Coupled-cluster response theory with linear-r_{12} corrections: The CC2-R12 model for excitation energies

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Coupled-cluster response theory for vertical excitation energies within the second-order approximate coupled-cluster singles-and-doubles model CC2, including linear-r_{12} corrections, is derived and implemented for *Ansätze* 1 and 2 of R12 theory. An orthonormal auxiliary basis set is used for the resolution-of-the-identity approximation in order to calculate the three- and four-electron integrals needed in R12 theory. The basis set convergence is investigated for a selected set of atoms and small molecules and it is found that in many cases the convergence is not improved. An analysis of the different contributions to excitation energies shows that the present scheme for the construction of the R12 pair functions leads in response theory to an unbalanced description of ground- and excited-state wave functions and needs to be generalized to carry the high accuracy of R12 methods over to response theory. © *2006 American Institute of Physics*.
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I. INTRODUCTION

Since Hylleraas[1] demonstrated in 1929 for the He atom that the inclusion of a correlation factor depending on the interelectronic distance r_{12} into the wave function leads to an excellent description of short-range electron correlation, much progress has been achieved in this field. In 1985, Kutzelnigg[2] proposed the linear-r_{12} *Ansatz* and already in 1987 the explicitly correlated second-order Møller-Plesset perturbation-theory model MP2-R12 was introduced.[3]

Much improvement has been achieved for this model in terms of different *Ansätze*, different approximations, and more efficient implementations (see Ref. 4 and references therein). In 2003, Manby[5] combined the MP2-R12 model with density-fitting techniques, and Ten-no and Manby improved the basis set convergence by rearranging three-electron integrals before using the resolution-of-the-identity (RI) approximation.[6] In 2005, Kordel *et al.*[7] developed the analytical calculation of first-order molecular properties such as quadrupole moments for the MP2-R12 theory. Furthermore, there are other explicitly correlated MP2 approaches available using various functions of r_{12} in place of the interelectronic distance r_{12} itself.[8–10] In particular, the use of nonlinear correlation factors such as $\exp(-\gamma r_{12})$ or $r_{12}\exp(-\gamma r_{12})$ has been shown[11,12] to be an efficient alternative to the conventional linear-r_{12} *Ansatz*. A recently published error analysis of explicitly correlated electronic structure theory by May *et al.*[13] underlines the importance of this new correlation factor.

Noga *et al.* combined the R12 approach with coupled-cluster (CC) theory to derive the explicitly correlated CC-R12 methods[14–16] CCSD-R12 and CCSD(T)-R12, which allow to obtain highly accurate results for ground-state energies. This was demonstrated in Refs. 17–24. Very recently, a CCSD(R12) method was introduced as an approximation to the CCSD-R12 model with less computational costs.[25]

The R12 and other related explicitly correlated wave functions are promising remedies for the slow basis set convergence of ground-state energies observed in conventional (orbital based) correlated wave-function methods of electronic structure theory. However, while the CC-R12 methods perform excellently for ground-state energies, nothing is yet known about the performance of R12 methods in the context of response theory, for example, for excitation energies or frequency-dependent properties. The calculation of molecular properties may be more difficult than the calculation of ground-state total energies. Methods giving accurate ground-state energies do not automatically provide the same accuracy for excitation energies and frequency-dependent properties. This was, for example, observed in recent studies with local correlation methods.[26,27]

In the present work, we shall investigate the basis set convergence of excitation energies and how this convergence

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can be improved by linear-r_{12} terms. For excitation energies, an established hierarchy[28,29] of CC models that converges systematically to the full configuration-interaction (CI) limit comprises the models CCS ($\mathcal{N}^4$), CC2 (Ref. 30) ($\mathcal{N}^5$), CCSD (Refs. 31–33) ($\mathcal{N}^6$), CC3 (Refs. 34 and 35) ($\mathcal{N}^7$), CCSDT ($\mathcal{N}^8$), and so on, with the scaling of the computational costs with the system size $\mathcal{N}$ given in parentheses. Within this hierarchy, molecular properties can be calculated with increasing accuracy and increasing computational costs.

In the present work, we derive the CC-R12 response theory for excitation energies for the CC2-R12 model with *Ansätze* 1 and 2 of Klopper and Samson,[36] the latter in a slightly modified form as proposed by Wind *et al.*[37] and Valeev.[38] For both *Ansätze*, the CC2-R12 model has been implemented in the integral-direct coupled-cluster program,[30,32,33] which is part of the DALTON program[39] package. An orthonormal auxiliary basis set can be used for the resolution-of-the-identity approximation to calculate the three- and four-electron integrals needed in R12 theory.

The paper is organized as follows: The equations for the CC2-R12 model are discussed in Sec. II. Computational aspects are discussed in Sec. III. Technical details such as employed basis sets, geometries, and programs are given in Sec. IV. Numerical results for atoms and molecules are presented in Sec. V, and the article is concluded in Sec. VI.

II. THEORY

A. The CC-R12 wave-function *Ansatz*

We start from the coupled-cluster wave function,

$$|\mathrm{CC}\rangle = \exp(\hat{T})|\mathrm{HF}\rangle, \tag{1}$$

where the reference state is the Hartree-Fock wave function and the cluster operator contains conventional single ($\hat{T}_1$) and double ($\hat{T}_2$) excitations as well as R12 double excitations ($\hat{T}_{2'}$),

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

For a closed-shell reference state $|\mathrm{HF}\rangle$, the excitation operators can be written as

$$\hat{T}_1 = \sum_{ai} t_a^i E_{ai} = \sum_{\mu_1} t_{\mu_1} \hat{\tau}_{\mu_1}, \tag{3}$$

$$\hat{T}_2 = \tfrac{1}{2} \sum_{abij} t_{ab}^{ij} E_{ai} E_{bj} = \sum_{\mu_2} t_{\mu_2} \hat{\tau}_{\mu_2}, \tag{4}$$

$$\hat{T}_{2'} = \tfrac{1}{2} \sum_{ijkl} c_{kl}^{ij} \sum_{\alpha\beta} w_{\alpha\beta}^{kl} E_{\alpha i} E_{\beta j} = \sum_{\mu_{2'}} t_{\mu_{2'}} \hat{\tau}_{\mu_{2'}}, \tag{5}$$

with

$$w_{\alpha\beta}^{kl} = \langle \varphi_\alpha(1) \varphi_\beta(2) | \hat{w}_{12} | \varphi_k(1) \varphi_l(2) \rangle. \tag{6}$$

The coupled-cluster amplitudes are denoted as t_{μ_i}, and for the single, double, and R12 double excitation operators, we use the notation $\hat{\tau}_{\mu_i}$. The amplitudes $t_{\mu_{2'}}$ are obtained by contracting the R12 amplitudes c_{kl}^{ij} with the integrals $w_{\alpha\beta}^{kl}$. The operators E_{ai} correspond to spin-free single excitations. They are described in detail in Ref. 40. We use the usual convention that i, j, …denote occupied and a, b, …unoccupied (virtual) orbitals. The index p is used for general molecular orbitals and α, β, …for orbitals of a complementary subspace (*vide infra*). The operator $\hat{T}_{2'}$ contains a particular form of double excitations, which we denote R12 double excitations. These are double excitations into the correlated pair functions,[41]

$$\hat{w}_{12} | \varphi_k(1) \varphi_l(2) \rangle, \tag{7}$$

which can be expressed with the help of a complementary orbital subspace $\{\varphi_\alpha\}$ as in Eqs. (5) and (6). For *Ansatz* 1, $\hat{w}_{12}$ is defined as

$$\hat{w}_{12} = (1 - \hat{P}_1)(1 - \hat{P}_2) r_{12}, \tag{8}$$

with the projection operator,

$$\hat{P}_1 = \sum_p |\varphi_p(1)\rangle\langle\varphi_p(1)|, \tag{9}$$

onto the finite one-electron orbital basis $\{\varphi_p\}$. In *Ansatz* 1, the orbital subspace $\{\varphi_\alpha\}$ consists of all orbitals that are orthogonal to the finite one-electron orbital basis $\{\varphi_p\}$. Hence, the union of $\{\varphi_\alpha\}$ and $\{\varphi_p\}$ forms a complete basis for the one-electron Hilbert space.

