Structures and harmonic vibrational frequencies for excited states of diatomic molecules with CCSD(R12) and CCSD(F12) models

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The equation-of-motion coupled-cluster method for excited states with the singles-and-doubles model (CCSD) has been implemented for ansatz 2 of the explicitly correlated CCSD(R12) and CCSD(F12) methods as part of the program package Dalton. In this model, an orthonormal complementary auxiliary basis set is used for the resolution-of-identity approximation in order to calculate the three-electron integrals needed for CCSD(R12) and CCSD(F12). The additional CCSD(R12) or CCSD(F12) terms introduced within ansatz 2, which are not present in ansatz 1, are derived and discussed with regard to the extra costs needed for their computation. As a first application the basis set convergence of equilibrium bond lengths and harmonic vibrational frequencies has been investigated for some singlet excited states of the diatomic molecules N_2, CO, BF, and BH. The calculated CCSD(F12) results show that the average absolute deviations of the bond lengths and frequencies from the basis set limits are below 0.1 pm and 5 cm^{-1} as well as 0.05 pm and 1 cm^{-1} for the triple- and quadruple-ζ basis sets, respectively. These deviations are shown to largely arise from the SCF basis set incompleteness errors. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3093947]

I. INTRODUCTION

It has been long-standing that correlated wave function based quantum chemical calculations suffer from the slow convergence of the correlation energy with the basis set. This is particularly well known to conventional wave function methods such as configuration interaction (CI), *n*th-order Møller–Plesset perturbation theory (MP*n*), and coupled-cluster (CC) theory. It has been recognized that this problem is due to the deficient representation of the cusp condition in the coalescent region of the electronic wave function when Slater determinants are built on one-electron basis functions. In the past decades, many efforts have been made to include a correlation factor depending on the interelectronic distance into the wave function[1–3] to improve the description of the short-range electron correlation. In particular the explicitly correlated so-called R12 approach has been systematically established for several standard wave function methods and leads, e.g., to the hierarchy of MP2-R12,[3] CCSD-R12, and CCSD(T)-R12 (Refs. 4–6) for accurate ground state correlation energies close to the basis set limit.[7–9] Recently, CCSD(R12) models with less computational costs were introduced[10,11] by treating the R12 cluster projection in analogy to the CC2 model.[12] The CCSD(R12) ground state correlation energies obtained with quadruple-ζ and triple-ζ basis sets have been shown to be superior to standard CCSD results computed using quintuple-ζ basis sets.[11] Very recently CCSD(T)-F12a and CCSD(T)-F12b approaches employing local orbitals and the diagonal fixed amplitude ansatz,[13] which excludes all off-diagonal R12/F12 amplitudes and parametrizes the diagonal R12/F12 amplitudes due to the cusp conditions,[14,15] have been developed by Adler *et al.*[16] The correlation contributions to relative energies (e.g., reaction energy, binding energy, interaction energy, etc.) given by CCSD(T)-F12a and CCSD(T)-F12b also demonstrate the same basis set convergence as the CCSD(T)(F12) model but with two orders of magnitude faster than standard CCSD(T) quintuple-ζ calculations.[16,17] This method is orbital invariant, size consistent, and free of geminal basis set superposition errors.[18,19] Last but not least, noniterative perturbative explicitly correlated $CCSD(2)_{\overline{R12}}$ and $CCSD(T)_{\overline{R12}}$ approaches which assume the extended Brillouin theorem for ansatz 2 to remove the coupling term between conventional doubles and R12 geminal functions in the zeroth-order Hamiltonian have been introduced by Valeev.[20,21] This perturbative method follows the formalism from Stanton and Gauss[22] which explores the perturbation expansion of the similarity-transformed Hamiltonian by Lödwin partitioning. $CCSD(2)_{\overline{R12}}$ and $CCSD(T)_{\overline{R12}}$ give the geminal correction to correlation energies requires only MP2-R12 and conventional CCSD(2) or CCSD(T) computations. The other interesting direction of explicitly correlated methods leads to the automated generation of full CCSD-R12 implementation using tensor contractions by Shiozaki *et al.*,[23,24] which serves as benchmarks for rigorous assessment of CCSD(R12) and $CCSD(2)_{\overline{R12}}$ approximations.

In the regard to the correlation factors, it has been further shown that nonlinear correlation factors[13,25] such as $e^{-\gamma r_{12}}$ or $r_{12}e^{-\gamma r_{12}}$ (i.e., F12 methods) are even more efficient alternatives to the original linear-r_{12} ansatz (i.e., R12 methods). The formal R12 or F12 double excitations occur only in the virtual space outside the finite basis sets in ansatz 1,[26]

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while in ansatz 2 (Ref. 27) the excitation space is also augmented by mixed replacements both inside and outside the orbital basis set. The strong orthogonality condition leads to explicitly correlated geminal functions orthogonal to the space spanned by the conventional double excitations. The explicit implementation of the additional required three-electron integrals, often encountered in the explicitly correlated methods, is avoided by inserting the resolution of the identity (RI) based on the complementary auxiliary basis set (CABS) approximation.[27] Other approximations involved in explicitly correlated methods are the so-called standard approximations to evaluate the commutators with the Fock operator.[28]

Beyond the ground state, excited states have been treated in the spirit of R12 corrections at the CC level. Fliegl *et al.*[29,30] extended CC2-R12 to compute excitation energies. Neiss and Hättig[31] implemented the CCSD(R12) response theory to evaluate polarizabilities and hyperpolarizabilities as yet in ansatz 1 only. The accelerated basis set convergence of these (hyper)polarizabilities and total energies of excited states have been observed to be similar to those of ground state total energies. By noting the fact that in the finite basis set ansatz 1 is less accurate than ansatz 2 due to a more restrictive explicitly correlated excitation space, it is desirable to incorporate ansatz 2 for excited states to the CCSD(R12) or CCSD(F12) method. Therefore in Sec. II of the present work, we derived and implemented the CC Jacobi matrix for CCSD(R12) and CCSD(F12) with ansatz 2 and report an implementation in the program package DALTON.[32]

Apart from extensive basis set convergence studies for correlation energies, a number of reports have appeared recently which focused on ground state molecular geometries and vibrational freqencies,[33–36] going through hierarchies of both one-electron basis sets and wave function correlation levels. Such studies are important since there is no guarantee that for molecular properties an identical convergence behavior will be observed as for energies.[36] However, nothing is yet known to the corresponding performance for excited states. Therefore we applied in the current report the new implementation to obtain equilibrium bond lengths and harmonic frequencies for a set of singlet excited states in N_2, CO, BF, and BH to assess the performance of CCSD(R12) and CCSD(F12) for excited state calculations.

II. THEORY AND IMPLEMENTATION

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

As usual in conventional CCSD,[37] the explicitly correlated CCSD-R12 or CCSD-F12 wave function is defined as

$$|\mathrm{CC}\rangle = e^{\hat{T}}|\mathrm{HF}\rangle, \tag{1}$$

where the reference state is the Hartree–Fock (HF) wave function and the cluster operator contains conventional single ($\hat{T}_1$), double ($\hat{T}_2$) and R12 or F12 double ($\hat{T}_{2'}$) replacements,

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

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

$$\hat{T}_1 = \sum_{ai} t_i^a E_{ai}, \tag{3}$$

$$\hat{T}_2 = \frac{1}{2}\sum_{aibj} t_{ij}^{ab} E_{ai}E_{bj}, \tag{4}$$

$$\hat{T}_{2'} = \frac{1}{2}\sum_{xiyj} c_{ij}^{xy} \sum_{\alpha\beta} w_{\alpha\beta}^{xy} E_{\alpha i}E_{\beta j}, \tag{5}$$

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 the singles, doubles, and R12 doubles cluster amplitudes, respectively. Throughout 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. With $\{x,y,\ldots\}$ we denote those molecular orbitals (MOs) that enter the R12 geminal functions,

$$\chi_{xy}(1,2) = \hat{w}_{12}\phi_x(1)\phi_y(2). \tag{6}$$

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. (6) 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.[30] In Eq. (6), $\hat{w}_{12}$ 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},

$$\hat{w}_{12} = \hat{Q}_{12} f_{12}. \tag{7}$$

The geminal function (6) can be expanded as a linear combination of orbital products in the complementary orbital space,

$$\chi_{xy}(1,2) = \sum_{\alpha\beta} w_{\alpha\beta}^{xy}\phi_\alpha(1)\phi_\beta(2), \tag{8}$$

with the geminal-orbital overlap $w_{\alpha\beta}^{xy}$ integrals,

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

The so-called R12 and F12 schemes refer to different correlation factors f_{12} in Eqs. (10) and (11), respectively,

$$f_{12} = r_{12}, \tag{10}$$

$$f_{12} = 1 - e^{-\gamma r_{12}}. \tag{11}$$

For ansatz 2, which is employed in the present study, $\hat{Q}_{12}$ is given by

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

where $\hat{O}_i$ and $\hat{V}_i$ project functions for electron i onto, respectively, the occupied and virtual spaces. In the basis set limit, $\hat{Q}_{12}$ becomes zero and the R12 contributions to cluster am-

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plitude equations disappear. The F12 correlation factor is represented in our implementation in the DALTON program[32] as a linear combination of six Gaussian functions. The only change needed to switch from the R12 to the F12 approach is a displacement of the correlation factor r_{12} by $1-e^{-\gamma r_{12}}$ in the integrals which involve geminal functions (6). Most of these integrals can be precalculated, once and for all, before the CC iterations and stored on file. For a more detailed discussion of the implementation we refer to Refs. 11 and 38.

