \sum_\mu \bar{t}_\mu \left(e_\mu(\epsilon,t) - i\frac{\mathrm{d}t_\mu}{\mathrm{d}t} \right). \tag{7}$$

The equations for the amplitudes and for the multipliers and their response to the external fields can be obtained from the quasi-energy Lagrangian by requiring that the time average $\{L(\epsilon,t)\}_T$ of the Lagrangian is

stationary in the Fourier components of the amplitudes $t(\epsilon,t)$ and the Langrangian multipliers $\bar{t}(\epsilon,t)$ [4–6].

In zeroth order one obtains the coupled cluster equations for the unperturbed system

$$\boldsymbol{e}(0) = \mathbf{0}, \tag{8}$$

and the equations for the zeroth-order multipliers

$$\bar{\boldsymbol{t}}^{(0)}\mathbf{A} = \boldsymbol{\eta}^{(0)}, \tag{9}$$

where the Jacobian $\mathbf{A}$ and the vector $\boldsymbol{\eta}^{(0)}$ are defined as

$$A_{\mu\nu} = \left(\frac{\mathrm{d}e_\mu}{\mathrm{d}t_\nu}\right)_0, \tag{10}$$

$$\eta_\nu^{(0)} = \left(\frac{\mathrm{d}\mathcal{W}}{\mathrm{d}t_\nu}\right)_0. \tag{11}$$

The index 0 indicates that the derivatives are taken at $\epsilon = 0$, i.e., for the unperturbed molecule. For explicit expressions see table I of Ref. [10]. According to the $2n+1$ and the $2n+2$ rules [18] we need for the quadratic response properties also the first order response for the amplitudes and for the multipliers, which are determined from

$$\boldsymbol{\xi}^A + (\mathbf{A} - \omega_A\mathbf{1})\,\boldsymbol{t}^A(\omega_A) = \mathbf{0}, \tag{12}$$

$$\boldsymbol{\eta}^A + \mathbf{F}\boldsymbol{t}^A(\omega_A) + \bar{\boldsymbol{t}}^A(\omega_A)\,(\mathbf{A} + \omega_A\mathbf{1}) = \mathbf{0}, \tag{13}$$

where the vectors $\boldsymbol{\eta}^A$ and $\boldsymbol{\xi}^A$ and the matrix $\mathbf{F}$ are defined by

$$\eta_\nu^A = \left(\frac{\partial^2\{L\}_T}{\partial\epsilon_A(\omega_A)\,\partial t_\nu^B(-\omega_A)}\right)_0, \tag{14}$$

$$\xi_\mu^A = \left(\frac{\partial^2\{L\}_T}{\partial\epsilon_A(\omega_A)\,\partial \bar{t}_\mu^B(-\omega_A)}\right)_0, \tag{15}$$

$$F_{\mu\nu} = \left(\frac{\partial^2\{L\}_T}{\partial t_\mu^A(\omega_A)\,\partial t_\nu^B(-\omega_A)}\right)_0. \tag{16}$$

We note, that these vectors and matrices are independent of the actual choice of operator B and the frequency ω_A. The linear and quadratic response functions are obtained taking the second and the third derivative of the time-averaged quasi-energy Lagrangian with respect to the field strengths. The frequency-dependent polarizability becomes accordingly

$$\boldsymbol{\alpha}_{AB}(\omega_A;\omega_B) = \tfrac{1}{2}\hat{P}^{\pm\omega}\{\boldsymbol{\eta}^A\boldsymbol{t}^B(\omega_B) + \mathbf{F}\boldsymbol{t}^A(\omega_A)\boldsymbol{t}^B(\omega_B) + \boldsymbol{\eta}^B\boldsymbol{t}^A(\omega_A)\}, \tag{17}$$

with $\omega_A = -\omega_B$, and for the frequency-dependent first hyperpolarizability one obtains

