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Frequency-dependent second hyperpolarizabilities using coupled cluster cubic response theory

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Abstract

The coupled cluster cubic response function is derived using a time-averaged quasienergy Lagrangian and Fourier component variational perturbation theory. The obtained expressions are in accord with the $2n+1$ and $2n+2$ rules. The first implementation of the cubic response function is reported for frequency-dependent second hyperpolarizabilities for a coupled cluster singles and doubles wavefunction and sample calculations are presented for hyperpolarizabilities of N_2 for several third-order optical processes. The results are in excellent agreement with recent experiments for electric field induced second harmonic generation. © 1998 Elsevier Science B.V.

1. Introduction

The frequency-dependent hyperpolarizabilities are the fundamental molecular parameters that enter in the description of many nonlinear optical phenomena. The theoretical understanding and accurate determination of the frequency-dependent hyperpolarizabilities is therefore important for example in the development of optical devices. In particular the recent discovery of an acceptor-substituted carotenoid with an extraordinarily large susceptibility for the third harmonic generation (THG) process has encouraged the search for organic compounds suitable for all-optical switches [1,2]. The ab initio determination of second- and third-order optical properties, i.e. frequency-dependent first and second hyperpolarizabilities, has been an active field of research for more than a decade. Most studies describe the frequency-dependence of the hyperpolarizabilities only at the uncorrelated time-dependent Hartree–Fock (TDHF) level or treat one or more of the electric fields by numerical differentiation and are thereby restricted to optical processes where these fields are static. The analytic treatment of four frequency-dependent fields is for example needed for the third harmonic generation process. Correlated calculations of general frequency-dependent second hyperpolarizabilities for two-electron systems have been reported by Bishop and Lam [3,4] and Bishop and coworkers [5,6], who employed explicitly correlated (CI-Hylleraas) wavefunctions. Recently the first implementation of a correlated approach which is applicable to many-electron systems has been reported by Jonsson et al. [7], using multiconfigurational self-consistent field (MCSCF) wavefunctions.

Dynamical electron correlation effects are important for an accurate description of higher-order response properties. For closed shell systems dynamical correlation is most efficiently dealt with using single reference based correlation methods. In partic-

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ular, second-order Møller–Plesset perturbation theory and coupled cluster methods have proven to be efficient. Coupled cluster based methods have the important advantage relative to approaches based on Møller–Plesset perturbation theory that the positions of the poles in the response functions are improved systematically. For example for the hierarchy CCS, CC2, CCSD and CC3 [8–10], the errors in the excitation energies have been found to be reduced by a factor of three at each step in the hierarchy.

In a previous publication we presented an implementation of frequency-dependent first hyperpolarizabilities using coupled cluster quadratic response theory [16]. In this Letter we extend this work to cubic response theory, i.e. to frequency-dependent fourth-order molecular properties. Coupled cluster linear and quadratic response functions have been derived previously using for example a dual state approach and a generalized Hellmann–Feynman theorem [11–13]. In general, response functions for nonvariational wavefunctions are most easily derived using time-dependent quasienergy Lagrangians and variational perturbation theory [14,15]. Derivations of the coupled cluster linear and quadratic response functions adopting this approach were given in Refs. [9,16]. In Section 2 we give an extension of this derivation to the cubic response function. The resulting expressions, which are in accord with the $2n+1$ and $2n+2$ rules [17,18,15] have been implemented for the coupled cluster singles and doubles wavefunction.

We present as a first application of the CCSD cubic response approach in Section 3 the second hyperpolarizabilities of the N_2 molecule for several optical processes, including third harmonic generation and electric field induced second harmonic generation.

2. Coupled cluster cubic response theory

To derive the working expressions for the calculation of coupled cluster cubic response functions we follow the same lines as in our previous Letter on the coupled cluster quadratic response function [16]. The cubic response function is thereby obtained as the analytic fourth derivative of the time-averaged real part of a variational quasienergy Lagrangian: consider a system that in its unperturbed state is described by the zeroth-order Hamiltonian $\hat{H}^{(0)}$ and apply a time-dependent one-electron perturbation $\hat{V}(t,\epsilon)$.

