Highly accurate CCSD(R12) and CCSD(F12) optical response properties using standard triple-ζ basis sets

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(Received 9 June 2009; accepted 21 July 2009; published online 17 August 2009)

Coupled-cluster response theory for frequency-dependent optical properties within the coupled-cluster singles-and-doubles model (CCSD) has been derived and implemented for ansatz 2 of the explicitly correlated CCSD(R12) and CCSD(F12) methods as part of the program package DALTON. The basis set convergence of static dipole moments, polarizabilities, and parallel averages of first and second hyperpolarizabilities has been investigated for Ne, BH, N_2, CO, and BF. The frequency-dependent results are presented for the electronic second-harmonic generation of N_2. With triple-ζ basis sets, the CCSD(F12) correlation contributions using ansatz 2 are close to the basis set limits for dipole moments and second hyperpolarizabilities; the CCSD(R12) results are better than the CCSD results obtained with at least quintuple-ζ basis sets for polarizabilities and first hyperpolarizabilities. The exponent of Slater-type correlation factor for CCSD(F12) ground state energy may not be optimal and has to be re-examined for response properties. We also suggest that the remaining one-electron basis set errors arising within the coupled-cluster singles should be reduced by allowing excitations into the auxiliary orbital space. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3204388]

I. INTRODUCTION

The reliable and accurate calculations of some ground state optical properties such as dipole moments, polarizabilities, and hyperpolarizabilities are computationally expensive since correlated wave function-based methods [e.g., coupled-cluster (CC)] have to be applied together with very large one-electron basis sets. This is due to the following twofold reasons: The low quality of wave functions obtained with small- or medium-sized basis sets as well as the steep increase in the computational costs which scale with the number of electrons n and basis functions N, for example, as $\mathcal{O}(n^2N^4)$ for CCSD and $\mathcal{O}(n^3N^4)$ for CCSD(T). Improving the basis set from, e.g., aug-cc-pVTZ (which just fulfills the minimum requirements for a correlated calculation of polarizabilities) to aug-cc-pVQZ (which is needed to exploit the accuracy of methods that account for connected triples) increases the computational costs by almost an order of magnitude. With the aug-cc-pV5Z basis the costs increase by another factor of ≈ 7. Therefore it is desirable to develop methods that can either improve the basis set convergence or reduce the cost scaling with n and N while still based on the virtue of systematically improvable wave function models. It has been known for decades that the cusp condition for correlated wave functions is in the coalescent region of two electrons poorly described with Slater determinants built from one-electron basis functions. In the past decades, the so-called explicitly correlated R12 methods, which introduce a correlation factor linearly (R12) or exponentially (F12) depending on the interelectronic distance into the wave function,[1–3] have been systematically established based on the common methods and give the hierarchy of MP2-R12,[3] CC2-R12, CCSD-R12, CCSD(T)-R12,[4–6] and CCSD(R12).[7,8] These variants lead to a significant improvement in the description of the short-range electron correlation and give high accuracies of at least quintuple-ζ quality with only triple-ζ basis sets for ground state correlation energies.[9–11]

Only recently have CC-R12 methods been used also in the framework of CC response theory to calculate higher-order properties (polarizabilities, etc.) and excited states. Fliegl *et al.*[12,13] extended CC2-R12 to compute excitation energies. Neiss *and* Hättig[14] implemented CCSD(R12) in the so-called ansatz 1 for response theory to evaluate polarizabilities and hyperpolarizabilities. The accelerated basis set convergence of these quantities has been observed to be similar to those of ground state correlation energies. We have recently derived and implemented equation-of-motion CCSD(R12) and CCSD(F12) approaches using the more accurate ansatz 2 to compute vertical transition energies for excited states.[15] The calculated CCSD(F12) bond distances and harmonic vibrational frequencies of some singlet excited states of diatomic molecules have demonstrated a much improved basis set convergence better than quintuple-ζ quality with only triple-ζ orbital basis sets.

In the current paper, we continue to report the derivation and implementation of the explicitly correlated contributions for frequency-dependent linear, quadratic, and cubic response functions with CCSD(R12) and CCSD(F12) models for ansatz 2. In the present implementation, which has been developed as a part of the program package DALTON,[16] a property of order n is evaluated as a full nth derivative of the

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time-averaged Lagrangian. In this way, zeroth-order cluster amplitudes and Lagrangian multipliers are sufficient for first-order properties (e.g., dipole moments); second-order properties (e.g., polarizabilities) need additionally the iterative solution of only first-order CC response amplitudes; third-order (e.g., first hyperpolarizabilities) and fourth-order properties (e.g., second hyperpolarizabilities) require additionally first-order Lagrangian multipliers and second-order CC response amplitudes, respectively.

The present paper is organized as follows: The explicitly correlated CCSD(R12) and CCSD(F12) models, their response functions, and the implementation are discussed, respectively, in parts A, B, and C of Sec. II. Computational and technical details are given in part A of Sec. III. The results for dipole moments and (hyper)polarizabilities for Ne, BH, BF, CO, and N_2 are presented and discussed in Sec. III. Finally the paper is concluded in Sec. IV.

II. THEORY AND IMPLEMENTATION

A. CCSD(R12) and CCSD(F12) models

Since the CCSD(R12) and CCSD(F12) methods for ground state energies and excitation energies have been described in detail in a number of references,[7,15,17] we will discuss the models only briefly. The exponential ansatz of conventional CCSD (Ref. 18) is extended by including R12 or F12 double replacements $\hat{T}_{2'}$,

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

For a closed shell reference $|\mathrm{HF}\rangle$, the spin-free cluster operators are

$$\hat{T}_1 = \sum_{ai} t_i^a E_{ai}, \tag{2}$$

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

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

where the operators E_{ai} and $E_{\alpha i}$ give the conventional and R12 single excitations. t_i^a, t_{ij}^{ab}, and c_{ij}^{xy} are singles, doubles, and R12 doubles cluster amplitudes, respectively. Through the paper $\{i,j,k,l,\ldots\}$ denotes a set of occupied orbitals, $\{a,b,c,d,\ldots\}$ virtual orbitals, and $\{\alpha,\beta,\ldots\}$ a complete space complementary to the occupied orbitals in ansatz 2. $\{x,y,\ldots\}$ are those conventional molecular orbitals (MOs) that enter the geminal-orbital overlap integral $w_{\alpha\beta}^{xy}$,

$$\begin{aligned} w_{\alpha\beta}^{xy} &= \langle \phi_\alpha(1)\phi_\beta(2)|\chi_{xy}(1,2)\rangle \\ &= \langle \phi_\alpha(1)\phi_\beta(2)|\hat{w}_{12}|\phi_x(1)\phi_y(2)\rangle. \end{aligned} \tag{5}$$

In principle, $x,y,\ldots$ can be any MOs due to the correlation projector enclosed in $\hat{w}_{12}$. Usually, only occupied MOs are used in Eq. (5) when calculating ground state energies and only a few additional virtual MOs have been included to accurately describe the excited electronic states of small molecules.[13] In Eq. (5), $\hat{w}_{12}$ is defined as the product of a projection operator $\hat{Q}_{12}$ and a correlation factor f_{12} which depends on the interelectronic distance r_{12},

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

The so-called R12 and F12 schemes refer to different definitions of the correlation factor f_{12}, which is just r_{12} in the R12 and $1-e^{-\gamma r_{12}}$ in the F12 methods. For ansatz 2 used in the present study $\hat{Q}_{12}$ is given by

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

where $\hat{O}_i$ and $\hat{V}_i$ project functions for electron i onto, respectively, the occupied and virtual spaces. For a more detailed discussion we refer to Refs. 8 and 19.

