



On the one-particle basis set relaxation in R12 based theories

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ARTICLE INFO

Article history:

Received 11 September 2008

Accepted 14 October 2008

Available online 22 October 2008

Keywords:

Explicitly correlated wave function

Hartree–Fock relaxation

R12 theory

Dual basis set

ABSTRACT

When the explicitly correlated R12/F12 theories are applied in combination with smaller one-particle orbital basis sets, the relaxation with respect to the one-particle limit basis becomes relevant. Starting from a single reference Slater determinant in a given computational orbital basis, two ways of coping with this effect within the coupled cluster R12 theory are compared. First is based on the full treatment of the correlation factor including its formal one-particle component, the second is based on a separate exponential expansion in terms of single excitations using a dual Hartree–Fock limit basis. Although, from the computational point of view the first approach would be preferable, its accuracy performance is somewhat worse. Using fixed one-particle basis set relaxed amplitudes in subsequent coupled cluster solution may be recommended.

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1. Introduction

It is well known that at the coalescence of two electrons the exact many-electron wave function must exhibit cusps, i.e. discontinuous first derivatives with respect to the inter-electronic coordinates [1]. However, the widely and most commonly used (multi) Slater determinantal wave functions never fully satisfy this condition. Even in the case of full configuration interaction such wave function behavior can only be achieved with an unreachable complete basis set. The convergence towards this limit is, nevertheless, extremely slow. In fact the error goes as $(L + 1)^{-3}$ [2,3], where L is the highest angular momentum function included in the (main computational) orbital basis (OBS) that should be still saturated for all included angular momenta. Alternatively, though not free from complications, the dependence on the inter-electronic coordinate can be explicitly introduced into the wave function, i.e. one works with explicitly correlated wave functions [4,5].

It was the jubilant Werner Kutzelnigg who more than 20 years ago showed that it was sufficient to introduce terms linear in r_{12} to an orbital product expansion in order to achieve that the error goes as $(L + 1)^{-7}$ rather than $(L + 1)^{-3}$ [6]. The latter work launched a new stream in the treatment of the dynamical electron correlation, since the idea provides an effective combination of the determinantal approach with explicit inclusion of the short range electron correlation. Approaches based on this idea are known as R12 methods. Their pioneering implementations came soon after by Klopper

and Kutzelnigg both in combination with low order perturbation or configuration interaction (CI) based theories [7–11], later followed by a generalization within the coupled cluster (CC) Ansatz [12–14] and multi-reference CI [15,16].

In order to avoid calculation of difficult three- and four-electron integrals constraints known as “the standard approximation” (SA) were introduced [17] and implied that the theories were plausible if the computational orbital basis set was saturated at the level of $3L_{\text{occ}}$, where L_{occ} is the highest angular momentum function involved in the space of occupied orbitals. This automatically means that such a basis contains the Hartree–Fock limit one, and, the generalized Brillouin condition (GBC) holds. Consequently, no single excitations to the space involving the complete orthogonal complement to the OBS (CCBS) were relevant. In addition, the extended Brillouin condition (EBC) was assumed, and the one-particle resolution of identity was considered as fully describable in the OBS.

Smaller OBSs in the R12 calculations were enabled by a separate description of the resolution of identity in terms of an extensive auxiliary set [18]. Since then a lot of development has been accomplished in this field [18–46]. Among others, it was found that the performance has been much improved if the linear r_{12} was in the Ansatz replaced by an alternative correlation factor, in particular the Slater type geminal suggested by Ten-no [25] proved to be superior. Accordingly, with this more general correlation factor a notation “F12” instead of “R12” has been often adopted in recent works. We rely on R12 in this work, even though the consideration below applies to a general correlation factor.

With turning to smaller OBSs, however, the assumption of GBC becomes far from being plausible. Practically, it means that errors introduced by the incompleteness of OBS at one-particle level become relevant and this deficiency must be treated. Quite recently,

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this problem has been addressed but only treated at the level of second order perturbation theory [36,37,40,45,47]. In the context of the coupled cluster theory, two ways of coping with this problem are compared in the following.

2. Theory

Having a single reference determinant $|\Phi\rangle$, the R12 coupled cluster (CC-R12) Ansatz [13] reads

$$|\Psi\rangle = e^{\hat{T}+\hat{\mathcal{R}}}|\Phi\rangle, \tag{1}$$

where $|\Psi\rangle$ is the target – in the limit exact – wave function, \hat{T} is the global excitation operator in the space describable by the OBS, $\hat{T} = \sum_n \hat{T}_n$, and $\hat{\mathcal{R}}$ is a special operator related to the correlation factor $F(r_{12})$. The latter is conveniently expressible in a second quantized normal ordered form with respect to the reference as

$$\hat{\mathcal{R}} = \hat{\mathcal{R}}_1 + \hat{\mathcal{R}}_2 = c_k^i \tilde{\mathcal{R}}_i^k + \frac{1}{4} c_{kl}^{ij} \tilde{\mathcal{R}}_{ij}^{kl}, \tag{2}$$

$$\tilde{\mathcal{R}}_i^k = \bar{F}_{ij}^{kl} \tilde{a}_i^j = F_a^k \tilde{a}_i^a, \tag{3}$$

$$\tilde{\mathcal{R}}_{ij}^{kl} = \frac{1}{2} \bar{F}_{\alpha\beta}^{kl} \tilde{a}_{ij}^{\alpha\beta} + \bar{F}_{ab}^{kl} \tilde{a}_{ij}^{ab}. \tag{4}$$

We use the same tensor notation convention as in Ref. [40] with i, j, k, l and a, b denoting occupied and virtual spin-orbitals within the OBS, respectively, whereas α, β are used to denote the CCBS. Einstein summation convention is applied throughout the paper.

