Extensions of r_{12} corrections to CC2-R12 for excited states

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As known since about two decades, R12 methods, which include terms linear in the interelectronic distance r_{12} in the wave function, improve substantially the basis set convergence of the ground state correlation energy. In a previous study, however, it was found that the same approach does not give a similar systematic improvement if applied to excited states in the framework of coupled cluster response theory. In the present work, we examine the reason for this behavior and show that the inclusion of additional orbitals in the construction of the r_{12} pair functions leads to an enhanced basis set convergence (and thus a balanced description) also for the excited states. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2335443]

I. INTRODUCTION

It is well known that traditional quantum chemical methods such as configuration interaction (CI), Møller-Plesset perturbation theory through order n (MPn), and coupled cluster theory suffer from the slow convergence of the correlation energy with the basis set size.[1] The reason for this behavior can be found in the deficient description of the Coulomb hole with Slater determinants built from one-electron basis functions. In the past years, it has been shown that so-called explicitly correlated linear r_{12} methods give a significant improvement in this regard, see, for example, Refs. 2–5. Common methods are Møller-Plesset perturbation theory through second order (MP2-R12) (Ref. 6) and coupled cluster singles and doubles (CCSD-R12);[7–9] a newer development is CCSD(R12) as an approximation for CCSD-R12.[10]

The computation of three and four electron integrals, which appear in explicitly correlated methods, can be avoided by resolution of the identity (RI) techniques, thus reducing drastically the costs of R12 methods, which makes them applicable to molecular systems of relevant size. While early implementations used the one-electron molecular orbital (MO) basis set also for the RI, newer codes allow the use of sufficiently large *auxiliary* basis sets for this purpose.[11,12]

Very recently, it was found that straightforward application of the same approach to calculations on excited states within the framework of coupled cluster (CC) response theory often fails to give useful improvements upon ordinary CC calculations.[13] In certain cases, the R12 correction to the wave function is strongly biased to the ground state and does not lead to a faster convergence of the excitation energy with basis set size. Analysis of the excitation energy contributions shows that in these cases the correlation contribution is rapidly convergent for the ground state, but not so for the excited state. The unbalanced description of ground and excited states would heavily restrict the applicability of R12 methods in the framework of response theory not only for excited states but also for (frequency-dependent) properties, which depend on a balanced description of ground and valence excited states.

The reason for the unbalanced description can be traced back to the choice of the r_{12} pair functions, which in MP2-R12 and CC-R12 methods are constructed from the orbitals occupied in the Hartree-Fock reference determinant (see Sec. II). As already suggested in Ref. 13, an appropriate generalization of the r_{12} pair functions might remedy the deficient description of the excited states. In the present work, we derive the changes needed for more general pair functions and show how they perform for ground and excited states.

II. THEORY

In CC-R12 methods the cluster operator $\hat{T}$ is augmented with $\hat{T}_{2'}$, which excites two electrons into an explicitly correlated r_{12} pair function,[10,13]

$$\hat{T}_{2'} = \frac{1}{2}\sum_{ijxy} c_{xy}^{ij}\hat{\tau}_{ixjy}, \tag{1}$$

where c_{xy}^{ij} is the cluster amplitude and $\hat{\tau}_{ixjy}$ the corresponding excitation operator. Throughout the paper we will use the

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convention that $i,j,\ldots$ denote occupied orbitals, $a,b,\ldots$ virtual orbitals, and $p,q,\ldots$ are arbitrary molecular orbitals. The indices $v,w,x,y,\ldots$ are used for the orbitals entering the r_{12} pair functions, which are of the form

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

The correlation operator $\hat{w}_{12}$ can be written in general as

$$\hat{w}_{12} = \hat{Q}_{12} f_{12}, \tag{3}$$

with f_{12} a function depending on the interelectronic distance and $\hat{Q}_{12}$ a projection operator, that can be chosen differently and leads to the so-called *Ansätze* 1 and 2:[11,13,14]

$$\textit{Ansatz 1: } \hat{Q}_{12} = (1-\hat{P}_1)(1-\hat{P}_2), \tag{4}$$

$$\textit{Ansatz 2: } \hat{Q}_{12} = (1-\hat{O}_1)(1-\hat{O}_2) - \hat{V}_1\hat{V}_2, \tag{5}$$

where

$$\hat{P}_1 = \sum_p |\phi_p(1)\rangle\langle\phi_p(1)|, \tag{6}$$

$$\hat{O}_1 = \sum_i |\phi_i(1)\rangle\langle\phi_i(1)|, \tag{7}$$

$$\hat{V}_1 = \sum_a |\phi_a(1)\rangle\langle\phi_a(1)|. \tag{8}$$

Note that we have chosen the formulation of *Ansatz* 2 proposed in Refs. 14 and 15, which ensures orthogonality between the conventional and the R12-double amplitudes and is therefore convenient for CC.