$$\begin{aligned}\boldsymbol{\beta}_{ABC}(\omega_A;\omega_B,\omega_C) = {}& \tfrac{1}{2}\hat{P}^{\pm\omega}\{\mathbf{G}\boldsymbol{t}^A(\omega_A)\boldsymbol{t}^B(\omega_B)\boldsymbol{t}^C(\omega_C) \\ & + \tfrac{1}{2}\hat{\mathbf{P}}^{ABC}\mathbf{B}\bar{\boldsymbol{t}}^A(\omega_A)\boldsymbol{t}^B(\omega_B)\boldsymbol{t}^C(\omega_C) \\ & + \tfrac{1}{2}\hat{\mathbf{P}}^{ABC}\mathbf{F}^A\boldsymbol{t}^B(\omega_B)\boldsymbol{t}^C(\omega_C) \\ & + \hat{\mathbf{P}}^{ABC}\mathbf{A}^A\bar{\boldsymbol{t}}^B(\omega_B)\boldsymbol{t}^C(\omega_C)\},\end{aligned} \tag{18}$$

with $\omega_A = -(\omega_B + \omega_C)$ and the matrices $\mathbf{G}$, $\mathbf{B}$, $\mathbf{F}^A$ and $\mathbf{A}^A$ defined as:

$$G_{\mu\nu\gamma} = \left(\frac{\partial^3\{L\}_T}{\partial t_\mu^A(\omega_A)\,\partial t_\nu^B(\omega_B)\,\partial t_\gamma^C(\omega_C)}\right)_0, \tag{19}$$

$$B_{\mu\nu\gamma} = \left(\frac{\partial^3\{L\}_T}{\partial \bar{t}_\mu^A(\omega_A)\,\partial t_\nu^B(\omega_B)\,\partial t_\gamma^C(\omega_C)}\right)_0, \tag{20}$$

$$F_{\mu\nu}^A = \left(\frac{\partial^3\{L\}_T}{\partial\epsilon_A(\omega_A)\,\partial t_\mu^B(\omega_B)\,\partial t_\nu^C(\omega_C)}\right)_0, \tag{21}$$

$$A_{\mu\nu}^A = \left(\frac{\partial^3\{L\}_T}{\partial\epsilon_A(\omega_A)\,\partial \bar{t}_\mu^B(\omega_B)\,\partial t_\nu^C(\omega_C)}\right)_0. \tag{22}$$

The operator $\hat{P}^{ABC}$ symmetrizes with respect to the perturbation indices A, B and C and the accompanied frequencies. In difference to Refs. [14–16] we use here a definition of the polarizabilities and hyperpolarizabilities that is explicitly symmetrized with respect to an overall sign change of the frequencies by the operator $\hat{P}^{\pm\omega}$ in order to keep only the symmetric part of the response functions which are identified with the physical properties, i.e., the polarizabilities and hyperpolarizabilities.

For the time-dependent non-approximated coupled cluster models with a fixed Hartree–Fock reference, i.e., non-relaxed orbitals, the quasi-energy Lagrangian can be written in the form:

$$L_{\text{non-app.}}(\epsilon,t) = \left\{\langle\mathrm{HF}| + \sum_{\mu_i}\bar{t}_{\mu_i}\langle\mu_i|\right\}\exp(-T) \times \left(H - i\frac{\mathrm{d}}{\mathrm{d}t}\right)\exp(T)|\mathrm{HF}\rangle \tag{23}$$

with

$$T = \sum_{\nu_i} t_{\nu_i} \tau_{\nu_i}, \tag{24}$$

where the labels μ_i, ν_i refer to an ordering with respect to the excitation class i, $i = 1, 2, \ldots$ and a numbering μ, ν within the excitation class. For CCS and CCSD the summations in (23) are restricted to $i = 1$, and $i = 1, 2$, respectively. The Lagrangian for the CC2 model is obtained from the CCSD Lagrangian by approximating the terms proportional to $\bar{t}_{\mu_2}$, i.e., the doubles amplitude equations:

