Frequency-dependent nonlinear optical properties with explicitly correlated coupled-cluster response theory using the CCSD(R12) model

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Response theory up to infinite order is combined with the explicitly correlated coupled-cluster singles and doubles model including linear-r_{12} corrections, CCSD(R12). The additional terms introduced by the linear-r_{12} contributions, not present in the conventional CCSD calculation, are derived and discussed with respect to the extra costs required for their evaluation. An implementation is presented up to the cubic response function for one-electron perturbations, i.e., up to frequency-dependent second hyperpolarizabilities. As first applications the authors computed the electronic polarizabilities and second hyperpolarizabilities of BH, N_2, and formaldehyde and show that the improvement in the one-electron basis set convergence known from the R12 method for ground state energies is retained for higher-order optical properties. Frequency-dependent results are presented for the second hyperpolarizability of N_2. © *2007 American Institute of Physics*.
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I. INTRODUCTION

The accurate calculation of frequency-dependent optical properties such as (hyper)polarizabilities is a demanding task that only very few methods can handle. The coupled-cluster (CC) method is able to provide accurate results over a wide range of frequencies with a consistent pole structure and has the advantages to be rather "black box" and systematically improvable. In particular, the iterative approximate triples model[1,2] CC3 has been shown[3–5] to yield highly accurate higher-order nonlinear optical properties as, e.g., the second hyperpolarizabilities of Ne and N_2. Such calculations require accurate one-electron basis sets, and the scaling of the computational costs with the number of electrons n and basis set size N are, however, for coupled-cluster calculations rather steep, e.g., for CCSD $\propto \mathcal{O}(n^2N^4)$ and for CC3 $\propto \mathcal{O}(n^3N^4)$. This limits present applications to rather small systems. Even worse, like any quantum chemical correlation method which is based on an expansion of the wave function in Slater determinants, coupled-cluster methods suffer from a very slow convergence of the correlation energy with the basis set, which prevents one from using small property-optimized basis sets. Even if one adopts extrapolation techniques (which presently are only well established for ground state energies), a set of calculations with basis sets up to quadruple- or quintuple-ζ quality are necessary to yield accurate results. Thus, methods with improved basis set convergence without loss in accuracy nor with a scaling worse than that of the conventional methods are very desirable.

In the last few years substantial progress has been made in the implementation of explicitly correlated so-called R12 and F12 methods,[6] making CC-R12 or CC-F12 to be obvious candidates to fulfill the above requirements. In R12 and F12 methods a few explicitly correlated two-electron pair functions are added to the manifold of orbital products which are used in the expansion of the wave function. Resulting three-electron integrals are avoided by inserting a resolution of the identity and the so-called standard approximations.[7–13] This made these methods applicable for molecules of relevant sizes. In fact, its implementation for second-order Møller-Plesset perturbation theory, MP2-R12, is nowadays a well established approach; see, e.g., Ref. 6 for a recent review.

A combination of R12 with coupled-cluster has been implemented by Noga *et al.* already in the early 1990s.[9,14,15] However, this implementation had been restricted to ground state energies and was not able to use an auxiliary basis set different from the orbital basis for the resolution of the identity, which prevented applications with small or moderate size basis sets. During the last two years, Fliegl *et al.*[16,17] presented a more general code without this problem for the explicitly correlated approximate coupled-cluster singles and doubles CC2-R12 and CCSD(R12) models, which has also been used for first pilot investigations[16,18] on the calculation of electronic excitation energies in the framework of CC-R12 response theory. Here, we use this as basis for the first implementation of higher-order nonlinear optical properties in the framework of CC-R12 response theory. In the current paper we derive the additional contributions to the response functions within the CCSD(R12) model with Ansatz 1 (*vide infra*) and present results of some first applications. Special focus is put on the question, whether the basis set convergence for the response properties is improved to a similar extent as it is for ground state energies. For *static* electric properties calculated as *orbital-relaxed* derivatives of the ground state energy this can be expected. In fact, this has already been investigated at the CCSD(T)-R12 level using finite difference techniques (see, e.g., Ref. 19 and references therein) and confirmed. In the *orbital-unrelaxed* response

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approach and, in particular, in the *frequency-dependent* case, the requirements on the wave function are, however, different, and it is not *a priori* clear if the performance found for a method for ground state energies carries over.

II. THEORY

A. The CCSD(R12) model

The CCSD(R12) model was recently introduced by Fliegl *et al.*[17] as an approximation to the full CCSD-R12 model. In both models the conventional CCSD excitation operator is extended by the R12 doubles excitation operator $\hat{T}_{2'}$,

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \hat{T}_{2'}, \tag{1}$$

where the excitation operators $\hat{T}_i$ $(i=1,2,2')$ are defined by

$$\hat{T}_1 = \sum_{ai} t_a^i E_{ai}, \tag{2}$$

$$\hat{T}_2 = \frac{1}{2}\sum_{aibj} t_{ab}^{ij} E_{ai} E_{bj}, \tag{3}$$

$$\hat{T}_{2'} = \frac{1}{2}\sum_{xiyj} c_{xy}^{ij} \sum_{\alpha\beta} w_{\alpha\beta}^{xy} E_{\alpha i} E_{\beta j}, \tag{4}$$

for a closed shell reference $|\mathrm{HF}\rangle$. The conventional singles and doubles cluster amplitudes are denoted t_a^i and t_{ab}^{ij}, respectively; the R12 cluster amplitudes are specified with c_{xy}^{ij}. The operators E_{ai} are spin-free single excitations. Throughout the paper we will use the convention that $i,j,\ldots$ denote occupied orbitals, $a,b,\ldots$ virtual orbitals, and $p,q,\ldots$ are arbitrary molecular orbitals (MOs). The orbitals $\alpha,\beta,\ldots$ span the subspace complementary to the MOs such that $\{\phi_p\}\oplus\{\phi_\alpha\}$ provides a formally complete one-electron basis. With x,y,v, and w we denote the MOs entering the R12 pair functions, which are defined as

$$\chi_{xy}(1,2) = \hat{w}_{12}\phi_x(1)\phi_y(2). \tag{5}$$

Usually, only occupied canonical orbitals are used (for ϕ_x and ϕ_y) to construct the pair functions but also canonical or noncanonical virtual orbitals may be included,[18] which can be necessary for an accurate description of excited electronic states and anisotropic properties of small molecules. In Eq. (5) $\hat{w}_{12}$ denotes a correlation operator which can be written as

$$\hat{w}_{12} = \hat{Q}_{12} f_{12}, \tag{6}$$

where f_{12} is a function depending on the interelectronic distance r_{12} and $\hat{Q}_{12}$ is a projection operator, which ensures that the pair functions χ_{xy} are orthogonal to products of MOs. With $f_{12}=r_{12}$ one obtains the usual R12 method and with, for example, $f_{12}=\exp(-\gamma r_{12})$ the so-called F12 method. The projection operator $\hat{Q}_{12}$ for Ansatz 1, which is used in the present study, is given by

$$\hat{Q}_{12} = (1-\hat{P}_1)(1-\hat{P}_2), \tag{7}$$

where

$$\hat{P}_i = \sum_p |\phi_p(i)\rangle\langle\phi_p(i)|. \tag{8}$$

Furthermore, we introduced in Eq. (4) the two-electron integrals over the correlation operator

$$w_{\alpha\beta}^{xy} = \langle\phi_\alpha(1)\phi_\beta(2)|\hat{w}_{12}|\phi_x(1)\phi_y(2)\rangle, \tag{9}$$

which are the expansion coefficients of the pair functions in the basis formed by products of complementary basis functions $\phi_\alpha(1)\phi_\beta(2)$. The CCSD-R12 energy is obtained from the expression

$$E = \langle \mathrm{HF}|\hat{H}\exp(\hat{T})|\mathrm{HF}\rangle, \tag{10}$$

with the cluster amplitudes determined by the equations

$$\Omega_{ai} = \langle {}_i^a|[\hat{F},\hat{T}_1] + \hat{\Phi}^T|\mathrm{HF}\rangle = 0, \tag{11}$$

$$\Omega_{aibj} = \langle {}_{ij}^{ab}|[\hat{F},\hat{T}_2+\hat{T}_{2'}] + \hat{\Phi}^T|\mathrm{HF}\rangle = 0, \tag{12}$$

$$\Omega_{xiyj} = \langle {}_{ij}^{xy}|[\hat{F},\hat{T}_2+\hat{T}_{2'}] + \hat{\Phi}^T|\mathrm{HF}\rangle = 0. \tag{13}$$

Above, $\hat{F}$ is the Fock operator, $\hat{\Phi}$ the electron fluctuation potential, and $\hat{\Phi}^T$ is defined as

$$\hat{\Phi}^T = \exp(-\hat{T})\hat{\Phi}\exp(\hat{T}). \tag{14}$$

The residual of the above equations is also known as the CC vector function. The projection manifolds are given by[18,20]

$$\langle {}_i^a| = \tfrac{1}{2}\langle \mathrm{HF}|E_{ai}^\dagger, \tag{15}$$

$$\langle {}_{ij}^{ab}| = \tfrac{1}{6}\langle \mathrm{HF}|(2E_{ai}^\dagger E_{bj}^\dagger + E_{aj}^\dagger E_{bi}^\dagger), \tag{16}$$

$$\langle {}_{ij}^{xy}| = \tfrac{1}{6}\sum_{\alpha\beta}(w^\dagger)_{xy}^{\alpha\beta}\langle \mathrm{HF}|(2E_{\alpha i}^\dagger E_{\beta j}^\dagger + E_{\alpha j}^\dagger E_{\beta i}^\dagger). \tag{17}$$