The singles, doubles, and R12 doubles projection manifolds can be spanned by

$$\left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| = \frac{1}{2}\langle \mathrm{HF}|E_{ai}^{\dagger}, \tag{13}$$

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \right| = \frac{1}{6}\langle \mathrm{HF}|(2E_{ai}^{\dagger}E_{bj}^{\dagger}+E_{aj}^{\dagger}E_{bi}^{\dagger}), \tag{14}$$

$$\left\langle \begin{matrix} \overline{xy} \\ ij \end{matrix} \right| = \frac{1}{6}\sum_{\alpha\beta}(w^{\dagger})_{xy}^{\alpha\beta}\langle \mathrm{HF}|(2E_{\alpha i}^{\dagger}E_{\beta j}^{\dagger}+E_{\alpha j}^{\dagger}E_{\beta i}^{\dagger}) = \sum_{\alpha\beta}(w^{\dagger})_{xy}^{\alpha\beta}\left\langle \begin{matrix} \overline{\alpha\beta} \\ ij \end{matrix} \right|, \tag{15}$$

where $\left\langle \begin{matrix} \overline{\alpha\beta} \\ ij \end{matrix} \right|$ is defined analogously to Eq. (14).

Let us turn to the additional R12 contributions to the CCSD cluster amplitude equations, which yield the CCSD-R12 model:

$$\Omega_{ai}^{(\mathrm{R12})} = \left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| [\tilde{\Phi},\hat{T}_{2'}]|\mathrm{HF}\rangle, \tag{16}$$

$$\Omega_{aibj}^{(\mathrm{R12})} = \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \right| [\hat{F},\hat{T}_{2'}]+\hat{\Phi}^{T}|\mathrm{HF}\rangle, \tag{17}$$

$$\Omega_{xiyj}^{(\mathrm{R12})} = \left\langle \begin{matrix} \overline{xy} \\ ij \end{matrix} \right| [\hat{F},\hat{T}_{2}+\hat{T}_{2'}]+\hat{\Phi}^{T}|\mathrm{HF}\rangle. \tag{18}$$

In the above, $\hat{F}$ is the Fock operator, $\hat{\Phi}$ the electron fluctuation potential, and $\tilde{\Phi}$ and $\hat{\Phi}^{T}$ are defined as similarity transformations with $\hat{T}_1$ and $\hat{T}$,

$$\tilde{\Phi} = e^{-\hat{T}_1}\hat{\Phi}e^{\hat{T}_1}, \tag{19}$$

$$\hat{\Phi}^{T} = e^{-\hat{T}}\hat{\Phi}e^{\hat{T}}. \tag{20}$$

Fliegl *et al.*[10] introduced the CCSD(R12) model by keeping only the lowest order in $\hat{T}_2'$ and $\hat{\Phi}^{\hat{T}}$ in a way similar to the CC2 doubles amplitudes, which yields

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

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

The R12 contributions to the singles equations are kept in the original form of Eq. (16), although the similarity transformation with $\hat{T}_1$ in $\tilde{\Phi}$ in Eqs. (21) and (22) are not important for ground state wave functions and correlation energies since the singles are not directly coupled with the HF reference determinant $|\mathrm{HF}\rangle$ due to Brillouin theorem. They are, however, kept to obtain with CCSD(R12) and CCSD(F12) coupled-cluster models which can be used in the framework of CC response theory to calculate excitation energies and higher-order properties for which the singles play a crucial role.

B. CCSD(R12) and CCSD(F12) Jacobi transformations

The coupled-cluster response theory or equation-of-motion coupled-cluster (EOM-CC) method has become a commonly used approach for excited states.[39–42] The development of EOM-CC also includes the combination of cluster and perturbation expansions.[43–47] In the present work, we extend EOM-CCSD due to R12 and F12 corrections for ansatz 2.

The EOM-CC excitation energies are obtained as eigenvalues ω of the Jacobi matrix

$$\mathbf{AR} = \omega\mathbf{SR}, \tag{23}$$

where $\mathbf{R}$ is the eigenvector. The elements of the Jacobi matrix $\mathbf{A}$ and the overlap matrix $\mathbf{S}$ are defined as

$$A_{\mu_i\nu_j} = \frac{\partial\Omega_{\mu_i}}{\partial t_{\nu_j}}, \tag{24}$$

$$S_{\mu_i\nu_j} = \langle\mu_i|\hat{\tau}_{\nu_j}|\mathrm{HF}\rangle, \tag{25}$$

where t_{ν_j} is the cluster amplitude and $\hat{\tau}_{\nu_j}$ denotes the corresponding excitation operator. Due to the use of the biorthogonal basis for the singles and conventional doubles space $\mathbf{S}$ has the following structure

$$\mathbf{S} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & S_{\mu_{2'}\nu_{2'}} \end{pmatrix}, \tag{26}$$

where only the block $S_{\mu_{2'}\nu_{2'}}$ is not a unit matrix since it occurs between two R12 projection manifolds which involve the nontrivial correlation factor $\hat{w}_{12}$. The elements of $S_{\mu_{2'}\nu_{2'}}$ can be expressed as

$$S_{xyij,x'y'i'j'} = \hat{P}_{ij}^{xy}\delta_{ii'}\delta_{jj'}X_{xy,x'y'}, \tag{27}$$

where

$$X_{xy,x'y'} = \langle\phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\hat{w}_{12}|\phi_{x'}(1)\phi_{y'}(2)\rangle, \tag{28}$$

with the particle permutation operator $\hat{P}_{ij}^{xy}$ defined as

$$\hat{P}_{ij}^{xy}\Omega_{ij}^{xy} = \Omega_{ij}^{xy}+\Omega_{ji}^{yx}. \tag{29}$$

Concerning the solution of the eigenvalue problem, Eq. (23), we note that the direct diagonalization of the Jacobi matrix $\mathbf{A}$ is not possible because of the tremendously huge dimensions of $\mathbf{A}$. Instead an iterative modified Davidson scheme is used which requires the implementation of the direct right contractions $\mathbf{AR}$ and $\mathbf{SR}$. The explicitly correlated contributions to the result of $\mathbf{AR}$ are for CCSD(R12) and CCSD(F12) with ansatz 2:

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TABLE I. R12 specific contributions to the Jacobi matrix transformations for CCSD(R12)/ansatz 2. These contributions are not present for CCSD(R12)/ansatz 1. We write the transformed result vectors as $\rho^{(\mathrm{R12})}_{aibj} = \rho^{C'}_{aibj} + \rho^{D'}_{aibj} + \rho^{E'}_{aibj}$ (doubles) and $\rho^{(\mathrm{R12})}_{xiyj} = \rho^{B'''}_{xiyj} + \rho^{C'''}_{xiyj} + \rho^{D'''}_{xiyj} + \rho^{E'''}_{xiyj} + \rho^{F'}_{xiyj}$ (R12 doubles). In the table, $\tilde{R}^{rs}_{pq} = 2R^{rs}_{pq} - R^{sr}_{pq}$, $\bar{r}^{rs}_{pq} = 2r'^{rs}_{pq} - r^{sr}_{pq}$, $L^{rs}_{pq} = 2g^{rs}_{pq} - g^{sr}_{pq}$, $\bar{\bar{r}}^{p'b}_{jk} = \Sigma_{xy} R^{xy}_{jk} r^{p'b}_{xy}$, and $\bar{\bar{r}}^{p'b}_{jk} = \Sigma_{xy} c^{xy}_{jk} r^{p'b}_{xy}$, where g^{rs}_{pq} and r^{rs}_{pq} are defined, respectively, in Eqs. (48) and (47). In this table, p' denotes the orthogonal auxiliary orbitals.