Fliegl *et al.*[7] introduced the CCSD(R12) model by keeping only the lowest order in $\hat{T}_{2'}$ but the full similarity transformation with the conventional cluster operator $e^{-\hat{T}_1+\hat{T}_2}\hat{\Phi}e^{\hat{T}_1+\hat{T}_2}$ in the spirit of the CC2 and CC3 models to define an approximate CCSD-R12 model through the following cluster amplitude equations:

$$\Omega_{ai}^{\mathrm{CCSD(R12)}} = \Omega_{ai}^{\mathrm{CCSD}} + \left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \middle| [\tilde{\Phi}, \hat{T}_{2'}] \middle| \mathrm{HF}\right\rangle, \tag{8}$$

$$\begin{aligned} \Omega_{aibj}^{\mathrm{CCSD(R12)}} = \Omega_{aibj}^{\mathrm{CCSD}} + \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [\hat{F}, \hat{T}_{2'}] + [\tilde{\Phi} + [\hat{\Phi}, \hat{T}_2], \hat{T}_{2'}] \right. \\ \left. \times |\mathrm{HF}\rangle, \right. \end{aligned} \tag{9}$$

$$\begin{aligned} \Omega_{xiyj}^{\mathrm{CCSD(R12)}} = \Omega_{xiyj}^{\mathrm{CCSD}} + \left\langle \begin{matrix} \overline{xy} \\ ij \end{matrix} \middle| [\hat{F}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\Phi} + [\tilde{\Phi}, \hat{T}_2] \right. \\ \left. \times |\mathrm{HF}\rangle. \right. \end{aligned} \tag{10}$$

Above, $\hat{F}$ is the Fock operator, $\hat{\Phi}$ is the electron fluctuation potential, and $\tilde{\Phi}$ is defined by a similarity transformation with $\hat{T}_1$,

$$\tilde{\Phi} = e^{-\hat{T}_1}\hat{\Phi}e^{\hat{T}_1}. \tag{11}$$

B. CCSD(R12) and CCSD(F12) response functions

In recent developments of CC response theory the linear,[20] quadratic,[21] and cubic[22] response functions have been derived and implemented for the standard CCSD ansatz as derivatives of a variational quasienergy Lagrangian. Such an analytical response approach has made it possible to derive higher-order response functions in a mathematically simple and transparent[23] manner. In the current paper we follow the same strategy for the CCSD(R12) and CCSD(F12) variants to identify additional explicitly correlated contributions to the linear, quadratic, and cubic response functions when ansatz 2 is applied.

We consider a Hermitian time-dependent one-particle periodic perturbation $\hat{V}(t)$ (e.g., an electric field),

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$$\hat{V}(t) = \sum_X \epsilon_X(\omega_X) e^{-i\omega_X t} \hat{X}, \tag{12}$$

where the sum over X accounts for the components of $\hat{V}(t)$ with the frequency ω_X and collects all monochromatic physical fields $\hat{X}$ that depend on the field strength $\epsilon_X(\omega_X)$ only linearly. We assume that the index X includes also the complex conjugate part $\epsilon_X^\dagger(-\omega_X)e^{i\omega_X t}\hat{X}^\dagger$ of each $\epsilon_X(\omega_X)e^{-i\omega_X t}\hat{X}$ with the conditions $\epsilon_X^\dagger(-\omega_X)=\epsilon_X(\omega_X)$ and $\hat{X}^\dagger=\hat{X}$. With $\hat{V}(t)$, one can define the perturbed Hamiltonian $\hat{H}(t)=\hat{H}_0+\hat{V}(t)$ and the quasienergy

$$Q(t) = \langle \mathrm{HF} | \left(\hat{H}(t) - i\frac{\partial}{\partial t} \right) e^{\hat{T}(t)} | \mathrm{HF} \rangle. \tag{13}$$

The time- and perturbation-dependent cluster equations are obtained by replacing in the time-independent equations $\hat{H}_0$ with $\hat{H}(t)-i(\partial/\partial t)$. The time-dependent CC wave function is parametrized with a time-dependent cluster operator $\hat{T}(t)=\Sigma_\mu t_\mu(t)\hat{\tau}_\mu$ but a time- and perturbation-independent reference state to ensure a corrected pole structure of the response functions. The time-dependent quasienergy Lagrangian has the form

$$\mathcal{L}(t) = Q(t) + \sum_\mu \bar{t}_\mu(t)\Omega_\mu(t), \tag{14}$$

where $\bar{t}_\mu(t)$ are the time-dependent Lagrangian multipliers which are determined by requiring that $\mathcal{L}(t)$ be stationary with respect to variations of the cluster amplitudes $t_\mu(t)$. The construction of Lagrangian in Eq. (14) implies that the oribtal-unrelaxed approach is used in order to avoid the transmission of singularities from the HF reference wave function into the pole structures of the CC response functions. In the present implementation, an nth order property is conveniently calculated as an nth order derivative of the time-averaged quasienergy Lagrangian with respect to field strengths rather than as derivatives of quasienergy in order to employ the $2n+1$ (e.g., cluster amplitude) and $2n+2$ (e.g., Lagrangian multiplier) rules.[23,24] The time average of $\mathcal{L}(t)$ reads

$$\{\mathcal{L}(t)\}_T = \frac{1}{T}\int_{-T/2}^{T/2} \mathcal{L}(t)dt, \tag{15}$$

which eliminates the term $i(\partial/\partial t)$ so that the analogy of time-independent variational CC response theory can be carried over to the time-dependent case straightforwardly. The frequency-dependent response functions are thus obtained as derivatives of the real part of $\{\mathcal{L}(t)\}_T$,

$$\langle\langle X_1; X_2, \ldots, X_n \rangle\rangle_{\omega_2,\ldots,\omega_n} = \left(\frac{d^n \,\mathrm{Re}[\{\mathcal{L}(t)\}_T]}{d\epsilon_{X_1}(\omega_1)\cdots d\epsilon_{X_n}(\omega_n)} \right)_0, \tag{16}$$

with the frequencies subject to the condition $\omega_1=-(\omega_2+\cdots+\omega_n)$. That in Eq. (16) only the real part of $\{\mathcal{L}(t)\}_T$ is taken introduces a symmetrization of the response functions which ensures that the response functions have the correct symmetries with respect to a sign change in the frequencies or complex conjugation. For CC-R12 models $\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle_{\omega_2,\ldots,\omega_n}$ can be decomposed into conventional CC contributions and R12 contributions,

$$\langle\langle X_1;X_2,\ldots,X_n\rangle\rangle_{\omega_2,\cdots,\omega_n} = \langle\langle X_1;X_2,\ldots,X_n\rangle\rangle^{\mathrm{CC}}_{\omega_2,\ldots,\omega_n} + \langle\langle X_1;X_2,\ldots,X_n\rangle\rangle^{\mathrm{R12}}_{\omega_2,\ldots,\omega_n}, \tag{17}$$

where the R12 contributions are defined as the derivatives of the explicitly correlated contributions from $\Omega^{\mathrm{R12}}_{ai}$, $\Omega^{\mathrm{R12}}_{aibj}$, $\Omega^{\mathrm{R12}}_{xiyj}$, and $\langle \mathrm{HF}|[\hat{H},\hat{T}_{2'}]|\mathrm{HF}\rangle$ to the Lagrangian. The expressions of the R12 contributions to first-order properties and linear, quadratic, and cubic response functions are formally similar to those of the conventional CC expressions,

$$\langle\langle X\rangle\rangle^{\mathrm{R12}}_0 = \bar{t}^{(0)}\xi^X(\omega_X), \tag{18}$$

$$\langle\langle X;Y\rangle\rangle^{\mathrm{R12}}_{\omega_Y} = \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{XY}\left\{\tfrac{1}{2}\mathbf{F}t^X(\omega_X)t^Y(\omega_Y) + \eta^X(\omega_X)t^Y(\omega_Y)\right\}, \tag{19}$$

$$\langle\langle X;Y,Z\rangle\rangle^{\mathrm{R12}}_{\omega_Y,\omega_Z} = \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{XYZ}\left\{\tfrac{1}{6}\mathbf{G}t^X(\omega_X)t^Y(\omega_Y)t^Z(\omega_Z) + \tfrac{1}{2}\mathbf{F}^X(\omega_X)t^Y(\omega_Y)t^Z(\omega_Z) + \tfrac{1}{2}\bar{t}^X(\omega_X)\mathbf{B}t^Y(\omega_Y)t^Z(\omega_Z) + \bar{t}^X(\omega_X)\mathbf{A}^Y(\omega_Y)t^Z(\omega_Z)\right\}, \tag{20}$$

$$\langle\langle X;Y,Z,W\rangle\rangle^{\mathrm{R12}}_{\omega_Y,\omega_Z,\omega_W} = \tfrac{1}{2}\hat{C}^{\pm\omega}\hat{P}^{XYZW}\left\{\tfrac{1}{4}\left[\eta^{ZW}(\omega_Z,\omega_W) + \tfrac{1}{2}\mathbf{F}t^{ZW}(\omega_Z,\omega_W)\right]t^{XY}(\omega_X,\omega_Y) + \tfrac{1}{6}\bar{t}^X(\omega_X)\mathbf{C}t^Y(\omega_Y)t^Z(\omega_Z)t^W(\omega_W) + \tfrac{1}{2}\bar{t}^X(\omega_X)\mathbf{B}^Y t^Z(\omega_Z)t^W(\omega_W)\right\}, \tag{21}$$

where t^X and t^{XY} are the first- and second-order response vectors which are defined as the first and second derivatives of the cluster amplitudes with respect to ϵ_X as well as ϵ_X and ϵ_Y, respectively. $\bar{t}^{(0)}$ and $\bar{t}^X$ are the zeroth- and first-order responses of the Lagrangian multipliers. The cubic response function of Eq. (21) needs the intermediate η^{XY},

$$\eta^{XY} = \hat{P}^{XY}\left\{\tfrac{1}{2}\mathbf{G}t^X(\omega_X)t^Y(\omega_Y) + \mathbf{F}^X t^Y(\omega_Y) + \bar{t}^Y(\omega_Y)\mathbf{B}t^X(\omega_X) + \bar{t}^Y(\omega_Y)\mathbf{A}^X\right\}. \tag{22}$$