$$\begin{aligned} L_{\mathrm{CC2}}(\epsilon, t) &= \langle \mathrm{HF}| H \exp(T_1 + T_2) |\mathrm{HF}\rangle \\ &+ \sum_{\mu_1} \bar{t}_{\mu_1} \langle \mu_1 | \hat{H} + [\hat{H}, T_2] |\mathrm{HF}\rangle \\ &+ \sum_{\mu_2} \bar{t}_{\mu_2} \langle \mu_2 | \hat{H} + [\hat{F} + \hat{V}(\epsilon, t), T_2] |\mathrm{HF}\rangle, \end{aligned} \tag{25}$$

where F is the unperturbed Fock operator and the T_1 transformed operators $\hat{O}$, $O = H, F, V$ are defined through

$$\hat{O} = \exp(-T_1) O \exp(T_1). \tag{26}$$

The approximation introduced going from CCSD to CC2 reduces the operation count from N^6 to N^5.

From the Lagrangians the expressions for the matrices **A**, **F**, **G**, **B**, $\mathbf{A}^A$ and $\mathbf{F}^A$ are derived straightforwardly for each of the coupled cluster models. We note, that for the implementation of the response equations and the response properties these matrices are not needed explicitly but only linear transformations of the types $\mathbf{A}t^X$, $\bar{t}^X\mathbf{A}$, $\mathbf{F}t^X$, $\mathbf{G}t^Xt^Y$, $\bar{t}^Y\mathbf{B}t^X$, $\bar{t}^X\mathbf{A}^A$, and $\mathbf{F}^At^X$.

The expressions for the Jacobian and the implementation of the transformation of a trial vector with **A** from the right and from the left are discussed in detail elsewhere [24,25]. The **F** matrix transformations $\mathbf{F}t^X$, and the **G** matrix transformations $\mathbf{G}t^Xt^Y$ will be discussed in detail in subsequent papers on the integral-direct implementation of coupled cluster polarizabilities and hyperpolarizabilities. Contractions of the **B** matrix with one vector from the left and one vector from the right, $\bar{t}^Y\mathbf{B}t^X$, can be calculated as **F** matrix transformations with the zeroth-order multipliers $\bar{t}^{(0)}$ exchanged by the response multipliers $\bar{t}^Y$ and the term that results from projections to the Hartree–Fock reference, $\langle \mathrm{HF}|[[H^{(0)}, T_1^X], \tau_1]|\mathrm{HF}\rangle$, excluded. Expressions for the transformations $\bar{t}^X\mathbf{A}^A$, and $\mathbf{F}^At^X$ can be obtained from the corresponding expressions for the Jacobian and the **F** matrix by exchanging the zeroth-order Hamiltonian $H^{(0)}$ with the one-electron operator H^A.

3. SHG and EOPE hyperpolarizabilities for FH

To demonstrate the usefulness of the coupled cluster quadratic response approach and our implementation we applied it to the second harmonic generation (SHG) and optical rectification (OR) hyperpolarizabilities of the FH molecule. For SHG we have $\omega_C = \omega_B = \omega$, while for OR $\omega_C = -\omega_B = \omega$. In the following we use the shorthand notation $\boldsymbol{\beta}^{\mathrm{SHG}}_{ABC}(\omega) = \boldsymbol{\beta}_{ABC}(-2\omega; \omega, \omega)$ and $\boldsymbol{\beta}^{\mathrm{OR}}_{ABC}(\omega) = \boldsymbol{\beta}_{ABC}(0; -\omega, \omega)$. The hyperpolarizabilities obtained through the linear electro-optic effect (LEOE), also known as the electro-optic Pockels effect (EOPE), where $\omega_B = \omega$ and $\omega_C = 0$, are identical to $\boldsymbol{\beta}^{\mathrm{OR}}$ except for a permutation of the indices: $\boldsymbol{\beta}^{\mathrm{LEOE}}_{ABC}(\omega) = \boldsymbol{\beta}^{\mathrm{OR}}_{CAB}(\omega)$.