For *Ansatz* 2, the operator $\hat{w}_{12}$ was in Ref. 10 chosen as

$$\hat{w}_{12} = (1 - \hat{O}_1)(1 - \hat{O}_2) r_{12}, \tag{10}$$

with

$$\hat{O}_1 = \sum_i |\varphi_i(1)\rangle\langle\varphi_i(1)|. \tag{11}$$

In the present article, however, we use the following equivalent but for coupled-cluster theory computationally more convenient form:[37,38]

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

with

$$\hat{V}_1 = \sum_a |\varphi_a(1)\rangle\langle\varphi_a(1)|. \tag{13}$$

Above, $\hat{O}_1$ is the projection operator onto the occupied and $\hat{V}_1$ the projection operator onto the virtual Hartree-Fock orbitals. The additional projection $(1 - \hat{V}_1 \hat{V}_2)$ keeps the R12 pair functions orthogonal to all orbital products included through the conventional (i.e., not R12) double excitations. For *Ansatz* 2, the indices α, β, … are defined in a manner different from *Ansatz* 1. In *Ansatz* 1, these indices denote the complementary basis. In *Ansatz* 2, however, they denote not only the virtual orbitals of the complementary basis but also the virtual orbitals of the finite one-electron basis. For *Ansatz* 2, the set $\{\varphi_\alpha\}$ forms a complete set together with the occupied orbitals $\{\varphi_i\}$.

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It is important to choose $\hat{w}_{12}$ as in Eq. (12) for two reasons: First, it ensures that the correct basis set limit is obtained independent of the approximations used for the evaluation of the R12 contributions, since all R12 contributions vanish in a complete one-electron orbital basis in *Ansatz* 2 as well as in *Ansatz* 1. Second, it circumvents numerical problems in the solution of the coupled-cluster ground-state amplitude and response equations, which otherwise occur when the R12 space becomes linearly dependent on the space spanned by products of virtual orbitals.

B. The CCSD-R12 and CC2-R12 models

As is usual in coupled-cluster theory, the cluster amplitudes t_μ are determined by solving the projected Schrödinger equation

$$\langle \mu | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle = 0. \tag{14}$$

The coupled-cluster energy is obtained as

$$E_{\text{CC-R12}} = \langle \mathrm{HF} | \hat{H} \exp(\hat{T}) | \mathrm{HF} \rangle. \tag{15}$$

For the closed-shell CCSD-R12 model, the cluster equation [Eq. (14)] can be written in more detail as

$$\Omega_{\mu_1} = \langle \mu_1 | [\hat{f}, \hat{T}_1] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}}, \hat{T}_2 + \hat{T}_{2'}] | \mathrm{HF} \rangle = 0, \tag{16}$$

$$\Omega_{\mu_2} = \langle \mu_2 | [\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \exp(-\hat{T}) \hat{\Phi} \exp(\hat{T}) | \mathrm{HF} \rangle = 0, \tag{17}$$

$$\Omega_{\mu_{2'}} = \langle \mu_{2'} | [\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \exp(-\hat{T}) \hat{\Phi} \exp(\hat{T}) | \mathrm{HF} \rangle = 0, \tag{18}$$

if the generalized Brillouin condition ($f^i_\alpha = f^\alpha_i = 0$) is assumed. Here, $\hat{f}$ is the Fock operator, $\hat{\Phi}$ is the electron fluctuation potential, and

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

The conventional singles and doubles projection manifolds are defined as[40]

$$\left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| = \frac{1}{2} \langle \mathrm{HF} | E^\dagger_{ai}, \tag{20}$$

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \right| = \frac{1}{6} \langle \mathrm{HF} | (2 E^\dagger_{ai} E^\dagger_{bj} + E^\dagger_{aj} E^\dagger_{bi}). \tag{21}$$

For the R12 doubles, we employ the projection manifold,

$$\left\langle \begin{matrix} \overline{kl} \\ ij \end{matrix} \right| = \sum_{\alpha\beta} (w^\dagger)^{\alpha\beta}_{kl} \left\langle \begin{matrix} \overline{\alpha\beta} \\ ij \end{matrix} \right|, \tag{22}$$

with

$$\left\langle \begin{matrix} \overline{\alpha\beta} \\ ij \end{matrix} \right|$$

defined analogously to Eq. (21). With this choice, the excitation operator and projection manifolds fulfill the equations

$$\left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| \hat{\tau}^b_j | \mathrm{HF} \rangle = \delta_{ab} \delta_{ij}, \tag{23}$$

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \right| \hat{\tau}^{cd}_{kl} | \mathrm{HF} \rangle = \hat{P}^{ab}_{ij} \delta_{ac} \delta_{bd} \delta_{ik} \delta_{jl}, \tag{24}$$

$$\left\langle \begin{matrix} \overline{kl} \\ ij \end{matrix} \right| \hat{\tau}^{k'l'}_{i'j'} | \mathrm{HF} \rangle = \hat{P}^{kl}_{ij} \delta_{ii'} \delta_{jj'} X_{kl,k'l'}, \tag{25}$$

where

$$X_{kl,k'l'} = \langle \varphi_k(1) \varphi_l(2) | \hat{w}^\dagger_{12} \hat{w}_{12} | \varphi_{k'}(1) \varphi_{l'}(2) \rangle, \tag{26}$$

and where $\hat{P}^{rs}_{pq}$ symmetrizes with respect to permutations of the electron indices in the following manner:

$$\hat{P}^{rs}_{pq} A^{rs}_{pq} = A^{rs}_{pq} + A^{sr}_{qp}. \tag{27}$$

The matrix elements

$$\left\langle \begin{matrix} \overline{kl} \\ ij \end{matrix} \right| \hat{\tau}^{ab}_{i'j'} | \mathrm{HF} \rangle$$

and

$$\left\langle \begin{matrix} \overline{ab} \\ ij \end{matrix} \right| \hat{\tau}^{kl}_{i'j'} | \mathrm{HF} \rangle$$

vanish not only in *Ansatz* 1 but also in *Ansatz* 2 by virtue of choosing the projection operator as in Eq. (12). Note that no approximations or truncations are invoked up to this point, except that we restrict the operator $\hat{T}$ to contain only single and double excitations, which defines the CCSD-R12 model, and that we use the generalized Brillouin condition.

Let us now turn to the CC2 model.[30] In the doubles equations for this model, the similarity transformation of the fluctuation potential $\hat{\Phi}$ is restricted to $\hat{T}_1$, that is, $\exp(-\hat{T}) \hat{\Phi} \exp(\hat{T})$ in Eqs. (17) and (18) is replaced by $\tilde{\hat{\Phi}} = \exp(-\hat{T}_1) \hat{\Phi} \exp(\hat{T}_1)$,

$$\Omega^{\text{CC2}}_{\mu_2} = \langle \mu_2 | [\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\hat{\Phi}} | \mathrm{HF} \rangle = 0, \tag{28}$$

$$\Omega^{\text{CC2}}_{\mu_{2'}} = \langle \mu_{2'} | [\hat{f}, \hat{T}_2 + \hat{T}_{2'}] + \tilde{\hat{\Phi}} | \mathrm{HF} \rangle = 0. \tag{29}$$

We note that the matrix elements $\langle \mu_2 | [\hat{f}, \hat{T}_{2'}] | \mathrm{HF} \rangle$ and $\langle \mu_{2'} | [\hat{f}, \hat{T}_2] | \mathrm{HF} \rangle$ vanish in *Ansatz* 1. These are the terms that couple the two sets of doubles equations. In *Ansatz* 2, these matrix elements are small but not zero.

C. CC2-R12 excitation energies

In the coupled-cluster response theory, excitation energies are obtained[42] as eigenvalues,

$$\mathbf{AR} = \omega \mathbf{SR}, \tag{30}$$

of the Jacobi matrix $\mathbf{A}$ defined as the first partial derivative of the vector function Ω_{μ_i} with respect to the cluster amplitudes t_{ν_j},

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TABLE I. Detailed expressions for the **V** intermediates in *Ansätze* 1 and 2. Two-electron Coulomb integrals are denoted as $g_{rs}^{pq}=\langle\varphi_r(1)\varphi_s(2)|1/r_{12}|\varphi_p(1)\varphi_q(2)\rangle$, integrals over the interelectronic distance as $r_{rs}^{pq}=\langle\varphi_r(1)\varphi_s(2)|r_{12}|\varphi_p(1)\varphi_q(2)\rangle$, and overlap integrals as S_{pq}; for the definition of the similarity transformed basis functions $\tilde{\varphi}_i$ and $\tilde{\varphi}_a$ see Eqs. (45) and (46).