Right hand side Jacobi matrix transformations $\rho_\mu = \Sigma_\nu A_{\mu\nu} R_\nu$	
$\rho^{C'}_{aibj} = -\left(\frac{1}{2} + \hat{P}_{ij}\right)\left[\Sigma_{p'k} \bar{\bar{r}}^{p'b}_{jk} C'_{p'kai} + \Sigma_{p'k} \bar{\bar{r}}^{p'b}_{jk} \tilde{C}'_{p'kai}\right]$	$C'_{p'kai} = g^{\bar{i}p'}_{k\bar{a}} - \Sigma_{dl} t^{ad}_{li} g^{p'd}_{lk}$
	$\tilde{C}'_{p'kai} = (g^{\bar{i}p'}_{k\bar{a}} + g^{\bar{i}p'}_{k\bar{a}}) - \Sigma_{dl} R^{ad}_{li} g^{p'd}_{lk}$
$\rho^{D'}_{aibj} = \frac{1}{2}\Sigma_{p'k}(2\bar{\bar{r}}^{bp'}_{jk} - \bar{\bar{r}}^{p'b}_{jk}) D'_{p'kai} + \frac{1}{2}\Sigma_{p'k}(2\bar{\bar{r}}^{bp'}_{jk} - \bar{\bar{r}}^{p'b}_{jk}) \tilde{D}'_{p'kai}$	$D'_{p'kai} = L^{p'\bar{i}}_{k\bar{a}} + \Sigma_{dl} \tilde{t}^{ad}_{il} L^{p'd}_{kl}$
	$\tilde{D}'_{p'kai} = (L^{p'\bar{i}}_{k\bar{a}} + L^{p'\bar{i}}_{k\bar{a}}) + \Sigma_{dl} \tilde{R}^{ad}_{il} L^{p'd}_{kl}$
$\rho^{E'}_{aibj} = \Sigma_{p'} \bar{\bar{r}}^{bp'}_{ij} E'^{1}_{p'a} + \Sigma_{p'} \bar{\bar{r}}^{bp'}_{ij} \tilde{E}'^{1}_{p'a} + \Sigma_c R^{bc}_{ij} E'^{1}_{ac} + \Sigma_c t^{bc}_{ij} \tilde{E}'^{1}_{ac}$	$E'^{1}_{p'a} = \Sigma_k (L^{p'\bar{k}}_{\bar{a}k} - L^{p'k}_{ak}) - \Sigma_{dlm} \tilde{t}^{la}_{lm} g^{dp'}_{lm}$
	$E'^{1}_{ac} = -\Sigma_{p'lm} \bar{\bar{t}}^{p'a}_{lm} L^{p'c}_{lm}$
	$\tilde{E}'^{1}_{p'a} = \Sigma_k (L^{p'\bar{k}}_{\bar{a}k} + L^{p'\bar{k}}_{\bar{a}k}) - \Sigma_{dlm} \tilde{R}^{da}_{lm} g^{dp'}_{lm}$
	$\tilde{E}'^{1}_{ac} = -\Sigma_{p'lm} \bar{\bar{t}}^{p'a}_{lm} L^{p'c}_{lm}$
$\rho^{B'''}_{xiyj} = \Sigma_{cd} t^{cd}_{ij} \bar{V}^{cd}_{xy}$	$\bar{V}^{cd}_{xy} = \Sigma_{\mu\nu} \bar{V}^{\mu\nu}_{xy} \Lambda^h_{\mu c} \Lambda^h_{\nu d}$
	$\bar{V}^{\mu\nu}_{xy} = -\hat{P}^{\mu\nu}_{xy} \Sigma_{mp'} r^{\bar{m}p'}_{xy} g^{\mu\nu}_{mp'}$
$\rho^{C'''}_{xiyj} = -\left(\frac{1}{2} + \hat{P}_{ij}\right)\Sigma_{p'b} r^{p'b}_{xy}\left[\Sigma_{cm} R^{cb}_{jm} C'''_{mip'c} + \Sigma_{cm} t^{cb}_{jm} \tilde{C}'''_{mip'c}\right]$	$C'''_{mip'c} = g^{\bar{i}c}_{mp'}$
	$\tilde{C}'''_{mip'c} = g^{\bar{i}c}_{mp'}$
$\rho^{D'''}_{xiyj} = \frac{1}{2}\Sigma_{p'b} r^{p'b}_{xy}\left[\Sigma_{cm} \tilde{R}^{bc}_{jm} D'''_{mcp'i} + \Sigma_{cm} \tilde{t}^{bc}_{jm} \tilde{D}'''_{mcp'i}\right]$	$D'''_{mcp'i} = L^{c\bar{i}}_{mp'}$
	$\tilde{D}'''_{mcp'i} = L^{c\bar{i}}_{mp'}$
$\rho^{E'''}_{xiyj} = \Sigma_{p'b} r^{p'b}_{xy}\left[\Sigma_c R^{bc}_{ji} E'''_{p'c} + \Sigma_c t^{bc}_{ji} \tilde{E}'''_{p'c}\right]$	$E'''_{p'c} = \Sigma_m (L^{c\bar{m}}_{p'm} - L^{cm}_{p'm})$
	$\tilde{E}'''_{p'c} = \Sigma_m L^{c\bar{m}}_{p'm}$
$\rho^{F'}_{xiyj} = \bar{V}^{ij}_{xy}$	$\bar{V}^{ij}_{xy} = \Sigma_{\mu\nu} \bar{V}^{\mu\nu}_{xy} \Lambda^h_{\mu i} \Lambda^h_{\nu j}$
	$\bar{V}^{\mu\nu}_{xy} = -\hat{P}^{\mu\nu}_{xy} \Sigma_{mp'} r^{\bar{m}p'}_{xy} g^{\mu\nu}_{mp'}$

$$\rho^{(\mathrm{R12})}_{ai} = \left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \middle| [\bar{\Phi}, \hat{T}_{2'}] + [\tilde{\Phi}, \hat{R}_{2'}] \middle| \mathrm{HF} \right\rangle, \tag{30}$$

$$\rho^{(\mathrm{R12})}_{aibj} = \left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \middle| [\hat{F}, \hat{R}_{2'}] + [\tilde{\Phi} + [\hat{\Phi}, \hat{T}_2], \hat{R}_{2'}] + [\bar{\Phi} + [\hat{\Phi}, \hat{R}_2], \hat{T}_{2'}] \middle| \mathrm{HF} \right\rangle, \tag{31}$$

$$\rho^{\mathrm{R12}}_{xiyj} = \left\langle \begin{matrix} \overline{xy} \\ ij \end{matrix} \middle| [\hat{F}, \hat{R}_2 + \hat{R}_{2'}] + \bar{\Phi} + [\tilde{\Phi}, \hat{R}_2] + [\bar{\Phi}, \hat{T}_2] \middle| \mathrm{HF} \right\rangle, \tag{32}$$

where $\bar{\Phi}$ is a fluctuation potential which is one index transformed with the single excitation part of the trial vector $\hat{R}_1$

$$\bar{\Phi} = \sum_{\mu_1} \left(\frac{\partial \tilde{\Phi}}{\partial t_{\mu_1}} \right) R_{\mu_1} = [\tilde{\Phi}, \hat{R}_1] \tag{33}$$

with $\tilde{\Phi}$ defined in Eq. (19). The vector **SR** takes the form

$$(\mathbf{SR})_{xyij} = \sum_{x'y'i'j'} S_{xyij,x'y'i'j'} R^{x'y'}_{ij} = \hat{P}^{xy}_{ij} \sum_{x'y'} X_{xy,x'y'} R^{x'y'}_{ij}. \tag{34}$$

C. $\hat{V}$ intermediates in the Jacobi transformations

In the CCSD(R12) or CCSD(F12) ground state energy calculation, the construction of matrix elements for $\tilde{\Phi}$ with geminal functions, which are collected in an intermediate as

$$\tilde{V}^{\mu\nu}_{xy} = \langle \phi_x(1) \phi_y(2) | \hat{w}^{\dagger}_{12} e^{-\hat{T}_1} \frac{1}{r_{12}} | \phi_\mu(1) \phi_\nu(2) \rangle \tag{35}$$

is one of the most expensive steps in the iterative solution of the cluster equations. Here μ and ν represent atomic orbitals

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TABLE II. Bond lengths R_e (pm) of diatomic molecules. Estimated basis set limits listed in the column headed with "∞" have been obtained by extrapolation from the d-aQZ and d-a5Z results as described in the text.