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

It is assumed that $\hat{V}(t,\epsilon)$ can be decomposed into a sum over Fourier components:

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

where $\hat{H}^X$ are (time-independent) one-electron operators and $\epsilon_X(\omega_X)$ the accompanied field strengths for frequency ω_X. In the case of hyperpolarizability calculations, $\hat{H}^X$ is a component of the dipole operator. We use a phase-isolated parametrization of the coupled cluster wavefunction:

$$|\mathrm{CC}(t,\epsilon)\rangle = \exp\left(-i\int_{t_0}^{t} dt'\, \mathscr{W}(t',\epsilon)\right) \times \exp(T(t,\epsilon))\,|\mathrm{HF}\rangle\,. \tag{3}$$

The cluster operator $T(t,\epsilon)$ can, based on the Fourier decomposition (2) of the perturbation operator, be written as a sum over Fourier components in each order of the field strengths:

$$T(t,\epsilon) = \sum_\mu t_\mu(t,\epsilon)\,\hat{\tau}_\mu = \sum_\mu \left(t_\mu^{(0)} + t_\mu^{(1)}(t,\epsilon) + \tfrac{1}{2}t_\mu^{(2)}(t,\epsilon) + .\right)\hat{\tau}_\mu\,, \tag{4}$$

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

$$t_\mu^{(2)}(t,\epsilon) = \sum_{XY} t^{XY}(\omega_X,\omega_Y)\,\epsilon_X(\omega_X) \times \epsilon_Y(\omega_Y)\, e^{-i(\omega_X+\omega_Y)t}\,. \tag{6}$$

The Hartree–Fock reference of the unperturbed molecule is used throughout. Orbital relaxation is thus not treated explicitly, but only approximately through the single excitation manifold of the coupled cluster parameters. The time-dependent quasienergy and the coupled cluster equations are obtained by projecting the time-dependent Schrödinger equation

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

$$\mathscr{W}(t,\epsilon) = \langle \mathrm{HF}| \left(\hat{H}(t,\epsilon) - i\frac{\mathrm{d}}{\mathrm{d}t} \right) \exp(T) |\mathrm{HF}\rangle$$

$$= \langle \mathrm{HF}| \hat{H}(t,\epsilon) \exp(T) |\mathrm{HF}\rangle, \quad (7)$$

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

$$= e_\mu(t,\epsilon) - i\frac{\mathrm{d}}{\mathrm{d}t} t_\mu(t,\epsilon) = 0\,. \quad (8)$$

The quasienergy and the time-dependent equations for the coupled cluster methods CCS, CCSD and CCSDT are obtained by truncating the cluster operator after the single, double or triple excitation level, respectively. The CC2 and CC3 methods are defined by further approximations to the CCSD and CCSDT equations respectively [8,9]. A variational formulation of coupled cluster response theory is obtained by combining the quasienergy (7) and the time-dependent coupled cluster Eq. (8) to the quasienergy Lagrangian:

$$L(t,\epsilon) = \mathscr{W}(t,\epsilon) + \sum_\mu \bar{t}_\mu \left(e_\mu(t,\epsilon) - i\frac{\mathrm{d}}{\mathrm{d}t} t_\mu \right). \quad (9)$$