Ansatz 1	*Ansatz* 2
$\tilde{V}_{kl}^{(1),ij}=\delta_{ik}\delta_{jl}-\hat{P}_{ij}^{kl}\Sigma_{pq'}r_{kl}^{pq'}\tilde{g}_{pq'}^{ij}+\Sigma_{pq}r_{kl}^{pq}\tilde{g}_{pq}^{ij}$	$\tilde{V}_{kl}^{(2),ij}=\delta_{ik}\delta_{jl}-\hat{P}_{ij}^{kl}\Sigma_{mq'}r_{kl}^{\bar{m}q'}\tilde{g}_{mq'}^{ij}+\Sigma_{mn}r_{kl}^{\bar{m}\bar{n}}\tilde{g}_{mn}^{ij}-\Sigma_{ab}r_{kl}^{ab}\tilde{g}_{\bar{a}\bar{b}}^{ij}$
$(V^{\dagger})_{\bar{a}m}^{(1),kl}=S_{\bar{a}k}\delta_{lm}-\Sigma_{pq'}r_{pq'}^{kl}g_{\bar{a}m}^{pq'}-\Sigma_{pq'}r_{pq'}^{lk}g_{m\bar{a}}^{pq'}+\Sigma_{pq}r_{pq}^{kl}g_{\bar{a}m}^{pq}$	$(V^{\dagger})_{\bar{a}m}^{(2),kl}=S_{\bar{a}k}\delta_{lm}-\Sigma_{mq'}r_{mq'}^{kl}g_{\bar{a}m}^{mq'}-\Sigma_{mq'}r_{mq'}^{lk}g_{m\bar{a}}^{mq'}+\Sigma_{mn}r_{mn}^{kl}g_{\bar{a}m}^{mn}-\Sigma_{cd}r_{cd}^{kl}g_{\bar{a}m}^{cd}$

$$A_{\mu_i\nu_j}=\frac{\partial\Omega_{\mu_i}}{\partial t_{\nu_j}}. \tag{31}$$

The metric **S** is defined by

$$S_{\mu_i\nu_j}=\langle\mu_i|\hat{\tau}_{\nu_j}|\mathrm{HF}\rangle; \tag{32}$$

detailed expressions for the different sub-blocks of **S** have been given in Eqs. (23)–(25). **S** can for CC2-R12 and CCSD-R12 be arranged as

$$S_{\mu_i\nu_j}=\begin{pmatrix}1 & 0 & 0\\ 0 & 1 & 0\\ 0 & 0 & S_{\mu_{2'}\nu_{2'}}\end{pmatrix}. \tag{33}$$

Note that the off-diagonal sub-blocks $S_{\mu_2\nu_{2'}}$ and $S_{\mu_{2'}\nu_2}$ vanish both in *Ansatz* 1 and in *Ansatz* 2 in its present form.

The R12 part of the product **SR** can be described with the help of the overlap matrix **X** of the MP2-R12 theory as

$$\sum_{i'j'mn}S_{ikjl,i'mj'n}R_{mn}^{i'j'}=\sum_{mn}X_{kl,mn}R_{mn}^{ij}, \tag{34}$$

with $X_{kl,mn}$ defined in Eq. (26). R_{mn}^{ij} denotes the R12 excitation component of a trial vector. The Jacobian **A** can for non-approximated coupled-cluster models be written as[40]

$$A_{\mu_i\nu_j}=\langle\mu_i|\exp(-\hat{T})[\hat{H},\hat{\tau}_{\nu_j}]\exp(\hat{T})|\mathrm{HF}\rangle; \tag{35}$$

for CC2-R12, the Jacobian takes the form

$$A_{\mu_i\nu_j}=\begin{pmatrix}\langle\mu_1|[\tilde{\tilde{H}},\hat{\tau}_{\nu_1}]+[[\tilde{\tilde{H}},\hat{\tau}_{\nu_1}],\hat{T}_2+\hat{T}_{2'}]|\mathrm{HF}\rangle & \langle\mu_1|[\tilde{\tilde{\Phi}},\hat{\tau}_{\nu_2}]|\mathrm{HF}\rangle & \langle\mu_1|[\tilde{\tilde{\Phi}},\hat{\tau}_{\nu_{2'}}]|\mathrm{HF}\rangle\\ \langle\mu_2|[\tilde{\tilde{\Phi}},\hat{\tau}_{\nu_1}]|\mathrm{HF}\rangle & \varepsilon_{\nu_2}\delta_{\mu_2\nu_2} & \langle\mu_2|[\hat{f},\hat{\tau}_{\nu_{2'}}]|\mathrm{HF}\rangle\\ \langle\mu_{2'}|[\tilde{\tilde{\Phi}},\hat{\tau}_{\nu_1}]|\mathrm{HF}\rangle & \langle\mu_{2'}|[\hat{f},\hat{\tau}_{\nu_2}]|\mathrm{HF}\rangle & \langle\mu_{2'}|[\hat{f},\hat{\tau}_{\nu_{2'}}]|\mathrm{HF}\rangle\end{pmatrix}, \tag{36}$$

with

$$\tilde{\tilde{H}}=\exp(-\hat{T}_1)\hat{H}\exp(\hat{T}_1) \tag{37}$$

and ε_{ν_2} equal to the difference of the four orbital energies involved in the double excitation. Note that the matrix elements $\langle\mu_2|[\hat{f},\hat{\tau}_{\nu_{2'}}]|\mathrm{HF}\rangle$ and $\langle\mu_{2'}|[\hat{f},\hat{\tau}_{\nu_2}]|\mathrm{HF}\rangle$ vanish for *Ansatz* 1 and are very small for *Ansatz* 2 in its present form.

D. Working equations

The working equations for the conventional CCSD and CC2 models have been described in the literature in several places. In particular, for the closed-shell case and for the operators and the projection manifolds used here, the expressions for the cluster equations and the Jacobi matrix can be found in Refs. 30, 32, and 33. We shall in the present article focus on the additional R12 contributions in the CC2-R12 model. For the doubles part of the cluster equations, these are

$$\left\langle\begin{matrix}\overline{ab}\\ ij\end{matrix}\right|[\hat{f},\hat{T}_{2'}]|\mathrm{HF}\rangle=\sum_{kl}C_{ab,kl}^{(ij)}c_{kl}^{ij}, \tag{38}$$

$$\left\langle\begin{matrix}\overline{kl}\\ ij\end{matrix}\right|[\hat{f},\hat{T}_2]||\mathrm{HF}\rangle=\sum_{ab}C_{kl,ab}^{(ij)}t_{ab}^{ij}, \tag{39}$$

with

$$C_{ab,kl}^{(ij)}=\langle\varphi_a(1)\varphi_b(2)|(\hat{f}_1+\hat{f}_2-\varepsilon_i-\varepsilon_j)\hat{w}_{12}|\varphi_k(1)\varphi_l(2)\rangle \tag{40}$$

and

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$$\left\langle \begin{matrix} \bar{kl} \\ ij \end{matrix} \right| [\hat{f},\hat{T}_{2'}]||\mathrm{HF}\rangle = \sum_{mn} B^{(ij)}_{kl,mn} c^{ij}_{mn}, \tag{41}$$

with

$$B^{(ij)}_{kl,mn} = \langle \varphi_k(1)\varphi_l(2)| \times \hat{w}^{\dagger}_{12}(\hat{f}_1+\hat{f}_2-\varepsilon_i-\varepsilon_j)\hat{w}_{12}|\varphi_m(1)\varphi_n(2)\rangle, \tag{42}$$

where the matrix **C** vanishes for *Ansatz* 1. These terms are known from MP2-R12 theory and their implementation has been discussed in detail in Ref. 36. We note here only that the resolution-of-the-identity approximation with an auxiliary basis set (ABS) is used to evaluate the three-electron integrals and that detailed expressions for **C** and **B** depend on the so-called standard approximations employed. Depending on the *Ansatz* used, the generalized and/or extended Brillouin conditions are employed. For the generalized Brillouin condition (GBC, $f^i_\alpha = f^\alpha_i = 0$) it is assumed that the occupied orbitals are eigenfunctions of the Fock operator. For the extended Brillouin condition (EBC, $f^a_\alpha = f^\alpha_a = 0$, with α in the complementary space) it is assumed that the orbital space is closed under the Fock operator. Both Brillouin conditions are assumed to be satisfied for *Ansatz* 1 while for *Ansatz* 2 only the GBC is employed.