In previous work, ϕ_x and ϕ_y where taken as the (active) occupied orbitals in the Hartree-Fock reference. As already stated in the Introduction, this choice is only apposite for the electronic ground state. However, if we wish to calculate a valence excited state, for example, the r_{12} pair functions must be able to describe the correlation between an electron in an excited (virtual) orbital and those in the occupied orbitals. This can be achieved by introducing additional *virtual* orbitals into the pair functions.

In order to keep the computational costs low, the number of additional orbitals should be small. Therefore, one should for the description of excited valence states (where the unexpected slow convergence of CC-R12 has been encountered) use virtual orbitals that provide a more compact description of the valence space than usually obtained with canonical orbitals—in particular, if basis sets with diffuse orbitals are used, as it is often necessary for accurate excitation energies. In our implementation, the additional r_{12} orbitals are determined before the CC-R12 (or MP2-R12) calculation by diagonalizing the virtual-virtual block of a conventional MP2 density matrix, thus yielding seminatural occupation numbers. Those with the largest occupation numbers are expected to have the greatest effect for inclusion into the additional r_{12} pair functions. After selection of the extra orbitals, the Fock matrix is for computational convenience diagonalized within the subspace of the additional seminatural virtual orbitals and has thus a block structure as shown in Fig. 1. This procedure has the advantage that only minor changes of the existing code were necessary: besides the fact that the number of the orbitals entering the pair functions has changed, the only new contributions are originating from the small off-diagonal nonzero blocks of the Fock matrix. We will therefore in the following only discuss the contributions to the R12 corrections that originate from the Fock operator.

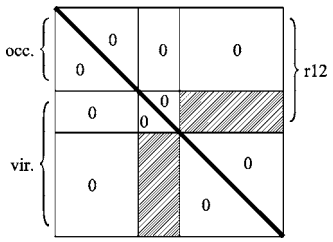


FIG. 1. Scheme of the Fock matrix entering the CC-R12 equations. Note that only the diagonal and the hatched blocks are nonzero.

A. Working equations

Commutators containing the Fock operator $\hat{f}$ appearing in (closed shell single reference) CC-R12 theory are

$$\langle {}^{\overline{ab}}_{ij}|[\hat{f},\hat{T}_{2'}]|\mathrm{HF}\rangle = \sum_{xy} C^{(ij)}_{ab,xy} c^{ij}_{xy}, \tag{9}$$

$$\langle {}^{\overline{xy}}_{ij}|[\hat{f},\hat{T}_{2}]|\mathrm{HF}\rangle = \sum_{ab} C^{(ij)}_{ab,xy} t^{ij}_{ab}, \tag{10}$$

$$\langle {}^{\overline{xy}}_{ij}|[\hat{f},\hat{T}_{2'}]|\mathrm{HF}\rangle = \sum_{vw} B^{(ij)}_{xy,vw} c^{ij}_{vw}, \tag{11}$$

with

$$C^{(ij)}_{ab,xy} = \langle\phi_a(1)\phi_b(2)|(\hat{f}_1+\hat{f}_2-\epsilon_i-\epsilon_j)\hat{w}_{12}|\phi_x(1)\phi_y(2)\rangle, \tag{12}$$

$$B^{(ij)}_{xy,vw} = \langle\phi_x(1)\phi_y(2)|\hat{w}^{\dagger}_{12}(\hat{f}_1+\hat{f}_2-\epsilon_i-\epsilon_j)\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle. \tag{13}$$

The projection manifolds for double excitations are chosen as[16]

$$\langle {}^{\overline{ab}}_{ij}| = \tfrac{1}{6}\langle\mathrm{HF}|(2E^{\dagger}_{ai}E^{\dagger}_{bj} + E^{\dagger}_{aj}E^{\dagger}_{bi}), \tag{14}$$

for ordinary and

$$\langle {}^{\overline{xy}}_{ij}| = \sum_{\alpha\beta} (\hat{w}^{\dagger}_{12})^{\alpha\beta}_{xy} \langle {}^{\overline{\alpha\beta}}_{ij}|, \tag{15}$$

for R12 doubles, where $\langle {}^{\overline{\alpha\beta}}_{ij}|$ is defined analogously to $\langle {}^{\overline{ab}}_{ij}|$, with α and β orbitals from the complementary subspace defined through $\hat{Q}_{12}$, that is, orbitals complementary to the MOs (*Ansatz 1*), or orbitals complementary to the occupied orbitals (*Ansatz 2*) (see Refs. 10 and 13 for details). Following Ref. 11, we rewrite the matrices **C** and **B** as