The time-average $\{L(t,\epsilon)\}_T$ of the quasienergy Lagrangian may now be required to be stationary with respect to variations of the amplitudes and the Lagrangian multipliers $\bar{t}_\mu$. Applying to the latter a similar expansion as for the cluster amplitudes in Eq. (4), this variational condition gives the response equations for the Fourier components of the amplitudes and the multipliers order by order in the perturbation strengths. In zeroth order one retains the coupled cluster equations of the unperturbed system and obtains the equation for the zeroth-order Lagrangian multipliers:

$$\eta^{(0)} + \bar{t}^{(0)} \boldsymbol{A} = 0\,. \quad (10)$$

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

$$(\boldsymbol{A} - \omega_X) t^X(\omega_X) = -\xi^X\,, \quad (11)$$

$$\bar{t}^X(\omega_X)(\boldsymbol{A} + \omega_X) = -\left(\eta^X + \boldsymbol{F} t^X(\omega_X)\right). \quad (12)$$

According to the $2n+1$ and $2n+2$ rules, we need for the cubic response function also the second-order response of the cluster amplitudes,

$$(\boldsymbol{A} - (\omega_X + \omega_Y)) t^{XY}(\omega_X, \omega_Y)$$

$$= -\left(\boldsymbol{B} t^X(\omega_X)\, t^Y(\omega_Y) + \boldsymbol{A}^X t^Y(\omega_Y) + \boldsymbol{A}^X t^X(\omega_X)\right), \quad (13)$$

but not the second-order response of the Lagrangian multipliers. The matrix $\boldsymbol{A}$ is the coupled cluster Jacobian for the unperturbed molecule,

$$\boldsymbol{A}_{\mu\nu} = \left(\frac{\partial e_\mu}{\partial t_\nu} \right)_0, \quad (14)$$

the vector $\eta^{(0)}$ is the derivative of the coupled cluster energy with respect to the amplitudes,

$$\eta_\mu^{(0)} = \left(\frac{\partial \mathscr{W}}{\partial t_\mu} \right)_0, \quad (15)$$

and the intermediates ξ^X, η^X, $\boldsymbol{F}$, $\boldsymbol{B}$ and $\boldsymbol{A}^X$ are defined as second and third derivatives of the Lagrangian:

$$\xi_\mu^X = \left(\frac{\partial^2 L}{\partial \epsilon_X(\omega_X)\, \partial \bar{t}_\mu} \right)_0, \quad (16)$$

$$\eta_\mu^X = \left(\frac{\partial^2 L}{\partial \epsilon_X(\omega_X)\, \partial t_\mu} \right)_0, \quad (17)$$

$$\boldsymbol{F}_{\mu\nu} = \left(\frac{\partial^2 L}{\partial t_\mu\, \partial t_\nu} \right)_0, \quad (18)$$

$$\boldsymbol{A}_{\mu\nu}^X = \left(\frac{\partial^3 L}{\partial \epsilon_X(\omega_X)\, \partial \bar{t}_\mu\, \partial t_\nu} \right)_0, \quad (19)$$

$$\boldsymbol{B}_{\mu\nu\gamma} = \left(\frac{\partial^3 L}{\partial \bar{t}_\mu\, \partial t_\nu\, \partial t_\gamma} \right)_0, \quad (20)$$

where the index 0 indicates that the derivatives are taken for zero perturbation strength. After the response equations have been solved, the response functions can be calculated as derivatives of the real part of the time-averaged quasienergy with respect to the field strengths. Employing the $2n+1$ rule for the amplitudes and the $2n+2$ rule for the La-

grangian multipliers we obtain the cubic response function as:

$$\gamma_{ABCD}(\omega_A;\omega_B,\omega_C,\omega_D) = -\left(\frac{\mathrm{d}^4\left\{\frac{1}{2}L(t,\epsilon)+\frac{1}{2}L(t,\epsilon)^*\right\}_T}{\mathrm{d}\epsilon_A(\omega_A)\,\mathrm{d}\epsilon_B(\omega_B)\,\mathrm{d}\epsilon_C(\omega_C)\,\mathrm{d}\epsilon_D(\omega_D)}\right)_0 \tag{21}$$