One obtains the CCSD(R12) model by truncating the equations for the R12 amplitudes, Eq. (13), to lowest order in $\hat{T}_{2'}$ and $\hat{\Phi}$ (counting $\hat{T}_1$, $\hat{T}_2$, and $\hat{F}$ as zero-order quantities), which yields

$$\Omega_{xiyj} = \langle {}_{ij}^{xy}|[\hat{F},\hat{T}_2+\hat{T}_{2'}] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}},\hat{T}_2]|\mathrm{HF}\rangle = 0, \tag{18}$$

with

$$\tilde{\hat{\Phi}} = \exp(-\hat{T}_1)\hat{\Phi}\exp(\hat{T}_1) \tag{19}$$

as a $\hat{T}_1$ similarity transformed fluctuation potential. In addition one would neglect in the equations for the conventional doubles amplitudes, Eq. (12), the contribution quadratic in the R12 amplitudes, i.e., the commutator $[[\hat{\Phi},\hat{T}_{2'}],\hat{T}_{2'}]$. Note, however, that $\langle {}_{ij}^{ab}|[[\hat{\Phi},\hat{T}_{2'}],\hat{T}_{2'}]|\mathrm{HF}\rangle$ vanishes for Ansatz 1, anyway. Specifically for Ansatz 1, the r_{12} corrections in the CCSD(R12) vector function become (additional to the conventional terms)

$$\Omega_{ai}^{(\mathrm{R12})} = \langle {}_i^a|[\tilde{\hat{\Phi}},\hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{20}$$

$$\Omega_{aibj}^{(\mathrm{R12})} = \langle {}_{ij}^{ab}|[\tilde{\hat{\Phi}},\hat{T}_{2'}] + [[\tilde{\hat{\Phi}},\hat{T}_2],\hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{21}$$

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$$\Omega_{xiyj}^{(\mathrm{R12})} = \langle {}^{xy}_{ij}|[\hat{F},\hat{T}_{2'}] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}},\hat{T}_2]|\mathrm{HF}\rangle. \quad (22)$$

The numerical deviations from the CCSD-R12 model introduced by these simplifications have been shown to be insignificant, provided that the MO basis set is large enough to make the R12 corrections small, which for ground state energies is usually the case for basis sets of about quadruple-ζ quality and better.[17] But also for smaller basis sets the CCSD(R12) model is well behaved in the sense that a larger amount of correlation energy than in conventional CCSD is retained, albeit not the full magnitude of CCSD-R12.[17] Note that all three methods, CCSD, CCSD(R12), and CCSD-R12, converge to exactly the same basis set limit and differ only in how fast this limit is approached.

B. Coupled-cluster response theory

To derive the equations for the response functions we consider a system—described in its unperturbed state by a time-independent Hamiltonian $\hat{H}_0$—which is subject to a periodic time-dependent perturbation,

$$\hat{H}(t) = \hat{H}_0 + \sum_j \epsilon_j \exp(-i\omega_j t)\hat{X}_j, \quad (23)$$

where $\hat{X}_j$ are Hermitian time-independent one-electron operators and ϵ_j the amplitudes of the field strengths. As usual in the CC response theory, we parametrize the time-dependent wave function as

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle, \quad (24)$$

where $\hat{T}$ depends through the amplitudes on the time t and $|\mathrm{HF}\rangle$ is the time-independent Hartree-Fock reference wave function for the unperturbed system. The expressions for the energy and the cluster equations must for the time-dependent case be generalized to

$$\mathcal{W}(t,\epsilon) = \langle \mathrm{HF}|\hat{H}(t)\exp(\hat{T})|\mathrm{HF}\rangle \quad (25)$$

and

$$\Omega_\mu(t,\epsilon) = \langle\bar{\mu}|\exp(-\hat{T})\left(\hat{H}(t) - i\frac{d}{dt}\right)\exp(\hat{T})|\mathrm{HF}\rangle = 0. \quad (26)$$

The real part of the time average of $\mathcal{W}(t,\epsilon)$ is the so-called quasienergy of the Floquet state[21] formed in the oscillating field. Frequency-dependent properties can conveniently be calculated[22,23] as derivatives of this quasienergy with respect to the field strengths. For CC methods, derivatives are most efficiently evaluated using a Lagrangian, since it allows to employ the $2n+1$ and $2n+2$ rules of variational perturbation theory.[22–25] The time-dependent quasienergy Lagrangian takes the form[23,24]

$$L(t,\epsilon) = \langle \mathrm{HF}|\hat{H}(t)\exp(\hat{T})|\mathrm{HF}\rangle + \sum_\mu \bar{t}_\mu(t)\langle\bar{\mu}|\exp(-\hat{T}) \times\left(\hat{H}(t) - i\frac{d}{dt}\hat{T}\right)\exp(\hat{T})|\mathrm{HF}\rangle, \quad (27)$$

where the Lagrangian multipliers $\bar{t}_\mu$ are determined by the requirement that the time average of $L(t,\epsilon)$ is stationary with respect to variations of the cluster amplitudes.

TABLE I. Building blocks for coupled-cluster response theory.

$A_{\mu\nu}=(\partial^2 L/\partial\bar{t}_\mu\partial t_\nu)_0$	$F_{\mu\nu}=(\partial^2 L/\partial t_\mu\partial t_\nu)_0$
$B_{\mu\nu\gamma}=(\partial^3 L/\partial\bar{t}_\mu\partial t_\nu\partial t_\gamma)_0$	$G_{\mu\nu\gamma}=(\partial^3 L/\partial t_\mu\partial t_\nu\partial t_\gamma)_0$
$C_{\mu\nu\gamma\delta}=(\partial^4 L/\partial\bar{t}_\mu\partial t_\nu\partial t_\gamma\partial t_\delta)_0$	$H_{\mu\nu\gamma\delta}=(\partial^4 L/\partial t_\mu\partial t_\nu\partial t_\gamma\partial t_\delta)_0$
$D_{\mu\nu\gamma\delta\eta}=(\partial^5 L/\partial\bar{t}_\mu\partial t_\nu\partial t_\gamma\partial t_\delta\partial t_\eta)_0$	$\xi_\mu^X=(\partial^2 L/\partial\epsilon_X\partial\bar{t}_\nu)_0$
$A_{\mu\nu}^X=(\partial^3 L/\partial\epsilon_X\partial\bar{t}_\mu\partial t_\nu)_0$	$\eta_\mu^X=(\partial^2 L/\partial\epsilon_X\partial t_\mu)_0$
$B_{\mu\nu\gamma}^X=(\partial^4 L/\partial\epsilon_X\partial\bar{t}_\mu\partial t_\nu\partial t_\gamma)_0$	$F_{\mu\nu}^X=(\partial^3 L/\partial\epsilon_X\partial t_\mu\partial t_\nu)_0$

Frequency-dependent response properties can be calculated as derivatives of the real part of the Lagrangian with respect to the amplitudes of the perturbations,[22–24]

$$\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle_{\omega_2,\ldots,\omega_n} = \frac{1}{2}\hat{C}^{\pm}\left(\frac{d^n L(t,\epsilon)}{d\epsilon_1,\ldots,d\epsilon_n}\right)_0. \quad (28)$$

In the last equation the operator $\hat{C}^{\pm}$, defined by $\hat{C}^{\pm}f(\omega_1,\omega_2,\ldots)=f(\omega_1,\omega_2,\ldots)+f(-\omega_1,-\omega_2,\ldots)^*$, symmetrizes with respect to an inversion of the signs of all frequencies and simultaneous conjugation, and the frequencies are subject to the condition $\omega_2+\cdots+\omega_n=-\omega_1$. The evaluation of the response functions and the calculation of the derivatives of the cluster amplitudes and Lagrangian multipliers require the implementation of the partial derivatives of L defined in Table I. All higher derivatives vanish since the Lagrangian is at most fourth order with respect to the cluster amplitudes. The linear response function, for example, can in terms of these intermediates be written as

$$\langle\langle A;B\rangle\rangle_{\omega_B} = \tfrac{1}{2}\hat{C}^{\pm}\left\{\tfrac{1}{2}\mathbf{F}t^A(\omega_A)t^B(\omega_B) + \eta^A t^B(\omega_B) + \eta^B t^A(\omega_B)\right\} \quad (29)$$

and requires the solution of the response equations for the first-order cluster amplitudes and the zeroth-order Lagrangian multipliers,

$$(\mathbf{A}-\omega\mathbf{S})t^X(\omega) = -\xi^X, \quad (30)$$

$$\bar{t}^{(0)}\mathbf{A} = -\eta^{(0)}. \quad (31)$$

In the last equations $\mathbf{S}$ contains the overlap matrix elements between the projection and excitation manifolds

$$S_{\nu\mu} = \langle\bar{\nu}|\hat{\tau}_\mu|\mathrm{HF}\rangle, \quad (32)$$

and the vector $\eta^{(0)}$ is defined by

$$\eta_\mu^{(0)} = \left(\frac{\partial\mathcal{W}}{\partial t_\mu}\right)_0. \quad (33)$$

Detailed expressions for CC response functions of arbitrary high order and the equations that have to be solved for the required derivatives of cluster amplitudes and Lagrangian multipliers are given in Ref. 24. (Note that in Ref. 24 and most other works on conventional CC models, it is assumed that excitation and projection manifolds are chosen such that $\mathbf{S}$ becomes a unit matrix, which is not easily possible for CC-R12 models because of the nontrivial integrals $w_{\alpha\beta}^{xy}$ that enter $\mathbf{S}$.) They require the implementation of contractions of the partial derivatives of the Lagrangian L listed in Table I with cluster amplitudes and Lagrangian multipliers to inter-

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mediates of rank 1, i.e., right hand side vectors, or rank 0, i.e., scalar quantities. The implementation of these contractions at the (conventional) CCSD level has been described in Refs. 26–28. Therefore, we restrict the discussion in the following sections to the additional contributions introduced by the linear-r_{12} corrections included in the CCSD(R12) model.