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$$C_{ab,xy}^{(ij)} = \langle \phi_a(1)\phi_b(2)|[\hat{f}_1+\hat{f}_2,\hat{w}_{12}]|\phi_x(1)\phi_y(2)\rangle + \langle \phi_a(1)\phi_b(2)|\hat{w}_{12}(\hat{f}_1+\hat{f}_2)|\phi_x(1)\phi_y(2)\rangle - (\epsilon_i+\epsilon_j) \times \langle \phi_a(1)\phi_b(2)|\hat{w}_{12}|\phi_x(1)\phi_y(2)\rangle, \tag{16}$$

$$B_{xy,vw}^{(ij)} = \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}[\hat{f}_1+\hat{f}_2,\hat{w}_{12}]|\phi_v(1)\phi_w(2)\rangle + \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|[\hat{w}_{12}^{\dagger},\hat{f}_1+\hat{f}_2]\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle + \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\hat{w}_{12}(\hat{f}_1+\hat{f}_2)|\phi_v(1)\phi_w(2)\rangle + \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|(\hat{f}_1+\hat{f}_2)\hat{w}_{12}^{\dagger}\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle - (\epsilon_i+\epsilon_j) \times \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle. \tag{17}$$

The orbitals ϕ_x, ϕ_y, ϕ_v, and ϕ_w entering the r_{12} pair functions can in the new approach be (1) only occupied orbitals or (2) occupied orbitals augmented with arbitrary virtual orbitals. The implementation of the addends in Eqs. (16) and (17) that contain the commutators $[\hat{f}_1+\hat{f}_2,\hat{w}_{12}]$ and $[\hat{w}_{12}^{\dagger},\hat{f}_1+\hat{f}_2]$ does not assume canonical occupied orbitals and therefore remains unchanged (see Ref. 11 for details). For the other terms containing the Fock operator, we assume in case of occupied orbitals that the generalized Brillouin condition (GBC) is fulfilled, that is, $\hat{f}\phi_i=\epsilon_i\phi_i$.[11] Acting on one of the *additional* virtual orbitals, however, the Fock operator yields (see Fig. 1)

$$\hat{f}\phi_x = \epsilon_x\phi_x + \sum_{a\neq x} f_{ax}\phi_a + \sum_{\alpha} f_{\alpha x}\phi_{\alpha}, \tag{18}$$

where α is (irrespectively of the *Ansatz* for $\hat{Q}_{12}$) an orbital of the space complementary to that spanned by the MO basis. Applying the extended Brillouin condition (EBC), that is, assuming that $f_{\alpha a}=f_{a\alpha}=0$, one obtains the modified expressions

$$C_{ab,xy}^{(ij)} = \langle \phi_a(1)\phi_b(2)|[\hat{f}_1+\hat{f}_2,\hat{w}_{12}]|\phi_x(1)\phi_y(2)\rangle + (\epsilon_x+\epsilon_y-\epsilon_i-\epsilon_j)r_{xy,ab} + \sum_{c\neq x} f_{xc}r_{cy,ab} + \sum_{c\neq y} f_{yc}r_{xc,ab}, \tag{19}$$

where

$$r_{xy,ab} = \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}|\phi_a(1)\phi_b(2)\rangle, \tag{20}$$

as well as

$$B_{xy,vw}^{(ij)} = \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}[\hat{f}_1+\hat{f}_2,\hat{w}_{12}]|\phi_v(1)\phi_w(2)\rangle + \tfrac{1}{2}\langle \phi_x(1)\phi_y(2)|[\hat{w}_{12}^{\dagger},\hat{f}_1+\hat{f}_2]\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle + \tfrac{1}{2}(\epsilon_x+\epsilon_y+\epsilon_v+\epsilon_w-2\epsilon_i-2\epsilon_j)X_{xy,vw} + \tfrac{1}{2}\Big(\sum_{a\neq x} f_{xa}X_{ay,vw} + \sum_{a\neq y} f_{ya}X_{xa,vw} + \sum_{a\neq v} f_{va}X_{xy,aw} + \sum_{a\neq w} f_{wa}X_{xy,va}\Big), \tag{21}$$

where

$$X_{xy,vw} = \langle \phi_x(1)\phi_y(2)|\hat{w}_{12}^{\dagger}\hat{w}_{12}|\phi_v(1)\phi_w(2)\rangle. \tag{22}$$

Note that f_{xa} is zero if $x\in$ occupied orbital space (see Fig. 1). Hence, the original formulation of **C** and **B** (Ref. 11) is recovered if only occupied orbitals are included in the construction of the r_{12} pair functions.