One of the most critical steps in the calculation of hyperpolarizabilities is the choice of the basis set. For the present investigation we employed the triply-augmented polarized valence correlation consistent triple zeta (t-aug-cc-pVTZ) basis sets of Woon and Dunning [26], which for the FH molecule consist of a (13s8p5d4f/9s5p4d)/[7s6p5d4f/6s5p4d] contraction. Based on test calculations of the static hyperpolarizabilities with basis sets of the x-aug-cc-pVXZ series (x = d, t, q and X = D, T, Q) we expect the CCSD results obtained with the chosen basis set to be converged within ±0.2 au, compared to the basis set limit.

Table 1 lists the results obtained for the dipole moment and the static polarizabilities and first hyperpolarizabilities at the equilibrium internuclear distance. For the dipole moment and for the longitudinal components of the (hyper-)polarizabilities the SCF results obtained with the t-aug-cc-pVTZ basis are close to the values calculated by Adamowicz and Bartlett [27] by combining a numerical Hartree–Fock with the finite field method. The static CCSDLR/QR results for the longitudinal components are close to the results obtained by Kondo et al. [19] for Sadlej's medium sized

Table 1
Static properties of the FH molecule. All ab initio values are given for the equilibrium internuclear distance, R_e = 1.7328 au. The direction of the positive z axis is from F to H

	μ_z	α_{zz}	α_{xx}	β_{zzz}	β_{zxx}
SCF [a]	0.756	5.758	4.494	−8.399	−0.510
CCSLR/QR [a]	0.756	6.060	4.673	−10.039	−1.001
CC2LR/QR [a]	0.691	6.789	5.664	−12.281	−2.790
CCSDLR/QR [a]	0.706	6.410	5.253	−9.841	−1.690
num. HF [b]	0.756	5.75		−8.5	
CAS 4420 [c]	0.7235	6.1983	5.093	−8.722	−1.045
CAS 6331 [c]	0.7225	6.167	5.028	−8.850	−1.102
CCSD [d]	0.7107	6.234	5.055	−8.854	−1.122
CCSD(T) [d]	0.7038	6.345	5.187	−9.185	−1.390
MP2 [e]	0.7069	6.4326	5.3975	−9.10	−1.25
CCSD [e]	0.7062	6.3440	5.2390	−9.24	−1.03
CCSD(T) [e]	0.7008	6.4378	5.3398	−9.62	−1.27
CCSDLR/QR [f]	0.6995	6.521		−9.869	
exp. [g]	0.707	6.40	5.08		

[a] This work.
[b] Ref. [27].
[c] Ref. [32], for a [8s6p4d3f/5s3p2d] basis.
[d] Ref. [28], basis B, [8s6p4d3f/5s3p2d].
[e] Ref. [29], for Sadlej's [5s3p2d/3s2p] basis augmented with a d-type cartesian function for hydrogen and 1s1p lone pair functions.
[f] Ref. [19], for Sadlej's [5s3p2d/3s2p] basis.
[g] Ref. [35], equilibrium vibrationless values estimated from experimental data and vibrational corrections.

polarized basis sets. The somewhat larger differences between the CCSDQR hyperpolarizabilities obtained in the present study and the CCSD finite field results given by Chong and Langhoff [28] and by Sekino and Bartlett [29] are partly due to differences in the basis sets and partly to the different treatment of the orbital relaxation.