In addition to the matrix elements known from MP2-R12 theory, we need for the R12 doubles equations also

$$\tilde{V}^{ij}_{kl} = \left\langle \begin{matrix} \bar{kl} \\ ij \end{matrix} \right| \tilde{\hat{\Phi}}|\mathrm{HF}\rangle = \langle \varphi_k(1)\varphi_l(2)|\hat{w}^{\dagger}_{12}\exp(-\hat{T}_1)\frac{1}{r_{12}} \times \exp(\hat{T}_1)|\varphi_i(1)\varphi_j(2)\rangle. \tag{43}$$

For the singles equations, we need to compute the contribution,

$$\left\langle \begin{matrix} \bar{a} \\ i \end{matrix} \right| [\tilde{\hat{\Phi}},\hat{T}_{2'}]|\mathrm{HF}\rangle = \sum_{klm}(2c^{im}_{kl}-c^{mi}_{kl})\langle\varphi_a(1)\varphi_m(2)|(1-\hat{T}_1)\frac{1}{r_{12}}\hat{w}_{12}|\varphi_k(1)\varphi_l(2)\rangle - \sum_{mnkl}(2c^{lk}_{mn}-c^{kl}_{mn})\langle\varphi_m(1)\varphi_n(2)\varphi_a(3)|\frac{1}{r_{12}}(1+\hat{T}_1)\hat{w}_{23}|\varphi_i(1)\varphi_l(2)\varphi_k(3)\rangle + \sum_{kmn}(2c^{ik}_{mn}-c^{ki}_{mn})\langle\varphi_a(1)\varphi_m(2)|\tilde{\hat{f}}_2\hat{w}_{12}|\varphi_k(1)\varphi_l(2)\rangle, \tag{44}$$

in addition to the terms of conventional CC2 or CCSD. $\tilde{\hat{f}}$ is a Fock operator computed from the modified density matrix $\rho(1,2)=2\Sigma_i\varphi^*_i(1)\tilde{\varphi}_i(2)$. If one introduces the similarity transformed basis,

$$\tilde{\varphi}_i = \varphi_i + \sum_a \varphi_a t^i_a, \tag{45}$$

$$\tilde{\varphi}_a = \varphi_a - \sum_i \varphi_i t^i_a, \tag{46}$$

to account for the contributions of $\hat{T}_1$ already in the integral transformation, the matrix element in the first term of Eq. (44) as well as $\tilde{V}^{ij}_{kl}$ in Eq. (43) can straightforwardly be evaluated similar to the V^{ij}_{kl} intermediate in MP2-R12, inserting, in particular, in the same way the ABS approximation (see Appendix). Detailed expressions for *Ansätze* 1 and 2 are given in Table I. The **V** intermediates are in the CC-R12 theory as in the MP2-R12 theory of particular importance since they are the Coulomb matrix elements between a product of two orbitals and a R12 pair function. The **B** matrix and the **V** intermediates are all what is needed for *Ansatz* 1 to implement the CC2-R12 vector function, since the second and third terms in Eq. (44) vanish for this *Ansatz*. For *Ansatz* 2 we implemented the matrix elements appearing in these two terms employing the ABS approximation as

$$-\sum_\beta w^{mn}_{a\beta}\tilde{g}^{i\beta}_{lk} \overset{\mathrm{ABS}}{\approx} -\sum_{p'} r^{mn}_{ap'}\left(\tilde{g}^{ip}_{kl}-\sum_p \tilde{g}^{ip}_{kl}S_{pp'}\right), \tag{47}$$

$$\sum_\beta w^{mn}_{a\beta}\tilde{f}^{k}_{\beta} \overset{\mathrm{ABS}}{\underset{\mathrm{GBC}}{\approx}} \sum_{p'} r^{mn}_{ap'}\left[\sum_{cl}(2g^{p'c}_{kl}-g^{p'c}_{lk})t^l_c - \sum_p\sum_{cl}(2g^{pc}_{kl}-g^{pc}_{lk})t^l_c S_{pp'}\right], \tag{48}$$

where we used the generalized Brillouin condition ($f^k_\beta = f^\beta_k = 0$) and a Schmidt orthogonalization to ensure that the auxiliary basis $\{\varphi_{p'}\}$ is orthogonal on the orbital space $\{\varphi_p\}$. All terms needed for the CC2-R12 vector functions of the *Ansätze* 1 and 2 are now available.

We shall next focus on the working equations for excitation energies. The eigenvalue problem of Eq. (30) is solved iteratively using a direct technique which avoids an explicit construction of the matrices **A** and **S**. It requires the implementation of the linear transformations **AR** and **SR**. Expressions for the latter have been given above in Eqs. (33)–(36). The expressions for **AR** can be derived straightforwardly from those for the vector function using Eq. (31). In particular, all terms which depend on the R12 and the conventional double excitation parts of the trial vector, R^{ij}_{kl} and R^{ij}_{ab} are obtained simply by replacing in the respective expressions for the vector function the doubles cluster amplitudes by the

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TABLE II. Detailed expressions for additional intermediates used to evaluate the transformation with the Jacobi matrix in *Ansätze* 1 and 2. For the notation used for the two-electron integrals, see the caption of Table I. Expressions for the intermediates $(V^\dagger)^{(2),kl}_{\bar{a}m}$ are obtained from those given in Table I for the $(V^\dagger)^{(2),kl}_{\bar{a}m}$. The orbitals $\bar{\varphi}_a$ are defined in Eq. (50).

Ansatz 1	*Ansatz* 2
$\bar{V}^{(1),ij}_{kl} = -\hat{P}^{kl}_{ij}\Sigma_{pq'} r^{pq'}_{kl}(g^{\bar{i}\bar{j}}_{pq'} + g^{\bar{i}\bar{j}}_{pq'}) + \Sigma_{pq} r^{pq}_{kl}(g^{\bar{i}\bar{j}}_{pq} + g^{\bar{i}\bar{j}}_{pq})$	$\bar{V}^{(2),ij}_{kl} = -\hat{P}^{kl}_{ij}\Sigma_{mq'}[r^{\bar{m}q'}_{kl} g^{\bar{i}\bar{j}}_{mq'} + r^{\bar{m}q'}_{kl}(g^{\bar{i}\bar{j}}_{mq'} + g^{\bar{i}\bar{j}}_{mq'})]$ $+ \hat{P}^{kl}_{ij}\Sigma_{mn}(r^{\bar{m}\bar{n}}_{kl} g^{\bar{i}\bar{j}}_{mn} + r^{\bar{m}\bar{n}}_{kl} g^{\bar{i}\bar{j}}_{mn}) - \hat{P}^{kl}_{ij}\Sigma_{ab} r^{ab}_{kl}(g^{\bar{i}\bar{j}}_{\bar{a}\bar{b}} + g^{\bar{i}\bar{j}}_{\bar{a}\bar{b}})$
	$\bar{f}_{kp'} = \Sigma_{cl}(2g^{p'c}_{kl} - g^{p'c}_{lk}) R^l_c - \Sigma_p \Sigma_{cl}(2g^{pc}_{kl} - g^{pc}_{lk}) R^l_c S_{pp'}$

doubles components of the trial vector. Somewhat more involved are the contributions that depend on the single excitation part of the trial vector R^i_a. The single excitation cluster amplitudes have mostly been accounted for by using the similarity transformed orbitals defined in Eqs. (45) and (46). Thus, the derivatives of the **V** intermediates, the integrals $g^{\bar{i}p'}_{kl}$ and $g^{\bar{i}p}_{kl}$, and the matrix $\bar{f}$ needed for the linear transformation **AR** are most conveniently evaluated by introducing orbitals transformed with the single excitation part of the trial vector:

$$\bar{\varphi}_i = \sum_a \varphi_a R^i_a, \tag{49}$$

$$\bar{\varphi}_a = -\sum_i \varphi_i R^i_a. \tag{50}$$

Detailed expressions for the new $\bar{\mathbf{V}}$ intermediates and the modified Fock matrix $\bar{f}^k_{p'}$ obtained thereby are given in Table II. The expressions for the CC2-R12 vector function and the linear transformations of the Jacobi and metric matrices discussed above have been implemented in the coupled-cluster program,[30,32,33] which is part of the DALTON program package.[39]

The sub-block $\langle \mu_{2'} | [\hat{f}, \hat{\tau}_{\nu_{2'}}] | \mathrm{HF} \rangle$, which we shall denote **B** for short, is a positive-definite matrix. However, if the approximations introduced into the R12 theory are inaccurate, for example, when a too small orbital basis or a too small auxiliary basis is used, it can happen in a practical calculation that this matrix has one or more negative eigenvalues. This is a very serious problem in a calculation of excitation energies, of course, yielding completely wrong results. In the calculations, one must ensure, for example, by enlarging the basis sets, that **B** is indeed a positive-definite matrix.

III. COMPUTATIONAL COSTS

The CC2-R12 model is an iterative method. In each iteration the residue of the cluster equations (i.e., the vector function) is evaluated and is used to update the singles-and-doubles and R12 doubles amplitudes until convergence is reached. A CC-R12 calculation is most conveniently started with a MP2-R12 calculation which gives as a side product all the integrals over the $\hat{w}_{12}$ operator needed later on, as well as all three-electron integrals needed to construct the matrix **B** and for *Ansatz* 2 also the matrix **C** on the fly. It provides also the initial guess for the amplitudes c^{ij}_{kl} and we calculate at this step a **V** intermediate with one atomic-orbital index from which $(V^\dagger)^{kl}_{\bar{a}m}$ can be obtained later on by a one-index transformation.