$$\begin{aligned}= -\tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{ABCD}\Bigg\{&\frac{1}{4!}\boldsymbol{H}t^A(\omega_A)t^B(\omega_B)\\ &\times t^C(\omega_C)t^D(\omega_D)\\ &+\frac{1}{3!}\bar{t}^A(\omega_A)\boldsymbol{C}t^B(\omega_B)t^C(\omega_C)t^D(\omega_D)\\ &+\tfrac{1}{2}\bar{t}^A(\omega_A)\boldsymbol{B}^Bt^C(\omega_C)t^D(\omega_D)\\ &+\tfrac{1}{4}\boldsymbol{G}t^{AB}(\omega_A,\omega_B)t^C(\omega_C)t^D(\omega_D)\\ &+\tfrac{1}{2}\bar{t}^A(\omega_A)\boldsymbol{B}t^{BC}(\omega_B,\omega_C)t^D(\omega_D)\\ &+\tfrac{1}{2}\boldsymbol{F}^At^{BC}(\omega_B,\omega_C)t^D(\omega_D)\\ &+\tfrac{1}{2}\bar{t}^A(\omega_A)\boldsymbol{A}^Bt^{CD}(\omega_C,\omega_D)\\ &+\tfrac{1}{8}\boldsymbol{F}t^{AB}(\omega_A)t^{CD}(\omega_C,\omega_D)\Bigg\},\end{aligned} \tag{22}$$

with $\omega_A = -\omega_B - \omega_C - \omega_D$. The operator $\hat{P}^{ABCD}$ symmetrizes with respect to the indices A, B, C, D of the perturbation operators and the associated frequencies and $\hat{C}^{\pm\omega}$ symmetrizes with respect to an overall sign inversion for the frequencies and simultaneous complex conjugation. The matrices $\boldsymbol{G}$, $\boldsymbol{F}^X$, $\boldsymbol{H}$, $\boldsymbol{C}$ and $\boldsymbol{B}^X$ are defined as partial third and fourth derivatives of the Lagrangian:

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

$$\boldsymbol{F}^X_{\mu\nu} = \left(\frac{\partial^3 L}{\partial\epsilon_X(\omega_X)\,\partial t_\mu\,\partial t_\nu}\right)_0, \tag{24}$$

$$\boldsymbol{H}_{\mu\nu\gamma\delta} = \left(\frac{\partial^4 L}{\partial t_\mu\,\partial t_\nu\,\partial t_\gamma\,\partial t_\delta}\right)_0, \tag{25}$$

$$\boldsymbol{C}_{\mu\nu\gamma\delta} = \left(\frac{\partial^4 L}{\partial\bar{t}_\mu\,\partial t_\nu\,\partial t_\gamma\,\partial t_\delta}\right)_0, \tag{26}$$

$$\boldsymbol{B}^X_{\mu\nu\gamma} = \left(\frac{\partial^4 L}{\partial\epsilon_X(\omega_X)\,\partial\bar{t}_\mu\,\partial t_\nu\,\partial t_\gamma}\right)_0. \tag{27}$$

From the Lagrangian the expressions for the vectors ξ^X and η^X and for the matrices $\boldsymbol{A}$, $\boldsymbol{F}$, $\boldsymbol{B}$, $\boldsymbol{G}$, $\boldsymbol{A}^X$, $\boldsymbol{F}^X$, $\boldsymbol{C}$, $\boldsymbol{H}$, and $\boldsymbol{B}^X$ are derived straightforwardly. We note, that the implementation of the response equations and the response functions does not require these matrices explicitly. All calculations can be carried out by means of linear transformations where the $\boldsymbol{A}$, $\boldsymbol{F}$, $\boldsymbol{A}^X$, $\boldsymbol{F}^X$ matrices are combined with a vector of response amplitudes or multipliers. Similar the matrices $\boldsymbol{B}$, $\boldsymbol{G}$, $\boldsymbol{B}^X$ are combined with two such vectors and $\boldsymbol{C}$ and $\boldsymbol{H}$ with three of them. These linear transformations can be implemented with a similar scaling of the operation count with the number of the orbitals and with similar memory and disk space requirements as the coupled cluster equations.