So far, we have made no assumptions concerning the CC-R12 model. The calculations reported in this publication are done as those reported in Ref. 13 using the CC2-R12 level of theory which is defined by the CC2-R12 vector functions,

$$\Omega_{ai} = \langle {}_{i}^{a}|[\hat{f},\hat{T}_1] + \tilde{\hat{\Phi}} + [\tilde{\hat{\Phi}},\hat{T}_2+\hat{T}_{2'}]|\mathrm{HF}\rangle = 0, \tag{23}$$

$$\Omega_{aibj} = \langle {}_{ij}^{\overline{ab}}|[\hat{f},\hat{T}_2+\hat{T}_{2'}] + \tilde{\hat{\Phi}}|\mathrm{HF}\rangle = 0, \tag{24}$$

$$\Omega_{xiyj} = \langle {}_{ij}^{\overline{xy}}|[\hat{f},\hat{T}_2+\hat{T}_{2'}] + \tilde{\hat{\Phi}}|\mathrm{HF}\rangle = 0, \tag{25}$$

with $\hat{\Phi}$ the electron fluctuation potential and

TABLE I. Analysis of the main contributions to the excitation energy of Be (in meV). Values in parentheses are relative to conventional 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-R12+	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+
sp	4981	4978 (−3)	4946 (−35)	735	892 (157)	896 (161)	−224	−225 (−1)	−646 (−422)
spd	4923	4921 (−2)	4930 (7)	834	894 (60)	895 (61)	−671	−672 (−1)	−823 (−152)
spdf	4923	4922 (−1)	4928 (5)	865	895 (30)	895 (30)	−773	−773 (0)	−838 (−65)
spdfg	4924	4924 (0)	4927 (3)	878	895 (17)	895 (17)	−807	−807 (0)	−841 (−34)
spdfgh	4925	4925 (0)	4927 (2)	883	895 (12)	895 (12)	−821	−821 (0)	−842 (−21)

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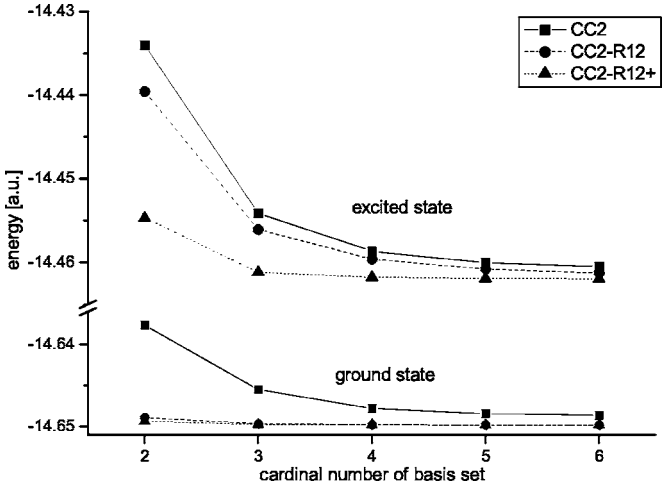


FIG. 2. Basis set dependence of ground and the ^1P $(2p \leftarrow 2s)$ excited state of Be (*Ansatz* 1, approximation B).

$$\tilde{\hat{\Phi}} = \exp(-\hat{T}_1)\hat{\Phi}\exp(\hat{T}_1). \tag{26}$$

For details on the theory and implementation of CC2-R12 excitation energies, the reader is referred to Ref. 13 and the references therein. The equations have been implemented in a local version of the DALTON program suite.[17]

III. COMPUTATIONAL DETAILS

We repeated the CC2-R12 culations of Ref. 13 adding seminatural virtual orbitals to the r_{12} orbital space for *Ansatz* 1, approximation B.[11] The linear r_{12} correlation factor was used. For molecules, the aug-cc-pVXZ basis sets were used, combined with the $19s14p8d6f4g3h2i$ $(9s6p4d3f2g$ for H) auxiliary basis from Ref. 11. Geometries were taken from Ref. 18 (R_{BH}=123.24 pm, R_{NN}=109.76 pm, R_{CO} =112.83 pm, and R_{BF}=126.25 pm). Furthermore, the frozen core approximation was adopted with inactive $1s^2$ orbitals from B to F.