$\hat{\mathcal{R}}_1$ evidently disappears if the computational basis reaches the Hartree–Fock limit. This can be to a great degree of accuracy achieved for small molecular systems. In this spirit the early stage R12 theories assumed the validity of GBC, i.e. that $f_i^z = f_x^z = 0$, with \hat{f} being the Fock operator. If the SA assumptions are at least approximately fulfilled, the $\hat{\mathcal{R}}_1$ could be safely disregarded. As follows from the preceding, the role of $\hat{\mathcal{R}}_1$ is related to the Hartree–Fock relaxation from OBS to the Hartree–Fock limit basis. Such one-particle basis set relaxation has to be treated when one wants to go to smaller OBSs – a permanent desire of quantum chemists.

Instead of following the Ansatz of Eq. (1) with $\hat{\mathcal{R}}_1$, in terms of CCBS, one can formally and with more variational freedom use a different Ansatz for the one-particle relaxation. Due to the Thouless theorem [48], an exact Hartree–Fock determinant (related to the same symmetry as the reference) is expressible as

$$|\Phi_\infty\rangle = e^{\hat{T}_1+\hat{T}_1^{\text{CCBS}}}|\Phi\rangle, \tag{5}$$

where

$$\hat{T}_1 = t_a^i \tilde{a}_i^a; \quad \hat{T}_1^{\text{CCBS}} = t_\alpha^i \tilde{a}_i^\alpha. \tag{6}$$

Similarly as $\hat{\mathcal{R}}_1$, \hat{T}_1^{CCBS} in fact relies to an orthogonal complement within the “mere” Hartree–Fock limit basis set instead of the full CCBS. For simplicity and the purpose of this paper, we used more general notation “CCBS”.

The form of $\hat{\mathcal{R}}_1$ can be understood as externally contracted \hat{T}_1^{CCBS} with individual excitations weighted by the pertinent values of the integrals over the correlation factor. Unlike Ansatz of Eq. (6), that at least in principle leads to an exact Hartree–Fock limit, the solution with $\hat{\mathcal{R}}_1$ is dependent from the choice of the reference.

In our consideration, let us only focus to the Hartree–Fock (HF) orbital relaxation, i.e. two- and more particle terms of $\hat{\mathcal{R}}$ and \hat{T} are ignored. It is clear that Ansatz of Eq. (5) cannot be exactly realized, but one can, approximately, use a finite complementary auxiliary basis set (CABS) [24] that somehow approaches the HF limit, making so the expansion of Eq. (6) realizable. On the other hand, with the Ansatz using $\hat{\mathcal{R}}_1$, one can in principle arrive at a mathematically exact solution, though, even in the limit of CCBS this solution is different from the aforementioned one. Such an “exact” solution

implies introducing three-particle integrals in the final equations. Again, close to the “exact” solution can be accomplished by using large enough CABS. We shall use the latter approximation, and, in the following, α, β, \dots refer to CABS.

The aim of this paper is to compare the performance of both $\hat{\mathcal{R}}_1$ and \hat{T}_1^{CABS} based approaches when applied within the CC and/or second order MP theories. The corresponding energies that reflect the CCBS (or more precisely the CABS) relaxation are given by

$$E_{\mathcal{R}_1} = \langle \Phi | e^{-\hat{T}_1 - \hat{\mathcal{R}}_1} \hat{H} e^{\hat{T}_1 + \hat{\mathcal{R}}_1} | \Phi \rangle, \tag{7}$$

$$E_{\text{CABS}} = \langle \Phi | e^{-\hat{T}_1 - \hat{T}_1^{\text{CABS}}} \hat{H} e^{\hat{T}_1 + \hat{T}_1^{\text{CABS}}} | \Phi \rangle, \tag{8}$$

while the pertinent amplitudes of \hat{T}_1 , $\hat{\mathcal{R}}_1$ and \hat{T}_1^{CABS} result from

$$0 = \langle \Phi | \tilde{a}_a^i e^{-\hat{T}_1 - \hat{\mathcal{R}}_1} \hat{H} e^{\hat{T}_1 + \hat{\mathcal{R}}_1} | \Phi \rangle, \tag{9}$$

$$0 = \langle \Phi | (\tilde{\mathcal{R}}^\dagger)_k^i e^{-\hat{T}_1 - \hat{\mathcal{R}}_1} \hat{H} e^{\hat{T}_1 + \hat{\mathcal{R}}_1} | \Phi \rangle \tag{10}$$

and

$$0 = \langle \Phi | \tilde{a}_a^i e^{-\hat{T}_1 - \hat{T}_1^{\text{CABS}}} \hat{H} e^{\hat{T}_1 + \hat{T}_1^{\text{CABS}}} | \Phi \rangle, \tag{11}$$