III. IMPLEMENTATION DETAILS

A. Vector function

The linear-r_{12} contributions to the vector function at the CCSD(R12) level can be expressed[17] using four intermediates corresponding to the Fock and overlap matrices and Coulomb integrals in conventional calculations. Introducing the R12-R12 Fock and overlap (super)matrices as, respectively

$$\mathcal{F}_{xy}^{vw} = \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}(\hat{f}(1)+\hat{f}(2))\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle \tag{34}$$

and

$$\mathcal{X}_{xy}^{vw} = \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle, \tag{35}$$

one can evaluate the matrix elements with the commutator between the Fock and the cluster operators according to

$$\begin{aligned}\langle {}_{ij}^{xy}|[\hat{F},\hat{T}_{2'}]|\mathrm{HF}\rangle &= \sum_{vw}(\mathcal{F}_{xy}^{vw} - (\epsilon_i+\epsilon_j)\mathcal{X}_{xy}^{vw})c_{vw}^{ij} \\ &= \sum_{vw}\mathcal{B}_{xy,vw}^{(ij)}c_{vw}^{ij}.\end{aligned} \tag{36}$$

We will use in the following $\mathcal{B}_{xy,vw}^{(ij)}$ as short hand notation for the expression in parentheses. Furthermore, one introduces

$$\mathcal{V}_{xy}^{\kappa\lambda} = \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\frac{1}{r_{12}}|\varphi_\kappa(1)\varphi_\lambda(2)\rangle, \tag{37}$$

$$(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy} = \langle \varphi_\kappa(1)\varphi_\lambda(2)|\frac{1}{r_{12}}\hat{w}_{12}|\phi_x(1)\phi_y(2)\rangle = (\mathcal{V}_{xy}^{\kappa\lambda})^* \tag{38}$$

as R12 Coulomb intermediates with two orbitals $\varphi_\kappa, \varphi_\lambda$ in the atomic orbital (AO) basis. From the latter two quantities one can calculate t_1 similarity transformed intermediates according to

$$\tilde{\mathcal{V}}_{xy}^{pq} = \sum_{\kappa\lambda}\Lambda_{\kappa p}^{h}\Lambda_{\lambda q}^{h}\mathcal{V}_{xy}^{\kappa\lambda}, \tag{39}$$

$$(\tilde{\mathcal{V}}^{\dagger})_{pq}^{xy} = \sum_{\kappa\lambda}\Lambda_{\kappa p}^{p}\Lambda_{\lambda q}^{p}(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy}, \tag{40}$$

with[29]

$$\Lambda_{\kappa p}^{h} = \sum_{q} C_{\kappa q}(1+t_{qp}), \tag{41}$$

$$\Lambda_{\kappa p}^{p} = \sum_{q} C_{\kappa q}(1-t_{pq}). \tag{42}$$

Above, $C_{\kappa q}$ are the MO coefficients and $t_{pq}=t_p^q$ if p is a virtual and q an occupied MO and 0 otherwise. Explicit expressions for the R12 specific contributions are given in Table II. The implementation of these intermediates is described in detail in Refs. 10 and 16. We note here only that a resolution-of-the-identity technique with an auxiliary basis set is used to approximate the three-electron integrals appearing in Eqs. (34), (37), and (38), and the usual standard approximations of R12 theory are employed to evaluate $\mathcal{F}_{xy}^{vw}$.

TABLE II. R12 specific contributions to the vector function for CCSD(R12)/Ansatz 1. In analogy to Ref. 29 we write the R12 contributions to the conventional singles and doubles parts of the vector function, Eqs. (20) and (21), as $\Omega_{ai}^{(\mathrm{R12})}=\Omega_{ai}^{G'}$ and $\Omega_{aibj}^{(\mathrm{R12})}=\Omega_{aibj}^{A'}+\Omega_{aibj}^{B'}+\Omega_{aibj}^{E'}$, and the R12 doubles part, Eq. (22), as $\Omega_{xiyj}^{(\mathrm{R12})}=\Omega_{xiyj}^{B'}+\Omega_{xiyj}^{E'}+\Omega_{xiyj}^{F'}$. The operator $\hat{P}_{ij}^{ab}$ is defined according to $\hat{P}_{ij}^{ab}\Omega_{aibj}=\Omega_{aibj}+\Omega_{bjai}$.

$\Omega_{ai}^{G'}=\Sigma_{xyk}(2c_{xy}^{ik}-c_{xy}^{ki})(\tilde{\mathcal{V}}^{\dagger})_{ak}^{xy}$		
$\Omega_{aibj}^{A'}=\Sigma_{klxy}c_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}t_{ab}^{kl}$	$\Omega_{aibj}^{B'}=\Sigma_{xy}c_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy}$	$\Omega_{aibj}^{E'}=-\hat{P}_{ij}^{ab}\Sigma_k E_{kj}^{(\mathrm{R12})}t_{ab}^{ik}$
$\Omega_{xiyj}^{B'}=\Sigma_{ab}t_{ab}^{ij}\tilde{\mathcal{V}}_{xy}^{ab}$	$\Omega_{xiyj}^{E'}=\Sigma_{vw}\mathcal{B}_{xy,vw}^{(ij)}c_{vw}^{ij}$	$\Omega_{xiyj}^{F'}=\tilde{\mathcal{V}}_{xy}^{ij}$

B. Partial derivatives independent on the perturbation

The explicit calculation of the partial derivatives of the Lagrangian as such is always avoided since storage of these huge intermediates would be only possible for very small systems. Rather, as indicated above, only contractions of the derivatives with trial vectors or derivatives of the cluster amplitudes or Lagrangian multipliers are computed and stored. In particular, the linear equations that determine the latter are solved iteratively using a Davidson-type scheme; for a more detailed discussion cf. Ref. 30. The final expressions for the additional contractions needed for the R12 specific contributions included in CCSD(R12)/Ansatz 1 are tabulated in Tables III and IV in the case of the (super)matrices **A**, **B**, **F**, **C**, and **G**. The additional terms for the R12 contributions to the vector function depend at most to third order on the cluster amplitudes. Therefore, no additional contributions arise for the matrices **D** and **H**. Furthermore, we listed in Table IV for **B** and **C** only the contributions to contractions of the form $\Sigma_{\mu\gamma}B_{\nu\mu\gamma}R_{\mu}^{A}R_{\gamma}^{B}$ and $\Sigma_{\mu\gamma\delta}C_{\nu\mu\gamma\delta}R_{\mu}^{A}R_{\gamma}^{B}R_{\delta}^{C}$. The contributions to contractions which involve the leftmost indices, i.e., to $\Sigma_{\nu\mu}L_{\nu}B_{\nu\mu\gamma}R_{\mu}^{A}$ and $\Sigma_{\nu\mu\gamma}L_{\nu}C_{\nu\mu\gamma\delta}R_{\mu}^{A}R_{\gamma}^{B}$, are easily obtained from the expressions for $\Sigma_{\mu}F_{\nu\mu}R_{\mu}^{A}$ and $\Sigma_{\mu\gamma}G_{\nu\mu\gamma}R_{\mu}^{A}R_{\gamma}^{B}$ by replacing the zeroth-order Lagrangian multipliers $\bar{t}_{\nu}$ by the elements of a "left" trial vector L_{ν} or derivatives of the Lagrangian multipliers. For compactness of the notation in Tables III and IV, we introduced the intermediates

$$E_{ij}^{(\mathrm{R12})} = \sum_{kxy}(2c_{xy}^{jk}-c_{xy}^{kj})(\mathcal{V}^{\dagger})_{ik}^{xy}, \tag{43}$$

$$\bar{E}_{ij}^{(\mathrm{R12})} = \sum_{kxy}(2R_{xy}^{jk}-R_{xy}^{kj})(\mathcal{V}^{\dagger})_{ik}^{xy}, \tag{44}$$