For the atoms beryllium and neon, different basis sets were used [Be: $20s17p14d11f8g5h$ as orbital and auxiliary basis; Ne: $20s14p11d9f7g5h3i$ as orbital basis and $32s24p18d15f12g9h6i$ as auxiliary basis (see Ref. 13)]. These calculations were performed without frozen cores.

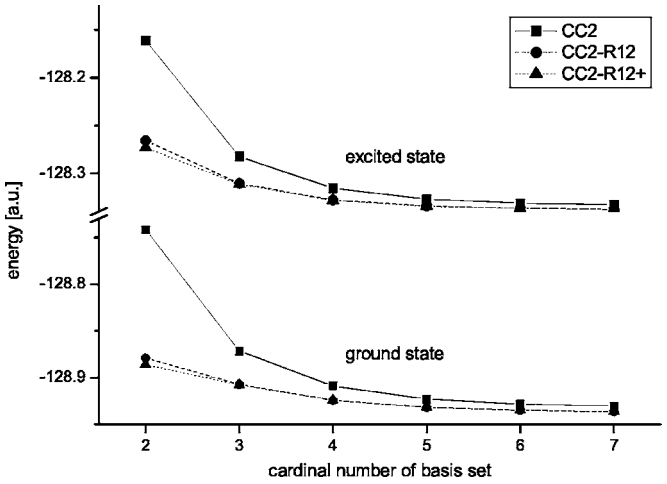


FIG. 3. Basis set dependence of ground and the ^1P $(3s \leftarrow 2p)$ excited state of Ne (*Ansatz* 1, approximation B).

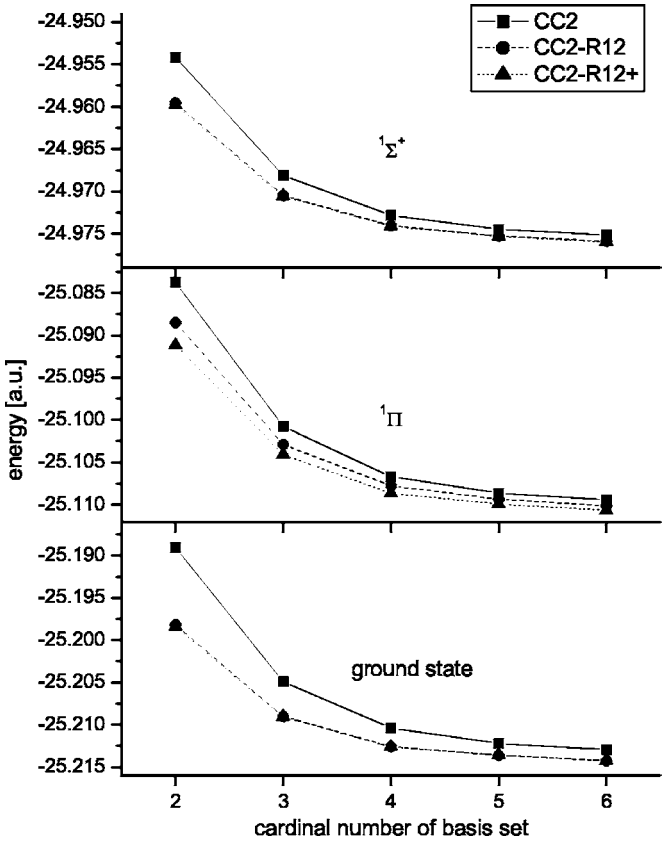


FIG. 4. Basis set dependence of ground and excited states of BH (*Ansatz* 1, approximation B).

IV. RESULTS AND DISCUSSION

A. Atoms

For the beryllium atom, the ^1P $(2p \leftarrow 2s)$ transition is examined. Since only the $1s$ and $2s$ orbitals are occupied in the HF reference, there are no r_{12} pair functions that could contribute to the excited state if one restricts the r_{12} orbitals to the occupied MOs as in the original formulation of CC2-R12 (all r_{12} pair functions of S symmetry). The unbalanced description of the ground and excited state leads to the fact that the excited state remains nearly unaffected by the R12 corrections, and thus, the overall excitation energy is too large. In Table I we analyze the main contributions of the excitation energy as already introduced in Ref. 13: the term $\langle R_1|[\tilde{\hat{H}},\hat{R}_1]|\mathrm{HF}\rangle$ mirrors the uncorrelated value of the excitation energy and the term $\langle R_1|[[\hat{H},\hat{T}_2+\hat{T}_{2'}],\hat{R}_1]|\mathrm{HF}\rangle$ measures the influence of dynamical correlation in the ground state, while $\langle R_1|[\tilde{\hat{H}},\hat{R}_2+\hat{R}_{2'}]|\mathrm{HF}\rangle$ describes the differential correlation effects between ground and excited states. The analysis shows that the first two contributions are quickly convergent for CC2-R12, but not the third one; for conventinal CC2 only the first shows fast convergence, indicating that the basis set is sufficient to describe the excited state qualitatively correct. However, if one includes a set of seminatural virtual p orbitals (indicated by CC2-R12+) also the results for the third