$$0 = \langle \Phi | \tilde{a}_\alpha^i e^{-\hat{T}_1 - \hat{T}_1^{\text{CABS}}} \hat{H} e^{\hat{T}_1 + \hat{T}_1^{\text{CABS}}} | \Phi \rangle, \tag{12}$$

respectively. Let us recall that such a CC approach is not variational, hence E_{CABS} may be different from an exact HF energy in the full (unified) OBS + CABS basis. Explicit forms of Eqs. (7), (9) and (10) can be easily extracted from our recent work [40], just by ignoring $\hat{\mathcal{R}}_2$ or \hat{T}_2 containing terms. Explicit forms of Eqs. (8), (11) and (12) are obvious from the conventional CC theory. Mere relaxation contributions to the energies in Eqs. (7) and (8) will be denoted by “ Δ ”.

Solution at the second order perturbation theory is not unique. Depending on the Hamiltonian partitioning one can or does not need to consider the coupling between the OBS and CABS spaces [36]. Let us restrict ourselves to references for which the Brillouin condition is fulfilled within the OBS space. In addition, and without loss of generality, we can assume that the Fock matrix is diagonalized separately in OBS and CABS spaces. Then, the energy contributions of Eqs. (7) and (8) restricted to second order read

$$\Delta E_{\mathcal{R}_1}^{(2)} = f_i^z F_a^i (c^{(1)})_j^i, \tag{13}$$

$$\Delta E_{\text{CABS}}^{(2)} = f_i^z (t^{(1)})_\alpha^i. \tag{14}$$

The aforementioned coupling can only be introduced in the determination of the first order $(c^{(1)})_j^i$ amplitudes via the system of coupled linear equations

$$0 = (f_a^a - f_i^i)(t^{(1)})_a^i + f_a^z F_\alpha^k (c^{(1)})_k^i, \tag{15}$$

$$0 = -F_k^z F_\alpha^z F_\alpha^i (c^{(1)})_i^i + F_k^z F_\alpha^i (c^{(1)})_i^i + F_k^z F_\alpha^i + F_k^z F_\alpha^i (t^{(1)})_a^i, \tag{16}$$

or for $(t^{(1)})_\alpha^i$ via

$$0 = (f_\alpha^z - f_i^i)(t^{(1)})_\alpha^i + f_\alpha^a (t^{(1)})_a^i, \tag{17}$$

$$0 = (f_a^a - f_i^i)(t^{(1)})_a^i + f_\alpha^z (t^{(1)})_\alpha^i. \tag{18}$$

Here, the $f_\alpha^z = f_i^z$ block of the Fock matrix is always treated as the perturbation. If f_α^z block is also treated as a perturbation the couplings disappear from the first order wave function. Contributing to the second order wave function, they only impact the third order energies. Second order energies reflecting the OBS–CABS coupling will be in the Tables denoted by “(c)”, otherwise by “(nc)”. Very recently, the Hartree–Fock corrections based essentially on Eqs. (14), (17) and (18) have been suggested in combination with a simple but fairly efficient approximate CCSD(T)-F12 approach [37], and implemented also for open shell systems at the second order level [45].

Alternatively, the OBS–CABS coupling in Eqs. (17) and (18) can be effectively considered using semicanonical orbitals [50] that

diagonalize the virtual–virtual block of the Fock matrix in the unified OBS + CABS space. This simple correction has been used in the dual basis second order Møller–Plesset (MP) theory [49].

Ansatz of $\hat{\mathcal{H}}$ defined by Eq. (2) leads to methods that provide results invariant with respect to rotations among occupied orbitals. Provided the leading term of the correlation factor is r_{12} , it follows from the cusp relations [1] that when the OBS approaches the complete limit the c -amplitude matrix related to \hat{R}_2 approaches 1/2 times the unit matrix for the singlet part, and 1/4 times the unit matrix for the triplet part, i. e. becomes diagonal. Correspondingly, with final OBSs one can assume (or force) diagonal amplitude matrices and $\hat{\mathcal{H}}$ operators in Eq. (2), but let the variational flexibility to the amplitudes. In fact, such an Ansatz has been used in the early development, but it leads to approaches that are not orbital invariant. On the other hand, this Ansatz results in a computationally much more favorable algorithms and also the numerical stability of the solved system of equations is better, in general. Hence, its use is still actual, especially when combined with localized orbitals. Accordingly, in the following section, we shall also show results using the diagonal restriction on $\hat{\mathcal{H}}_1$. Those are labeled by “(d)”.

Though seemingly Eqs. (15) and (16) are somewhat more complicated than Eqs. (17) and (18), the computational demands within the full MP2-R12 are approximately the same. This is due to the fact that F_{2z}^k can be calculated as a byproduct in MP2-R12 steps related to $\hat{\mathcal{H}}_2$. In both approaches, construction of the CABS–CABS block of the Fock matrix is computationally most expensive, but this block is in parts used in (non-approximated) MP2-R12, anyway. Two-electron repulsion integrals with two CABS functions involved are needed in this case.