Comparing the different coupled cluster models we observe an unexpected progression in the series CCS, CC2 and CCSD: the CCS model gives for all polarizability and hyperpolarizability components of FH results between the respective SCF and CCSD numbers, while CC2 overestimates the correlation contributions which results in unexpected large discrepancies between the CC2 and CCSD hyperpolarizabilities. It is not clear whether this is a result of an accidentally good agreement for CCS or if the CC2 model gives an insufficient description of the correlation effects in FH. We also note a large difference between the CC2 and MP2 hyperpolarizabilities. However, a closer analysis for a more representative set of molecules is necessary to get a better picture of the performance of the particular coupled cluster response models for the calculation of hyperpolarizabilities.

In Table 2 we give CCS-, CC2- and CCSD-QR results for SHG and OR hyperpolarizabilities at typical laser frequencies. Of particular interest are the results for the SHG hyperpolarizabilities at a wavelength of 694.3 nm, because they can be compared with experimental results of Dudley and Ward [30]. The experimental data must be compared with the hyperpolarizability component

$$\boldsymbol{\beta}_{\parallel} = \sum_i \tfrac{1}{5}(\boldsymbol{\beta}_{iiz} + \boldsymbol{\beta}_{izi} + \boldsymbol{\beta}_{zii}), \tag{27}$$

where the z axis is that of the permanent dipole moment. Eq. (27) reduces for the SHG and OR hyperpolarizabilties of a linear molecule to

$$\boldsymbol{\beta}_{\parallel}(\omega) = \tfrac{1}{5}\big(3\boldsymbol{\beta}_{zzz}(\omega) + 2\boldsymbol{\beta}_{zxx}(\omega) + 4\boldsymbol{\beta}_{xzx}(\omega)\big). \tag{28}$$

The main contribution to $\boldsymbol{\beta}_{\parallel}$ comes from the longitudinal component of the electronic contribution $\boldsymbol{\beta}_{zzz}$. We have plotted the result obtained for $\boldsymbol{\beta}_{zzz}$ with the three coupled cluster models CCS, CC2 and CCSD as a function of the frequency in Fig. 1. As comparison we included the CAS4220 and the SCF results of Ref. [32]. Fig. 1 reflects the points discussed for static hyperpolarizabilities: the SCF and CAS4220 results are too small due to the missing or underestimated correlation contribution, the CCS results are accidentally almost the same as the CCSD results, while the CC2 model overshoots by about 2 au.

A similar sensitivity to the correlation treatment is exhibited by the dispersion of $\boldsymbol{\beta}_{zzz}$. To compare the frequency dependence obtained in the different methods, we calculated the coefficient A_{zzz} [33]:

$$\boldsymbol{\beta}^{\mathrm{SHG}}_{zzz}(\omega) = \boldsymbol{\beta}_{zzz}(0)\left(1 + 6\omega^2 A_{zzz} + \mathcal{O}(\omega^4)\right), \tag{29}$$

$$A_{zzz} = \lim_{\omega\to 0} \frac{\boldsymbol{\beta}^{\mathrm{SHG}}_{zzz}(\omega) - \boldsymbol{\beta}_{zzz}(0)}{6\omega^2 \boldsymbol{\beta}_{zzz}(0)}. \tag{30}$$

We obtained 2.55, 3.42 and 3.17 for the CCS, the CC2 and the CCSD dispersion curves. The respective val-

Table 2
Hyperpolarizabilities for the FH molecule for R_e = 1.7328 au. The direction of the positive z axis is from F to H

	λ/ nm	$\beta_{zzz}(\omega)$			$\beta_{zxx}(\omega)$			$\beta_{xzx}(\omega)$		
		CCS	CC2	CCSD	CCS	CC2	CCSD	CCS	CC2	CCSD
static	∞	−10.039	−12.281	−9.841	−1.001	−2.790	−1.690	−1.001	−2.790	−1.690
SHG	1319	−10.225	−12.588	−10.069	−1.002	−2.873	−1.724	−1.037	−2.939	−1.778
	694.3	−10.738	−13.445	−10.702	−1.002	−3.103	−1.818	−1.145	−3.402	−2.051
	488.8	−11.539	−14.816	−11.706	−0.992	−3.474	−1.958	−1.340	−4.307	−2.576
OR	1319	−10.100	−12.382	−9.916	−1.016	−2.846	−1.724	−1.005	−2.825	−1.707
	694.3	−10.263	−12.651	−10.116	−1.059	−2.999	−1.819	−1.016	−2.917	−1.753
	488.8	−10.500	−13.046	−10.408	−1.123	−3.239	−1.968	−1.033	−3.056	−1.822