and

$$\bar{\Lambda}_{\kappa p}^{h} = \sum_{q} C_{\kappa q}R_{qp}, \tag{45}$$

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TABLE III. R12 specific contributions to the Jacobi matrix transformations for CCSD(R12)/Ansatz 1. Similar to Table II, we write the result vectors for a contraction of a vector $\mathbf{R}$ with the right index of $\mathbf{A}$ as $\rho_{ai}^{(\mathrm{R12})}={}^{1}\rho_{ai}^{G'}+{}^{2'}\rho_{ai}^{G'}$ (singles part), $\rho_{aibj}^{(\mathrm{R12})}={}^{1}\rho_{aibj}^{B'}+{}^{2}\rho_{aibj}^{A'}+{}^{2}\rho_{aibj}^{E'}+{}^{2'}\rho_{aibj}^{B'}+{}^{2'}\rho_{aibj}^{A'}+{}^{2'}\rho_{aibj}^{E'}$ (doubles part), and $\rho_{xiyj}^{(\mathrm{R12})}={}^{1}\rho_{xiyj}^{E'}+{}^{2}\rho_{xiyj}^{B'}+{}^{2'}\rho_{xiyj}^{F'}$ (R12 doubles part) and for a contraction with a vector $\mathbf{R}$ with the left index of $\mathbf{A}$ as $\rho_{ai}^{(\mathrm{R12})}={}^{1}\rho_{ai}^{G'}+{}^{2}\rho_{ai}^{B'}+{}^{2'}\rho_{ai}^{F'}$ (singles part), $\rho_{aibj}^{(\mathrm{R12})}={}^{2}\rho_{aibj}^{A'}+{}^{2}\rho_{aibj}^{E'}+{}^{2'}\rho_{aibj}^{B'}$ (doubles part), and $\rho_{xiyj}^{(\mathrm{R12})}={}^{1}\rho_{xiyj}^{G'}+{}^{2}\rho_{xiyj}^{B'}+{}^{2}\rho_{xiyj}^{A'}+{}^{2}\rho_{xiyj}^{E'}+{}^{2'}\rho_{xiyj}^{E'}$ (R12 doubles part), where the left upper indices indicate the block of the trial vector entering the contraction. The operator $\hat{P}_{ij}^{xy}$ is defined analogously to $\hat{P}_{ij}^{ab}$ (see Table II).

Right hand side Jacobi matrix transformations $\rho_\mu=\Sigma_\nu A_{\mu\nu}R_\nu$

${}^{1}\rho_{ai}^{G'}=-\Sigma_j E_{ji}^{(\mathrm{R12})}R_a^j$		${}^{2'}\rho_{ai}^{G'}=\Sigma_{xyk}(2R_{xy}^{ik}-R_{xy}^{ki})(\tilde{\mathcal{V}}^{\dagger})_{ak}^{xy}$
${}^{1}\rho_{aibj}^{B'}=\Sigma_{xy}c_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy}$	${}^{2}\rho_{aibj}^{A'}=\Sigma_{klxy}c_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}R_{ab}^{kl}$	${}^{2}\rho_{aibj}^{E'}=-\hat{P}_{ij}^{ab}\Sigma_k E_{kj}^{(\mathrm{R12})}R_{ab}^{ik}$
${}^{2'}\rho_{aibj}^{B'}=\Sigma_{xy}R_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy}$	${}^{2'}\rho_{aibj}^{A'}=\Sigma_{klxy}R_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}t_{ab}^{kl}$	${}^{2'}\rho_{aibj}^{E'}=-\hat{P}_{ij}^{ab}\Sigma_k\bar{E}_{kj}^{(\mathrm{R12})}t_{ab}^{ik}$
${}^{2'}\rho_{xiyj}^{E'}=\Sigma_{vw}\mathcal{B}_{xy,vw}^{(ij)}R_{vw}^{ij}$	${}^{1}\rho_{xiyj}^{F'}=\tilde{\mathcal{V}}_{xy}^{ij}$	${}^{2}\rho_{xiyj}^{B'}=\Sigma_{ab}R_{ab}^{ij}\tilde{\mathcal{V}}_{xy}^{ab}$

Left hand side Jacobi matrix transformations $\rho_\mu=\Sigma_\nu R_\nu A_{\nu\mu}$

${}^{1}\rho_{ai}^{G'}=-\Sigma_j E_{ij}^{(\mathrm{R12})}R_a^j$		${}^{1}\rho_{xiyj}^{G'}=\hat{P}_{ij}^{xy}\Sigma_a R_a^i(2(\tilde{\mathcal{V}}^{\dagger})_{aj}^{xy}-(\tilde{\mathcal{V}}^{\dagger})_{ja}^{xy})$
${}^{2}\rho_{xiyj}^{B'}=\Sigma_{ab}R_{ab}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy}$	${}^{2}\rho_{xiyj}^{A'}=\Sigma_{abkl}R_{ab}^{ij}t_{ab}^{kl}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}$	${}^{2}\rho_{xiyj}^{E'}=-\hat{P}_{ij}^{xy}\Sigma_{abkl}R_{ab}^{kj}t_{ab}^{kl}(2(\tilde{\mathcal{V}}^{\dagger})_{il}^{xy}-(\tilde{\mathcal{V}}^{\dagger})_{li}^{xy})$
${}^{2}\rho_{ai}^{B'}=-\Sigma_{xybkl}R_{ba}^{kl}c_{xy}^{kl}(\tilde{\mathcal{V}}^{\dagger})_{bi}^{xy}$	${}^{2}\rho_{aibj}^{A'}=\Sigma_{klxy}c_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}R_{ab}^{kl}$	${}^{2}\rho_{aibj}^{E'}=-\hat{P}_{ij}^{ab}\Sigma_k E_{jk}^{(\mathrm{R12})}R_{ab}^{ik}$
${}^{2'}\rho_{xiyj}^{E'}=\Sigma_{vw}\mathcal{B}_{xy,vw}^{(ij)}R_{vw}^{ij}$	${}^{2'}\rho_{ai}^{F'}=\Sigma_{xyj}R_{xy}^{ij}\tilde{\mathcal{V}}_{xy}^{aj}$	${}^{2'}\rho_{aibj}^{B'}=\Sigma_{xy}R_{xy}^{ij}\tilde{\mathcal{V}}_{xy}^{ab}$

$$\bar{\Lambda}_{\kappa p}^{p}=-\sum_{q}C_{\kappa q}R_{pq}, \tag{46}$$

$$\bar{\mathcal{V}}_{xy}^{ij}=\sum_{\kappa\lambda}(\bar{\Lambda}_{\kappa i}^{h}\Lambda_{\lambda j}^{h}+\Lambda_{\kappa i}^{h}\bar{\Lambda}_{\lambda j}^{h})\mathcal{V}_{xy}^{\kappa\lambda}, \tag{47}$$

with $R_{pq}=R_p^q$ if p is a virtual and q an occupied MO and 0 otherwise, i.e., transformations with the singles part of trial vectors are absorbed in the AO to MO transformation by using $\bar{\mathbf{\Lambda}}^p$ and $\bar{\mathbf{\Lambda}}^h$ as generalized MO coefficients. Furthermore, a short hand notation for derivatives of $\hat{T}_1$ similarity transformed intermediates with respect to the singles amplitudes is used, e.g.,

$$(\bar{\mathcal{V}}^{\dagger})_{ab}^{xy}=\sum_{\kappa\lambda}(\bar{\Lambda}_{\kappa a}^{p}\Lambda_{\lambda b}^{p}+\Lambda_{\kappa a}^{p}\bar{\Lambda}_{\lambda b}^{p})(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy}. \tag{48}$$

For the vector $\eta^{(0)}$, which appears in the equation that determines the zeroth-order Lagrangian multipliers $\bar{t}^{(0)}$, Eq. (31), one obtains just one additional term given by

$$\eta_{xiyj}^{(0)}=4(\mathcal{V}^{\dagger})_{ij}^{xy}-2(\mathcal{V}^{\dagger})_{ji}^{xy}. \tag{49}$$

TABLE IV. R12 specific contributions to the **F**, **B**, **G**, and **C** matrix transformations for CCSD(R12)/Ansatz 1. The result vectors for the **F** matrix transformations are $\rho_{ai}^{(\mathrm{R12})}={}^{2'}\rho_{ai}^{G'}+{}^{1}\rho_{ai}^{B'}+{}^{2'}\rho_{ai}^{B'}+{}^{1}\rho_{ai}^{F'}$ (singles part), $\rho_{aibj}^{(\mathrm{R12})}={}^{2'}\rho_{aibj}^{A'}+{}^{2'}\rho_{aibj}^{E'}$ (doubles part), and $\rho_{xiyj}^{(\mathrm{R12})}={}^{1}\rho_{xiyj}^{G'}+{}^{1}\rho_{xiyj}^{B'}+{}^{2}\rho_{xiyj}^{A'}+{}^{2}\rho_{xiyj}^{E'}$ (R12 doubles part), those for the **B** matrix transformations are $\rho_{ai}^{(\mathrm{R12})}={}^{12'}\rho_{ai}^{G'}$ (singles part), $\rho_{aibj}^{(\mathrm{R12})}={}^{11}\rho_{aibj}^{B'}+{}^{22'}\rho_{aibj}^{A'}\ {}^{12'}\rho_{aibj}^{B'}+{}^{12'}\rho_{aibj}^{E'}$ (doubles part), and $\rho_{xiyj}^{(\mathrm{R12})}={}^{11}\rho_{xiyj}^{F'}$ (R12 doubles part). The **G** matrix transformations exhibit only an additional singles ($\rho_{ai}^{(\mathrm{R12})}={}^{12'}\rho_{ai}^{B'}$) and R12 doubles part ($\rho_{xiyj}^{(\mathrm{R12})}={}^{11}\rho_{xiyj}^{B'}$), while to the **C** matrix transformations an extra doubles term is added ($\rho_{aibj}^{(\mathrm{R12})}={}^{112'}\rho_{aibj}^{B'}$). The permutation operators $\hat{P}^{AB}$ and $\hat{P}^{ABC}$ are defined by $\hat{P}^{AB}\rho(AB)=\rho(AB)+\rho(BA)$ and $\hat{P}^{ABC}\rho(ABC)=\rho(ABC)+\rho(BCA)+\rho(CAB)$.