The implementation of the transformations of a trial vector with the Jacobian from the left and from the right are discussed in detail in Refs. [19,20]. The implementation of the transformations involving the $\boldsymbol{F}$ and the higher-order response matrices will be subject to forthcoming publications on the integral-direct implementation of coupled cluster response properties.

3. Frequency-dependent second hyperpolarizabilities for N_2

To illustrate the capabilities of the coupled cluster cubic response approach we have computed the frequency-dependent second hyperpolarizability for the N_2 molecule for the Kerr effect, degenerate four wave mixing (DFWM), electric field induced second harmonic generation (ESHG) and third harmonic generation (THG). Using the notation of Section 2, the aforementioned optical effects are described by the hyperpolarizabilities $\gamma^{\mathrm{Kerr}}_{ABCD}(\omega) = \gamma_{ABCD}(-\omega;0,0,\omega)$, $\gamma^{\mathrm{DFWM}}_{ABCD}(\omega) = \gamma_{ABCD}(-\omega;\omega,\omega,-\omega)$, $\gamma^{\mathrm{ESHG}}_{ABCD}(\omega) = \gamma_{ABCD}(-2\omega;\omega,\omega,0)$ and $\gamma^{\mathrm{THG}}_{ABCD}(\omega) = \gamma_{ABCD}(-3\omega;\omega,\omega,\omega)$. For the electric induced second harmonic generation accurate experimental data has been reported by Mizrahi and Shelton [21–23] covering a broad range of wavelengths between 457.9 and 694.3 nm. The broad range of frequencies is especially useful for the comparison with ab initio calculations as it allows, to some extent, to distinguish between errors present for the static property and errors due to the frequency-dependence.

Table 1
Hyperpolarizabilities (in au) for the N_2 molecule

	$\bar{\alpha}$	$\Delta\alpha$	γ_{xxxx}	γ_{xxzz}	γ_{zzzz}	$\gamma_{\|\|}$
CCSD [a]	11.67	4.49	781.6	312.8	1179.5	903.0
CASSCF [b]	11.606	4.341	758	310	1162	0.5885
CCSD(T) [c]			860	370	1290	1010
QCISD(T) [d]	11.807	4.632	802	335	1258	0.5946
QCISD(T) [e]	11.81 ± 0.12	4.70 ± 0.09	810	339	1272	0.5956 ± 5
exp.	11.74 ± 0.12 [f]	4.59 ± 0.05 [f]				0.5917 ± 5 [g]

[a] Present work, t-aug-cc-pVTZ basis set (13s8p5d4f)/[7s6p5d4f], $r_{N_2} = 2.074$ bohr.
[b] CAS MCSCF quadratic response, [8s6p4d3f] basis, $r_{N_2} = 2.0743$ bohr, Ref. [25].
[c] CCSD(T) in a [5s3p2d] basis, $r_{N_2} = 2.0743$ bohr, Ref. [31].
[d] QCISD(T) in a [8s6p3d1f] basis plus estimated corrections for the inclusion of further *d*- and *f*-functions, $r_{N_2} = 2.0743$ bohr, Ref. [26].
[e] QCISD(T) of Ref. [26] including an estimate for the effect of zero point vibrational averaging.
[f] Constrained dipole oscillator strength distribution, Ref. [32].
[g] Extrapolation to the static limit of the ESHG results of Ref. [21–23] corrected for the rovibrational contribution, Ref. [23].