In the CCSD-R12 treatment beyond the second order, integrals involving three CABS functions are needed. With \hat{T}_1^{CABS} relaxation, these integrals are used whenever the amplitudes of \hat{T}_1^{CABS} are updated, i. e. usually in each iteration. In fact, if \hat{T}_1^{CABS} would be used without further restrictions in CCSD-R12, only a limited overall computational saving with respect to the full CCSD-R12 calculation using larger basis set would be gained.

With $\hat{\mathcal{H}}_1$ the situation is more favorable, since the c -amplitudes do not contain indices of CABS. Mere amplitude independent matrix elements F_{2z}^k , F_k^z contained in $\hat{\mathcal{H}}_1$ are contracted via the CABS index. Hence, one can in principle precalculate effective intermediate matrices [40], so that integrals involving three CABS indices are only needed in a single step. On the other hand, in most general case of CCSD-R12, these precalculated matrices may bear up to eight indices of OBS, even though mostly involving occupied orbitals. Density fitting or Cholesky decomposition techniques are needed to reduce the unpleasant scaling. From this point of view the $\hat{\mathcal{H}}_1$ based approach leads to more effective algorithm.

Significant savings in CCSD-R12 would be accomplished if either $\hat{\mathcal{H}}_1$ or \hat{T}_1^{CABS} are precalculated via resolving the one-particle basis set relaxation as here and using the resulting amplitudes fixed in the subsequent full CCSD-R12 treatment. Present work should contribute to exploring the potential of such implementations.

3. Results and discussion

The aforementioned approaches treating the one-particle basis set deficiency were tested for F^- and a set of seven small molecules including $\text{CH}_2(^1A_1)$, NH_3 , H_2O , HF , CO , N_2 , and F_2 . Geometries have been taken as in Ref. [40].

For the purpose of this study the OBS + CABS basis does not need to be very close to the Hartree–Fock limit, since the unified OBS + CABS basis set serves as a reference basis for the Hartree–Fock energies. We have thus chosen aug-cc-pCV5Z [51–53] as

our reference from which subsets defined in Table 1 have been used as OBSs. For curiosity, we went even to very small OBSs at the level of minimal bases which would hardly be reliable in highly accurate calculations. Nevertheless, the results may provide useful information to be used in treating large molecular systems with alternative approaches.

Although the OBSs with the given sizes are by far not optimal, we have a well defined reference space and no functions need be removed due to the linear dependencies in the unified basis set.

At the end of this section, results for a larger test example represented by the uracil molecule ($\text{C}_4\text{H}_4\text{N}_2\text{O}_2$) with aug-cc-pV5Z reference basis are given.

In all calculations the linear r_{12} correlation factor was considered.

For F^- only the sp sets are relevant to the ground state Hartree–Fock energy, hence we have separated these results in Table 2. A difference of 0.1 E_h between the HF energy with 3s2p and with the reference basis set reflects how much the occupied orbitals are changed from neutral atom to the anion. Since the basis was optimized on atoms, for them already the 2s1p provides HF energies closely approaching the full reference limit, so that their inclusion into this study was irrelevant.

Total relaxed energies for the hydrates and N_2 , CO , F_2 are given in Tables 3 and 4, respectively. Individual contributions are collected in Tables 5 and 6.

As expected, the fully relaxed E_{CABS} energies with either OBS are very close to the Hartree–Fock reference. Even with the smallest minimal or DZ quality OBSs these relaxed energies are within 10 m E_h of the reference values, while the unrelaxed OBS energies

Table 1

Definitions of the main orbital basis sets (OBS). The complementary auxiliary basis sets (CABS) are defined as complements to OBS within the aug-cc-pCV5Z sets. N denotes the number of basis functions in the pertinent set.

OBS (non-H/H)	Description	N_{OBS}	N_{CABS}
2s1p/1s	(14s8p/5s) \rightarrow [2s1p/1s] ^a	5/1	176/79
3s2p1d/2s1p	[2s1p/1s] + (1s1p1d/1s1p) ^b	14/5	167/75
4s3p2d/3s2p	[2s1p/1s] + (2s2p2d/2s2p) ^b	23/9	158/71
5s4p3d/4s3p	[2s1p/1s] + (3s3p3d/3s3p) ^b	32/13	149/67
6s5p4d/5s4p	[2s1p/1s] + (4s4p4d/4s4p) ^b	41/17	140/63
6s5p4d3f/5s4p3d	[2s1p/1s] + (4s4p4d3f/4s4p3d) ^c	62/32	119/48
cc-pV5Z	[2s1p/1s] + (4s4p4d3f2g1h/4s4p3d2f1g)	91/55	90/25
aug-cc-pCV5Z ^d	[2s1p/1s] + (9s9p8d6f4g2h/5s5p4d3f2g)	181/80	

^a First contracted functions from cc-pV5Z [51].

^b nsnnpd/nsnp uncontracted functions from cc-pV5Z with highest exponents.

^c 3f/3d sets added from cc-pV5Z.

^d Reference basis set.

Table 2

One-particle basis set relaxed energies and their contributions (in E_h) for F^- . Basis sets are defined in Table 1, while only the sp sets need to be considered. Reference aug-cc-pCV5Z energy is $-99.459263 E_h$.