		CCSD					CCSD(R12)		CCSD(F12)	
Molecule	State	d-aDZ	d-aTZ	d-aQZ	d-a5Z	∞	d-aTZ	d-aQZ	d-aTZ	d-aQZ
N_2	$a'\ ^1\Sigma_u^-$	126.7	125.4 125.3[a]	125.1	125.0	124.9	125.2 125.0[a]	124.9	125.1 125.0[a]	124.9
	$a\ ^1\Pi_g$	122.0	120.7 120.6[a]	120.3	120.2	120.1	120.4 120.3[a]	120.2	120.4 120.2[a]	120.2
	$w\ ^1\Delta_u$	126.2	124.9 124.7[a]	124.5	124.4	124.4	124.6 124.5[a]	124.4	124.6 124.4[a]	124.4
CO	$A\ ^1\Pi$	124.5	123.1 122.8[a]	122.5	122.4	122.3	122.7 122.4[a]	122.3	122.6 122.4[a]	122.3
	$B\ ^1\Sigma^+$	112.7	111.6 111.4[a]	111.2	111.1	111.0	111.3 111.1[a]	110.0	111.2 111.0[a]	111.0
	$C\ ^1\Sigma^+$	112.6	111.5 111.2[a]	111.0	110.9	110.8	111.2 111.0[a]	110.9	111.1 110.9[a]	110.9
BF	$A\ ^1\Pi$	135.1	131.1 130.7[a]	130.5	130.3	130.2	130.7 130.3[a]	130.3	130.6 130.2[a]	130.3
	$B\ ^1\Sigma^+$	123.7	121.2 120.9[a]	120.7	120.6	120.5	121.0 120.6[a]	120.6	120.9 120.5[a]	120.6
	$C\ ^1\Sigma^+$	125.2	122.5 122.1[a]	122.0	121.9	121.8	122.3 121.9[a]	121.9	122.2 121.8[a]	121.9
BH	$A\ ^1\Pi$	124.4	122.4 122.3[a]	122.2	122.1	122.1	122.3 122.2[a]	122.2	122.3 122.1[a]	122.1
	$B\ ^1\Sigma^+$	123.4	121.8 121.7[a]	121.6	121.6	121.5	121.7 121.6[a]	121.6	121.7 121.5[a]	121.6

[a]Corrections from HF/d-a5Z PECs.

(AOs). If O denotes the number of occupied orbitals (which is assumed to be approximately equal to the number of MOs x,y used to construct the geminal functions) and N and N' stand for the size of, respectively, the AO and auxiliary basis sets, the costs for $\tilde{V}_{xy}^{\mu\nu}$ scale with $\mathcal{O}(O^2N^4+O^3N^2(N+N'))$ in ansatz 2. Equation (35) can be rewritten as (see Fliegl *et al.*[29]):

$$\tilde{V}_{xy}^{\mu\nu} = \langle \phi_x(1)\phi_y(2)|f_{12}\tilde{Q}_{12}^{\dagger}\frac{1}{r_{12}}|\phi_\mu(1)\phi_\nu(2)\rangle. \tag{36}$$

In the CABS approach $\tilde{Q}_{12}^{\dagger}$ becomes

$$\tilde{Q}_{12}^{\dagger} = 1 - \tilde{O}_1\hat{P}_2' - \tilde{O}_2\hat{P}_1' - \hat{P}_1\hat{P}_2, \tag{37}$$

where $\hat{P}_i'$ is a projector onto the manifold of complementary orthogonal auxiliary basis functions and the $\hat{T}_1$-transformed orbital projectors $\tilde{O}_i$ are defined as

$$\tilde{O}_i = \hat{O}_i + \hat{T}_1(i) = \sum_m |\tilde{\phi}_m(i)\rangle\langle\phi_m(i)|, \tag{38}$$

with

$$\tilde{\phi}_m(i) = \phi_m(i) + \sum_a t_m^a\phi_a(i). \tag{39}$$

For the Jacobi transformations we define a $\bar{\mathbf{V}}$ intermediate as counterpart of $\tilde{\mathbf{V}}$ as

$$\bar{V}_{xy}^{\mu\nu} = \sum_m \left(\frac{\partial\tilde{V}_{xy}^{\mu\nu}}{\partial t_m^a}\right)R_m^a = \langle\phi_x(1)\phi_y(2)|f_{12}\bar{Q}_{12}^{\dagger}\frac{1}{r_{12}}|\phi_\mu(1)\phi_\nu(2)\rangle, \tag{40}$$

with the projector $\bar{Q}_{12}^{\dagger}$ given by

$$\bar{Q}_{12}^{\dagger} = \sum_m \left(\frac{\partial\tilde{Q}_{12}^{\dagger}}{\partial t_m^a}\right)R_m^a. \tag{41}$$

In the CABS approach $\bar{Q}_{12}^{\dagger}$ becomes just

$$\bar{Q}_{12}^{\dagger} = -\hat{R}_1(1)\hat{P}_2' - \hat{R}_1(2)\hat{P}_1', \tag{42}$$

where $\hat{R}_1(i)$ can be in first quantization expressed as

$$\hat{R}_1(i) = \sum_m |\bar{\phi}_m(i)\rangle\langle\phi_m(i)|, \tag{43}$$

with

$$\bar{\phi}_m(i) = \sum_a R_m^a\phi_a(i). \tag{44}$$

According to Eqs. (35)–(44) $\tilde{V}_{xy}^{\mu\nu}$ and $\bar{V}_{xy}^{\mu\nu}$ can be evaluated through the following integral contractions:

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TABLE III. Harmonic vibrational frequencies ω_e (cm^{-1}) of diatomic molecules. Estimated basis set limits listed in the column headed with ∞ have been obtained by extrapolation from the d-aQZ and d-a5Z results as described in the text.

		CCSD				CCSD(R12)			CCSD(F12)	
Molecule	State	d-aDZ	d-aTZ	d-aQZ	d-a5Z	∞	d-aTZ	d-aQZ	d-aTZ	d-aQZ
N_2	$a'\ ^1\Sigma_u^-$	1709	1714 1711[a]	1725	1727	1730	1725 1722[a]	1729	1724 1721[a]	1729
	$a\ ^1\Pi_g$	1827	1830 1836[a]	1848	1851	1854	1846 1851[a]	1854	1847 1852[a]	1854
	$w\ ^1\Delta_u$	1726	1733 1734[a]	1744	1746	1749	1744 1745[a]	1748	1744 1745[a]	1748
CO	$A\ ^1\Pi$	1510	1561 1566[a]	1581	1587	1592	1579 1583[a]	1589	1580 1584[a]	1589
	$B\ ^1\Sigma^+$	2184	2221 2230[a]	2244	2249	2253	2241 2248[a]	2252	2246 2254[a]	2253
	$C\ ^1\Sigma^+$	2219	2259 2267[a]	2281	2285	2289	2277 2284[a]	2289	2282 2289[a]	2289
BF	$A\ ^1\Pi$	1127	1258 1260[a]	1271	1275	1279	1271 1273[a]	1278	1275 1277[a]	1278
	$B\ ^1\Sigma^+$	1580	1704 1708[a]	1715	1718	1720	1714 1717[a]	1720	1717 1720[a]	1720
	$C\ ^1\Sigma^+$	1487	1620 1625[a]	1632	1635	1637	1630 1635[a]	1637	1633 1638[a]	1637
BH	$A\ ^1\Pi$	2229	2303 2309[a]	2321	2323	2326	2312 2318[a]	2324	2314 2320[a]	2324
	$B\ ^1\Sigma^+$	2360	2390 2395[a]	2398	2399	2400	2397 2403[a]	2400	2398 2403[a]	2400

[a]Corrections from HF/d-a5Z PECs.

$$\tilde{V}_{xy}^{\mu\nu} = s_{xy}^{\mu\nu} - \sum_{pq} r_{xy}^{pq} g_{pq}^{\mu\nu} - \hat{P}_{xy}^{\mu\nu} \sum_{mp'} r_{xy}^{\bar{m}p'} g_{mp'}^{\mu\nu}, \tag{45}$$

$$\bar{V}_{xy}^{\mu\nu} = -\hat{P}_{xy}^{\mu\nu} \sum_{mp'} r_{xy}^{\bar{m}p'} g_{mp'}^{\mu\nu}, \tag{46}$$

where p and p' are, respectively, orbital and complementary auxiliary basis functions which satisfy $\langle p|p'\rangle=0$. $\hat{P}_{xy}^{\mu\nu}$ is defined in analogy to $\hat{P}_{ij}^{xy}$. The integrals used in the above equations are given by

$$r_{pq}^{rs} = \langle \phi_p \phi_q | f_{12} | \phi_r \phi_s \rangle, \tag{47}$$

$$g_{pq}^{rs} = \langle \phi_p \phi_q | \frac{1}{r_{12}} | \phi_r \phi_s \rangle, \tag{48}$$

$$s_{pq}^{rs} = \langle \phi_p \phi_q | f_{12} \frac{1}{r_{12}} | \phi_r \phi_s \rangle. \tag{49}$$

s_{pq}^{rs} becomes $\delta_{pr}\delta_{qs}$ when the linear r_{12} correlation factor is used. In the present study we obtain $\bar{V}_{xy}^{\mu\nu}$ from Eq. (46) which demonstrates a simplified structure compared to the derivation for CC2-R12 in Ref. 29 as we restrict here to the CABS instead of the general ABS approach. Therefore the efforts of implementing the integral contraction for $\bar{V}_{xy}^{\mu\nu}$ intermediate in the right hand transformation are much reduced affording only $\mathcal{O}(O^3N^2N')$ floating point operations.