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TABLE II. Analysis of the main contributions to the $A\ ^1\Pi$ excitation energy of BH (in meV). Values in parentheses are relative to conventional 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-R12+	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+
aug-cc-pVDZ	2800	2798 (−2)	2797 (−3)	1012	1133 (121)	1136 (124)	−970	−1009 (−39)	−1077 (−107)
aug-cc-pVTZ	2803	2802 (−1)	2802 (−1)	1181	1237 (56)	1237 (56)	−1216	−1217 (−1)	−1248 (−32)
aug-cc-pVQZ	2803	2802 (−1)	2802 (−1)	1239	1268 (29)	1269 (30)	−1284	−1285 (−1)	−1308 (−24)
aug-cc-pV5Z	2802	2802 (0)	2802 (0)	1261	1280 (19)	1280 (19)	−1310	−1310 (0)	−1326 (−16)
aug-cc-pV6Z	2802	2802 (0)	2802 (0)	1271	1287 (16)	1288 (17)	−1322	−1322 (0)	−1337 (−15)

contribution are substantially improved: both the ground and excited states converge quickly with the cardinal number of the basis set (see Table I and Fig. 2). (Total energies are provided in supplementary material.[19])

Let us now turn to the neon atom, for which we studied the ^1P $(3s \leftarrow 2p)$ transition. In this case, there are occupied orbitals of p as well as of s symmetries, and the excitation energies using either the original form of CC2-R12 or with additional r_{12} orbitals give very similar results, both yielding an improvement over conventional CC2 (Fig. 3). The data shown for CC2-R12+ were obtained by adding one set of s and p orbitals. The energy of ground and excited states is lowered by approximately the same (small) amount. However, the small effect of the additional seminatural orbitals is not very surprising due to the Rydberg character of the excited state, which in turn means that the correlation effects between an electron in the diffuse $3s$ orbital and the remaining electrons are tiny. We also tested to include *canonical* virtual orbitals, which are more diffuse. The results (data not shown) are again very similar to those achieved before, except that the **B** matrix possesses negative eigenvalues in all basis sets employed.

B. Molecules

BH. For BH we investigated the $A\ ^1\Pi$ and $B\ ^1\Sigma^+$ states, corresponding to $\pi \leftarrow \sigma$ (= highest occupied molecular orbital (HOMO)←lowest unoccupied molecular orbital (LUMO)) and $\sigma^* \leftarrow \sigma$ transitions, respectively.

For the calculations with seminatural additional orbitals in the r_{12} space, one orbital of σ, π_x, and π_y symmetries were included, respectively. The results are plotted in Fig. 4 and an analysis of the excitation energies is provided in Tables II and III.

In case of the $A\ ^1\Pi$ state we observe a similiar behavior than for the Be atom described before: While the first term converges nicely for all three methods (CC2, CC2-R12, and CC2-R12+), an overall quick convergence can only be achieved by CC2-R12+, which is not unexpected, because there are no occupied orbitals of suitable symmetry.

For the $B\ ^1\Sigma^+$ state, however, the situation is different. By looking at the analysis given in Table III, one recognizes that the *third* term shows nice convergence for all methods, whereas the other two terms are clearly inferior. This means that even the uncorrelated part of the excitation energy is not converged, making, for example, an extrapolation very questionable. Obviously, the basis sets used are not flexible enough to describe this excitation properly, which is a prerequisite for high accuracy, since the R12 methods cannot correct for this deficiency.

N_2. In case of the nitrogen molecule, three states are under inspection that can be classified as $\pi^* \leftarrow \sigma$ and $\pi^* \leftarrow \pi$ transitions. Therefore, additional r_{12} orbitals of π^* symmetry are expected to have the largest influence on the results, and we included the π_x^* and π_y^* seminatural virtual orbitals with the largest occupation number in the r_{12} active space. Results for the (total) energies are presented in Fig 5.

Note that the results again converge fast to the correct limiting value and that the excited states are affected more by the additional r_{12} orbitals than the ground state. Once more, the conventional excitation energies benefit heavily from the fact that the basis set errors of ground and excited states largely compensate each other, although the total energies are more rapidly convergent using CC-R12 (see supplementary material[19]).