F matrix transformations $\rho_\mu=\Sigma_\nu F_{\mu\nu}R_\nu$

${}^{2'}\rho_{ai}^{G'}=-\Sigma_j\bar{E}_{ij}^{(\mathrm{R12})}\bar{t}_a^j$		${}^{1}\rho_{xiyj}^{G'}=\hat{P}_{ij}^{xy}\Sigma_a\bar{t}_a^i(2(\tilde{\mathcal{V}}^{\dagger})_{aj}^{xy}-(\tilde{\mathcal{V}}^{\dagger})_{ja}^{xy})$
${}^{1}\rho_{xiyj}^{B'}=\Sigma_{ab}\bar{t}_{ab}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy}$	${}^{2}\rho_{xiyj}^{A'}=\Sigma_{abkl}\bar{t}_{ab}^{ij}R_{ab}^{kl}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}$	${}^{2}\rho_{xiyj}^{E'}=-\hat{P}_{ij}^{xy}\Sigma_{abkl}\bar{t}_{ab}^{kj}R_{ab}^{kl}(2(\tilde{\mathcal{V}}^{\dagger})_{il}^{xy}-(\tilde{\mathcal{V}}^{\dagger})_{li}^{xy})$
${}^{1}\rho_{ai}^{B'}=-\Sigma_{xybkl}\bar{t}_{ba}^{kl}c_{xy}^{kl}(\tilde{\mathcal{V}}^{\dagger})_{bi}^{xy}$	${}^{2'}\rho_{aibj}^{A'}=\Sigma_{klxy}R_{xy}^{ij}(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}\bar{t}_{ab}^{kl}$	${}^{2'}\rho_{aibj}^{E'}=-\hat{P}_{ij}^{ab}\Sigma_k\bar{E}_{jk}^{(\mathrm{R12})}\bar{t}_{ab}^{ik}$
${}^{2'}\rho_{ai}^{B'}=-\Sigma_{xybkl}\bar{t}_{ba}^{kl}R_{xy}^{kl}(\tilde{\mathcal{V}}^{\dagger})_{bi}^{xy}$		
${}^{1}\rho_{ai}^{F'}=\Sigma_{xyj}\bar{c}_{xy}^{ij}\tilde{\mathcal{V}}_{xy}^{aj}$		

B matrix transformations $\rho_\mu=\Sigma_{\nu\gamma}B_{\mu\nu\gamma}R_\nu^A R_\gamma^B$

${}^{12'}\rho_{ai}^{G'}=-\hat{P}^{AB}\Sigma_j(\bar{E}_{ji}^{(\mathrm{R12})})^A(R_a^j)^B$	
${}^{11}\rho_{aibj}^{B'}=\hat{P}^{AB}\Sigma_{xy}c_{xy}^{ij}\Sigma_{\kappa\lambda}(\bar{\Lambda}_{\kappa a}^{p})^A(\bar{\Lambda}_{\lambda b}^{p})^B(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy}$	${}^{22'}\rho_{aibj}^{A'}=\hat{P}^{AB}\Sigma_{xykl}(R_{xy}^{ij})^A(R_{ab}^{kl})^B(\tilde{\mathcal{V}}^{\dagger})_{kl}^{xy}$
${}^{12'}\rho_{aibj}^{B'}=\hat{P}^{AB}\Sigma_{xy}(R_{xy}^{ij})^A((\tilde{\mathcal{V}}^{\dagger})_{ab}^{xy})^B$	${}^{22'}\rho_{aibj}^{E'}=-\hat{P}^{AB}\hat{P}_{ij}^{ab}\Sigma_k(\bar{E}_{kj}^{(\mathrm{R12})})^A(R_{ab}^{ik})^B$
${}^{11}\rho_{xiyj}^{G'}=\hat{P}^{AB}\Sigma_{\kappa\lambda}(\bar{\Lambda}_{\kappa i}^{h})^A(\bar{\Lambda}_{\lambda j}^{h})^B\tilde{\mathcal{V}}_{xy}^{\kappa\lambda}$	

G matrix transformations $\rho_\mu=\Sigma_{\nu\gamma}G_{\mu\nu\gamma}R_\nu^A R_\gamma^B$

${}^{11}\rho_{xiyj}^{B\prime}=\hat{P}^{AB}\Sigma_{ab}\bar{t}_{ab}^{ij}\Sigma_{\kappa\lambda}(\bar{\Lambda}_{\kappa a}^{p})^A(\bar{\Lambda}_{\lambda b}^{p})^B(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy}$
${}^{12'}\rho_{ai}^{B'}=-\hat{P}^{AB}\Sigma_{xybkl}\bar{t}_{ba}^{kl}(R_{xy}^{kl})^A((\tilde{\mathcal{V}}^{\dagger})_{bi}^{xy})^B$

C matrix transformations $\rho_\mu=\Sigma_{\nu\gamma\delta}C_{\mu\nu\gamma\delta}R_\nu^A R_\gamma^B R_\delta^C$

${}^{112'}\rho_{aibj}^{B'}=\hat{P}^{ABC}\Sigma_{xy}(R_{xy}^{ij})^A\Sigma_{\kappa\lambda}(\bar{\Lambda}_{\kappa a}^{p})^B(\bar{\Lambda}_{\lambda b}^{p})^C(\mathcal{V}^{\dagger})_{\kappa\lambda}^{xy}$

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TABLE V. CCSD(R12) contributions to ξ^X, η^X, and $\mathbf{A}^X$, $\mathbf{F}^X$, $\mathbf{B}^X$ matrix transformations for Ansatz 1. Note that, apart from the additional R12 doubles terms, only corrections to the singles parts of the result vectors of η^X and the $\mathbf{F}^X$ matrix transformations occur.

Contribution to ξ^X	
$\xi^X_{xiyj}=\Sigma_{vw}(\mathcal{W}^{vw}_{xy}c^{ij}_{vw}-\hat{P}^{xy}_{ij}\mathcal{X}^{vw}_{xy}\Sigma_k c^{ik}_{vw}\bar{X}^j_k)$	
Contributions to η^X	
$\eta^X_{ai}=-\Sigma_{xyvw}\Sigma_{kl}\bar{c}^{ki}_{xy}c^{kl}_{vw}\mathcal{X}^{vw}_{xy}X^a_l$	$\eta^X_{xiyj}=\Sigma_{vw}(\mathcal{W}^{xy}_{vw}\bar{c}^{ij}_{vw}-\hat{P}^{xy}_{ij}\mathcal{X}^{xy}_{vw}\Sigma_k\bar{c}^{ik}_{vw}\bar{X}^k_j)$
$\mathbf{A}^X$ matrix transformations $\rho^X_\mu=\Sigma_\nu A^X_{\mu\nu}R_\nu$	
${}^1\rho^X_{xiyj}=-\hat{P}^{xy}_{ij}\Sigma_{vw}\mathcal{X}^{vw}_{xy}\Sigma_k c^{ik}_{vw}\bar{X}^j_k$	${}^{2'}\rho^X_{xiyj}=\Sigma_{vw}(\mathcal{W}^{vw}_{xy}R^{ij}_{vw}-\hat{P}^{xy}_{ij}\mathcal{X}^{vw}_{xy}\Sigma_k R^{ik}_{vw}\bar{X}^j_k)$
$\mathbf{F}^X$ matrix transformations $\rho^X_\mu=\Sigma_\nu F^X_{\mu\nu}R_\nu$	
${}^{2'}\rho^X_{ai}=-\Sigma_{xyvw}\Sigma_{kl}\bar{c}^{ki}_{xy}R^{kl}_{vw}\mathcal{X}^{vw}_{xy}X^a_l$	${}^1\rho^x_{xiyj}=-\hat{P}^{xy}_{ij}\Sigma_{vw}\mathcal{X}^{xy}_{vw}\Sigma_k\bar{c}^{ik}_{vw}\bar{X}^k_j$
$\mathbf{B}^X$ matrix transformations $\rho^X_\mu=\Sigma_{\nu\gamma}B^X_{\mu\nu\gamma}R^A_\nu R^B_\gamma$	
${}^{12'}\rho^X_{xiyj}=-\hat{P}^{AB}\Sigma_{vw}\mathcal{X}^{xy}_{vw}\Sigma_k(R^{ik}_{vw})^A(\bar{X}^k_j)^B$	