D. Working equations

The working equations for calculating excitation energies for conventional CC2 (Ref. 48) and CCSD,[49] CC2-R12 (both ansatz 1 and 2) (Refs. 29 and 30) and CCSD(R12)/ansatz 1 (Ref. 31) have been given in several reports. In this study we focus on the additional R12 contributions in CCSD(R12)/ansatz 2 which are not present in CCSD(R12)/ansatz 1. The detailed expressions are listed in Table I. In analogy to conventional CCSD in Ref. 49, we identify global and local intermediates for CCSD(R12)/ansatz 2 in Table I to achieve a significant reduction in operation counts. From Table I, the global intermediates include $C_{p'kai}$, $D_{p'kai}$, $E'^1_{p'a}$, E'^1_{ac}, $C'''_{mip'c}$, $D'''_{mip'c}$, and $E'''^1_{p'c}$, which are constructed after convergence of the CCSD(R12) cluster amplitudes. They are stored on disk and read back when needed during the Jacobi right hand transformation Eq. (23). Local intermediates are corresponding quantities capped with tildes in Table I, which depend on $\hat{R}_1$ or $\hat{R}_2$ trial vectors and have to be recalculated in each linear transformation. Therefore, the respective contractions of both global and local intermediates with four-index vectors require for each trial vector about twice as much computational time as an iteration solely for the cluster equations. In the following discussions we focus on the contributions of local intermediates only.

Following the strategy described in Ref. 49, the $\tilde{C}'_{p'kai}$ and $\tilde{D}'_{p'kai}$ local intermediates are evaluated in each iteration

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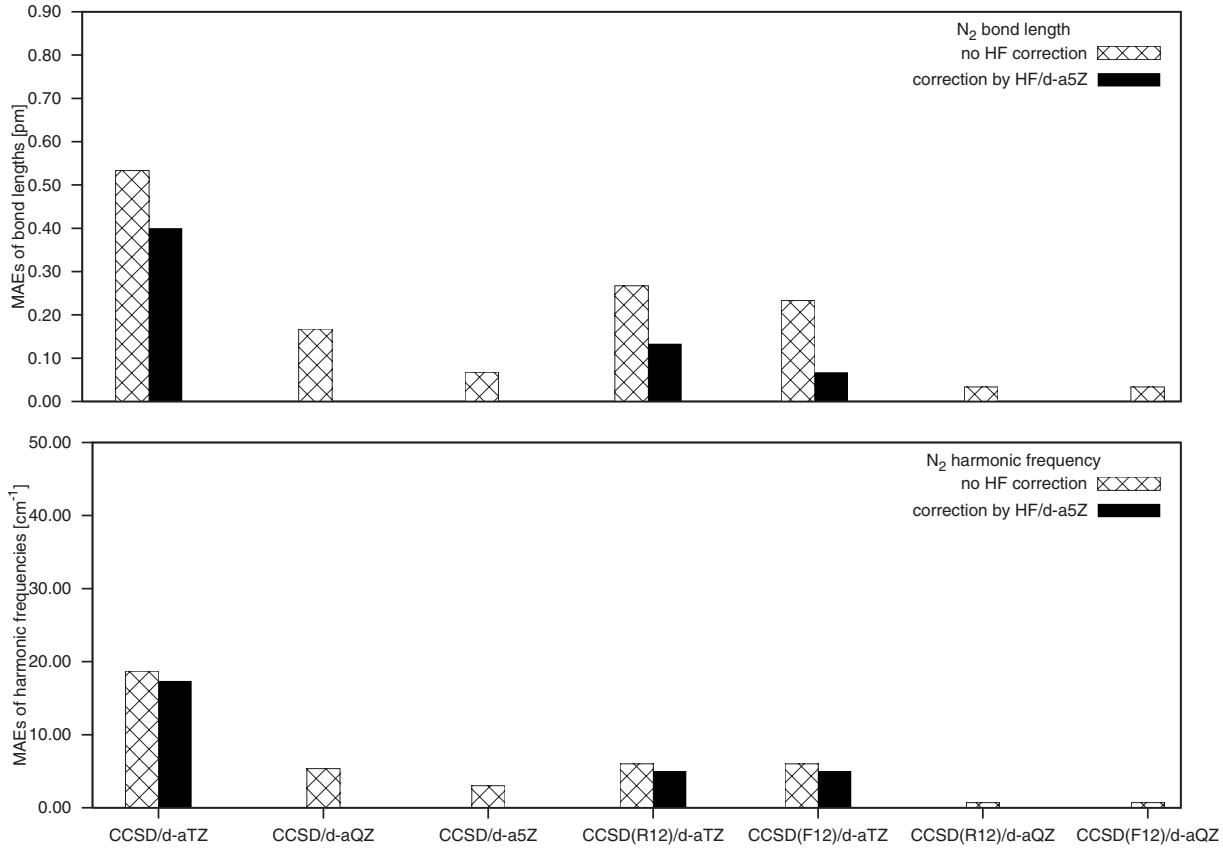


FIG. 1. The MAEs of calculated CCSD(R12) and CCSD(F12) bond lengths (top) and harmonic frequencies (bottom) for N_2 compared to the estimated basis set limits.

with the first index δ or δ' initially in the AO basis and stored on disk and transformed later to the CABS basis p',

$$\tilde{C}'_{p'kai} = \sum_{\delta+\delta'} C_{\delta p'} \tilde{D}'_{\delta kai}, \tag{50}$$

$$\tilde{D}'_{p'kai} = \sum_{\delta+\delta'} C_{\delta p'} \tilde{D}'_{\delta kai}. \tag{51}$$

Above, $\tilde{C}'_{\delta kai}$ and $\tilde{D}'_{\delta kai}$ include the additional R_2-dependent contributions of $-\Sigma_{dl} R_{li}^{ad} g_{lk}^{\delta d}$ and $\Sigma_{dl} \tilde{R}_{li}^{ad} L_{kl}^{\delta d}$ for CCSD(R12)/ansatz 2 while in the conventional CCSD linear transformation only R_1-dependent contributions exist.

$\tilde{E}'^{1}_{p'a}$ is obtained as by-product of the $\tilde{C}_{p'kai}$ and $\tilde{D}_{p'kai}$ intermediates by accumulating the traces of the R_1- and R_2-dependent contributions,

$$\tilde{E}'^{1}_{p'a} = \frac{3}{2} \sum_k \tilde{C}_{p'kak} - \frac{1}{2} \sum_k \tilde{D}_{p'kak}, \tag{52}$$

where $\tilde{C}_{p'kai}$ and $\tilde{D}_{p'kai}$ are similarly defined as $\tilde{C}'_{p'kai}$ and $\tilde{D}'_{p'kai}$ except that the prefactors of the R_2-dependent parts differ by $\frac{1}{2}$. The contribution from $\tilde{E}'^{1}_{p'a}$ can be absorbed into $\tilde{C}'_{p'kai}$ and $\tilde{D}'_{p'kai}$ intermediates by the simple modification

$$\tilde{C}'_{p'kai} \leftarrow \tilde{C}'_{p'kai} - \tfrac{1}{2} \delta_{ki} \tilde{E}'^{1}_{p'a}, \tag{53}$$

$$\tilde{D}'_{p'kai} \leftarrow \tilde{D}'_{p'kai} + \tfrac{1}{2} \delta_{ki} \tilde{E}'^{1}_{p'a}. \tag{54}$$

The $\tilde{E}'^{1}_{bc}$ local intermediate is conveniently obtained similar to the H-term in the conventional CCSD linear transformation[49] due to their similar structures,

$$\tilde{E}'^{1}_{bc} = -\sum_{lm}^{\delta+\delta'} \left[\sum_{xy} (2R_{lm}^{xy} - R_{ml}^{xy}) r_{xy}^{\delta b} \right] g_{lm}^{\delta c}. \tag{55}$$

with the contravariant back transformed AO index δ on $r_{xy}^{\delta b}$. The main difference is that one hole virtual index c on the integral $g_{lm}^{\delta c}$ replaces the original occupied i.