In the following n denotes the number of occupied orbitals and N and N' stand for the size of, respectively, the atomic orbital and auxiliary basis sets. The most expensive step in the iterative solution of the cluster equations is the evaluation of the three-electron integrals for the intermediate $\tilde{\mathbf{V}}$ which scales with $n^4N(N+N')$ for *Ansatz* 1 and with $n^4(N^2+nN')$ for *Ansatz* 2. We note at this point that for *Ansatz* 1 this $\mathcal{N}^6$ step could be avoided during the iterative solution of the cluster equations as described in Ref. 25 for CCSD-R12, if an additional intermediate is calculated in advance with n^2N^4 costs. For CC2-R12 we avoid in the present implementation any steps scaling worse than n^3N^3 and iterative steps scaling worse than $n^4N(N+N')$. The terms involving the matrices **B** and **C** scale as n^6 and n^4N^2, respectively.

Due to three-electron integrals needed in explicitly correlated methods, CC2-R12 calculations are more expensive than conventional CC2 calculations, for which the computational costs scale with nN^4. However, this is mainly a problem for second-order methods as CC2 and MP2. R12 calculations will not be significantly more expensive at higher-order coupled-cluster levels. A main perspective of the present work lies in its future extension to methods such as CCSD and CC3. Compared to the coupled-cluster singles-and-doubles model CCSD, which scales with n^2N^4 and n^3N^3 in each iteration, the CCSD(R12) model (of which the iterative R12 part scales as n^4N^2) has already proven to be an efficient approach for ground-state energy calculations. Although the scaling of the CC2-R12 method is unfavorable in comparison with the conventional CC2 method, the R12 terms in higher-order methods such as CCSD(R12) or CCSD-R12 do not require terms that scale worse than those already present in the conventional CCSD model (n^2N^4).

IV. COMPUTATIONAL DETAILS

All CC2-R12 calculations were carried out in the standard approximation B of the R12 theory,[36] in which all integrals are evaluated. The results were obtained with the DALTON program[39] using aug-cc-pV*X*Z basis sets[43–45] for the orbital basis and the 19*s*14*p*8*d*6*f*4*g*3*h*2*i* basis (9*s*6*p*4*d*3*f*2*g* for H) of Ref. 36 for the auxiliary basis. The calculations were carried out at experimental bond lengths (r_e values) taken from Ref. 46 for BH, CO, N_2, and BF, and the frozen-core approximation was used for the 1*s* orbitals. The frozen-core approximation was not employed in the calculations on the atoms Be and Ne.

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TABLE III. Calculated vertical $^1P(2p \leftarrow 2s)$ excitation energies of Be with *Ansatz* 2 and approximation B (in eV), using a $20s17p14d11f8g5h$ orbital and auxiliary basis set (almost identical results are obtained with *Ansatz* 1).

Basis	CC2	CC2-R12
sp	5.541	5.696
spd	5.207	5.267
spdf	5.145	5.174
spdfg	5.126	5.143
spdfgh	5.119	5.130
Estimated limit	5.109	

TABLE IV. Calculated vertical $^1P(3s \leftarrow 2p)$ excitation energies of Ne with *Ansätze* 1 and 2 and approximation B (in eV), using a $20s14p11d9f7g5h3i$ orbital and $32s24p18d15f12g9h6i$ auxiliary basis set.

Basis	CC2	A1	A2
sp	15.808	16.683	16.673
spd	16.030	16.232	16.351
spdf	16.137	16.219	16.292
spdfg	16.215	16.258	16.288
spdfgh	16.244	16.275	16.286
spdfghi	16.257	16.283	16.285
Estimated limit	16.279		

The CC2-R12 calculations on Be were carried out using a $20s17p14d11f8g5h$ basis set that was used both as orbital and as auxiliary basis. This basis was constructed from an uncontracted $18s$ Partridge3 basis[43] by adding two diffuse s functions and by adding polarization functions with exponents generated from the formula[47]

$$\eta_l = \eta_s \frac{2l+3}{5}, \tag{51}$$

where l is the angular momentum quantum number of the polarization functions, η_l are their exponents and η_s the exponents of the corresponding set of most diffuse s functions. For Ne, we used a $20s14p11d9f7g5h3i$ orbital and a $32s24p18d15f12g9h6i$ auxiliary basis set.[36,37]

Extrapolations to the basis set limit were attempted using the formula[48]

$$E_\infty = \frac{(X^3 E_X - Y^3 E_Y)}{(X^3 - Y^3)}, \tag{52}$$

where E_X and E_Y are the excitation energies obtained in the basis sets with cardinal numbers X and Y, respectively. (For the Be and Ne basis sets $L_{\max}+1$ is used as the cardinal number.) This formula has proven to be useful for ground-state correlation energies, but it is not yet clear how well it applies to excitation energies. We nevertheless use it here to obtain at least some estimate of the basis set limit for the calculated CC2 excitation energies. We choose $X=5$ and $Y=6$ for the extrapolation, assuming that the uncorrelated contribution to the excitation energy is almost converged for such large basis sets. For Ne, we even use $X=6$ and $Y=7$.

V. RESULTS AND DISCUSSION

A. Atoms

The calculated CC2-R12 excitation energies for *Ansätze* 1 and 2 for Ne and Be are listed in Tables III and IV. The conventional CC2 results are included for comparison.

For Be, the excitation energies for the $^1P(2p \leftarrow 2s)$ transition are investigated using a single basis both as auxiliary basis and as orbital basis. The CC2-R12 excitation energies for *Ansätze* 1 and 2 are almost identical in this case. The operators $\hat{w}_{12}$ of Eqs. (8) and (12) are identical when the auxiliary basis equals the orbital basis, and one would expect identical results. However, small and in this case negligible differences occur due to the different manner in which the standard approximations are implemented in both *Ansätze*.

For all basis sets the CC2-R12 excitation energies are slightly larger than the corresponding conventional CC2 re-

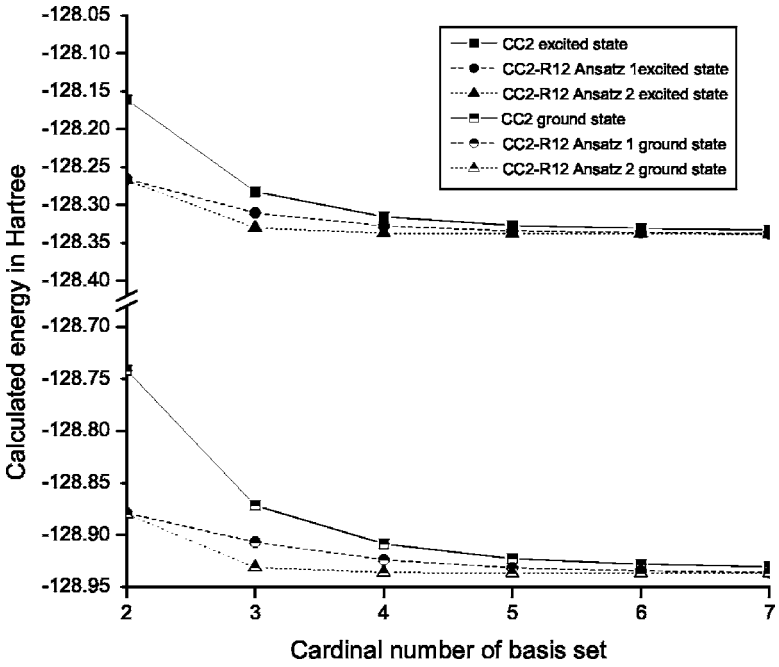


FIG. 1. Calculated energies (in E_h) of the ground and excited states of Ne.

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TABLE V. Calculated vertical excitation energies of BH with *Ansätze* 1 and 2 and approximation B (in eV), using an *spdfghi* auxiliary basis set.

	$B\ ^1\Sigma^+$			$A\ ^1\Pi$		
Basis	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	6.393	6.494	6.505	2.866	2.985	3.033
aug-cc-pVTZ	6.444	6.491	6.490	2.834	2.888	2.899
aug-cc-pVQZ	6.465	6.491	6.492	2.823	2.852	2.856
aug-cc-pV5Z	6.469	6.486	6.486	2.819	2.838	2.839
aug-cc-pV6Z	6.472	6.486	6.483	2.817	2.834	2.831
Estimated limit	6.476			2.814		

sults. Nevertheless a clear convergence of the CC2-R12 results to the basis set limit is observed, although the convergence is found to be slower than in the conventional CC2 model. The difference between the CC2-R12 and the extrapolated basis set limit is 0.021 eV in the largest basis, while without the R12 *Ansatz* the difference is 0.01 eV.