	OBS			
	3s2p	4s3p	5s4p	6s5p
E_{OBS}	-99.369070	-99.380042	-99.412976	-99.455426
$E_{\hat{\mathcal{H}}_1}$	-99.447262	-99.453417	-99.457525	-99.456787
E_{CABS}	-99.469268	-99.466625	-99.462779	-99.459320
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(nc)$	-0.048496	-0.034129	-0.009546	-0.000816
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(nc, d)$	-0.047275	-0.034150	-0.009465	-0.000814
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(c)$	-0.092436	-0.082767	-0.038603	-0.001163
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(c, d)$	-0.091326	-0.082573	-0.038773	-0.001166
$\Delta E_{\hat{\mathcal{H}}_1}$	-0.078192	-0.073375	-0.044548	-0.001361
$\Delta E_{\hat{\mathcal{H}}_1}(d)$	-0.077532	-0.073265	-0.044778	-0.001365
$\Delta E_{\text{CABS}}^{(2)}(nc)$	-0.056508	-0.034956	-0.011493	-0.001704
$\Delta E_{\text{CABS}}^{(2)}(c)$	-0.111556	-0.093135	-0.041382	-0.002682
ΔE_{CABS}	-0.100197	-0.086583	-0.049802	-0.003894

Table 3

One-particle basis set relaxed energies (in E_h) for NH_3 , H_2O , CH_2 and HF. Basis sets are defined in Table 1.

OBS	E_{OBS}	$E_{\hat{\mathcal{H}}_1}$	E_{CABS}
H_2O			
2s1p/1s	-75.913515	-76.025814	-76.071700
3s2p1d/2s1p	-75.999522	-76.030217	-76.069060
4s3p2d/3s2p	-76.025713	-76.046092	-76.067662
5s4p3d/4s3p	-76.051292	-76.060046	-76.067402
6s5p4d/5s4p	-76.065308	-76.066022	-76.067332
6s5p4d3f/5s4p3d	-76.066981	-76.067101	-76.067318
cc-pV5Z	-76.067076	-76.067197	-76.067318
aug-cc-pCV5Z	-76.067318		
NH_3			
2s1p/1s	-56.060632	-56.191566	-56.228744
3s2p1d/2s1p	-56.159262	-56.198241	-56.225955
4s3p2d/3s2p	-56.183322	-56.209095	-56.225012
5s4p3d/4s3p	-56.208918	-56.219967	-56.224864
6s5p4d/5s4p	-56.223447	-56.224139	-56.224887
6s5p4d3f/5s4p3d	-56.224613	-56.224702	-56.224880
cc-pV5Z	-56.224727	-56.224801	-56.224880
aug-cc-pCV5Z	-56.224880		
CH_2			
2s1p/1s	-38.778221	-38.885185	-38.900165
3s2p1d/2s1p	-38.843448	-38.879523	-38.896958
4s3p2d/3s2p	-38.867865	-38.891187	-38.896153
5s4p3d/4s3p	-38.883748	-38.894069	-38.895973
6s5p4d/5s4p	-38.895369	-38.895661	-38.895973
6s5p4d3f/5s4p3d	-38.895832	-38.895854	-38.895971
cc-pV5Z	-38.895876	-38.895901	-38.895971
aug-cc-pCV5Z	-38.895971		
HF			
2s1p/1s	-99.968265	-100.035160	-100.074878
3s2p1d/2s1p	-100.026633	-100.039037	-100.072160
4s3p2d/3s2p	-100.045042	-100.054764	-100.070993
5s4p3d/4s3p	-100.060769	-100.064630	-100.070728
6s5p4d/5s4p	-100.069075	-100.069493	-100.070649
6s5p4d3f/5s4p3d	-100.070428	-100.070493	-100.070638
cc-pV5Z	-100.070488	-100.070563	-100.070638
aug-cc-pCV5Z	-100.070638		

Table 4

One-particle basis set relaxed energies (in E_h) for N_2 , F_2 and CO. Basis sets are defined in Table 1.

OBS	E_{OBS}	$E_{\hat{\mathcal{H}}_1}$	E_{CABS}
N_2			
2s1p	-108.745422	-108.962687	-109.006655
3s2p1d	-108.805204	-108.929266	-109.000412
4s3p2d	-108.925731	-108.980878	-108.993982
5s4p3d	-108.969697	-108.979572	-108.992969
6s5p4d	-108.988980	-108.992713	-108.992953
6s5p4d3f	-108.992317	-108.992732	-108.992925
cc-pV5Z	-108.992678	-108.992810	-108.992924
aug-cc-pCV5Z	-108.992924		
F_2			
2s1p	-198.730424	-198.761767	-198.774238
3s2p1d	-198.732897	-198.763276	-198.774169
4s3p2d	-198.744539	-198.771047	-198.773621
5s4p3d	-198.761174	-198.767379	-198.773183
6s5p4d	-198.769090	-198.772326	-198.773138
6s5p4d3f	-198.772615	-198.772799	-198.773097
cc-pV5Z	-198.772819	-198.772865	-198.773096
aug-cc-pCV5Z	-198.773096		
CO			
2s1p	-112.566460	-112.749311	-112.802372
3s2p1d	-112.639024	-112.733403	-112.796155
4s3p2d	-112.733631	-112.775110	-112.791394
5s4p3d	-112.775025	-112.780798	-112.790666
6s5p4d	-112.787094	-112.790270	-112.790667
6s5p4d3f	-112.790252	-112.790459	-112.790641
cc-pV5Z	-112.790533	-112.790553	-112.790640
aug-cc-pCV5Z	-112.790640		