The operator $\hat{C}^{\pm\omega}$ symmetrizes a function with respect to an inversion of the signs of all frequencies $\{\omega\}$ and simultaneous complex conjugation, i.e., $\hat{C}^{\pm\omega}f(\omega)=f(\omega)+f^*(-\omega)$. The operator $\hat{P}^{AB\cdots}$ generates all permutations of the indices $A,B,\ldots$ of the perturbation operators together with their accompanied frequencies. The perturbation-independent $\mathbf{B}$, $\mathbf{C}$, $\mathbf{F}$, and $\mathbf{G}$ quantities as well as perturbation-dependent counterparts $\mathbf{F}^X$, $\mathbf{A}^X$, $\mathbf{B}^X$, and η^X involve partial derivatives of the Lagrangian to various orders (see Table 1 in Ref. 14 for original definitions). For the explicitly correlated parts to the response functions these quantities have to be defined as derivatives of only the explicitly correlated part of the Lagrangian. An additional difference compared to conventional CC

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contributions is that for the cubic response function the explicitly correlated part of **H** vanishes for the CCSD(R12) and CCSD(F12) models. This is because **H** is a fourth-order partial derivative of the Lagrangian with respect to cluster amplitudes while the explicitly correlated part of the vector function $\Omega_\mu^{R12}(t)$ depends at most to third order on cluster amplitudes. When a higher-order response than cubic is calculated, the R12 part of the **D** matrix, which is the first partial derivative of **H** with respect to the Lagrangian multipliers, also vanishes. In the current work, we have identified η^X, ξ^X, and the Jacobi matrix **A** as basic quantities which we have analytically derived for ansatz 2 of CCSD(R12) and treated others, rather than pursuing their explicit working equations, by means of finite difference based on these.

As seen in the above equations, before the response functions can be completed one needs to evaluate the responses of the cluster amplitudes t^X and t^{XY} and the Lagrangian multipliers $\bar{t}^X$ which are at least one order lower than the corresponding response functions. For example, the quadratic response function needs only the first-order response of cluster amplitudes and multipliers and the cubic response additionally only the second-order response of the cluster amplitudes. The great advantage of the variational Lagrangian scheme is that the number of response equations is significantly reduced. The response equations for the cluster amplitudes $t_\mu^{(n)}$ and Lagrangian multipliers $\bar{t}_\mu^{(n)}$ at any order n are in general of the form

$$-\mathbf{A}t^{(n)}(\omega_1,\ldots,\omega_n)=\xi^{(n)}(\omega_1,\ldots,\omega_n), \tag{23}$$

$$-\bar{t}^{(n)}(\omega_1,\ldots,\omega_n)\mathbf{A}=\bar{\xi}^{(n)}(\omega_1,\ldots,\omega_n), \tag{24}$$

where the Jacobi matrix **A** is defined as

$$A_{\mu\nu}=\left(\frac{\partial\Omega_\mu}{\partial t_\nu}\right)_0. \tag{25}$$

For example, the first- and second-order right hand side vectors for the amplitude response equations are

$$\xi^{(1)}=\xi^X(\omega_X), \tag{26}$$

$$\xi^{(2)}=\hat{P}^{XY}\left\{\tfrac{1}{2}\mathbf{B}t^X(\omega_X)t^Y(\omega_Y)+\mathbf{A}^X t^Y(\omega_Y)\right\}. \tag{27}$$

The zero- and first-order right hand side vectors for the Lagrangian multipliers are

$$\bar{\xi}^{(0)}=\eta^{(0)}, \tag{28}$$

$$\bar{\xi}^{(1)}=\eta^X(\omega_X)+\mathbf{F}t^X(\omega_X), \tag{29}$$

with $\eta^{(0)}$ obtained as the first partial derivative of the unperturbed CCSD(R12) energy with respect to the cluster amplitudes. The R12 contribution to $\eta^{(0)}$ is independent of any amplitude, and therefore the R12 contributions to those intermediates (e.g., **F**) that involve a further partial derivative of $\eta^{(0)}$ with respect to amplitudes vanish.

C. Implementation

1. Jacobi left hand side transformation

The Jacobi transformations from both the right [see Eq. (23)] and left [see Eq. (24)] sides are the most expensive iterative steps in response calculations. The Jacobi right hand side transformation **AR** for CCSD(R12) with ansatz 2 has been derived and discussed in our previous report.[15] In the present paper, we will discuss the Jacobi left hand side transformation,

$$\rho^L=\zeta\mathbf{A}, \tag{30}$$

where ζ is the left eigenvector (e.g., Lagrangian multiplier $\bar{t}^{(n)}$) and **A** the Jacobi matrix defined in Eq. (25). Explicit expressions for the additional R12 contributions to ρ^L that are not present in CCSD(R12) ansatz 1 which has been discussed in Ref. 14 are given in Table I. All equations have been derived based on the complementary auxiliary basis set (CABS) approach[25] and $\{p',q',\ldots\}$ denotes in the following the set of CABS orbitals. Compared to ansatz 1, several extra contributions are found to both singles, conventional doubles, and R12 doubles due to the augmented R12 virtual space in ansatz 2.

The singles contributions of $\rho_{ai}^{C'}$, $\rho_{ai}^{D'}$, $\rho_{ai}^{C'''}$, and $\rho_{ai}^{D'''}$ are the computationally most demanding terms in a CCSD(R12) response calculation since they involve three virtual and one CABS orbital indices and have to be computed in every iteration. In order to reduce the operation counts, the computations of these terms are driven by the $\tilde{P}$- and $\tilde{Q}$-local intermediates (see Table I) that depend on the left trial vector ζ. These local intermediates have to be iteratively recalculated and stored on disk in each linear transformation and read back again when thereafter needed. The most expensive steps to obtain the singles contributions are therefore the computations of the $\tilde{P}$ and $\tilde{Q}$ that scale as O^3V^2N', where O and V denote the number of occupied and virtual orbitals and N' stands for the size of auxiliary basis sets. The remaining singles contributions of $\rho_{ai}^{F'}$, $\rho_{ai}^{B'''}$, $\rho_{ai}^{H'}$, and $\rho_{ai}^{I'}$ are less expensive by at least one order of magnitude, since they can be computed as contractions of the defined global intermediates (see Table I) with the vector ζ or ζ-transformed integrals that involve only one virtual index. These global intermediates are independent of the left vector and constructed at once when the CCSD(R12) cluster amplitudes are converged.

The contributions to the double excitation part ρ_{aibj} of the result vector have been implemented as contractions of the vector ζ or ζ-dependent intermediates with precalculated global intermediates. Among these contractions, the computationally most demanding ones are again the C', D', C''', and D''' contributions, which require a total operation count of $2O^3V^3+2O^3V^2N'$. Although the global intermediates $C'_{bi,ck}$ and $D'_{bi,ck}$ scale as O^3V^2N', they are precalculated once after the cluster amplitude equations have been solved.

Finally the most expensive iterative step for ρ_{xiyj} is the construction of the $\tilde{M}$ local intermediates for $\rho_{xiyj}^{C'}$ and $\rho_{xiyj}^{D'}$ terms (see Table I) with an operation count of $2O^3V^2N'$,

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TABLE I. CCSD(R12) specific contributions to the Jacobi matrix transformations from the left for CCSD(R12)/ansatz 2. These contributions are not present for CCSD(R12)/ansatz 1. We write the transformed result vectors as $\rho_{ai}^{(\mathrm{R12})}=\rho_{ai}^{C'}+\rho_{ai}^{D'}+\rho_{ai}^{E'}+\rho_{ai}^{F'}+\rho_{ai}^{H'}+\rho_{ai}^{I'}+\rho_{ai}^{B'''}+\rho_{ai}^{C'''}+\rho_{ai}^{D'''}+\rho_{ai}^{E'''}$, $\rho_{aibj}^{(\mathrm{R12})}=\rho_{aibj}^{C'}+\rho_{aibj}^{D'}+\rho_{aibj}^{E'}+\rho_{aibj}^{E''}+\rho_{aibj}^{C'''}+\rho_{aibj}^{D'''}+\rho_{aibj}^{E'''}$ (conventional doubles), and $\rho_{xiyj}^{(\mathrm{R12})}=\rho_{xiyj}^{C'}+\rho_{xiyj}^{D'}+\rho_{xiyj}^{E'}+\rho_{xiyj}^{H'}+\rho_{xiyj}^{I'}$ (R12 doubles). In the table, the transformed integrals are $L_{pq}^{rs}=2g_{pq}^{rs}-g_{pq}^{sr}$, $\bar{t}_{kl}^{bp'}=\Sigma_{xy}\zeta_{kl}^{xy}r_{xy}^{bp'}$ and $\bar{t}_{kl}^{bp'}=\Sigma_{xy}c_{kl}^{xy}r_{xy}^{bp'}$, where $g_{pq}^{rs}=\langle\phi_p\phi_q|1/r_{12}|\phi_r\phi_s\rangle$ and $r_{pq}^{rs}=\langle\phi_p\phi_q|f_{12}|\phi_r\phi_s\rangle$.