For Ne we calculated the excitation energies for the $^1P(3s \leftarrow 2p)$ transition. A very large auxiliary basis is used in this case to make sure that the errors introduced by the ABS approximation are negligible. We observe that the results for *Ansatz* 2 are always slightly larger than those for *Ansatz* 1, and the results for both *Ansätze* are larger than the conventional CC2 results. All *Ansätze* converge to the same limit and the convergence of *Ansatz* 2 is faster than for *Ansatz* 1. In the largest basis, the difference between CC2-R12 and the estimated basis set limit is only 0.004 eV, which shows that the limit is almost reached with an *spdfghi* basis set. Without the R12 *Ansatz* the remaining basis set error is in this case about three times larger.

In Fig. 1, the basis set convergence of the total energy of the ground and excited states of Ne is given in comparison with conventional CC2. Both CC2-R12 *Ansätze* converge to the same limit. In this example, we observe a similar convergence for the excited state as for the ground state.

B. Molecules

The results for the four investigated molecules are presented in Tables V–VII. For BH, the $B\ ^1\Sigma^+$ and $A\ ^1\Pi$ transitions have been studied. With conventional CC2 the excitation energies for the $^1\Sigma^+$ state increase with increasing basis set, whereas the CC2-R12 excitation energies decrease for both *Ansätze*. The CC2-R12 excitation energies are again larger than their CC2 counterparts. The transition energies for the $^1\Pi$ state decrease with increasing cardinal number.

The convergence of the excitation energies is in this case for the Σ^+ state faster with CC2-R12, although the result in the largest basis deviates by 0.01 eV from the estimated limit. However, as noted above, this limit might be inaccurate. For the $^1\Pi$ state the convergence is faster without R12. At each step in this basis set hierarchy the variation of the CC2-R12 results is considerably larger than for the conventional CC2 results.

Also for the BF molecule (Table VI), the CC2-R12 excitation energies for *Ansätze* 1 and 2 are close to each other, with the results for *Ansatz* 2 slightly larger than those for *Ansatz* 1. The conventional CC2 results decrease smoothly with increasing basis set for the $^1\Pi$ state, but for the two $^1\Sigma^+$ states the convergence is somewhat irregular and the extrapolated limits are probably not reliable for the latter two states. Again, the R12 results seem to converge somewhat slower than the results of the calculations without R12.

For CO (Table VII), the conventional CC2 energies decrease from the triple zeta basis set onwards for all investigated transitions, which are the two lowest $^1\Sigma^+$ states and the first $^1\Pi$ transition. The CC2-R12 results decrease monotonically from double to hextuple zeta, as for all the cases investigated so far. The deviations from the estimated limits for the largest basis set are 0.08 eV for $B\ ^1\Sigma^+$, 0.05 eV for $C\ ^1\Sigma^+$, and 0.01 eV for $^1\Pi$.

For the excitation into the $^1\Sigma^+$ states, the deviations are larger than those obtained in the previous examples, but in these cases also the conventional CC2 results in the aug-cc-pV6Z basis differ still by 0.06 and 0.03 eV from the extrapolated limits. The slower convergence for these states is probably related to their partial Rydberg character.

The results for N_2 are given in Table VIII. The CC2 results converge rapidly in this case and no fluctuations are observed. The extrapolated limits are considered to be trust-

TABLE VI. Calculated vertical excitation energies of BF with *Ansätze* 1 and 2 and approximation B (in eV), using an *spdfghi* auxiliary basis set.

	$B\ ^1\Sigma^+$			$C\ ^1\Sigma^+$			$A\ ^1\Pi$		
Basis	CC2	A1	A2	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	8.212	8.309	8.342	8.618	8.709	8.737	6.521	6.594	6.659
aug-cc-pVTZ	8.268	8.313	8.316	8.655	8.701	8.701	6.457	6.484	6.502
aug-cc-pVQZ	8.274	8.299	8.299	8.642	8.668	8.668	6.437	6.453	6.456
aug-cc-pV5Z	8.271	8.288	8.287	8.631	8.648	8.648	6.428	6.437	6.438
aug-cc-pV6Z	8.247	8.261		8.603	8.617		6.424	6.429	
Estimated limit							6.419		

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TABLE VII. Calculated vertical excitation energies of CO with *Ansätze* 1 and 2 and approximation B (in eV), using an *spdfghi* auxiliary basis set.

	$B\,^1\Sigma^+$			$C\,^1\Sigma^+$			$A\,^1\Pi$		
Basis	CC2	A1	A2	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	11.086	11.213	11.268	11.624	11.755	11.807	8.772	8.867	8.970
aug-cc-pVTZ	11.103	11.163	11.178	11.622	11.685	11.699	8.687	8.725	8.761
aug-cc-pVQZ	11.067	11.100	11.108	11.595	11.629	11.638	8.668	8.687	8.699
aug-cc-pV5Z	11.007	11.030	11.033	11.544	11.568	11.571	8.662	8.675	8.679
aug-cc-pV6Z	10.965	10.984		11.519	11.539		8.660	8.669	
Estimated limit	10.907			11.485			8.657		

worthy, since they are within 0.001 eV of the conventional CC2 results obtained in the hextuple zeta basis set. We see again the same trends as for the other molecules for the CC2-R12 results: *Ansätze* 1 and 2 yield results which are very close to each other, with the values for *Ansatz* 2 always slightly larger than those for *Ansatz* 1, and again CC2-R12 seems to converge slower than conventional CC2. In the largest basis, the deviations from the estimated basis set limits amount still to 0.01–0.02 eV.

C. Analysis of R12 contributions to excitation energies

For ground-state energies, the R12 *Ansatz* is known to greatly improve the convergence to the basis set limit when the dominant source of error is dynamic correlation. To understand the unexpected slow convergence found for excitation energies, we need to look closely at the individual correlation contributions to the latter. However, for excitation energies the separation into an uncorrelated and a correlated contribution is problematic, since in contrast to ground states there is for excited states no undisputable noncorrelated reference model as Hartree-Fock and even the character of the wave function (i.e., the most important Slater determinants) can change upon the inclusion of dynamic correlation.

Therefore, we introduce for analysis of the coupled-cluster response results for excitation energies a decomposition into characteristic contributions, which is motivated from the structure of the Jacobian in Eqs. (35) and (36). For CC2 and CCSD, the excitation energy can (avoiding for notational convenience a separation into conventional and R12 doubles) be written as

$$\omega = \frac{1}{\mathbf{R}^\dagger \mathbf{S} \mathbf{R}} (\mathbf{R}_1^\dagger \mathbf{A}_{11} \mathbf{R}_1 + \mathbf{R}_1^\dagger \mathbf{A}_{12} \mathbf{R}_2 + \mathbf{R}_2^\dagger \mathbf{A}_{21} \mathbf{R}_1 + \mathbf{R}_2^\dagger \mathbf{A}_{22} \mathbf{R}_2). \tag{53}$$

The denominator is only a normalization constant which can be chosen as 1 by appropriate normalization of the eigenvectors $\mathbf{R}$. For single excitation dominated transitions, as investigated in the present study, $\|\mathbf{R}_2\| \ll \|\mathbf{R}_1\|$ and the last two terms (almost) cancel each other because

$$\mathbf{R}_2^\dagger (\mathbf{A}_{21} \mathbf{R}_1 + \mathbf{A}_{22} \mathbf{R}_2) = \omega \mathbf{R}_2^\dagger \mathbf{S}_{22} \mathbf{R}_2 = \mathcal{O}(\|\mathbf{R}_2\|^2) \approx 0, \tag{54}$$

and we can restrict the discussion to the first two terms. Introducing the shorthand notation $\langle R_i| = \Sigma_{\mu_i} \langle \mu_i|$ (with $i=1$, 2), the first term can be split into the two matrix elements $\langle R_1|[\tilde{\hat{H}}, \hat{R}_1]|\mathrm{HF}\rangle$, which can be called a "singles only" term and considered as the uncorrelated value, and $\langle R_1|[[\hat{H}, \hat{T}_2], \hat{R}_1]|\mathrm{HF}\rangle$, which describes the effect of dynamic correlation in the ground state on the excitation energy and is thus usually positive. The second term, the matrix element $\langle R_1|[\tilde{\hat{H}}, \hat{R}_2]|\mathrm{HF}\rangle$, describes a contribution from the differential correlation effects between the ground and the excited state. It is thus usually negative and in most cases of the same order of magnitude as $\langle R_1|[[\hat{H}, \hat{T}_2], \hat{R}_1]|\mathrm{HF}\rangle$. The final results are therefore very sensitive to the balance between these two terms, i.e., between dynamic correlations in the ground- and excited-state wave functions. In CC-R12 one gets for both matrix elements, in addition to the contribution from the conventional doubles, a R12 contribution from the R12 parts of the amplitudes and the trial vector, $T_{2'}$ and $R_{2'}$, respectively.