C. Derivatives of the Lagrangian containing the perturbation

The remaining contributions to the response equations depend explicitly on the perturbation operator $\hat{X}$, where we restrict ourselves to a one-electron operator. For example, for

$$\xi^X_\mu=\langle\mu|\exp(-\hat{T})\hat{X}\exp(\hat{T})|\mathrm{HF}\rangle, \tag{50}$$

one obtains with Ansatz 1 of R12 theory only a single additional contribution,

$$\xi^X_{xiyj}=\langle {}^{xy}_{ij}|[\tilde{\hat{X}},\hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{51}$$

where $\tilde{\hat{X}}=\exp(-\hat{T}_1)\hat{X}\exp(\hat{T}_1)$. With the two-electron intermediate

$$\mathcal{W}^{vw}_{xy}=\langle\phi_x(1)\phi_y(2)|\hat{w}^\dagger_{12}(\hat{X}(1)+\hat{X}(2))\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle, \tag{52}$$

the elements ξ^X_{xiyj} can be evaluated as stated in Table V. The new intermediate $\mathcal{W}^{vw}_{xy}$ is formally very similar to the R12-R12 Fock matrix $\mathcal{F}^{vw}_{xy}$, but since $\hat{X}$ can be any one-electron operator we adopted in our current implementation a more general strategy for its evaluation: to avoid the coding of new two-electron integrals we insert an approximate resolution of the identity as

$$\hat{w}^\dagger_{12}\hat{X}(1)\hat{w}_{12}\overset{\text{Ansatz 1}}{=}f_{12}(1-\hat{P}_1)\hat{X}(1)(1-\hat{P}_1)(1-\hat{P}_2)f_{12}, \tag{53}$$

$$\overset{\text{ABS}}{\approx}f_{12}(\hat{P}'_1-\hat{P}_1)\hat{X}(1)(\hat{P}'_1-\hat{P}_1)(\hat{P}'_2-\hat{P}_2)f_{12}, \tag{54}$$

where $\hat{P}'$ is the projector on the basis used to resolve the identity and is defined similar to $\hat{P}$ in Eq. (8). This leads for $\mathcal{W}^{vw}_{xy}$ to the expression

$$\begin{aligned}\mathcal{W}^{vw}_{xy}=\hat{P}^{vw}_{xy}\Bigg[&\sum_{p'q'}w^{p'q'}_{xy}\Bigg(\sum_{s'}X^{s'}_{p'}w^{vw}_{s'q'}-\sum_s X^s_{p'}w^{vw}_{sq'}\Bigg)\\&-\sum_{pq'}w^{pq'}_{xy}\Bigg(\sum_{s'}X^{s'}_p w^{vw}_{s'q'}-\sum_s X^s_p w^{vw}_{sq'}\Bigg)\\&-\sum_{p'q}w^{p'q}_{xy}\Bigg(\sum_{s'}X^{s'}_{p'}w^{vw}_{s'q}-\sum_s X^s_{p'}w^{vw}_{sq}\Bigg)\\&+\sum_{pq}w^{pq}_{xy}\Bigg(\sum_{s'}X^{s'}_p w^{vw}_{s'q}-\sum_s X^s_p w^{vw}_{sq}\Bigg)\Bigg].\end{aligned} \tag{55}$$

Note that in this approximation $\mathcal{W}^{vw}_{xy}$ vanishes if the resolution of the identity is done in the basis of molecular orbitals. On the other hand, an appealing feature of this implementation is that it requires only integrals already available and that it can be used for any (even nonmultiplicative) one-electron operator.

The expressions for all other partial derivatives of the Lagrangian that depend on the one-electron perturbations, η^X, $\mathbf{A}^X$, $\mathbf{F}^X$, and $\mathbf{B}^X$, follow from those of ξ^X_{xiyj} by further differentiation with respect to cluster amplitudes and contraction with Lagrangian multipliers. Explicit expressions for the additional contributions induced by the linear-r_{12} corrections at the CCSD(R12) level are given in Table V.

IV. COMPUTATIONAL DETAILS

The reponse properties for the CCSD(R12) model have been implemented in the coupled-cluster module of the DALTON program.[31] As examples for a first investigation of the performance of this approach, we have chosen the three molecules BH, N_2, and formaldehyde H_2CO. The bond distances were fixed at 2.329 a.u. for BH (Ref. 32) and 2.074 a.u. for N_2.[5] For formaldehyde the structure from Ref. 33 ($r_{CO}=120.3$ pm, $r_{CH}=109.9$ pm, $\angle_{HCH}=116.5°$) was used. The calculations for BH and N_2 were carried out without frozen core approximation. For formaldehyde the 1*s* orbitals of C and O were frozen in the coupled-cluster calculations. Since the time- and field-dependent coupled-cluster wave function $|\mathrm{CC}\rangle$ is parametrized based on the Hartree-Fock reference for the unperturbed system, Eq. (24), orbitals are not allowed to relax with respect to the perturbations. For a dis-

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TABLE VI. Static electronic polarizabilities for N_2 in a.u. computed at the SCF, CCSD, and CCSD(R12) levels of theory using the d-aug-cc-pV*X*Z basis set family. Values in parentheses are relative to the SCF result in the same basis.

Cardinal No. *X*Z	α_{xx} SCF	α_{xx} CCSD	α_{xx} CCSD(R12)	α_{zz} SCF	α_{zz} CCSD	α_{zz} CCSD(R12)
DZ	9.774	10.212 (0.438)	10.064 (0.290)	15.003	14.800 (−0.203)	14.605 (−0.398)
TZ	9.834	10.174 (0.340)	10.112 (0.278)	15.044	14.665 (−0.379)	14.594 (−0.450)
QZ	9.835	10.130 (0.295)	10.100 (0.265)	15.034	14.609 (−0.425)	14.575 (−0.459)
5Z	9.832	10.106 (0.274)	10.089 (0.257)	15.029	14.577 (−0.452)	14.558 (−0.471)
6Z	9.832	10.096 (0.264)	10.082 (0.250)	15.028	14.565 (−0.463)	14.549 (−0.479)
Limit	9.831±0.001	10.081±0.001		15.027±0.001	14.549±0.003	

cussion of the effects of orbital relaxation on higher-order properties, the reader is referred to Refs. 5 and 34–37. We mention here only that the orbital-relaxed approach is inappropriate for correlated calculations on frequency-dependent properties, as singularities from the Hartree-Fock reference would spoil the pole structure of the results at the correlated level. Also, for frequency-independent properties the orbital-relaxed approach is with coupled-cluster wave functions often not an improvement.

The orbital basis sets are taken from the cc-pV*X*Z family with X=D, T, Q, 5, 6, augmented with a varying number of diffuse functions (see Sec. V). As auxiliary basis sets for the resolution of the identity, we used the decontracted correlation-consistent basis sets with one higher cardinal number $X+1$ and the same augmentation level as the orbital basis. Because of the absence of a cc-pV7Z basis, we applied in the case of the cc-pV6Z basis the 19*s*14*p*8*d*6*f*4*g*3*h*2*i* auxiliary basis set described in Ref. 10. The largest calculation performed contained 574 orbital and 476 auxiliary basis functions.

All calculations employed the complementary auxiliary basis set (CABS+) approach of Valeev,[13] which essentially means that the (approximate) resolution of the identity is done in the union of the orbital and the auxiliary basis sets. Standard approximation[10] B and the standard linear-r_{12} correlation factor of R12 theory, i.e.,

$$f_{12} = r_{12} = |\mathbf{r}(1) - \mathbf{r}(2)|, \tag{56}$$

were used throughout.

In the case of BH we performed calculations without and with additional seminatural virtual orbitals extending the R12 orbital space which were obtained by diagonalization of the virtual-virtual block of a conventional MP2 density matrix (we added one orbital of σ, π_x, and π_y symmetries, respectively).[18] For N_2 and formaldehyde no additional virtual orbitals were added, since calculations using the smaller basis sets (where additional orbitals should have the greatest effect) did not indicate the need to do so.

V. RESULTS

A. Static polarizability of N_2

Results for the dipole polarizability of N_2 are presented in Table VI. For comparison, Hartree-Fock self-consistent field (SCF) and conventional CCSD results are shown as well. Extrapolated SCF values were obtained from QZ-5Z and 5Z-6Z extrapolations assuming an exponential [$\sim\exp(-X)$] convergence behavior. The error was assessed as (up-rounded) half difference between the two extrapolations. The SCF values for both components of the polarizability are practically converged (errors below 1%) with d-aug-cc-pVTZ for α_{xx} and d-aug-cc-pVQZ for α_{zz}, respectively.

The correlation contributions for CCSD were calculated as the difference between the CCSD response and SCF results (given in parentheses in Table VI) and were extrapolated assuming a similar convergence behavior as for the correlation energy, i.e., $\sim X^{-3}$. For α_{xx} one obtains 0.250 a.u. as correlation contribution both from QZ-5Z and 5Z-6Z extrapolations. Adding the estimated uncorrelated limit of 9.831 a.u., we obtain 10.081±0.001 a.u., where the error is estimated as described above for the SCF extrapolation. For the zz component the extrapolated basis set limits for the correlation contribution are −0.484 a.u. (QZ-5Z) and −0.478 a.u. (5Z-6Z), leading to a best estimate of 14.549±0.003 a.u. for α_{zz}. Note that for both components the extrapolated limits are reproduced by the CCSD(R12) calculation in the d-aug-cc-pV6Z basis set within the estimated error bars.