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

Singles

$$\rho_{ai}^{C'D'}=\tfrac{1}{2}\Sigma_{bkp'}(\tilde{P}'_{bkip'}L_{k\bar{b}}^{p'a}-\tilde{Q}'_{bkip'}g_{k\bar{b}}^{ap'})-\tfrac{1}{2}\Sigma_{mkp'}(\tilde{P}'_{akmp'}L_{ki}^{p'\bar{m}}-\tilde{Q}'_{akmp'}g_{ki}^{\bar{m}p'})$$

$$\rho_{ai}^{C'''D'''}=\Sigma_{bkp'}\tilde{P}'''_{bkip'}g_{kp'}^{ba}-\tfrac{1}{2}\Sigma_{bkp'}(\tilde{P}'''_{bkip'}+\tilde{Q}'''_{bkip'})g_{kp'}^{ab}$$

$$\rho_{ai}^{E'E'''}=\Sigma_{bp'}(\tilde{Y}'_{p'b}L_{bi}^{p'a}+\tilde{Y}'''_{p'b}L_{p'i}^{ba})-\Sigma_{p'}\tilde{Y}'_{p'a}F_i^{p'}$$

$$\rho_{ai}^{F'B'''}=-\Sigma_{klp'}\bar{t}_{kl}^{ap'}\Omega_{p'kli}^{F'B'''}$$

$$\rho_{ai}^{H'I'}=-\Sigma_b\zeta_i^bE'_{ba}+\Sigma_{bj}\zeta_j^bD'_{ai,bj}$$

$$\tilde{P}'_{bkip'}=\Sigma_{lc}(2\bar{t}_{lk}^{cp'}-\bar{t}_{kl}^{cp'})\zeta_{li}^{cb}$$
$$\tilde{Q}'_{bkip'}=\Sigma_{lc}\bar{t}_{kl}^{cp'}(2\zeta_{il}^{cb}+\zeta_{li}^{cb})$$
$$\tilde{P}'''_{bkip'}=\Sigma_{lc}(2t_{lk}^{cb}-t_{kl}^{cb})\bar{t}_{li}^{cp'}$$
$$\tilde{Q}'''_{bkip'}=\Sigma_{lc}t_{kl}^{cb}(2\bar{t}_{il}^{cp'}+\bar{t}_{li}^{cp'})$$
$$\tilde{Y}'_{p'b}=\tfrac{1}{4}\Sigma_k(\tilde{P}'_{bkkp'}+\tilde{Q}'_{bkkp'})$$
$$\tilde{Y}'''_{p'b}=\tfrac{1}{4}\Sigma_k(\tilde{P}'''_{bkkp'}+\tilde{Q}'''_{bkkp'})$$
$$\Omega_{p'kli}^{F'B'''}=g_{ip'}^{kl}+\Sigma_{cd}t_{kl}^{cd}g_{ip'}^{cd}$$

See below for general forms of E'_{ba} and $D'_{ai,bj}$

Conventional doubles

$$\rho_{aibj}^{C'}=-\tfrac{1}{2}\Sigma_{kc}(2\zeta_{kj}^{ac}+\zeta_{jk}^{ac})C'_{bi,ck}$$
$$\rho_{aibj}^{D'}=\tfrac{1}{2}(2-\hat{P}_{ij})\Sigma_{kc}\zeta_{ik}^{ac}D'_{bj,ck}$$
$$\rho_{aibj}^{E'}=-\Sigma_{p'}L_{ij}^{ap'}\Sigma_{klc}\bar{t}_{kl}^{cp'}\zeta_{kl}^{cb}+\Sigma_c\zeta_{ij}^{ac}E'_{cb}$$
$$\rho_{aibj}^{E''}=\Sigma_{xy}\zeta_{ij}^{xy}C_{xy,ab}^{(ij)}$$
$$\rho_{aibj}^{C'''}=-\tfrac{1}{2}\Sigma_{p'm}(2\bar{t}_{mj}^{ap'}+\bar{t}_{jm}^{ap'})C'''_{imp'b}$$
$$\rho_{aibj}^{D'''}=\tfrac{1}{2}(2-\hat{P}_{ij})\Sigma_{p'm}\bar{t}_{im}^{ap'}D'''_{jbp'm}$$
$$\rho_{aibj}^{E'''}=\Sigma_{p'}\bar{t}_{ij}^{ap'}E'''_{p'b}$$

$$C'_{bi,ck}=-\Sigma_{p'l}\bar{t}_{lk}^{cp'}g_{li}^{bp'}$$
$$D'_{bj,ck}=\Sigma_{p'l}(2\bar{t}_{kl}^{cp'}-\bar{t}_{lk}^{cp'})L_{jl}^{bp'}$$
$$E'_{cb}=-\Sigma_{p'lm}\bar{t}_{ml}^{cp'}L_{ml}^{bp'}$$

$$C'''_{imp'b}=g_{ip'}^{\bar{m}b}$$
$$D'''_{jbp'm}=L_{jp'}^{b\bar{m}}$$
$$E'''_{p'b}=\Sigma_m(L_{p'm}^{b\bar{m}}-L_{p'm}^{bm})$$

R12 doubles

$$\rho_{xiyj}^{C'D'}=\tfrac{1}{2}\Sigma_{bp'}r_{xy}^{bp'}\tilde{M}_{bi,j}^{p'}$$
$$\rho_{xiyj}^{E'}=\Sigma_{bp'}r_{xy}^{bp'}\Sigma_a(\zeta_{ij}^{ba}E'_{p'a}+L_{ij}^{p'a}\tilde{Y}_{ab})$$

$$\tilde{M}_{bi,j}^{p'}=-\Sigma_{ak}\{(2\zeta_{ik}^{ab}+\zeta_{ki}^{ab})C'_{akp'j}+(2-\hat{P}_{ij})\zeta_{ki}^{ab}D'_{akp'j}\}$$
$$\tilde{Y}_{ab}=\Sigma_{mnc}t_{mn}^{ca}\zeta_{mn}^{cb}$$
$$E'_{p'a}=\Sigma_k(L_{\bar{a}k}^{p'\bar{k}}-L_{ak}^{p'k})-\Sigma_{dlm}(2t_{lm}^{da}-t_{lm}^{ad})g_{lm}^{dp'}$$

$$\rho_{xiyj}^{H'}=-\Sigma_{kp'}(2g_{ij}^{\bar{k}p'}-g_{ji}^{\bar{k}p'})\Sigma_ar_{xy}^{ap'}\zeta_k^a$$
$$\rho_{xiyj}^{I'}=\Sigma_{ap'}\zeta_i^a(2r_{xy}^{ap'}-r_{yx}^{ap'})\Sigma_{bk}(2g_{kj}^{bp'}-g_{jk}^{bp'})t_k^b$$
$$\rho_{xiyj}^{E'''}=\Sigma_{ab}\zeta_{ij}^{ab}C_{ab,xy}^{(ij)}$$

while the global intermediates $C'_{akp'j}$ and $D'_{akp'j}$ that are available from the solution of ground state cluster equations are converged.