Detailed results for an analysis of the excitation energies along the above lines are given for three examples, the

TABLE VIII. Calculated vertical excitation energies of N_2 with *Ansätze* 1 and 2 and approximation B (in eV), using an *spdfghi* auxiliary basis set.

	$a'\,^1\Sigma_u^-$			$a\,^1\Pi_g$			$w\,^1\Delta_u$		
Basis	CC2	A1	A2	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	10.486	10.630	10.759	9.569	9.690	9.822	11.016	11.108	11.278
aug-cc-pVTZ	10.377	10.437	10.486	9.481	9.529	9.577	10.918	10.955	11.017
aug-cc-pVQZ	10.371	10.399	10.419	9.467	9.489	9.507	10.909	10.922	10.949
aug-cc-pV5Z	10.373	10.395	10.401	9.465	9.481	9.488	10.907	10.920	10.931
aug-cc-pV6Z	10.374	10.391	10.391	9.465	9.477	9.478	10.907	10.918	10.921
Estimated limit	10.375			9.465			10.907		

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TABLE IX. Analysis of the different CC2-R12 contributions (in meV) to the investigated excitation energies of Be in comparison with CC2.

	$\langle R_1\|[\tilde{\hat{H}},\hat{R}_1]\|\mathrm{HF}\rangle$		$\langle R_1\|[[\hat{H},\hat{T}_2+\hat{T}_{2'}],\hat{R}_1]\|\mathrm{HF}\rangle$		$\langle R_1\|[\tilde{\hat{H}},\hat{R}_2+\hat{R}_{2'}]\|\mathrm{HF}\rangle$	
Basis	CC2	CC2-R12	CC2	CC2-R12	CC2	CC2-R12
sp	4981	4978	735	892	−224	−225
spd	4923	4921	834	894	−671	−672
spdf	4923	4922	865	895	−773	−773
spdfg	4924	4924	878	895	−807	−807
spdfgh	4925	4925	883	895	−821	−821

$^1P(2s\leftarrow 2p)$ transition in Be and the $B\ ^1\Sigma^+$ and $A\ ^1\Pi$ states of BH; similar trends have been found also for the other excited states investigated in the present work.

The results for Be are listed in Table IX. In this case the contribution arising from dynamic correlation in the ground state is of the order of 0.7–0.9 eV, depending on the basis set, and is with CC2-R12 already practically converged in the smallest basis (*sp*), while in conventional CC2 the convergence is considerably slower. However, the largest basis set error and slowest convergence arise in the contribution from the double excitation part of the eigenvector, which has as expected the opposite sign. This contribution remains basically unchanged upon inclusion of the R12 terms. For the $^1P(2s\leftarrow 2p)$ transition of Be, this has a simple explanation: the ground-state configuration of Be is $1s^22s^2$ and since the R12 pair functions are constructed by multiplying all products of occupied orbitals with the correlation factor $\hat{w}_{12}$, there are in this case no pair functions or R12 double excitations with a symmetry appropriate to contribute to this transition. The conventional CC2 results for the excitation energies in Table III only seem to converge faster because of a fortunate cancellation of the basis set errors in the two correlation contributions.

For the $B\ ^1\Sigma^+$ state of BH the situation is different (Table X). In this case the correlation contribution arising from the doubles contribution to the eigenvector converges both with and without the R12 *Ansatz* very quickly and the overall convergence of the excitation energies is dominated by the basis set errors in the singles-only term and the correlation contributions arising from the ground-state cluster amplitudes. Since the errors in the singles-only term are as large as those in the contribution of $\hat{T}_2$, the suppositions for the extrapolation formula [Eq. (52)] might not be given. The limit given in Table V might indeed be inaccurate. Anyway, for the individual contributions we see for this state a slightly better convergence for CC2-R12 than for conventional CC2. For the $A\ ^1\Pi$ state, however, we again find a similar situation as for the $^1P(2s\leftarrow 2p)$ transition of Be: a very fast convergence of the singles-only term and a (in this case almost complete) cancellation of the two correlation contributions (Table XI). Again, CC2-R12 only improves the convergence of the contribution arising from the dynamic correlation in the ground state since the R12 part of the eigenvector vanishes for symmetry reasons. Therefore, the excitation energies are overestimated by CC2-R12 in the small basis sets since the positive contribution of the ground-state amplitudes is included with much higher accuracy than the negative contribution of excited-state doubles.

VI. SUMMARY AND CONCLUSIONS

In this paper, the fundamental equations for the CC-R12 response theory have been derived and implemented for the calculation of excitation energies with the approximate coupled-cluster singles-and-doubles model CC2. This allowed a first application of the coupled-cluster response theory for vertical excitation energies with terms linear in the interelectronic distance r_{12} included in the wave-function *Ansatz*.

After investigating a small set of atoms and molecules, we find that the results we have obtained with the present approach, where the R12 pair functions are chosen as it is standard for ground-state correlation energies, are not always as fast as anticipated. In several cases, CC2-R12 does not give a faster convergence of the excitation energies to the basis set limit than conventional CC2. Furthermore, for both *Ansätze* most CC2-R12 results are larger than the excitation energies calculated without the R12 terms included, in particular, with small basis sets and with *Ansatz* 2.

An analysis of the investigated excitation energies shows

TABLE X. Analysis of the different CC2-R12 contributions (in meV) to the investigated $B\ ^1\Sigma^+$ excitation energies of BH in comparison with CC2.

	$\langle R_1\|[\tilde{\hat{H}},\hat{R}_1]\|\mathrm{HF}\rangle$			$\langle R_1\|[[\hat{H},\hat{T}_2+\hat{T}_{2'}],\hat{R}_1]\|\mathrm{HF}\rangle$			$\langle R_1\|[\tilde{\hat{H}},\hat{R}_2+\hat{R}_{2'}]\|\mathrm{HF}\rangle$		
Basis	CC2	A1	A2	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	6295	6281	6268	884	1001	1040	−970	−976	−983
aug-cc-pVTZ	6214	6207	6201	1044	1099	1107	−1004	−1006	−1009
aug-cc-pVQZ	6188	6184	6182	1099	1129	1132	−1014	−1015	−1016
aug-cc-pV5Z	6171	6169	6168	1120	1139	1140	−1015	−1016	−1016
aug-cc-pV6Z	6164	6162	6162	1130	1146	1144	−1015	−1016	−1016

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TABLE XI. Analysis of the different CC2-R12 contributions (in meV) to the investigated $A\ ^1\Pi$ excitation energies of BH in comparison with CC2.

	$\langle R_1\|[\tilde{\hat{H}},\hat{R}_1]\|\mathrm{HF}\rangle$			$\langle R_1\|[[\hat{H},\hat{T}_2+\hat{T}_{2'}],\hat{R}_1]\|\mathrm{HF}\rangle$			$\langle R_1\|[\tilde{\hat{H}},\hat{R}_2+\hat{R}_{2'}]\|\mathrm{HF}\rangle$		
Basis	CC2	A1	A2	CC2	A1	A2	CC2	A1	A2
aug-cc-pVDZ	2800	2798	2799	1012	1133	1181	−970	−1009	−1009
aug-cc-pVTZ	2803	2802	2802	1181	1237	1247	−1216	−1217	−1217
aug-cc-pVQZ	2803	2802	2802	1239	1268	1272	−1284	−1285	−1285
aug-cc-pV5Z	2802	2802	2801	1261	1280	1282	−1310	−1310	−1310
aug-cc-pV6Z	2802	2802	2802	1271	1287	1285	−1322	−1322	−1322

that, as expected, the description of the singles contributions to excitation energies is usually equally good for conventional CC2 and CC2-R12 with both *Ansätze*. However, from the two dynamical correlation contributions arising from the doubles parts of, respectively, the ground-state amplitudes and the excited-state eigenvector, the R12 *Ansatz* improves in the present approach only the former (positive) contribution considerably, while the latter (negative) contribution is only marginally changed by R12. This unbalanced treatment of the ground- and excited-state contributions to the excitation energies is seen for several of the investigated states and explains the observed slow convergence behavior. Conventional CC2 (and other CC response methods) benefits from a fortunate cancellation of the basis set error in the two terms and therefore appears to converge for excitation energies in most cases faster than if the R12 terms are included. Since *Ansatz* 2 covers an even larger fraction of the (ground state) correlation than *Ansatz* 1, the effects are slightly more pronounced with *Ansatz* 2 than with *Ansatz* 1.