differ by more than a 100 mE_h . Deviations of the CC relaxed energies from the reference ones are largest for the diatomics with triple bonds and the anion, whereas the differences are much smaller for the investigated hydrates and F_2 . Non-variational nature of the CC approach allows, however, that the relaxed energies are below the “exact” variational limit – the HF energy with the reference basis. With the increasing OBS, the relaxed CC energies converge to this limit, somewhat surprisingly, from below. On the other hand, such a behavior might be related to the pertinent choice of the reference basis and its splitting. Based merely on these results, any generalization of the trends would be premature.

Computationally much less demanding approach with $\hat{\mathcal{H}}_1$ does not provide energies so close to the reference ones; but still about 80% of the relaxation effects is recovered even for the smallest OBSs. Contrary to the previous case, by increasing the OBS size the reference values are approached from above, although, not always smoothly. Paradoxically, with more extensive OBSs when the relaxation effects are very small, the relative performance of the $\hat{\mathcal{H}}_1$ based approach is somewhat deteriorated, apparently due to the lack of variational freedom that is needed to recover the tiny contributions accurately.

From the pragmatic point of view, one would appreciate accurate second order corrections. Indeed, the overall performance is fairly good and, this major contribution usually covers about 90% of the total HF relaxation when the \hat{T}_1^{CABS} approach is used, but the coupling between the OBS and CABS space must be included. Such a result is, of course, not surprising. Knizia and Werner have demonstrated this on a larger set of molecules, including also properties such as ionization potentials and electron affinities [45] for the OBS of aug-cc-pVTZ quality.

Paradoxically, with smaller basis sets, the second order may, and often provides a seemingly more accurate relaxation corrections than the full CC treatment. Such a behavior is, however, hardly a priori predictable. In extreme cases, such as for F^- or N_2 with smaller OBS, the second order correction is even more over-shot than the fully CC relaxed E_{CABS} value.

Relative to the \hat{T}_1^{CABS} counterparts, at the second order level, the $\hat{\mathcal{H}}_1$ based results mimic the situation for the fully relaxed ones, i. e. the corrections are significantly lower. As expected, also here the OBS–CABS coupling is essential.

Non-invariant diagonal $\hat{\mathcal{H}}_1$ approach removes the long range excitations. Indeed, its performance was best for the F^- anion, when all the excitations are localized on a single atom, and the calculated relaxation energies differed by a small fraction of mE_h from their invariant counterparts. For brevity, in Tables 5 and 6 we only show the final non-invariant $\hat{\mathcal{H}}_1$ based relaxation energies, since the trends were the same at the second order level. Here one sees that the diagonal approach may fail badly, especially with smaller OBS.

Table 7 with the results for the much larger uracil molecule just confirm the aforementioned trends.

4. Conclusions

This study has been aimed at a comparison of two approaches to correct for the Hartree–Fock relaxation effects that arise when the explicitly correlated R12 based approaches start from reference determinantal wave functions determined by using basis sets that are not close to the Hartree–Fock limit.

Having such a reference, the first approach follows the R12 Ansatz when the basis set incompleteness is treated via inclusion of terms linearly depending on the inter-electronic coordinate (or more generally a related correlation factor). Within the second quantized formalism with normal ordering related to the reference, the deficiency of the orbital basis at the one-particle level

Table 5Energy contributions (in mE_h) for NH₃, H₂O, CH₂ and HF. Basis sets are defined in Table 1.