2. ξ^X and η^X intermediates

ξ^X and η^X are important perturbation-dependent intermediates that are used not only to solve the first-order right and left response equations [see Eqs. (26) and (29)] but also to construct the $\mathbf{F}^{\mathbf{X}}$ and $\mathbf{A}^{\mathbf{X}}$ matrices. Explicit expressions for the additional R12 contributions to ξ^X and η^X with ansatz 2 are given in Table II. Formally, the perturbation operator $\hat{X}$ appears in ξ^X and η^X in terms which are similar to contributions of the Fock operator to the ground state cluster equations. However, in difference to those contributions we can for the perturbation operators not apply a Brillouin condition to simplify the expressions. To avoid perturbation-dependent two-electron integrals of the form $\langle\phi_x\phi_y|\hat{w}_{12}^\dagger(\hat{X}_1+\hat{X}_2)\hat{w}_{12}|\phi_v\phi_w\rangle$ we thus use an approximate resolution of the identity in the combined MO and CABS basis:

$$\hat{w}_{12}^\dagger(\hat{X}_1+\hat{X}_2)\approx\hat{w}_{12}^\dagger[(\hat{P}_1+\hat{P}'_1)\hat{X}_1(\hat{P}_1+\hat{P}'_1)\times(\hat{P}_2+\hat{P}'_2)\hat{X}_2(\hat{P}_2+\hat{P}'_2)],\tag{31}$$

where $\hat{P}'_i=\Sigma_{p'}|\phi_{p'}(i)\rangle\langle\phi_{p'}(i)|$ is the projector on the CABS basis of the electron i to resolve the identity

$$1\approx\hat{P}_i+\hat{P}'_i.\tag{32}$$

ξ^X and η^X are calculated in a noniterative approach based on converged zero-order cluster amplitudes and Lagrangian multipliers, driven by the perturbation-dependent intermediates in the current implementation, ${}^XV_{\alpha a}^{xy}$ and ${}^XV_{\alpha q'}^{xy}$, which are defined in Table II. Here α is the index which runs over both one-electron atomic and CABS orbitals. ${}^XV_{\alpha a}^{xy}$ and ${}^XV_{\alpha q'}^{xy}$ are independent of CC cluster amplitudes and can be precalculated and stored, once and for all. The computational costs of ξ^X and η^X are minor since the most expensive terms for ξ_{aibj}^X and η_{aibj}^X scale as only O^4V^2 and are noniterative.

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TABLE II. Complete CCSD(R12) contributions to ξ^X and η^X using ansatz 2. In the table, the overlap matrix element between geminal functions is given as $S^{vw}_{xy}=\langle\phi_x(1)\phi_y(2)|\hat{w}^\dagger_{12}\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle$. $X^s_r=\langle\phi_r|\hat{X}|\phi_s\rangle$ is the property integral over two general orbitals ϕ_r and ϕ_s. The particle permutation operator $\hat{P}^{rs}_{pq}$ is defined as $\hat{P}^{rs}_{pq}\xi^{rs}_{pq}=\xi^{rs}_{pq}+\xi^{sr}_{qp}$. $C_{\kappa q}$ are MO coefficients and $t_{qp}=t^p_q$ if p is a virtual and q an occupied MO and 0 otherwise.

Contributions to $\xi^X_\mu=(\partial^2\mathcal{L}/\partial\epsilon_X(\omega_X)\partial\bar{t}_\mu)_0$

Singles

$\xi^X_{ai}=\Sigma_{jxy}c^{xy}_{ji}\Sigma_\alpha\Lambda^p_{\alpha j}{}^X V^{xy}_{\alpha a}$

Conventional doubles

$\xi^X_{aibj}=\hat{P}^{ab}_{ij}\Sigma_{xy}c^{xy}_{ij}\Sigma_\alpha\Lambda^p_{\alpha a}{}^X V^{xy}_{\alpha b}$

R12 doubles

$\xi^X_{xiyj}=\Sigma_{vw}c^{vw}_{ij}(\tilde{W}^{vw}_{xy}+\bar{W}^{vw}_{xy})-\hat{P}^{xy}_{ij}\Sigma_{vw}S^{vw}_{xy}\Sigma_k c^{vw}_{ik}X^{\tilde{j}}_k$

$\xi'^X_{xiyj}=\hat{P}^{xy}_{ij}\Sigma_{ab}t^{ab}_{ij}\Sigma_\alpha\Lambda^h_{\alpha a}{}^X V^{xy}_{\alpha b}$

Contributions to $\eta^X_\mu=(\partial^2\mathcal{L}/\partial\epsilon_X(\omega_X)\partial t_\mu)_0$

Singles

$\eta^X_{ai}=-\Sigma_{bkl}\bar{t}^{ab}_{kl}\Sigma_{xy}c^{xy}_{kl}\Sigma_\alpha\Lambda^p_{\alpha i}{}^X V^{xy}_{\alpha b}$

$\eta'^X_{ai}=-\Sigma_{xyvw}\Sigma_{kl}\bar{c}^{xy}_{ki}c^{vw}_{kl}S^{vw}_{xy}X^a_l$

$-\Sigma_{klp'}\Sigma_{vw}\bar{c}^{vw}_{kl}r^{ap'}_{vw}\Sigma_{xy}c^{xy}_{kl}\Sigma_\alpha\Lambda^p_{\alpha i}{}^X V^{xy}_{\alpha p'}$,

Conventional doubles

$\eta^X_{aibj}=\hat{P}^{ab}_{ij}\Sigma_{xy}\bar{c}^{xy}_{ij}\Sigma_\alpha\Lambda^h_{\alpha a}{}^X V^{xy}_{\alpha b}$

R12 doubles

$\eta^X_{xiyj}=\hat{P}^{xy}_{ij}\Sigma_a\bar{t}^a_i\Sigma_\alpha\Lambda^p_{\alpha j}{}^X V^{xy}_{\alpha a}$

$\eta'^X_{xiyj}=\hat{P}^{xy}_{ij}\Sigma_{ab}\bar{t}^{ab}_{ij}\Sigma_\alpha\Lambda^p_{\alpha a}{}^X V^{xy}_{\alpha b}$

$\eta''^X_{xiyj}=\Sigma_{vw}[\bar{c}^{vw}_{ij}(\tilde{W}^{xy}_{vw}+\bar{W}^{xy}_{vw})-\hat{P}^{xy}_{ij}S^{xy}_{vw}\Sigma_k\bar{c}^{vw}_{ik}\tilde{X^k_j}]$

Related intermediates

${}^X V^{xy}_{\alpha a}=\Sigma_{p'}X^{p'}_\alpha r^{xy}_{p'a}$

${}^X V^{xy}_{\alpha q'}=\Sigma_b X^b_\alpha r^{xy}_{bq'}+\Sigma_{p'}X^{p'}_\alpha r^{xy}_{p'q'}$

$\tilde{W}^{vw}_{xy}=\hat{P}^{vw}_{xy}\{\Sigma_{p'c}r^{p'cX}_{xy}V^{vw}_{p'c}+\Sigma_{p'q'}r^{p'q'X}_{xy}V^{vw}_{p'q'}\}$

$\bar{W}^{vw}_{xy}=\hat{P}^{vw}_{xy}\Sigma_{cq'}r^{cq'}_{xy}\Sigma_\alpha\Lambda^p_{\alpha c}{}^X V^{vw}_{\alpha q'}$

Transformation matrices

$\Lambda^h_{\kappa p}=\Sigma_q C_{\kappa q}(1+t_{qp})$

$\Lambda^p_{\kappa p}=\Sigma_q C_{\kappa q}(1-t_{pq})$

3. Matrix transformations for higher derivatives of Lagrangian

The remaining quantities needed for the response functions, Eqs. (18)–(21), are the matrices **B**, **C**, **F**, **G**, $\mathbf{F}^X$, $\mathbf{A}^X$, and $\mathbf{B}^X$, which are defined as partial third and fourth derivatives of the Lagrangian with respect to cluster amplitudes and multipliers. These matrix transformations are obtained by using a finite difference scheme based on **A**, ξ^X, and η^X. The computational costs for finite differences can be significantly reduced by noting the following facts. First of all, we realize that the finite difference computations are only involved in noniterative procedures, i.e., the computations of response functions [see Eqs. (18)–(21)] and right hand side vectors $\xi^{(n)}$ and $\eta^{(n)}$ [see Eqs. (26)–(29)] in the response equations [see Eqs. (23) and (24)]. Second, it has been implemented such that we apply the finite difference scheme only to lower-order matrix transformations from which some higher-order matrix transformations are derived as follows:

$$\bar{t}^X(\omega_X)\mathbf{B}t^Y t^Z=\mathbf{F}(\bar{t}^X)t^Y t^Z \quad \text{and} \quad \bar{t}^X(\omega_X)\mathbf{A}^Y t^Z=\eta^Y(\bar{t}^X)t^Z, \tag{33}$$

$$\bar{t}^X(\omega_X)\mathbf{C}t^Y t^Z=\mathbf{G}(\bar{t}^X)t^Y t^Z \quad \text{and} \quad \bar{t}^X(\omega_X)\mathbf{B}^Y t^Z=\mathbf{F}^Y(\bar{t}^X)t^Z. \tag{34}$$

In the above equations, the $\mathbf{G}(\bar{t}^X)t^Y t^Z$ is the most expensive transformation since it cannot be reduced to a first derivative of an available analytical intermediate as all other matrix transformations. As one example for implementing the finite difference, the $\mathbf{F}(\bar{t}^X)t^Y t^Z$ is calculated as

$$\sum_{\mu\nu}F_{\mu\nu}(\bar{t}^X)t^Y_\mu t^Z_\nu=\sum_\mu t^Y_\mu\sigma^{XZ}_\mu, \tag{35}$$

with

$$\sigma^{XZ}_\mu=\sum_\nu\frac{\rho^L_\mu(\bar{t}^X,t_\nu+\delta t^Z_\nu)-\rho^L_\mu(\bar{t}^X,t_\nu-\delta t^Z_\nu)}{2\delta}, \tag{36}$$

where ρ^L_μ is the Jacobi left hand side transformation that has been discussed previously and is calculated analytically. For the calculations reported below we used $\delta=10^{-6}$ a.u. with which, for example, the CCSD polarizabilities and first and second hyperpolarizabilities can be well reproduced at the numerical accuracy of 10^{-5} a.u. compared to the results obtained with analytically derived matrix transformations.