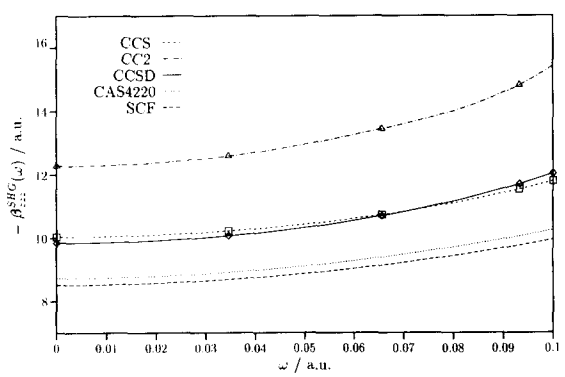


Fig. 1. The dispersion of $\beta_{zzz}^{SHG}(\omega)$ at the equilibrium internuclear distance, R_e = 1.7328 au. For the SCF and the CAS4220 curves we used the respective fits to the expression $\beta^{SHG}(\omega) \approx \beta(0)(1 + 6\omega^2 A)$, given in Ref. [32].

ues for the SCF and CAS4220 curves are 2.83 and 2.94 [32]. Thus, CCS and SCF underestimate the dispersion for β_{zzz}, while CC2 overestimates it. The dispersion of the CAS4220 curve is intermediate between the SCF dispersion and the CCSD dispersion.

At the CCSD quadratic response level we obtain for the electronic contribution to $\beta_{\parallel}$ at the equilibrium distance R_e = 1.7328 au and at the experimental wavelength of 694.3 nm the result of −8.789 au. The effect of vibrational averaging has been calculated in Ref. [32] for the CAS4220 results at 694.3 nm as −0.65 au. The purely vibrational contribution has been calculated by Bishop and Kirtman [34] as $\beta_{\parallel,vib}$ = −0.35 au. If we add these estimates to our CCSD result we obtain an estimate for the first hyperpolarizability of the FH molecule of $\beta_{\parallel}^{SHG}$ = −9.8 au. Our final result is only slightly outside the error bounds of the experimental value of -10.9 ± 0.95 au [30]. Previous theoretical studies of Sekino and Bartlett [31,29] and Jaszuński et al. [32] have given $\beta_{\parallel}$ significantly outside the experimental error bars. The differences between the present result and those obtained in previous theoretical investigations are mainly due to the larger values obtained for the static hyperpolarizability components, i.e., they can be traced to differences in basis sets, treatment of orbital relaxation and correlation effects. To obtain a more definite validation of the experiment the contributions of triple excitations and the remaining basis set errors have to be investigated and more accurate corrections are needed for vibrational averaging and for the purely vibrational contribution.

In summary, we have implemented the quadratic response functions for the coupled cluster models CCS, CC2 and CCSD for general frequency-dependent first hyperpolarizabilities. A first application to the SHG and OR hyperpolarizabilities of the FH molecule shows that coupled cluster quadratic response theory combined with the $2n + 1$ and $2n + 2$ rules for the response amplitudes and multipliers provides an efficient approach for the ab initio calculation of nonlinear optical properties. A more detailed study of the role of orbital relaxation effects and the contributions from triple excitations is necessary to obtain a clear understanding of the accuracy obtained for the hyperpolarizabilities at particular levels in the coupled cluster hierarchy.