The $\tilde{C}'''_{mip'c}$ and $\tilde{D}'''_{mip'c}$ local intermediates need the precalculation of integrals $g_{m\delta}^{\bar{ic}}$ and $L_{m\delta}^{\bar{ic}}$ with two occupied, one virtual and one AO index. The local AO intermediate $\tilde{E}'''_{\delta c}$ is obtained as the trace of $L_{m\delta}^{\bar{ic}}$,

$$\tilde{E}'''_{\delta c} = \sum_m L_{m\delta}^{\bar{mc}}. \tag{56}$$

$g_{m\delta}^{\bar{ic}}$, $L_{m\delta}^{\bar{ic}}$ and $\tilde{E}'''_{\delta c}$ are all precalculated and stored on files in loops over δ and δ'. The AO-to-MO transformations of δ and δ' are carried out later, which leads to $g_{mp'}^{\bar{ic}}$, $L_{mp'}^{\bar{ic}}$, and $\tilde{E}'''_{p'c}$. Employing the same strategy as in Eqs. (53) and (54), we incorporate $\tilde{E}'''_{p'c}$ in the diagonals of $\tilde{C}'''_{mip'c}$ and $\tilde{D}'''_{mip'c}$,

$$\tilde{C}'''_{mmp'c} \leftarrow \tilde{C}'''_{mmp'c} - \tfrac{1}{2} \tilde{E}'''_{p'c}, \tag{57}$$

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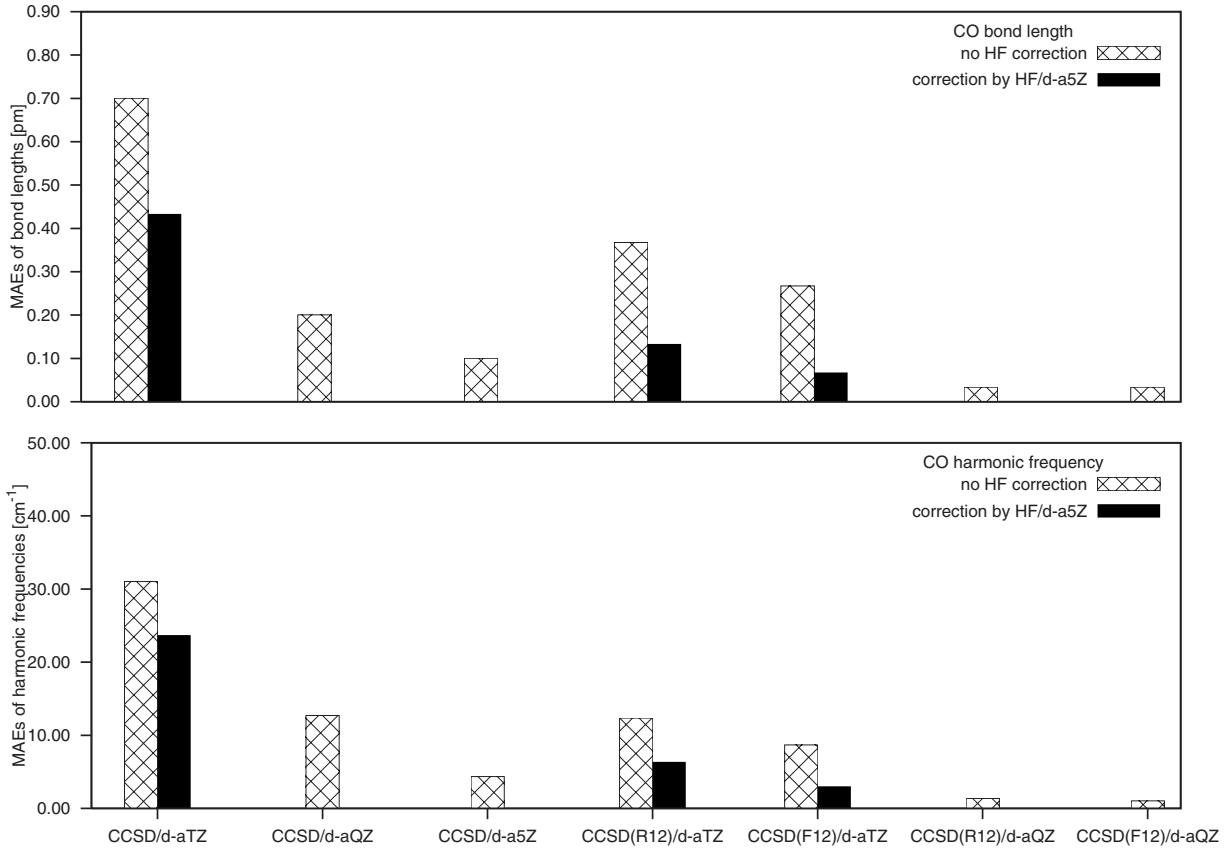


FIG. 2. The MAEs of calculated CCSD(R12) and CCSD(F12) bond lengths (top) and harmonic frequencies (bottom) for CO compared to the estimated basis set limits.

$$\tilde{D}'''_{mmp'c} \leftarrow \tilde{D}'''_{mmp'c} + \tfrac{1}{2}\tilde{E}'''_{p'c}. \tag{58}$$

Thus, the contributions to R12 doubles projections are obtained as

$$\rho_{xiyj}^{C'''+D'''+E'''} = \sum_{p'b} r_{xy}^{p'b}\rho_{ij}^{p'b}, \tag{59}$$

where the new quantity $\rho_{ij}^{p'b}$ consists of both the contributions from $\tilde{C}'''_{mip'c}$ and $\tilde{D}'''_{mip'c}$,

$$\rho_{ij}^{p'b} = \sum_{cm}\left[\frac{1}{2}\bar{t}_{jm}^{bc}\tilde{D}'''_{mip'c}\left(\frac{1}{2}+\hat{P}_{ij}\right)t_{jm}^{cb}\tilde{C}'''_{mip'c}\right]. \tag{60}$$

In the above, the modified amplitude $\bar{t}_{jm}^{bc}$ is defined in Table I.

The most expensive step arising from the R12 contributions in the linear transformation with the Jacobian matrix is found to be the evaluation of $\bar{V}_{xy}^{\mu\nu}$, which requires about $N^2N'O^3$ operations. However, we need to stress that the calculation of $\bar{V}_{xy}^{\mu\nu}$ is evidently cheaper than that of $\tilde{V}_{xy}^{\mu\nu}$ in the ground state calculation in the CABS approach. Besides, the calculation of the $\tilde{C}'_{p'kai}$ and $\tilde{D}'_{p'kai}$ intermediates is time consuming. Their R_2-dependent parts are quite demanding, scaling with $\mathcal{O}(N'V^2O^3)$. We often encounter the evaluation of two-electron integrals with two occupied, one virtual and one complementary orbital index. These processes need a few times of $N^3N'+N^2N'O^2+NN'VO^2$ operations, which occurs to the R_1-dependent parts of $\tilde{C}'_{p'kai}$ and $\tilde{D}'_{p'kai}$. Generally, the computational costs of the linear transformation for CCSD(R12)/ansatz 2 are approximately two to three times that of the conventional CCSD scheme, if the size of the auxiliary basis set is similar to that of the orbital basis set. In particular, we observe that a CCSD(R12) calculation using the Dunning basis set with the cardinal number of X is always faster than a conventional CCSD calculation with $X+1$. Thus as will be seen, in Secs. III and IV, the CCSD(R12) calculations provide accurate results at significantly lower costs than standard CCSD implementations.

III. APPLICATIONS

A. Computational details

The linear transformations for CCSD(R12) and CCSD(F12) for ansatz 2 have been implemented in the coupled-cluster code of the DALTON program package.[32] We have selected four diatomic molecules N_2, CO, BF, and BH for a first application of these models to calculate equilibrium geometries and harmonic vibrational frequencies for singlet excited states. All calculations have been carried out with frozen-core approximations for the $1s$ orbitals at the atoms B, C, N, and O. The Dunning cc-pVXZ basis set family,[50] doubly augmented with diffusions (d-aXZ in abbrevation) due to the presence of several Σ^+ states with Rydberg characters, has been applied with X=D, T, Q, and 5 for conventional CCSD. The CCSD(R12) and CCSD(F12) calculations have been performed with d-aTZ and d-aQZ orbital basis. As auxiliary basis sets, we took the cc-pVTZ-RI basis[51] which uses uncontracted $8s6p5d3f1g$ functions for