III. APPLICATIONS

A. Computational details

We have applied the above implementation of CCSD(R12) and CCSD(F12) response functions to compute the dipole moments, polarizabilities, and hyperpolarizabilities of Ne as well as BH, N_2, CO, and BF. The bond distances were fixed at 1.232 Å for BH,[26] 1.098 Å for N_2,[27] 1.128 Å for CO,[26] and 1.262 Å for BF.[26] All calculations have been carried out with frozen-core approximations for the 1*s* orbitals at the atoms Ne, B, C, N, O, and F. The

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TABLE III. Total electric dipole moments for BH, BF, and CO molecules at the CCSD as well as CCSD(R12) and CCSD(F12) levels for both ansatz 1 (A1) and ansatz 2 (A2).

	BH					BF					CO				
		CCSD(R12)		CCSD(F12)			CCSD(R12)		CCSD(F12)			CCSD(R12)		CCSD(F12)	
	CCSD	A1	A2	A1	A2	CCSD	A1	A2	A1	A2	CCSD	A1	A2	A1	A2
t-aVTZ	0.555	0.558	0.560	0.558	0.562	0.341	0.339	0.338	0.338	0.335	0.0563	0.0528	0.0513	0.0524	0.0483
t-aVQZ	0.559	0.560	0.561	0.560	0.561	0.336	0.336	0.335	0.335	0.334	0.0504	0.0487	0.0479	0.0485	0.0472
t-aV5Z	0.560					0.335					0.0487				
Approximate ∞	0.561					0.334					0.0471				

standard Dunning n-aug-cc-pVXZ (n-aVXZ in abbreviation) family[28] augmented with a varying number of diffuse functions (n=q for Ne, n=t for other molecules, and n=d for frequency-dependent calculations) has been applied with X=T, Q, and 5 for conventional CCSD. For the Ne atom, a CCSD calculation with the q-aV6Z basis has also been performed. It is necessary to use diffuse functions for the calculations in order to avoid sometimes nonmonotonic or scattered results with respect to the cardinal numbers of the basis sets. Moreover, for small molecules the outer valence space important to dipole moments and (hyper)polarizabilities may be described accurately via the diffuse basis functions and the electronic cusp region is left responsible for the major part of basis set incompleteness errors. The CCSD(R12) and CCSD(F12) calculations have been performed with n-aVTZ and n-aVQZ orbital basis sets for Ne and with the n-aVTZ basis for the molecules. The aV6Z basis has been applied as CABS basis for all calculations in order to make sure that the errors introduced by the CABS approximation are only minor. The exponents of F12 exponential geminal functions are, respectively, 1.6, 1.8, 1.2, 1.3, and 0.9 for Ne, N_2, CO, BF, and BH, which are taken over from our previous work.[15]

All R12 and F12 calculations have employed the CABS+approach by Valeev,[25] which essentially means that the RI is done in the union of the orbital and the auxiliary basis sets. Standard approximation B (Ref. 29) was used throughout for the matrix elements of the geminal functions over the Fock operator. In the present calculations, we have only included occupied orbitals to construct the R12 and F12 geminal functions.

For the comparison the CCSD basis set limits of the static properties were estimated by adding the Hartree–Fock (HF) results for the t-aV5Z basis (but q-aV6Z for Ne atom) to the basis set limits for the correlation contribution which were extrapolated from CCSD/t-aV5Z and CCSD/t-aVQZ results using[30]

$$P_\infty \approx \frac{X^3 P_X - (X-1)^3 P_{X-1}}{X^3 - (X-1)^3}, \tag{37}$$

where X stands for the cardinal number of the basis set n-aVXZ, and P_∞, P_X, and P_{X-1} are the correlation contributions to the properties at the infinite, n-aVXZ, and n-aV($X-1$)Z basis sets, respectively.

As higher-order properties, we have computed the parallel isotropic averages of the first and second hyperpolarizabilities, $\beta_\parallel$ and $\gamma_\parallel$, according to the definitions[31]

$$\beta_\parallel = \frac{1}{5}\sum_\xi (\beta_{z\xi\xi} + \beta_{\xi z\xi} + \beta_{\xi\xi z}), \tag{38}$$

$$\gamma_\parallel = \frac{1}{15}\sum_{\xi\eta} (\gamma_{\xi\xi\eta\eta} + \gamma_{\xi\eta\xi\eta} + \gamma_{\xi\eta\eta\xi}), \tag{39}$$

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

B. Electric dipole moments

We first discuss the performance of the CCSD(R12) and CCSD(F12) methods with ansatz 2 for the total electric dipole moments of the diatomic molecules. For comparison, the standard CCSD and CCSD(R12) and CCSD(F12) results using ansatz 1 are given in Table III. The correlation contributions were calculated as the difference between the CCSD [or CCSD(R12)/CCSD(F12)] and HF results, which are plotted in Fig. 1. The approximate basis set limits were obtained by adding the HF/t-aV5Z results to the CCSD basis set limits for correlation contributions estimated from QZ-5Z extrapolations according to Eq. (37), since the HF dipole moments (not given) have been observed to be converged within 0.0002 a.u. which is sufficient for the present purposes.

The comparison with CCSD reveals that the CCSD(F12) model with ansatz 2 gives with the t-aVTZ basis dipole moments which are better converged than the t-aV5Z results for the conventional CCSD calculation. The absolute deviations from the CCSD basis set limits for correlation contributions

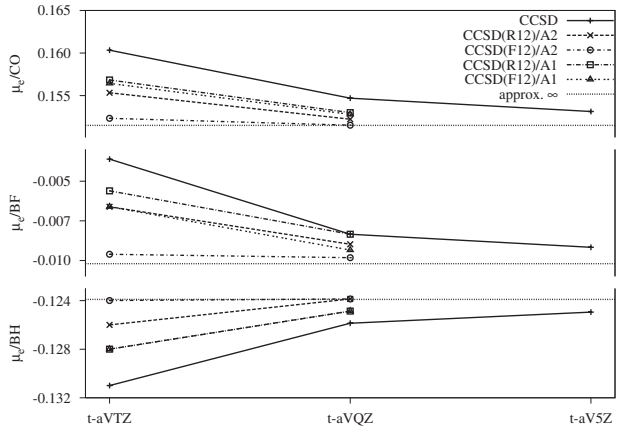


FIG. 1. Basis set convergence of the correlation contributions to total electric dipole moments μ_e for BH (bottom), BF (middle), and CO (top) diatomic molecules (in a.u.) using the t-aVXZ basis sets with triply augmented diffuse functions. A1 and A2 stand for ansatz 1 and ansatz 2, respectively.

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TABLE IV. Static polarizabilities α_{zz} and second hyperpolarizabilities $\gamma_{\|}$ for Ne atom in a.u. at the CCSD as well as CCSD(R12) and CCSD(F12) levels for both ansatz 1 (A1) and ansatz 2 (A2).

	CCSD		CCSD(R12)/A1		CCSD(R12)/A2		CCSD(F12)/A1		CCSD(F12)/A2	
Ne	α_{zz}	$\gamma_{\|}$	α_{zz}	$\gamma_{\|}$	α_{zz}	$\gamma_{\|}$	α_{zz}	$\gamma_{\|}$	α_{zz}	$\gamma_{\|}$
q-aVTZ	2.702	114.5	2.683	111.8	2.669	110.1	2.681	111.7	2.658	109.0
q-aVQZ	2.686	111.2	2.677	110.0	2.670	109.2	2.676	109.8	2.667	108.7
q-aV5Z	2.676	110.2	2.670	109.5			2.669	109.4		
q-aV6Z	2.671	110.0								
Approximate ∞	2.666	109.3								

are only 0.0002, 0.0009, and 0.0008 a.u. for BH, BF, and CO, respectively. With t-aVQZ basis sets the CCSD(F12)/ansatz 2 calculations lead to the results which are very close to the estimated basis set limits and may even surpass their accuracy. The CCSD(R12)/ansatz 2 results perform evidently worse than CCSD(F12) in parallel with the observations for ground state correlation energies. When the less accurate ansatz 1 is applied, both CCSD(R12) and CCSD(F12) models improve the basis set convergence by only one cardinal number compared to conventional CCSD.