Further comparison of the conventional CCSD and the CCSD(R12) values reveals that the explicitly correlated calculations in a basis with cardinal number X provide correlation contributions with accuracies corresponding to conventional calculations with X increased by one and two steps in the cc-pV*X*Z hierarchy, which pretty much parallels what is observed for ground state correlation energies.[10,17]

B. Static polarizability of BH

In Fig. 1 the computed α_{xx} and α_{zz} components of the electronic polarizability of BH are shown. This molecule is an example where the necessity to include additional virtual orbitals in the R12 orbital manifold is apparent: since there are no occupied orbitals of π symmetry in BH, with only occupied orbitals included in the construction of pair functions [Eq. (5)], there would be no suitable pairs for describing $\pi \leftarrow \sigma$ excitations,[18] which, however, are necessary for an accurate description of α_{xx}. Consequently, CCSD(R12) with only occupied orbitals used for construction of the pair functions is able to improve α_{zz}, but the basis set convergence of α_{xx} is even inferior to what is obtained with con-

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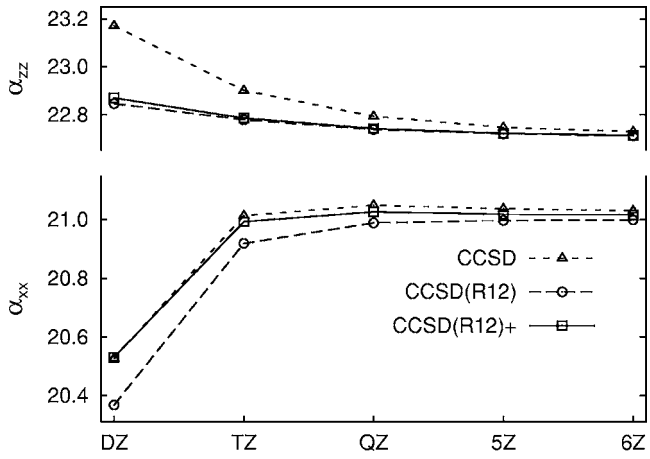


FIG. 1. Basis set convergence of the static electronic polarizabilities for BH (in a.u.) with the aug-cc-pV*X*Z basis sets. The cardinal number *X* is indicated in the ordinate. CCSD(R12)+ denotes the CCSD(R12) method adopting additional nonoccupied orbitals for constructing the R12 pair functions, see text.

ventional CCSD for this component. To remedy this behavior we added three additional seminatural virtual orbitals[18] of π_x, π_y, and σ symmetries (i.e., those with the largest occupation numbers) to the R12 space. The results are labeled CCSD(R12)+ in Fig. 1. They show that a small extension of the orbital manifold used for the construction of the pair functions rectifies the basis set convergence of α_{xx} (which in that case is accidentally already fast for conventional CCSD), while that of α_{zz} remains nearly unchanged. From the three approaches only CCSD(R12)+ reveals a fast basis set convergence for *both* components of the polarizability.

C. Static polarizability of formaldehyde

Table VII contains the data obtained for the three components of the static electronic part of the dipole polarizability. Errors of the estimated limits of the SCF polarizability were concluded from the absolute difference of TZ-QZ and QZ-5Z extrapolations, in an analogous way to N_2. CCSD errors were estimated from DZ-TZ and TZ-QZ extrapolations.

The obtained results corroborate what has been observed above for the nitrogen molecule: with CCSD(R12) the basis set convergence is clearly accelerated for all components of the polarizability. The quadruple-zeta results agree with the estimated basis set limits within their uncertainties, but might be more accurate than the latter. Note that such extrapolation is not always possible or reliable for properties. In particular, in the frequency-dependent case it will break down close to poles.

D. Second hyperpolarizabilities of N_2 and formaldehyde

As example for higher-order properties we computed the second hyperpolarizabilities of N_2 and formaldehyde (H_2CO). For the former we also calculated frequency-dependent results for the electric-field induced second-harmonic generation (ESHG) process. We use the usual convention[38] for the frequency arguments, $\gamma^{\mathrm{ESHG}}_{\mu\nu\eta\xi}(\omega) = \gamma_{\mu\nu\eta\xi}(-2\omega;\omega\omega,0)$, which leads for the parallel isotropic average of the second hyperpolarizability $\gamma_{\|}$ to the definition[38]

$$\gamma_{\|} = \frac{1}{15}\sum_{\xi\eta}(\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\eta\xi} + \gamma_{\xi\eta\xi\eta}), \tag{57}$$

with $\xi, \eta = x, y, z$.

The values in Tables VIII and IX reveal similar features as discussed before for the polarizability: the CCSD(R12) method significantly accelerates the basis set convergence. For N_2 we find that apart from the three smallest basis sets, d-aug-cc-pVDZ, t-aug-cc-pVDZ, and d-aug-cc-pVTZ, which are insufficient to describe γ qualitatively correct and exhibit also at the SCF level large basis sets errors, the results obtained with CCSD(R12) are of an accuracy which is first obtained by conventional CCSD with the cardinal number *X* increased by at least one further level. For formaldehyde this behavior is already seen for the smallest basis set employed (d-aug-cc-pVDZ).

Looking in more detail at the convergence of the correlation contribution in the triply augmented series for N_2, one finds that the conventional CCSD values decrease by 73.3, 23.4, 10.5, and 4.2 a.u. when going stepwise from DZ to 6Z. For the CCSD(R12) model, however, the corresponding steps are 40.2, 12.8, 6.2, and 3.5 a.u. Thus, albeit the changes are smaller in magnitude, they become similar for the largest basis sets. We suspect that this is a consequence of the fact that the basis sets used are optimized for *conventional* correlated wave function methods, but not for explicitly correlated methods.

TABLE VII. Static electronic polarizabilities for formaldehyde in a.u. computed at the SCF, CCSD, and CCSD(R12) levels of theory using the d-aug-cc-pV*X*Z basis set family. The frozen core approximation was used. Values in parentheses are relative to the SCF result in the same basis.

Cardinal No. *X*Z	α_{xx}			α_{yy}			α_{zz}		
	SCF	CCSD	CCSD(R12)	SCF	CCSD	CCSD(R12)	SCF	CCSD	CCSD(R12)
DZ	12.466	13.000 (0.534)	12.845 (0.379)	16.280	17.819 (1.539)	17.543 (1.263)	21.226	22.539 (1.313)	22.240 (1.014)
TZ	12.489	12.972 (0.483)	12.915 (0.426)	16.307	17.608 (1.301)	17.511 (1.204)	21.240	22.332 (1.092)	22.227 (0.987)
QZ	12.495	12.924 (0.429)	12.897 (0.402)	16.299	17.498 (1.199)	17.452 (1.153)	21.224	22.223 (0.999)	22.174 (0.950)
5Z	12.493	⋯	⋯	16.296	⋯	⋯	21.221	⋯	⋯
Limit	12.492±0.003	12.888±0.039 (0.396±0.033)		16.294±0.001	17.419±0.038 (1.125±0.037)		21.219±0.002	22.150±0.034 (0.931±0.032)	

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TABLE VIII. Static electronic second hyperpolarizability $\gamma_{\|}$ for N_2 in a.u. computed at the SCF, CCSD, and CCSD(R12) levels of theory using the *n*-aug-cc-pV*XZ* basis set family. Values in parentheses indicate the correlation contributions obtained by subtracting the SCF values.

	SCF[a]		CCSD[a]		CCSD(R12)	
	augmentation *n*		augmentation *n*		augmentation *n*	
Cardinal No. *XZ*	d	t	d	t	d	t
DZ	672.0	669.2	937.6 (265.6)	935.4 (266.2)	883.7 (211.7)	881.7 (212.5)
TZ	697.1	710.1	895.3 (198.2)	903.0 (192.9)	874.5 (177.4)	882.4 (172.3)
QZ	709.9	713.2	880.7 (170.8)	882.7 (169.5)	870.6 (160.7)	872.7 (159.5)
5Z	713.9	714.3	873.2 (159.3)	873.3 (159.0)	867.6 (153.7)	867.6 (153.3)
6Z	714.4	714.7	869.2 (154.8)	869.5 (154.8)	864.5 (150.1)	864.5 (149.8)
Limit	714.7±0.2		863.3±3.3(148.6±3.1)			

[a]Values taken from Ref. 5.

The results for the dynamic electronic ESHG hyperpolarizabilities $\gamma_{\|}^{\mathrm{ESHG}}(\omega)$ for several frequencies in the optical regime (Table X) indicate that the improved basis set convergence of CCSD(R12) also applies to the dispersion, which is related to the position at the lowest pole(s) and the corresponding residues. The CCSD(R12)/t-aug-cc-pVTZ results deviate at most by 1 a.u. (i.e., by less than 1%) from the conventional CCSD/t-aug-cc-pVQZ values, which can hardly be achieved by extrapolation techniques. This is also reflected by the best theoretical estimates (Table X) for $\gamma_{\|}^{\mathrm{ESHG}}(\omega)$, which have been calculated by first correcting the CCSD(R12)/t-aug-cc-pVQZ values for $\gamma_{\|}(\omega)$ for the remaining basis set error by scaling them as $\gamma_{\|}^{6Z}(\omega) \approx \gamma_{\|}^{QZ}(\omega) \cdot \gamma_{\|}^{6Z}(0)/\gamma_{\|}^{QZ}(0)$ and then correcting for higher-order correlation effects and zero-point vibrational (ZPV) averaging by adding the differences between the basis set extrapolated CC3 and CCSD results and the ZPV correction calculated at the CC3/t-aug-cc-pVTZ level (both taken from Ref. 5). Down to 632.8 nm these results agree well with the experimental values within the error bars of the latter and for the remaining frequencies the deviations are less than twice the experimental uncertainty (i.e., less than 2%).