All calculations for the N_2 molecule were performed at its equilibrium bond length of $r_e = 2.074$ au. We have used the triply-augmented correlation consistent polarized valence triple zeta (t-aug-cc-pVTZ) basis of Woon and Dunning [24], which for the nitrogen atom consists of a (13s8p5d4f)/[7s6p5d4f] contraction. Based on the results of Ref. [24], the t-aug-cc-pVTZ basis sets are expected to yield static second hyperpolarizabilities for correlated methods to within a few percent of the basis set limits. The accuracy of the dispersion of polarizabilities and hyperpolarizabilities is in the normal disper-

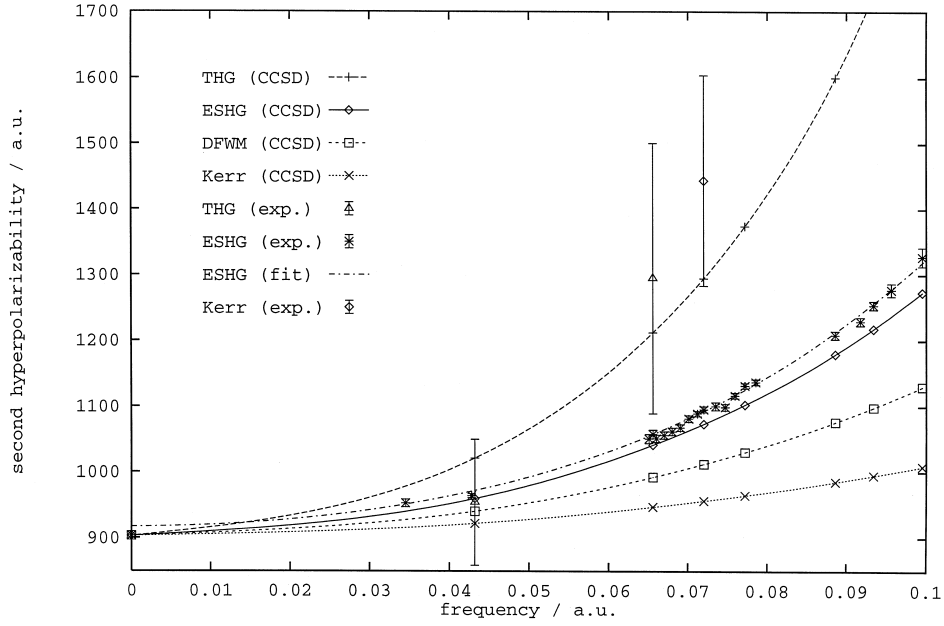


Fig. 1. Frequency-dependent hyperpolarizability for N_2. For the THG, ESHG and DFWM process we have plotted $\gamma_{||}$, while for the Kerr process γ_K is shown. For references for the experimental results see caption of Table 2. The plot includes additional ESHG results from Refs. [21–23], not listed in Table 2. The parameters for the fit through the experimental ESHG results have been taken from Ref. [23].

Table 2
Hyperpolarizabilities (in au) for the N_2 molecule for $r_e = 2.074$ bohr [a]