C. Ne atom

The Ne atom is considered an instructive yet simple case to study the (hyper)polarizability. The CCSD, CCSD(R12), and CCSD(F12) polarizabilities (α_{zz}) and parallel average of the second hyperpolarizability ($\gamma_{\|}$) are compared in Table IV and Fig. 2. The explicitly correlated calculations in a basis with the cardinal number X provide correlation contributions to both α_{zz} and $\gamma_{\|}$ with accuracies corresponding to standard CCSD calculations with $X+1$ for ansatz 1 and $X+2$ for ansatz 2 in the q-aVXZ hierarchy. For CCSD(R12)/ansatz 2 and CCSD(F12)/ansatz 2 the absolute deviations of α_{zz} with q-aVTZ are only, respectively, 0.004 and 0.007 a.u. from the CCSD basis set limits, while for ansatz 1 the deviations are as large as 0.02 a.u. for both the R12 and the F12 results.

Interestingly, as seen in Fig. 2 for the polarizability, the CCSD(R12) model with ansatz 2 appears to give α_{zz} closer

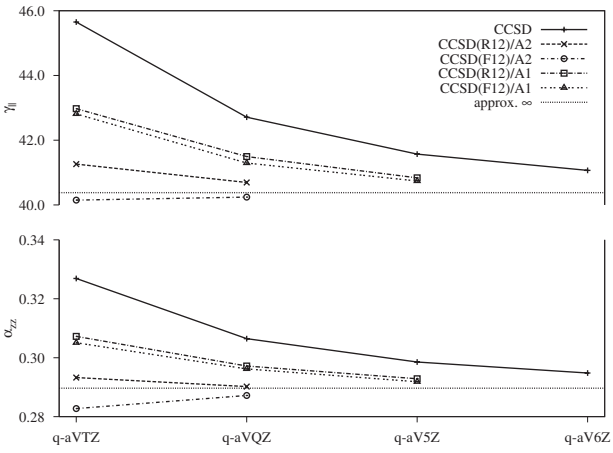


FIG. 2. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and second hyperpolarizabilities $\gamma_{\|}$ for Ne atom (in a.u.) using the q-aVXZ basis sets with quadruply augmented diffuse functions. A1 and A2 stand for ansatz 1 and ansatz 2, respectively.

to the basis set limit than CCSD(F12), which is opposite to the trend observed for ground state correlation energies. But such an effect is not seen for $\gamma_{\|}$ and CCSD(F12)/ansatz 2 in a q-aVTZ set achieves an accuracy which is even better than that of standard CCSD in a q-aV6Z set. There are at least two factors that can possibly bias the CCSD(F12) results. The selected γ exponent in the F12 geminal function customized for ground state correlation energies may be not optimal for polarizabilities and hyperpolarizabilities. In addition, the accuracies of the results might now be limited by the convergence of contributions from the singles excitations, which are treated in the same one-electron basis set as in conventional CCSD calculation.

D. BH molecule: A critical case

The BH molecule has been a critical case for assessing the CCSD(R12) or CCSD(F12) response theory. The lack of occupied orbitals with π symmetry in BH leads to a geminal function that is not suitable to describe $\sigma \rightarrow \pi$ excitations. This limits the accuracy when excitation energies for excited states with π symmetry[12] and the xx component of the static polarizability (α_{xx}) (Ref. 14) are calculated, unless a few pairs of virtual orbitals with π symmetry are included in the construction of the geminal functions. However, this does not necessarily affect the parallel components of the polarizability (α_{zz}) and the first and second hyperpolarizabilities ($\beta_{\|}$ and $\gamma_{\|}$) presented in Table V and Fig. 3. For α_{zz} with t-aVTZ basis CCSD(R12)/ansatz 2 gives an absolute deviation of only 0.0006 a.u. from the basis set limit for the correlation contribution. For $\beta_{\|}$ and $\gamma_{\|}$, the smallest deviations occur for CCSD(F12) results with only about 1% and 6% errors with respect to the basis set limit for the correlation contribution, respectively.

E. BF, CO, and N_2 molecules

We have carried out CCSD(R12) and CCSD(F12) calculations for BF, CO, and N_2 molecules with the triple-ζ basis sets and compared them to the standard CCSD results in the t-aVXZ (X=T, Q, 5) hierarchy. The results for static α_{zz}, α_{xx}, $\beta_{\|}$, and $\gamma_{\|}$ are presented in Table V and Figs. 4–6. With the CCSD(R12)/ansatz 2 model the basis set convergence is rather accelerated for all components of the polarizabilities and first hyperpolarizabilities. For CCSD(R12) the polarizabilities are with t-aVTZ basis converged at least as close to the basis set limit as for conventional CCSD with the t-aV5Z basis. But the CCSD(F12) calculations evidently underesti-

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TABLE V. Static polarizabilities α_{zz} and α_{xx} and first and second hyperpolarizabilities $\beta_\parallel$ and $\gamma_\parallel$ for BH, BF, CO, and N_2 molecules in a.u. at the CCSD as well as CCSD(R12) and CCSD(F12) levels for ansatz 2 (A2).

	CCSD				CCSD(R12)/A2				CCSD(F12)/A2			
BH	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$
t-aVTZ	23.005	20.995	64.657	10763.9	22.877	20.912	63.162	10614.7	22.814	20.867	62.141	10530.5
t-aVQZ	22.903	21.011	63.388	10642.2	22.846	20.980	62.629	10572.5	22.828	20.964	62.349	10547.5
t-aV5Z	22.868	21.015	62.905	10593.1								
Approximate ∞	22.838	21.016	62.314	10539.8								
	CCSD				CCSD(R12)/A2				CCSD(F12)/A2			
BF	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$
t-aVTZ	18.146	20.050	53.529	6246.3	17.993	19.963	52.665	6156.2	17.933	19.926	51.830	6086.9
t-aVQZ	18.039	20.025	52.406	6172.2								
t-aV5Z	18.002	20.014	52.130	6144.7								
Approximate ∞	17.966	20.003	51.826	6111.3								
	CCSD				CCSD(R12)/A2				CCSD(F12)/A2			
CO	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$	α_{zz}	α_{xx}	$\beta_\parallel$	$\gamma_\parallel$
t-aVTZ	15.712	11.880	25.255	1410.2	15.582	11.800	25.067	1375.5	15.532	11.762	24.808	1357.2
t-aVQZ	15.636	11.840	25.035	1381.6								
t-aV5Z	15.606	11.824	24.978	1370.2								
Approximate ∞	15.577	11.807	24.899	1359.3								
	CCSD				CCSD(R12)/A2				CCSD(F12)/A2			
N_2	α_{zz}	α_{xx}	$\gamma_\parallel$		α_{zz}	α_{xx}	$\gamma_\parallel$		α_{zz}	α_{xx}	$\gamma_\parallel$	
t-aVTZ	14.676	10.187	907.7		14.574	10.114	883.0		14.538	10.079	872.4	
t-aVQZ	14.629	10.153	890.8									
t-aV5Z	14.605	10.137	883.3									
Approximate ∞	14.584	10.123	874.2									

mate α_{zz}, α_{xx}, and $\beta_\parallel$ compared to the CCSD(R12) results, which is similar to the above observation for the Ne atom. Comparing BF to BH, we have found that CCSD(R12) indeed accelerates the basis set convergence of α_{xx}. For BF the occupied orbitals with π symmetry are automatically included in the construction of the geminal functions, which provides the required degrees of freedom for the correlation contribution.

The obtained static second hyperpolarizabilities $\gamma_\parallel$ confirm the strength of CCSD(R12) and CCSD(F12) with ansatz 2: Already the calculations in a triple-ζ basis set give results that are rather close to the basis set limits.

F. Frequency-dependent $\gamma_\parallel$ of N_2

As example for frequency-dependent higher-order properties we computed the parallel average of the second hyper-

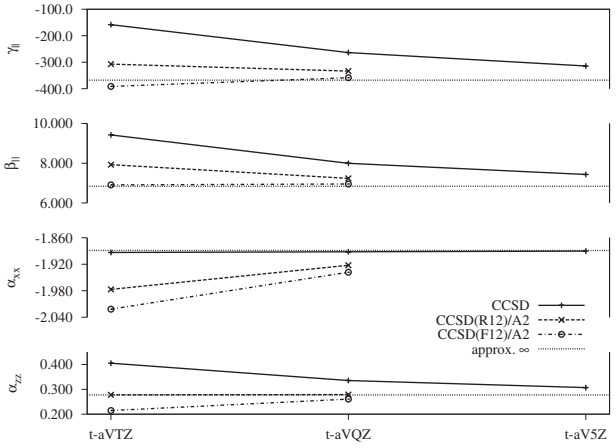


FIG. 3. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and α_{xx} and first and second hyperpolarizabilities $\beta_\parallel$ and $\gamma_\parallel$ for BH (in a.u.) using the t-aV*X*Z basis sets with triply augmented diffuse functions. A2 stands for ansatz 2.