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References

[1] D.P. Shelton and J.E. Rice, Chem. Rev. 94 (1994) 3.
[2] P. Jørgensen, H.J.A. Jensen and J. Olsen, J. Chem. Phys. 89 (1988) 3654.
[3] H. Hettema, H.J.A. Jensen, P. Jørgensen and J. Olsen, J. Chem. Phys. 97 (1992) 1174.
[4] K. Sasagane, F. Aiga and R. Itoh, J. Chem. Phys. 99 (1993) 3738.
[5] O. Christiansen, P. Jørgensen and C. Hättig, to be published.
[6] H. Koch, to be published.
[7] F. Aiga, K. Sasagane and R. Itoh, Int. J. Quantum Chem. 51 (1994) 87.
[8] C. Hättig and B.A. Heß, Chem. Phys. Lett. 233 (1995) 359.
[9] F. Aiga and R. Itoh, Chem. Phys. Lett. 251 (1996) 372.
[10] O. Christiansen, H. Koch and P. Jørgensen, Chem. Phys. Lett. 243 (1995) 409.
[11] O. Christiansen, H. Koch and P. Jørgensen, J. Chem. Phys. 103 (1995) 7429.
[12] H. Koch, O. Christiansen and P. Jørgensen, Chem. Phys. Lett. 244 (1995) 75.
[13] H.J. Monkhorst, Int. J. Quantum Chem. S11 (1977) 421.
[14] E. Dalgaard and H.J. Monkhorst, Phys. Rev. A 28 (1983) 1217.
[15] H. Koch and P. Jørgensen, J. Chem. Phys. 93 (1990) 3333.
[16] R. Kobayashi, H. Koch and P. Jørgensen, Chem. Phys. Lett. 219 (1994) 30.
[17] T. Helgaker and P. Jørgensen, Theor. Chim. Acta 75 (1989) 111.
[18] P. Jørgensen and T. Helgaker, J. Chem. Phys. 89 (1988) 1560.
[19] A.E. Kondo, P. Piecuch and J. Paldus, J. Chem. Phys. 104 (1996) 8566.
[20] P.E.S. Wormer and W. Rijks, Phys. Rev. A 33 (1986) 2928.
[21] D. Spelsberg, T. Lorenz and W. Meyer, J. Chem. Phys. 99 (1993) 7845.
[22] T. Helgaker and P. Jørgensen, Adv. Quantum Chem. 19 (1988) 183.
[23] F. Aiga, K. Sasagane and R. Itoh, J. Chem. Phys. 99 (1993) 3779.
[24] O. Christiansen, H. Koch, A. Halkier, P. Jørgensen, T. Helgaker and A.M. Sanchez de Meras, J. Chem. Phys. 105 (1996) 6921.
[25] A. Halkier, H. Koch, O. Christiansen, P. Jørgensen and T. Helgaker, J. Chem. Phys., submitted.
[26] D.E. Woon and T. H. Dunning, J. Chem. Phys. 100 (1994) 2975.
[27] L. Adamowicz and R.J. Bartlett, J. Chem. Phys. 84 (1986) 4988; 87 (1987) 7250(E).
[28] D.P. Chong and S.R. Langhoff, J. Chem. Phys. 93 (1990) 570.
[29] H. Sekino and R.J. Bartlett, J. Chem. Phys. 98 (1993) 3022.
[30] J. Dudley and J. Ward, J. Chem. Phys. 82 (1985) 4673.
[31] H. Sekino and R.J. Bartlett, J. Chem. Phys. 84 (1986) 2726.
[32] M. Jaszuński, P. Jørgensen and H.J.Å. Jensen, Chem. Phys. Lett. 191 (1992) 293.
[33] D.M. Bishop, J. Chem. Phys. 95 (1991) 5489.
[34] D.M. Bishop and B. Kirtman, J. Chem. Phys. 95 (1991) 2646.
[35] G.H.F. Diercksen and A. Sadlej, J. Chem. Phys. 75 (1981) 1253.