VI. ADDITIONAL COSTS

For the future perspectives of CC-R12 response methods it is important that they do not just converge faster with the size of the one-electron basis set but also provide a better cost/performance ratio. The two key issues in this respect are the evaluation of the additional integrals needed for the R12 terms and the additional computational costs during the iterative solution of the ground state cluster and the response equations.

Prior to the iterative solution of the CCSD(R12) equations, the global intermediates $\mathcal{V}_{xy}^{\kappa\lambda}$ and $\mathcal{W}_{xy}^{vw}$ are precomputed after an initial MP2-R12 calculation, which provides (besides $\mathcal{B}$ and $\mathcal{X}$) the required integrals for r_{12} as a by-product. We denote the number correlated electrons with n and the number of orbital and auxiliary basis functions with N and N', respectively, and assume for simplicity $n \ll N \approx N'$. The most expensive intermediate needed for a CCSD(R12) calculation[16,17] is $\mathcal{V}_{xy}^{\kappa\lambda}$ [where κ and λ are two AO indices, cf. Eq. (37)] for which computational effort scales as $\mathcal{O}(n^2N^2(N+N')^2)$. The costs for the computation of the additional intermediate $\mathcal{W}_{xy}^{vw}$, which is needed for the calculation of properties, scale with $\mathcal{O}(n^4(N+N')^2)$. However, these steps are noniterative and contribute in a CCSD(R12) response calculation for (hyper)polarizabilities, which requires typically the (iterative) solution of several equations, only a small amount to the total computational cost. The additional contractions required for the R12 terms during the iterations, however, scale at most as $\mathcal{O}(n^4N^2)$, see from the equations given in Table II. This is also what one would expect considering that (after the computation of $\mathcal{V}_{xy}^{\kappa\lambda}$) most R12 terms are related to conventional contributions, but with two virtual orbitals replaced by the orbitals that appear in the R12 pair functions, and that the costs for the most demanding conventional contribution scale with $\mathcal{O}(n^2N^4)$.

Also for the final (super)matrix vector products needed to evaluate the response properties from the derivatives of the amplitudes and Lagrangian multipliers, all R12 contributions could be implemented such that the additional effort scales at most with $\mathcal{O}(n^4N^2)$. Moreover, the prefactors could be kept small by combining at several places intermediates for conventional contributions with those for corresponding R12 contributions and thereby avoiding the calculation of similar contractions several times. Test calculations with small molecules show indeed that the timings for the additional contractions are quite small compared to those for the conventional contributions; typically these R12 contributions are only responsible for about 10% or less of the total time for CCSD(R12) calculation.

TABLE IX. Static electronic second hyperpolarizability $\gamma_{\|}$ for formaldehyde in a.u. computed at the SCF, CCSD, and CCSD(R12) levels of theory using the d-aug-cc-pV*XZ* basis set family. The frozen core approximation was used.

Cardinal No. *XZ*	SCF	CCSD	CCSD(R12)
DZ	1833.1	3262.0 (1428.9)	3062.7 (1229.6)
TZ	1941.1	3209.2 (1268.1)	3136.5 (1195.4)
QZ	1944.9	3128.1 (1183.2)	3093.1 (1148.2)
5Z	1946.3	⋯	⋯
Limit	1947±1	3068±40(1121±39)	

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TABLE X. Frequency-dependent electronic ESHG hyperpolarizability $\gamma_{\parallel}(\omega)$ for N_2 in a.u. computed at the CCS, CCSD, and CCSD(R12) levels of theory using the t-aug-cc-pV*X*Z basis set family. A best theoretical estimate (Est.) obtained by correcting for a remaining basis set error, higher-order correlation effects, and zero-point vibrational averaging (see text for details) is given in the ninth column. The last two columns list the best estimates from Ref. 5 and the experimental ESHG values from Refs. 40 and 41.

		CCS		CCSD		CCSD(R12)				
λ (nm)	ω (a.u.)	TZ[a]	QZ	TZ[a]	QZ	TZ	QZ	Est.	Ref. 5	Expt.
∞	0.000 000	825.2	828.5	903.0	882.7	882.4	872.7	914.1	912.9	917±9
1055.0	0.043 188	870.1	873.7	959.2	936.9	936.7	925.9	973.2	971.2	
694.3	0.065 625	935.0	938.7	1041.1	1015.6	1015.7	1003.2	1059.4	1056.1	1057.6±6.4
632.8	0.072 003	960.3	963.9	1073.1	1046.3	1046.6	1033.4	1093.1	1089.3	1095.6±4.6
590.0	0.077 226	983.3	987.0	1102.8	1074.8	1075.2	1061.3	1124.1	1120.0	1132.0±4.2
514.5	0.088 558	1042.7	1046.5	1179.6	1148.4	1149.1	1133.5	1205.5	1200.4	1208.7±6.2
488.0	0.093 368	1072.2	1076.0	1218.1	1185.3	1186.1	1169.7	1246.2	1240.6	1253.3±6.3
457.9	0.099 505	1114.2	1118.1	1273.4	1238.1	1239.1	1221.5	1304.7	1298.6	1327.5±14.3

[a]Values reported in Ref. 5.

For the applications reported in this Communication, mostly the evaluation of the additional integrals during the MP2-R12 calculation and (to a smaller extent) the computation of the $\mathcal{V}_{xy}^{\kappa\lambda}$ intermediate (which has to be done in direct mode in the present implementation) are responsible for the prolonged duration of the CCSD(R12) response calculations. In particular, we observed that for any basis set used in this study the CCSD(R12) calculation is always faster than a conventional CCSD calculation using a $(X+1)$Z basis.

VII. CONCLUSION AND OUTLOOK

We reported the first implementation of an explicitly correlated coupled-cluster approach for the calculation of frequency-dependent properties as polarizabilities and hyperpolarizabilities. First applications demonstrate that the improved basis set convergence of the correlation energy obtained with explicitly correlated methods as CCSD(R12) for the ground state transfers to (frequency-dependent) higher-order response properties. With the approximation used for the presented examples, CCSD(R12) with Ansatz 1, we obtained usually in an *n*-aug-cc-pV*X*Z basis $(n=d,t)$ results with an accuracy which with conventional CCSD is first obtained with the *n*-aug-cc-pV$(X+1)$Z or larger basis sets. Problems related to an inappropriate manifold of R12 pair functions for small highly symmetric molecules can be easily rectified by including a few unoccupied orbitals in the construction of the pair functions.

As demonstrated by the results for, e.g., the frequency-dependent second hyperpolarizability of N_2 in Table X and previous results for excitation energies,[16,18] the approach improves systematically not only the static properties but also their frequency dependence including the pole structure. It is an important advantage of CC-R12 response methods compared to basis set extrapolation techniques that they do not rely on a separation into noncorrelated and correlation contributions, which is problematic, e.g., for frequency-dependent properties, if the dispersion contribution becomes large, for electronic excitation energies, or for properties of excited states.

Already in this first implementation of CCSD(R12) response theory the computational efforts to evaluate the R12 contributions (after the primary MP2-R12 calculation) are only a small fraction of the total computational costs and the cost/performance ratio is significantly improved compared to conventional CCSD. However, several approaches to further enhance the efficiency and accuracy of explicitly correlated methods have already been devised and implemented for ground state energies during the last few years, which have not yet been applied in the present implementation, see, e.g., Ref. 6 for a recent review. The costs for the evaluation of the additional integrals can be reduced by using the resolution-of-the-identity or density-fitting technique for two-electron integrals.[11] The basis set convergence can further be improved by switching to the so-called Ansatz 2 of R12 theory, which requires the implementation of a number of additional terms compared to the Ansatz 1 used here, but provides an even more accurate description of electron correlation.[16,39] This is especially true if generalized correlation factors (such as the slater functions used in the F12 methods) instead of the linear-r_{12} correlation factor of the R12 methods are used.[39]

An important issue are also basis sets. As pointed out in Sec. V D, there are indications that with the *n*-aug-cc-pVXZ basis sets the convergence of CCSD(R12) for hyperpolarizabilities might slow down for high angular momenta. It will probably be possible to improve the performance by using AO basis sets optimized, or at least customized, for R12 or F12 calculations. For example, the high angular momentum functions which play a prominent role in current correlation-consistent basis sets are less important for explicitly correlated calculations. More detailed investigations on the requirements for the auxiliary basis used to resolve the identity are also necessary. It should include the AO basis, as it is automatically done in the CABS approach, and in addition augment this basis such that an accurate representation of operators appearing in the three-electron integrals is obtained. Work along the above lines is in progress in our laboratories.

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