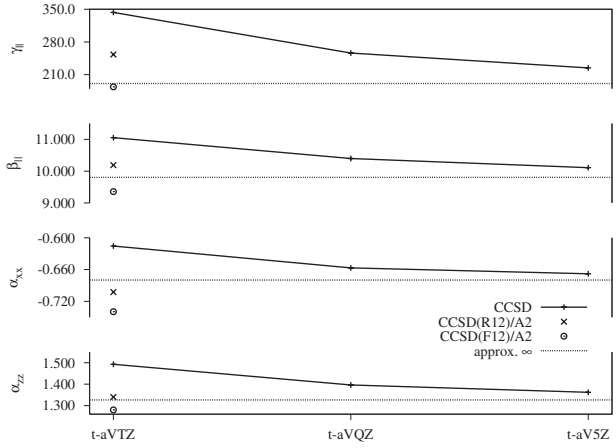


FIG. 4. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and α_{xx} and first and second hyperpolarizabilities $\beta_\parallel$ and $\gamma_\parallel$ for BF (in a.u.) using the t-aV*X*Z basis sets with triply augmented diffuse functions. A2 stands for ansatz 2.

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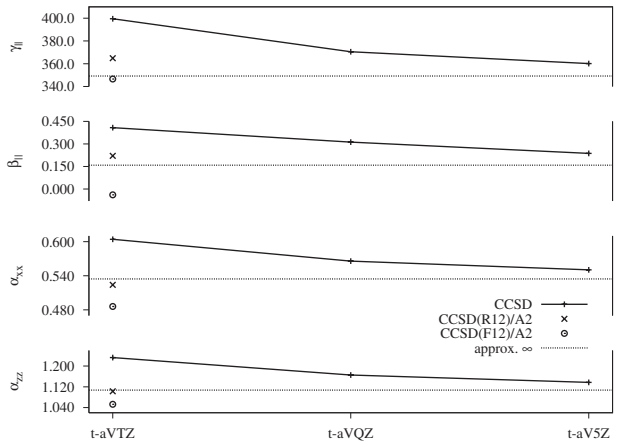


FIG. 5. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and α_{xx} and first and second hyperpolarizabilities $\beta_\parallel$ and $\gamma_\parallel$ for CO (in a.u.) using the t-aV*XZ* basis sets with triply augmented diffuse functions. A2 stands for ansatz 2.

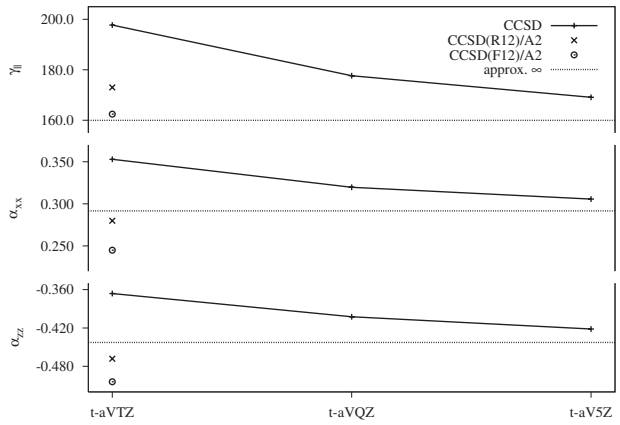


FIG. 6. Basis set convergence of the electronic correlation contributions to static polarizabilities α_{zz} and α_{xx} and second hyperpolarizabilities $\gamma_\parallel$ for N_2 atom (in a.u.) using the t-aV*XZ* basis sets with triply augmented diffuse functions. A2 stands for ansatz 2.

polarizability for N_2. The computed CCSD, CCSD(R12), and CCSD(F12) electronic second-harmonic generations (ESHGs) $\gamma_\parallel^{\mathrm{ESHG}}(\omega)$ are given in Table VI for various frequencies. The basis set limit at frequency ω has been estimated by a multiplicative scheme:

$$\gamma_\parallel^{\infty}(\omega) \approx \gamma_\parallel^{5Z}(\omega)\left(\frac{\gamma_\parallel^{\infty}(0)}{\gamma_\parallel^{5Z}(0)}\right), \tag{40}$$

where the $\gamma_\parallel^{\infty}(0)$ is obtained by applying the extrapolation scheme described in Sec. III A. This estimation is based on the observation that the scaling factor for $\gamma_\parallel(0)$ with d-aV*XZ* and d-aV*YZ* basis sets can be approximately transferred to $\gamma_\parallel(\omega)$. We note that with such a simple correction the basis set errors of CCSD calculations can be estimated more accurately for the low frequencies than for the higher ones.

The calculated ESHG results indicate that both CCSD(R12) and CCSD(F12) models using ansatz 2 tremendously improve the basis set convergence of the dispersion, which are better than the CCSD/d-aV5Z values. The deviations compared to the basis set limits are less than 10 a.u. (i.e., less than 1%). The largest deviation occurs for the shortest wavelength example probably mainly because of a larger numerical uncertainty of $\gamma_\parallel^{\infty}(\omega)$ estimated according to Eq. (40) for short wavelengths. Moreover, the CCSD(F12) results show a slightly larger deviation than the CCSD(R12) ones, which implies again that the exponent in the Slater-type correlation factor customized for the ground state correlation energy may not be optimal for the calculation of polarizabilities and hyperpolarizabilities.

IV. CONCLUSIONS

In this paper, the explicitly correlated methods CCSD(R12) and CCSD(F12) with ansatz 2 have been generalized and implemented for calculating one-electron first-, second-, third-, and fourth-order optical response properties, and the implementations of response functions, left hand side Jacobi matrix transformations, and perturbation-dependent intermediate matrices have in the program package DALTON been discussed. The most expensive steps occur for the C', D', C''', and D''' contributions with operation counts of a few times $O^3V^2(N'+V)$.

As corroborated with what has been observed for ground state correlation energies, the CCSD(F12) method with ansatz 2 obtains correlation contributions to dipole moments and second hyperpolarizabilities in a triple-ζ basis with an accuracy which with conventional CCSD is first obtained in a quintuple-ζ or larger basis set. The CCSD(R12) method with ansatz 2 gives also correlation contributions to polarizabilities in triple-ζ basis sets with quintuple-ζ quality, while CCSD(F12)/ansatz 2 has slightly larger errors due to an underestimation of the polarization. Considering the correlation contributions to $\beta_\parallel$, the CCSD(R12) and CCSD(F12) models demonstrate variant relative performances that are intermediate between those for computing α and $\gamma_\parallel$, i.e., the CCSD(R12) results for $\beta_\parallel$ are for CO better than, for BF competitive with, and for BH less accurate than the CCSD(F12) results. Possible remedies for CCSD(F12) may be that the exponent of the Slater-type correlation factor obtained for CCSD(F12) ground state calculations needs a

TABLE VI. The dynamic ESHG second hyperpolarizabilities $\gamma_\parallel^{\mathrm{ESHG}}(\omega)$ for N_2 in a.u. at the CCSD as well as CCSD(R12) and CCSD(F12) levels for ansatz 2 (A2).

Frequencies		CCSD				CCSD(R12)/A2	CCSD(F12)/A2
λ (nm)	ω (a.u.)	d-aVTZ	d-aVQZ	d-aV5Z	Estimate ∞	d-aVTZ	d-aVTZ
1055.0	0.043 188	956.5	943.4	937.2	926.7	929.2	918.2
694.3	0.065 625	1038.8	1023.0	1015.8	1004.3	1007.9	995.6
457.9	0.099 505	1272.3	1248.1	1237.8	1223.8	1230.6	1214.0

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more careful re-examination for response properties and the contributions from the CC singles should be improved by allowing excitations into the CABS space to reduce the remaining one-electron basis set error. However, already without these possible improvements CCSD(F12)/ansatz 2 gives overall first-order properties and polarizabilities and hyperpolarizabilities in triple-ζ basis sets with accuracies which are difficult to reach in conventional CCSD.

ACKNOWLEDGMENTS

This work has been supported by the DFG priority program SPP1145 "Modern and universal first-principles methods for many-electron systems in chemistry and physics."

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