Even though the $^1P(2s \leftarrow 2p)$ transition of Be and the $A\ ^1\Pi$ state of BH analyzed in Sec. V C are two extreme cases as here the R12 doubles part of the eigenvectors *must* vanish for symmetry reasons with the present approach for constructing the R12 pair functions, they clearly show that the reason for the unexpected slow convergence of the excitation energies with CC2-R12 is related to a diminished balance in the two correlation contributions that arise from the ground-state and the excited-state doubles, $\hat{T}_2+\hat{T}_{2'}$ and $\hat{R}_2+\hat{R}_{2'}$. Apparently, the construction of the R12 pair functions from only products of occupied orbitals in Eq. (7) is an efficient choice for the ground-state energies and properties derived as analytic derivatives thereof, but leads in response theory to a bias towards the unperturbed ground state. For excitation energies an accurate description of the differential correlation effects, described in response theory by the doubles part of the eigenvector, is essential. The studied examples made apparent that these are only partially covered with the present scheme, which leads in small basis sets to an overestimation of the excitation energies since the ground state is described with higher accuracy than the excited state.

A possible remedy to the unbalanced treatment of ground- and excited-state correlation effects could be the inclusion of additional pair functions such as $\hat{w}_{12}|\varphi_i(1)\varphi_a(2)\rangle$, where φ_a should be the most important virtual orbitals involved in the investigated transitions. Since the introduction of two inequivalent indices (as i and a) would considerably complicate the implementation, a slightly different but symmetric scheme, where the correlated pair functions are constructed as $\hat{w}_{12}|\varphi_u(1)\varphi_v(2)\rangle$ with φ_u and φ_v taken from a set comprised of occupied and the most important virtual orbitals might be more convenient. Such a scheme is expected to provide a balanced treatment of the ground and excited states, which is not only needed for excitation energies, but also for the calculation of frequency-dependent properties, as polarizabilities and hyperpolarizabilities, within the framework of the CC-R12 response theory. The inclusion of such new pair functions for CC-R12 response methods will be the subject of future work, but preliminary results[49] indicate that they indeed help to improve the convergence of excitation energies. When this problem will be solved, the adaption of the CABS approach[38] and of new correlation factors such as the function $r_{12}\exp(-\gamma r_{12})$ proposed by Tew and Klopper[12] could further improve the performance and computational efficiency of the CC-R12 response methods.

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APPENDIX: INTRODUCTION OF THE ABS APPROXIMATION IN CC-R12

During the derivation of the working equations in Sec. II D the auxiliary basis set approximation (ABS) has been employed several times. Here we give additional information on how the ABS is inserted in detail. Generally, the ABS approximation is introduced as proposed by Klopper and Samson[36] to avoid three-electron integrals, i.e., for *Ansatz* 1 we substitute in the correlation factor,

$$w_{12} = (1 - \hat{P}_1 - \hat{P}_2 + \hat{P}_1\hat{P}_2)r_{12}, \tag{A1}$$

the second and third terms by

$$\hat{P}_1 \rightarrow \hat{P}_1\hat{P}_{2'}, \quad \hat{P}_2 \rightarrow \hat{P}_2\hat{P}_{1'}, \tag{A2}$$

where the projection operators $\hat{P}_{1'}$ and $\hat{P}_{2'}$, defined by

$$\hat{P}_{2'} = \sum_{p'} |\phi_{p'}(2)\rangle\langle\phi_{p'}(2)|, \tag{A3}$$

provide an approximate resolution of the identity in an or-

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thonormal auxiliary basis set $\{\phi_{p'}\}$. For *Ansatz* 2 we follow a similar procedure with $\hat{O}_1$ in place of $\hat{P}_1$. For example, we obtain the following expression for the product $\hat{w}_{12}^{\dagger}(1/r_{12})$ in *Ansatz* 2:

$$\hat{w}_{12}^{\dagger}\frac{1}{r_{12}} \overset{\text{ABS}}{\approx} 1 - r_{12}\hat{O}_1\hat{P}_{2'}\frac{1}{r_{12}} - r_{12}\hat{O}_2\hat{P}_{1'}\frac{1}{r_{12}} + r_{12}\hat{O}_1\hat{O}_2\frac{1}{r_{12}} - r_{12}\hat{V}_1\hat{V}_2\frac{1}{r_{12}}. \tag{A4}$$

In the CC-R12 theory one often encounters operators similarity transformed with either $\exp(\hat{T})$ or $\exp(\hat{T}_1)$, as, e.g., in the intermediate $\tilde{\mathbf{V}}$ in Eq. (43). The latter is defined as the matrix representation of

$$\hat{w}_{12}^{\dagger}\exp(-\hat{T}_1)\frac{1}{r_{12}}\exp(\hat{T}_1) = \hat{w}_{12}^{\dagger}\exp(-\hat{T}_1(1)-\hat{T}_1(2))\frac{1}{r_{12}}\exp(\hat{T}_1(1)+\hat{T}_1(2)), \tag{A5}$$

where we have used that, as any one-electron operator, $\hat{T}_1$ can be expanded as $\hat{T}_1=\Sigma_i\hat{T}_1(i)$, where $\hat{T}_1(i)$ is the contribution which acts on electron i or, to be more specific, $\hat{T}_1(i)$ excites the electron i from an occupied orbital into a virtual orbital. The leftmost operator exponential can in the calculation of matrix elements be accounted for by using for the ket state the similarity transformed basis in Eqs. (45) and (46) as described, e.g., in Ref. 40 and will in the following not be discussed further.

Since the same electron cannot be promoted twice from an occupied to a virtual orbital, $(\hat{T}_1(i))^2$ and all higher powers of $\hat{T}_1(i)$ vanish and thus

$$\hat{w}_{12}^{\dagger}\exp(-\hat{T}_1(1)-\hat{T}_1(2))\frac{1}{r_{12}} = \hat{w}_{12}^{\dagger}(1-\hat{T}_1(1))(1-\hat{T}_1(2))\frac{1}{r_{12}}. \tag{A6}$$

Furthermore, $(1-\hat{P}_i)\hat{T}_1(i)=0$ since $(1-\hat{P}_i)$ projects out any contribution where electron i is in a virtual (or occupied) orbital contained in the basis set. Thus, we have for *Ansatz* 1 the identity

$$\hat{w}_{12}^{\dagger}\exp(-\hat{T}_1(1)-\hat{T}_1(2))\frac{1}{r_{12}} = \hat{w}_{12}^{\dagger}\frac{1}{r_{12}}, \tag{A7}$$

and the ABS approximation can be inserted as described above.

For *Ansatz* 2, however, the projection included in $\hat{w}_{12}$ leads to somewhat more complicated expressions. We first rewrite Eq. (12) as

$$\hat{w}_{12}^{\dagger} = r_{12}[(1-\hat{O}_1)(1-\hat{O}_2)-\hat{V}_1\hat{V}_2]. \tag{A8}$$

For the contribution of the last term in the brackets on the right-hand side to the operator product that appears in the **V** intermediates one obtaines

$$r_{12}\hat{V}_1\hat{V}_2(1-\hat{T}_1(1))(1-\hat{T}_1(2))\frac{1}{r_{12}} = r_{12}\tilde{\hat{V}}_1\tilde{\hat{V}}_2\frac{1}{r_{12}}, \tag{A9}$$

with the modified projection operators defined with the help of the similarity transformed virtual orbitals in Eq. (46) as $\tilde{\hat{V}}_1=\Sigma_a|\varphi_a(1)\rangle\langle\tilde{\varphi}_a(1)|$. Using that $\hat{T}_1(i)\hat{O}_i=\hat{T}_1(i)$ and $\hat{O}_i\hat{T}_1(i)=0$, the contribution from the second term in the brackets in Eq. (A8) can be rewritten as

$$r_{12}(1-\hat{O}_1)(1-\hat{O}_2)(1-\hat{T}_1(1))(1-\hat{T}_1(2))\frac{1}{r_{12}} = r_{12}(1-\tilde{\hat{O}}_1)(1-\tilde{\hat{O}}_2)\frac{1}{r_{12}}, \tag{A10}$$

with $\tilde{\hat{O}}_1=\Sigma_j|\tilde{\varphi}_j(1)\rangle\langle\varphi_j(1)|$, where $\tilde{\varphi}_j$ are the similarity transformed occupied orbitals from Eq. (45). Now the ABS approximation can be introduced in almost the same manner as in MP2-R12 [Eq. (A2)] as

$$r_{12}[1-\tilde{\hat{O}}_1\hat{P}_{2'}-\tilde{\hat{O}}_2\hat{P}_{1'}+\tilde{\hat{O}}_1\tilde{\hat{O}}_2-\tilde{\hat{V}}_1\tilde{\hat{V}}_2]\frac{1}{r_{12}}. \tag{A11}$$

A similar approach leads to the expressions given for the additional **V** intermediates that are used to evaluate the transformation of trial vectors with the Jacobi matrix **A**.

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