CO and BF. For completeness, vertical excitation energies of CO and BF, which we want to discuss together here, are shown in Tables IV and V. The excitations into $^1\Sigma^+$ states can be classified as $\sigma^* \leftarrow \sigma$ transitions, while those to $^1\Pi$ states are of the $\pi^* \leftarrow \sigma$ type. We observe that by inclusion of additional orbitals nearly only the $^1\Pi$ states are affected. This can be rationalized by the fact that (1) there are no occupied π^* orbitals in either case and (2) that the $^1\Pi$ states are va-

TABLE III. Analysis of the main contributions to the $B\ ^1\Sigma^+$ excitation energy of BH (in meV). Values in parentheses are relative to conventional 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-R12+	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+
aug-cc-pVDZ	6295	6281 (−14)	6281 (−14)	884	1001 (117)	1005 (121)	−970	−976 (−6)	−981 (−11)
aug-cc-pVTZ	6214	6207 (−7)	6207 (−7)	1044	1099 (55)	1100 (56)	−1004	−1006 (−2)	−1008 (−4)
aug-cc-pVQZ	6188	6184 (−4)	6184 (−4)	1099	1129 (30)	1129 (30)	−1014	−1015 (−1)	−1016 (−2)
aug-cc-pV5Z	6171	6169 (−2)	6196 (−2)	1120	1139 (19)	1140 (20)	−1015	−1016 (−1)	−1017 (−2)
aug-cc-pV6Z	6164	6162 (−2)	6162 (−2)	1130	1146 (16)	1146 (16)	−1015	−1016 (−1)	−1017 (−2)

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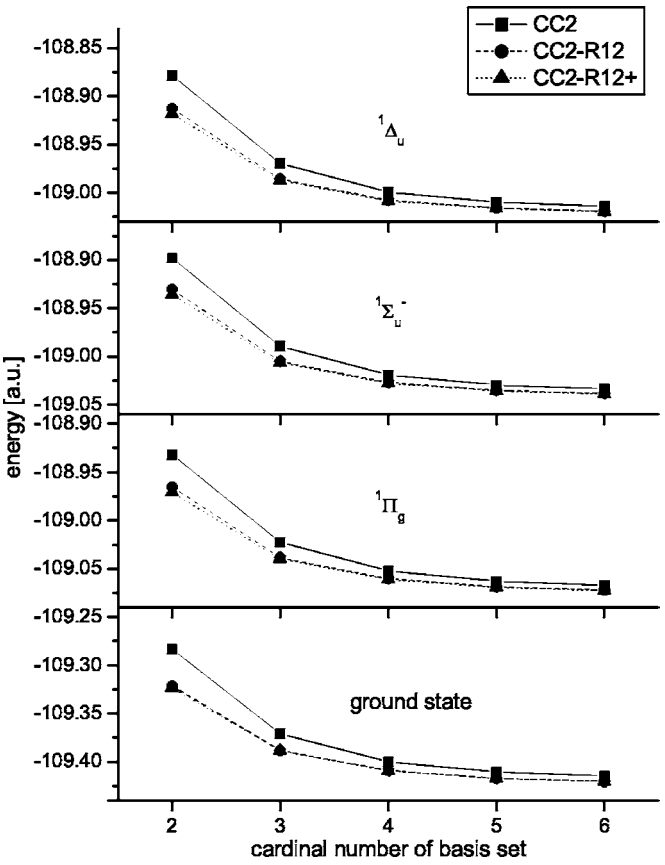


FIG. 5. Basis set dependence of ground and excited states of N_2 (*Ansatz* 1, approximation B).

lence states while the $^1\Sigma^+$ states have largely Rydberg character. Thus, similar arguments as discussed for the ^1P state of Ne apply to these states. In addition, analysis of the excitation energies reveals that the convergence of the one-electron contribution to the excitation energy is only for the $^1\Pi$ states satisfactory, not for the $^1\Sigma^+$ states, similiar to BH. Therefore, we report no estimated limits for $^1\Sigma^+$ states.

C. Remarks on the choice of the additional r_{12} orbitals

The results show that inclusion of additional r_{12} orbitals is mandatory for calculations on excited states if there are no occupied orbitals that can generate r_{12} pair functions of the symmetry of the investigated excited states. Moreover, it will also be important to include the most important (seminatural) virtual orbitals for valence excited states for an accurate description of the correlation between electrons in the virtual orbital and those in the remaining occupied orbitals. For excited states with predominantly Rydberg character the inclusion of additional orbitals is less important.