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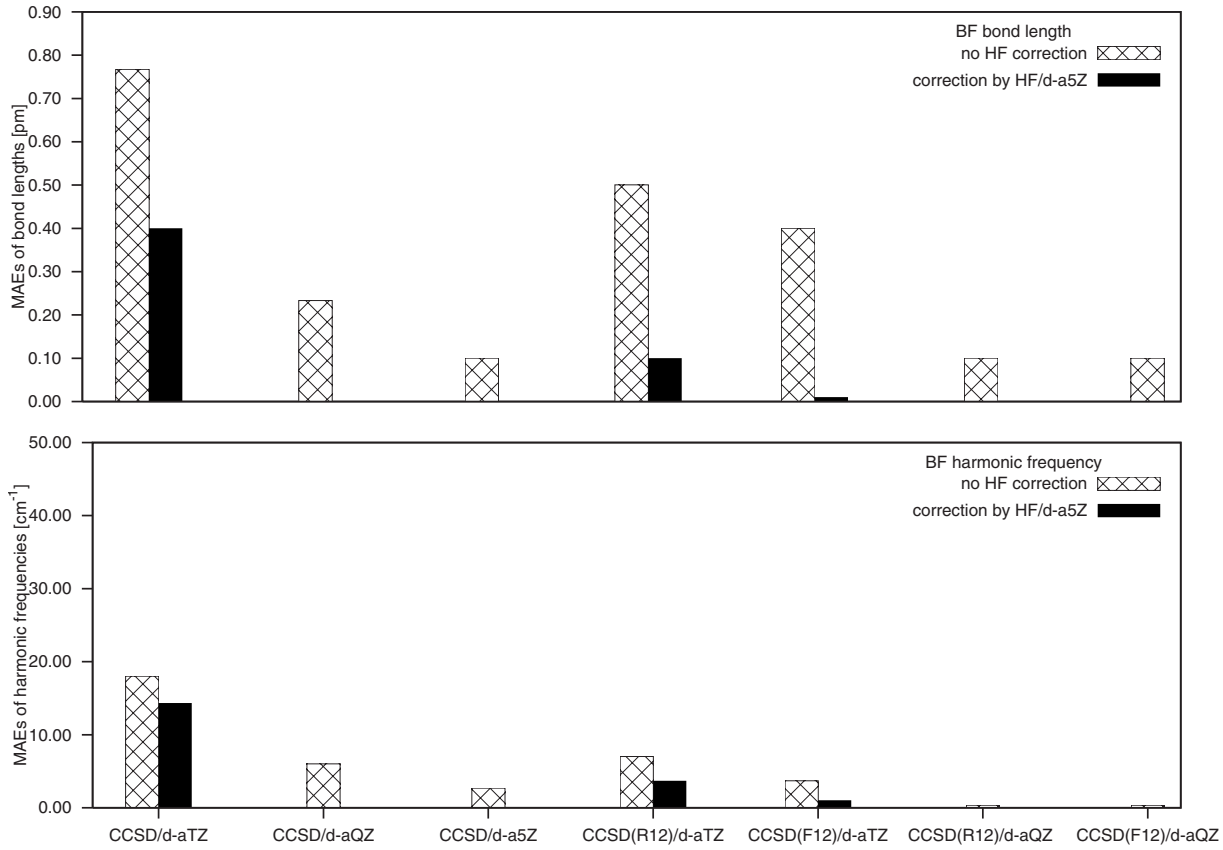


FIG. 3. The MAEs of calculated CCSD(R12) and CCSD(F12) bond lengths (top) and harmonic frequencies (bottom) for BF compared to the estimated basis set limits.

N, C, B, and F and $4s3p2d1f$ functions for H. The exponents of F12 exponential geminal functions are 1.8, 1.2, 1.3, and 0.9 for N_2, CO, BF, and BH, respectively, which were optimized to obtain the minima of the ground state correlation energies for the molecules.

All R12 and F12 calculations have employed the CABS+ approach by Valeev,[27] which essentially means that the RI is done in the union of the orbital and the auxiliary basis sets. Standard approximation B (Ref. 26) 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.

Numerical potential energy curves (PECs) have been obtained by computing several grid points with a bond length increment of 0.01 a.u. The PECs were fitted by sixth-order polynomial functions to ten points around the minima. We only report the equilibrium bond lengths within 0.1 pm. However, more digits were actually required for sufficient accuracies of the computed harmonic frequencies. The force constants have been calculated as the second derivatives at the minima of the PECs according to a simple three-point formula,

$$k = \frac{E_{+\delta} + E_{-\delta} - 2E_0}{\delta^2}, \tag{61}$$

where E_0 is the total energy at the equilibrium bond length r_0 and $E_{+\delta}$ and $E_{-\delta}$ are the total energies interpolated at $r_0+\delta$ and $r_0-\delta$ (δ=0.5 pm). The obtained norms of molecular gradients were below 0.0001 a.u. and lead to numerical uncertainties of harmonic frequencies of about 1 cm^{-1}. For the comparison with CCSD(R12) and CCSD(F12) the CCSD basis set limit PECs were estimated by adding the HF/d-a5Z energies to the basis set limits of correlation energies obtained by extrapolating the CCSD/d-aQZ and CCSD/d-a5Z results using[52]

$$E_\infty \approx \frac{X^3 E_X - Y^3 E_Y}{X^3 - Y^3}, \tag{62}$$

where X, Y stand for the cardinal numbers of basis sets d-aXZ and d-aYZ, and E_∞, E_X, and E_Y are the correlation energies at the infinite, d-aXZ, and d-aYZ basis sets, respectively. The basis set limits of the bond lengths and harmonic frequencies were then estimated from the minima and second derivatives of the extrapolated PECs. In order to have an independent test of the so estimated basis set limits we also carried out CCSD calculations in the a6Z basis sets. For most states the a6Z results agree well with both the d-a5Z numbers and the estimated basis set limits and show that these numbers are well converged. However, for the states with larger Rydberg contributions (e.g., BF $C\ ^1\Sigma^+$), the a6Z results are not accurately enough converged to serve as benchmarks for the d-a5Z results and the extrapolated basis set limits. Therefore we did not include them in Tables II and III.

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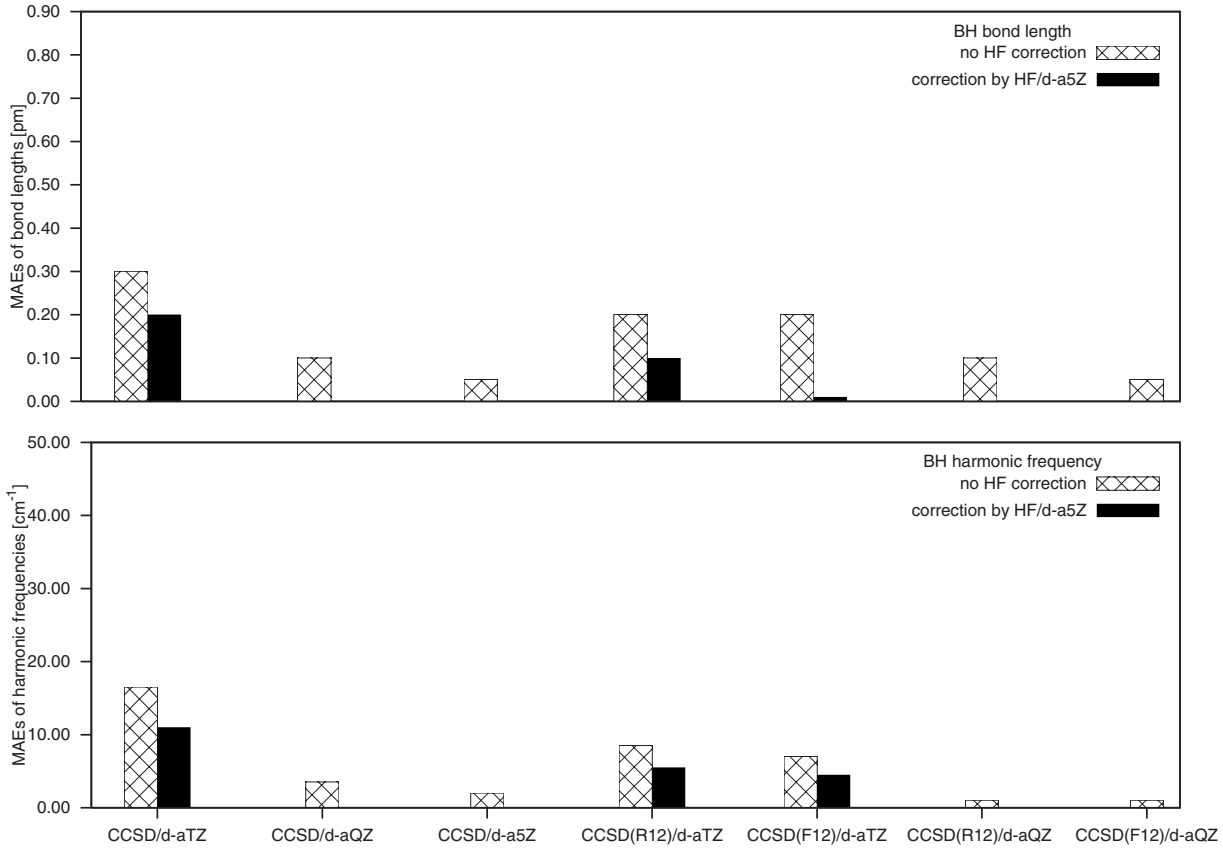


FIG. 4. The MAEs of calculated CCSD(R12) and CCSD(F12) bond lengths (top) and harmonic frequencies (bottom) for BH compared to the estimated basis set limits.