	λ/nm	γ_{xxxx}	γ_{xxzz}	γ_{xzzx}	γ_{zxxz}	γ_{zzxx}	γ_{zzzz}	$\gamma_{\|\|}$	$\gamma_{\|\|}^{\text{expt}}$ [b]
ESHG	1055	828.9	330.9	333.3	334.3	332.9	1255.7	959.2	
	694.3	897.4	357.2	363.3	365.9	362.2	1367.0	1041.1	1057.6 ± 6.4 [c]
	632.8	924.2	367.4	375.1	378.3	373.7	1410.6	1073.1	1095.6 ± 4.6 [c]
	590.0	949.0	376.8	386.1	389.9	384.4	1451.1	1102.8	1132.0 ± 4.2 [c]
	514.5	1013.1	401.1	414.6	420.2	411.9	1556.1	1179.6	1208.7 ± 6.2 [c]
	488.0	1045.1	413.2	429.0	435.5	425.7	1608.9	1218.1	1253.3 ± 6.3 [c]
	457.9	1091.0	430.4	449.8	457.6	445.5	1684.6	1273.4	1327.5 ± 14.3 [c]
THG	1055	880.4	352.0	352.0	356.3	356.3	1339.3	1020.7	954 ± 95 [d]
	694.3	1040.0	415.5	415.5	427.9	427.9	1601.0	1212.2	1295 ± 206 [e]
	632.8	1108.0	442.6	442.6	458.9	458.9	1713.8	1294.2	
	590.0	1174.1	468.9	468.9	489.2	489.2	1824.0	1374.2	
	514.5	1360.3	543.2	543.2	575.5	575.5	2137.7	1600.5	
	488.0	1462.7	584.0	584.0	623.5	623.5	2312.0	1725.5	
	457.9	1621.2	647.4	647.4	698.6	698.6	2584.3	1919.9	
DFWM	1055	812.7	324.9	327.3	327.3	324.9	1229.6	940.0	
	694.3	856.5	342.0	348.2	348.2	342.0	1300.3	992.1	
	632.8	873.2	348.5	356.2	356.2	348.5	1327.2	1012.0	
	590.0	888.4	354.4	363.5	363.5	354.4	1351.9	1030.1	
	514.5	927.0	369.2	382.3	382.3	369.2	1414.5	1076.1	
	488.0	945.8	376.4	391.6	391.6	376.4	1445.1	1098.7	
	457.9	972.4	386.6	404.8	404.8	386.6	1488.3	1130.4	
Kerr	1055	796.9	319.3	318.3	319.2	318.3	1204.1	921.5	
	694.3	817.6	328.3	325.8	328.0	325.8	1237.5	946.7	
	632.8	825.3	331.6	328.6	331.3	328.6	1249.9	956.0	1443 ± 160 [f]
	590.0	832.1	334.5	331.0	334.2	331.0	1261.0	964.4	
	514.5	849.1	341.8	337.1	341.4	337.1	1288.4	985.0	
	488.0	857.1	345.3	340.0	344.9	340.0	1301.4	994.8	
	457.9	868.2	350.1	344.0	349.6	344.0	1319.4	1008.4	

[a] At the tabulated wavelengths 1055, 696.3, 632.8, 590.0, 514.5, 488.0, and 457.9 nm we used in the calculations the frequencies 0.04318801, 0.06562487, 0.07200276, 0.07722602, 0.08855850, 0.09336752, and 0.09950502 au, respectively.

[b] The experimental result for γ_{N_2}/γ_{He} of Refs. [21,22,28,29] were converted to absolute hyperpolarizabilities using the ab initio results for γ_{He} of Ref. [5].

[c] Refs. [21,22]. [d] Ref. [29]. [e] Ref. [28]. [f] Ref. [30].

sion region, i.e. below the first dipole-allowed transitions, mainly determined by the accuracy of the respective excitation energies.

In Table 1 we have compiled the results obtained for the static polarizabilities and hyperpolarizabilities. The CCSD cubic response values for the components of the static hyperpolarizability compare well with the results of other ab initio studies, in particular with the CAS MCSCF calculation of Luo et al. [25] and a recent QCISD(T) study of Archibong and Thakkar [26]. The effect of zero point vibrationally averaging on the isotropic hyperpolarizability $\bar{\gamma}$ has been estimated in Ref. [26] at the SDQ-MP4 level to be ≈ 10 au, which agrees well with the value of ≈ 9 au found by Luo et al. at the CAS MCSCF level [25]. If we add the estimate of 10 au to the CCSD cubic response result, we obtain 913 au, in nearly perfect agreement with Sheltons experiment

In Table 2 we compare the CCSD cubic response results for the frequency-dependent hyperpolarizabilities with the results of several experiments. For the ESHG and THG process the experimental results have to be compared with [27]:

$$\gamma_{\parallel} = \tfrac{1}{15} \sum_{\xi\eta} (\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\xi\eta} + \gamma_{\eta\xi\xi\eta}), \qquad (28)$$

while for the Kerr effect one has to compare with [27]:

$$\gamma_K = \tfrac{3}{2} (\gamma_{\parallel} - \gamma_{\perp}),$$
$$\gamma_{\perp} = \tfrac{1}{15} \sum_{\xi\eta} (\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\xi\eta} - \gamma_{\eta\xi\xi\eta}). \qquad (29)$$