We also tested the stability of the results if one includes more virtual orbitals than necessary. For example, for N_2 one could include two sets of π^* symmetry, or an additional σ orbital (which would result from occupation numbers as natural choice). In either case, we find that the results remain largely unchanged. Excitation energies differ only in the meV range. This is a very pleasant result, since it means that one can restrict the number of additional orbitals to a small set.

For excited states, it seems important that the r_{12} pair functions are able to correlate (in a balanced way) all strongly interacting electron pairs in the valence region. This will probably also be the case for many other applications of coupled cluster response theory. So far, mostly seminatural orbitals were investigated, since they provide a simple way to select the most important correlating or valence orbitals. Regarding the use of canonical virtual orbitals, we found that they often lead to negative eigenvalues of the matrix **B** (as already mentioned for Ne), which is probably due to a unfavorable interplay between the diffuse character of the low lying virtual orbitals and the RI and EBC approximations applied to compute the matrix **B**. A related problem is that the calculations also tend to become unstable if *too many* (seminatural) virtual orbitals are added to the r_{12} space, since the matrix **B** is often not positive definite anymore.

As the eigenvalues of **B** are an upper bound for the excitation energies, this leads to negative excitation energies and turns the overall results questionable. In the special case of Ne investigated here, the negative eigenvalues of the matrix **B** are related to core excitations and have a magnitude of ca. −5000 eV. Because of the large distance and the vanishing overlap to physical excitations, these can be safely ignored.

V. CONCLUSION AND OUTLOOK

We have shown that augmentation of the orbital space used for the construction of the r_{12} pair functions in CC-R12 with a few (seminatural) virtual orbitals ensures an accurate description also for excited states. Total energies of excited states converge then similarly fast with the cardinal number of the basis set as those of the ground states already do with the original choice of pair functions. The previously found

TABLE IV. Calculated vertical excitation energies of CO in eV (*Ansatz* 1, approximation B).

	$B\,^1\Sigma^+$			$C\,^1\Sigma^+$			$A\,^1\Pi$		
Basis	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+
aug-cc-pVDZ	11.086	11.213	11.213	11.624	11.755	11.756	8.772	8.867	8.800
aug-cc-pVTZ	11.103	11.163	11.162	11.622	11.685	11.685	8.687	8.725	8.702
aug-cc-pVQZ	11.067	11.100	11.100	11.595	11.629	11.630	8.668	8.687	8.670
aug-cc-pV5Z	11.007	11.030	11.029	11.544	11.568	11.568	8.662	8.675	8.664
aug-cc-pV6Z	10.965	10.984	10.983	11.519	11.539	11.538	8.660	8.669	8.660
Estimated limit	⋯			⋯			8.657		

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TABLE V. Calculated vertical excitation energies of BF in eV (*Ansatz* 1, approximation B).

	$B\ ^1\Sigma^+$			$C\ ^1\Sigma^+$			$A\ ^1\Pi$		
Basis	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+	CC2	CC2-R12	CC2-R12+
aug-cc-pVDZ	8.212	8.309	8.310	8.618	8.709	8.713	6.521	6.594	6.547
aug-cc-pVTZ	8.268	8.313	8.313	8.655	8.701	8.701	6.457	6.484	6.472
aug-cc-pVQZ	8.274	8.299	...[a]	8.642	8.668	...[a]	6.437	6.453	...[a]
aug-cc-pV5Z	8.271	8.288	8.287[a]	8.631	8.648	8.648[a]	6.428	6.437	6.428[a]
aug-cc-pV6Z	8.247	8.261	8.260	8.603	8.617	8.617	6.424	6.429	6.421
Estimated limit	...			...			6.419		

[a]The matrix **B** has negative eigenvalues.

imbalance in the treatment of ground and excited states and the resulting slow convergence of excitation energies for excited valence states disappears usually already after inclusion of a few additional seminatural virtual orbitals in the subspace used for the generation of the explicitly correlated r_{12} pair functions. The R12 technique might not much facilitate the calculation of vertical excitation energies, for which the basis set convergence is usually not conditioned by dynamic electron correlation and are, anyway, rarely needed with an accuracy beyond $\approx$0.1 eV. But for accurate potential energy surfaces and equilibrium structures of excited states or frequency-dependent (nonlinear) optical (ground or excited state) properties, where the basis set convergence is determined by dynamic electron correlation, the proposed extension of the orbital set for the construction of the pair functions should offer an efficient possibility to retain the high accuracy of CC-R12 methods known from ground state potentials. Future work will focus on extending the developed CC2-R12 and CCSD(R12) implementations for higher-order response properties such as (hyper-) polarizabilities. Along this line, excited state energies are the first step.

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