OBS	$\Delta E_{\mathcal{R}_1}^{(2)}(nc)$	$\Delta E_{\mathcal{R}_1}^{(2)}(c)$	$\Delta E_{\mathcal{R}_1}$	$\Delta E_{\mathcal{R}_1}(d)$	$\Delta E_{\text{CABS}}^{(2)}(nc)$	$\Delta E_{\text{CABS}}^{(2)}(c)$	ΔE_{CABS}
<i>H₂O</i>							
2s1p/1s	-91.368	-92.589	-112.298	-68.972	-133.943	-136.495	-158.185
3s2p1d/2s1p	-16.314	-25.229	-30.695	-25.295	-46.507	-63.148	-69.538
4s3p2d/3s2p	-8.659	-17.240	-20.379	-16.981	-26.629	-36.742	-41.950
5s4p3d/4s3p	-2.343	-7.074	-8.754	-7.755	-6.806	-13.248	-16.110
6s5p4d/5s4p	-0.596	-0.656	-0.714	-0.502	-1.733	-1.822	-2.024
6s5p4d3f/5s4p3d	-0.072	-0.101	-0.120	-0.115	-0.223	-0.281	-0.337
cc-pV5Z	-0.065	-0.099	-0.121	-0.125	-0.133	-0.192	-0.242
<i>NH₃</i>							
2s1p/1s	-99.212	-101.137	-130.933	-109.883	-140.298	-143.437	-168.111
3s2p1d/2s1p	-21.082	-30.607	-38.979	-37.121	-44.566	-59.415	-66.694
4s3p2d/3s2p	-14.693	-21.290	-25.773	-27.757	-27.420	-36.167	-41.690
5s4p3d/4s3p	-2.871	-8.793	-11.049	-11.674	-6.723	-12.855	-15.946
6s5p4d/5s4p	-0.585	-0.644	-0.693	-0.586	-1.246	-1.302	-1.440
6s5p4d3f/5s4p3d	-0.059	-0.078	-0.088	-0.080	-0.191	-0.230	-0.266
cc-pV5Z	-0.039	-0.060	-0.073	-0.055	-0.086	-0.123	-0.152
<i>CH₂</i>							
2s1p/1s	-84.211	-86.260	-106.964	-81.777	-104.544	-106.394	-121.944
3s2p1d/2s1p	-22.095	-29.669	-36.074	-32.362	-34.123	-46.626	-53.510
4s3p2d/3s2p	-16.136	-20.349	-23.321	-17.496	-19.433	-24.680	-28.288
5s4p3d/4s3p	-3.289	-8.405	-10.321	-8.815	-4.891	-9.883	-12.225
6s5p4d/5s4p	-0.242	-0.265	-0.292	-0.243	-0.501	-0.540	-0.604
6s5p4d3f/5s4p3d	-0.015	-0.019	-0.022	-0.016	-0.097	-0.117	-0.139
cc-pV5Z	-0.016	-0.021	-0.025	-0.015	-0.058	-0.076	-0.095
<i>HF</i>							
2s1p/1s	-57.924	-58.308	-66.895	-11.085	-94.064	-95.585	-106.613
3s2p1d/2s1p	-5.279	-11.146	-12.404	-4.283	-31.350	-42.844	-45.528
4s3p2d/3s2p	-2.834	-8.592	-9.723	-3.824	-17.215	-23.564	-25.951
5s4p3d/4s3p	-1.113	-3.234	-3.861	-1.894	-4.463	-4.499	-9.959
6s5p4d/5s4p	-0.347	-0.380	-0.418	-0.172	-1.371	-1.429	-1.574
6s5p4d3f/5s4p3d	-0.039	-0.055	-0.065	-0.060	-0.143	-0.178	-0.210
cc-pV5Z	-0.044	-0.062	-0.075	-0.076	-0.091	-0.122	-0.150

is reflected via appearance of a formal one-particle part of the correlation factor operator \mathcal{R}_1 .

Second approach is based on a separate treatment of the one-particle basis set relaxation via utilization of the Thouless theorem, i.e. through an exponential type expansion involving (conventional) single excitation operator into the space spanned by a Har-

tree-Fock limit basis. The practical solution in both cases is related to an extended auxiliary one-particle basis set, instead of the Hartree-Fock limit one.

The one-particle basis set relaxation has been treated via non-variational coupled cluster (singles) approach that does not necessarily lead to energies bond from above. However, the calculated

Table 6Energy contributions (in mE_h) for N₂, F₂ and CO. Basis sets are defined in Table 1.

OBS	$\Delta E_{\mathcal{R}_1}^{(2)}(nc)$	$\Delta E_{\mathcal{R}_1}^{(2)}(c)$	$\Delta E_{\mathcal{R}_1}$	$\Delta E_{\mathcal{R}_1}(d)$	$\Delta E_{\text{CABS}}^{(2)}(nc)$	$\Delta E_{\text{CABS}}^{(2)}(c)$	ΔE_{CABS}
<i>N₂</i>							
2s1p	-221.687	-221.761	-217.265	-139.509	-270.969	-271.152	-261.233
3s2p1d	-78.333	-116.276	-124.062	-102.118	-119.486	-190.159	-195.208
4s3p2d	-41.416	-52.434	-55.148	-31.790	-46.257	-63.595	-68.251
5s4p3d	-3.974	-8.311	-9.875	-11.115	-12.452	-20.300	-23.272
6s5p4d	-3.152	-3.417	-3.733	-2.946	-3.440	-3.664	-3.973
6s5p4d3f	-0.303	-0.370	-0.415	-0.182	-0.478	-0.555	-0.608
cc-pV5Z	-0.080	-0.111	-0.131	-0.103	-0.157	-0.210	-0.246
<i>F₂</i>							
2s1p	-29.086	-29.087	-31.343	-14.733	-39.710	-39.715	-43.814
3s2p1d	-21.626	-27.482	-30.378	-16.509	-29.864	-37.148	-41.271
4s3p2d	-13.996	-23.736	-26.509	-12.521	-16.104	-25.984	-29.082
5s4p3d	-2.205	-5.330	-6.206	-4.075	-6.694	-10.430	-12.009
6s5p4d	-2.850	-2.977	-3.236	-2.461	-3.573	-3.728	-4.048
6s5p4d3f	-0.123	-0.168	-0.184	-0.030	-0.333	-0.422	-0.481
cc-pV5Z	-0.020	-0.040	-0.046	-0.023	-0.148	-0.229	-0.277
<i>CO</i>							
2s1p	-181.000	-182.128	-182.852	-102.338	-233.003	-235.464	-235.912
3s2p1d	-62.544	-89.489	-94.378	-66.758	-101.810	-150.739	-157.131
4s3p2d	-31.851	-40.318	-41.479	-20.517	-39.675	-53.290	-57.763
5s4p3d	-2.657	-4.862	-5.773	-5.740	-8.820	-13.608	-15.641
6s5p4d	-2.723	-2.918	-3.176	-2.896	-3.172	-3.305	-3.573
6s5p4d3f	-0.170	-0.194	-0.207	-0.123	-0.338	-0.367	-0.389
cc-pV5Z	-0.014	-0.019	-0.020	-0.013	-0.085	-0.100	-0.108