In the static limit $\gamma_{\parallel}$ and γ_K become identical with the static isotropic average $\bar{\gamma} = \frac{1}{5} \sum_{\xi\eta} \gamma_{\xi\xi\eta\eta}(0)$, while $\gamma_{\perp}(0) = \frac{1}{3} \bar{\gamma}$. In Fig. 1 we have displayed the data of Table 2. For the electric field induced second harmonic generation the CCSD values compare well with the experimental results of Mizrahi and Shelton [21–23], with deviations of only 1.5–4.1%. From Fig. 1 and Table 2 it can be seen that the deviation increases with increasing frequency, indicating that the CCSD cubic response dispersion curve is slightly too flat. This is most likely due to the neglect of connected triple excitations in the CCSD model, which leads to a small overestimation of the first dipole-allowed ($^1\Sigma_u^-$) excitation energy of N_2 [8].

For the third harmonic generation process in the N_2 molecule two experimental studies have been published: one by Ward and New [28] for a wavelength of 694.3 nm and a more recent one by Lehmeier et al. [29] for $\lambda = 1055$ nm. Ward and New determined the ratio between the THG hyperpolarizability of N_2 and He $\gamma^{\mathrm{THG}}_{N_2} / \gamma^{\mathrm{THG}}_{\mathrm{He}} = 26.75 \pm 4.25$. Using the accurate ab initio results for the THG hyperpolarizability for He of Bishop and Pipin [5] one obtains $\gamma^{\mathrm{THG}}_{N_2}(\lambda = 694.3\,\mathrm{nm}) = 1295 \pm 206$ au, which can be compared with the CCSD cubic response result $\gamma^{\mathrm{THG}}_{\parallel} = 1212.2$ au for the same wavelength. Taking into account the large uncertainity of the experimental result, the two numbers are in fair agreement. As for the ESHG process, the CCSD cubic response result is smaller than the experimental value. In contrast, Lehmeier et al. obtained at $\lambda = 1055$ nm a ratio of $\gamma^{\mathrm{THG}}_{N_2} / \gamma^{\mathrm{THG}}_{\mathrm{He}} = 21.1 \pm 2.1$, corresponding to $\gamma^{\mathrm{THG}}_{N_2} = 954 \pm 95$ au, which is somewhat smaller than our CCSD value $\gamma^{\mathrm{THG}}_{\parallel} = 1020.7$ au. This value even falls below the CCSD curve for the ESHG process. Of course, it is in principle possible that this is an effect of the pure vibrational contribution which we have not included in our present study, but it is more likely that the correct THG hyperpolarizability is at the upper end of the experimental error bars of Ref. [29]. In any case, from a theoretical analysis [27] it is known that for small frequencies the dispersion contributions to the electronic Kerr, DFWM, ESHG and THG hyperpolarizabilities have approximately the ratio 1:2:3:6. For this reason we also conclude, that the experimental result for the Kerr hyperpolarizability from Ref. [30] is too large by about 50%.

4. Conclusions

We have derived the coupled cluster cubic response function as the fourth derivative of the real part of the time-averaged quasienergy. Employing a quasienergy Lagrangian and variational perturbation theory, we have obtained computationally efficient expressions in accord with the $2n+1$ and $2n+2$ rules. We have implemented the cubic response function for the CCSD wavefunction. A first application to the frequency-dependent hyperpolarizabilities of N_2 for several optical processes has shown that coupled cluster cubic response theory for a CCSD wavefunction is an efficient and accurate approach for the ab initio calculation of third-order nonlinear

optical properties. We obtained in particular the ESHG hyperpolarizability for a wide range of frequencies within a few percent of the accurately determined experimental values.

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