B. Equilibrium structures

The optimized bond lengths of some singlet excited states using frozen-core CCSD, CCSD(R12), and CCSD(F12) are tabulated in Table II. The mean absolute errors (MAEs) relative to the estimated basis set limits are plotted in the upper parts of Figs. 1–4. The slow convergence of bond lengths obtained with standard CCSD method is expected. With the triple-ζ basis the MAEs for N_2, CO, BF, and BH molecules are about 0.53, 0.70, 0.77, and 0.30 pm, respectively. The bond lengths of most of these states still deviate from the basis set limits by 0.1 pm even with the quintuple-ζ basis. For all investigated states the CCSD(R12) and CCSD(F12) results with the quadruple-ζ basis are intermediate between the standard CCSD results in the d-a5Z basis and the extrapolated basis set limits.

From Table II, we notice that with the triple-ζ basis sets the improvements obtained with the CCSD(R12) and CCSD(F12) calculations seem to be less satisfactory. However, it needs to be pointed out that it is not the R12 or F12 method that should be blamed. With this basis set the largest remaining error in the explicitly correlated calculations arise not from the treatment of dynamic electron correlation, but from the uncorrelated mean field contributions to the total energies. This becomes obvious when the triple-ζ results are approximately corrected for this error by adding to the energy differences between HF response calculations in d-a5Z and d-aTZ basis sets. The so corrected CCSD(R12) and CCSD(F12) results (cf. the second row for each state in Table II) agree for all states within 0.1 pm with the CCSD/d-a5Z benchmark. However, the standard CCSD results with this correction in the triple-ζ basis set deviate for most states still by 0.2–0.4 pm from this benchmark.

The MAEs of the CCSD, CCSD(R12), and CCSD(F12) in the different basis sets and the triple-ζ results corrected for HF errors are shown in Figs. 1–4. It can be immediately seen that the improvements of the correlation treatment in the CCSD(R12) and CCSD(F12) methods and of the HF correction for the triple-ζ results are significant when we compare with the basis set limits. The CCSD(R12) and particularly CCSD(F12) results in the triple-ζ basis corrected for the HF error have an accuracy which in the standard CCSD calculation is first reached with quintuple-ζ basis sets. With quadruple-ζ basis sets the CCSD(R12) and CCSD(F12) results are (even without HF corrections) comparably accurate or even surpass the standard CCSD/d-a5Z calculations.

We also observe that, although the exponential correlation factor of the F12 method has been widely applied to achieve faster basis set convergence of correlation energies than the linear factor of the R12 method, for the bond lengths of the excited states reported here such an advantage appears minor by only 0.1 pm for triple-ζ basis sets and is almost undiscernible for quadruple-ζ ones.

C. Harmonic frequencies

The CCSD, CCSD(R12), and CCSD(F12) results for harmonic frequencies are presented in Table III. The MAEs

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are plotted at the lower parts in Figs. 1–4. Again, the conventional CCSD frequencies of most states are not converged to the basis set limits by a few wavenumbers even with the quintuple-ζ basis. As a comparison, it is clear that in Table III with the quadruple-ζ basis the CCSD(R12) and CCSD(F12) results indeed make significant improvements and bring all frequencies very close to the basis set limits which cannot be achieved by the conventional CCSD method with the same basis sets.

The R12/F12 results for frequencies with the triple-ζ basis seem again to be less satisfactory and have only the qualities of CCSD quadruple-ζ for most excited states. The slow basis set convergence of some excited states is mainly due to the fact that the applied orbital basis sets in this study were tailored to ground states and thus do not contain sufficiently diffuse functions and cause the low quality of the HF reference states. We have therefore followed the same route used for the correction of the bond lengths to approximately upgrade CCSD(R12) and CCSD(F12) harmonic frequencies in the d-aTZ orbital basis with HF/d-a5Z corrections. The corrected frequencies are given in the second row for each excited state in Table III. The MAEs are given with black bars in Figs. 1–4. The HF/d-a5Z corrections to the R12/F12 results obtained with the triple-ζ basis have pronounced effects. For example, the CCSD(F12) frequencies of all Σ^+ states with the triple-ζ basis even approach the basis set limits within the accuracy of the present calculations. The frequencies of N_2 $a\,^1\Pi_g$ and $w\,^1\Delta_u$ states are brought to quintuple-ζ qualities. The more difficult cases are the $A\,^1\Pi$ states of BH, CO, and BF which have the qualities with CCSD(F12)/d-aTZ calculations close to quadruple-ζ, quintuple-ζ, and ∞, respectively. We want also to mention the irregular changes of frequencies due to the corrections for $a'\,^1\Sigma_u^-$ of N_2. For this state the basis set errors at the HF level have the opposite sign of the errors in the correlation contribution so that they partially cancel each other. If the HF basis set corrections are added this error cancellation is lost.

For the harmonic frequencies no evident advantage of the exponential over the linear correlation factor for all excited states when quadruple-ζ basis sets are applied. But when using the smaller triple-ζ basis sets, CCSD(F12) becomes more advantageous than CCSD(R12) by about 3 and 5 cm^{-1} only for Rydberg-like Σ^+ states of BF and CO, respectively.

IV. CONCLUSIONS AND OUTLOOKS

In this paper, the explicitly correlated methods CCSD(R12) and CCSD(F12) for ansatz 2 have been extended to describe excited states. The equations of the coupled-cluster Jacobi right hand linear transformations adapted to these models have been derived and implemented in the program DALTON. This has allowed the first application of CCSD(R12) and CCSD(F12) methods for ansatz 2 to equilibrium bond lengths and harmonic frequencies of singlet excited states.

The implemented CCSD(R12) and CCSD(F12) methods for ansatz 2 are more expensive than those for ansatz 1 due to the efforts for the additional contributions to the linearly transformed vectors. The most expensive step is the computation of the R_1-transformed V intermediates which scales with $N^2N'O^3$ in the CABS approach. We have observed that for N_2 the computational time of the CCSD(R12) method for one iteration for vertical excitation energies is much shorter by a factor of 3 with variations of the excitation energies by only about 1 meV when using aQZ as auxiliary basis sets than a6Z. Thus, it is important to develop optimized auxiliary basis sets with reduced dimensions in order to avoid unnecessary computational costs.

The basis set convergence of equilibrium bond lengths and harmonic frequencies of some singlet excited states of N_2, CO, BF, and BH diatomic molecules have been compared for CCSD(R12) and CCSD(F12) calculations using doubly augmented d-aTZ and d-aQZ basis sets to CCSD/d-aXZ (X=D, T, Q, and 5) results. We have also found that the convergence of these properties is not as fast as might be anticipated with the triple-ζ basis set. The reason for this is, however, no longer the slow convergence of the correlation contribution given by CCSD(R12) and CCSD(F12), but now the remaining basis set errors of the HF contribution with the triple-ζ basis set. A simple and pragmatically useful scheme which replaces the HF contribution from the d-aTZ total energy of the excited state by the d-a5Z one has been able to upgrade most of the CCSD(R12)/d-aTZ and CCSD(F12)/d-aTZ results to CCSD/d-a5Z quality. We have also found that for the equilibrium bond lengths and harmonic frequencies the exponential correlation factor of CCSD(F12) only slightly improves the convergence for the triple-ζ basis upon the linear r_{12} factor of CCSD(R12). When a larger quadruple-ζ basis set was used the differences between CCSD(R12) and CCSD(F12) methods have been found to be below 0.1 pm and 1 cm^{-1}. However with smaller basis sets the improvements will be more significant particularly to some Rydberg-like excited states.

The implementation of excitation energies as we have done in this work is an important intermediate step toward accurate calculations of optical polarizabilities and hyperpolarizabilities within the CCSD(R12) and CCSD(F12) methods for ansatz 2. These quantities require the implementation of intermediates which depend on higher derivatives with respect to cluster amplitudes. In this direction, the linear transformation is the first step and proceeding work will focus on higher-order properties.

Another important issue is to include single excitations into the CABS basis which provides a perturbative correction for the basis set error in the HF reference. This has been shown to almost entirely remove the HF basis set errors if an MP2 singles energy correction $\Delta E = 2\Sigma_{i\alpha} t_i^\alpha f_i^\alpha$ is added.[16] On the correlation side, moreover, a further simplification of our implementation is possible so as to enhance the cost efficiency as we have observed that some contributions to the transformed vectors ρ_μ are minor but computationally expensive. Also the costs for the evaluation of additional two-electron integrals can be reduced by using the density-fitting technique,[53] so that the explicitly correlated coupled-cluster response models can become cost-efficient alternatives for larger molecules.

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