Table 7

One-particle basis set relaxed energies and their contributions (in E_h) for Uracil. Main orbital basis sets are defined in Table 1, while CABS in this case was constructed as the complement to the OBS within the aug-cc-pV5Z basis.^a

OBS	5s4p3d/4s3p	6s5p4d3f/5s4p3d
E_{OBS}	-412.588630	-412.653599
$E_{\hat{\mathcal{H}}_1}$	-412.619749	-412.654138
E_{CABS}	-412.655393	-412.655259
$E_{Ref.}^a$	-412.655217	-412.655217
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(nc)$	-0.011307	-0.000376
$\Delta E_{\hat{\mathcal{H}}_1}^{(2)}(c)$	-0.026784	-0.000497
$\Delta E_{\hat{\mathcal{H}}_1}$	-0.031119	-0.000539
$\Delta E_{CABS}^{(2)}(nc)$	-0.034348	-0.001379
$\Delta E_{CABS}^{(2)}(c)$	-0.058367	-0.001531
ΔE_{CABS}	-0.066761	-0.001660

^a Geometry N@N; reference energy: -412.655217 E_h taken from [54].

values reflect the pure Hartree–Fock relaxation content within a more general full CCSD-R12.

Our results show that with the first approach the convergence with the increasing OBS towards the limit basis was achieved from above, with the second approach from below. This approach with “conventional” single excitations to CABS leads to a faster convergence since in principle the wave function Ansatz is exact, and the deviations are caused just by the non-variational treatment.

In comparison with the fully relaxed counterparts, the second order corrections are fairly accurate as soon as the OBS–CABS coupling is included. Also the non-invariant diagonal $\hat{\mathcal{H}}_1$ approach is generally unreliable.

Though, concerning the computational complexity the $\hat{\mathcal{H}}_1$ based approach would be preferable in the exact CCSD-R12 treatment, its performance is somewhat worse in comparison with variationally more flexible \hat{T}_1^{CABS} . Unlike $\hat{\mathcal{H}}_1$, however, in full CCSD-R12 treatment the latter requires involvement of two-electron integrals bearing three CABS indices together with several matrix multiplications involving CABS in each iteration, making so the \hat{T}_1^{CABS} relaxation in full CCSD-R12 treatment in attractive. CCSD-R12 using fixed $\hat{\mathcal{H}}_1$ or \hat{T}_1^{CABS} after resolving the one-particle basis set relaxation may be an attractive and feasible alternative.

Acknowledgements

One of us (JN) greatly appreciates the fruitful discussions, collaboration and friendship with Prof. Werner Kutzelnigg, to whom this article is dedicated at the happy occasion of his 75th birthday.

This work has been supported by the Grant Agency of the Ministry of Education of the Slovak Republic and Slovak Academy of Sciences (VEGA Project No. 2/6182) as well as by the Slovak Research and Development Agency (APVV 20-018405, LPP0031-07). This work has benefitted from the Centers of Excellence program of the Slovak Academy of Sciences (COMCHEM, Contract No. II/1/2007).

References

- [1] T. Kato, Commun. Pure Appl. Math. 10 (1957) 15.
- [2] R.N. Hill, J. Chem. Phys. 83 (1985) 1173.
- [3] W. Kutzelnigg, J.D. Morgan III, J. Chem. Phys. 96 (1992) 4484.
- [4] W. Klopper, in: P. v. R. Schleyer, N.L. Allinger, T. Clark, J. Gasteiger, P.A. Kollman, H.F. Schaefer III, P.R. Schreiner (Eds.), Encyclopedia of Computational Chemistry, vol. 4, Wiley, Chichester, 1998, p. 2351.
- [5] J. Rychlewski (Ed.), Explicitly Correlated Wave Functions in Chemistry, Physics, Progress in Theoretical Chemistry, Physics, vol. 13, Kluwer Academic Publisher, Dordrecht, Boston, London, 2003.
- [6] W. Kutzelnigg, Theor. Chim. Acta 68 (1985) 445.
- [7] W. Klopper, W. Kutzelnigg, Chem. Phys. Lett. 134 (1986) 17.
- [8] V. Termath, W. Klopper, W. Kutzelnigg, J. Chem. Phys. 94 (1991) 2002.
- [9] W. Klopper, W. Kutzelnigg, J. Chem. Phys. 94 (1991) 2020.
- [10] W. Klopper, R. Röhse, W. Kutzelnigg, Chem. Phys. Lett. 178 (1991) 455.
- [11] W. Klopper, Chem. Phys. Lett. 186 (1991) 583.
- [12] J. Noga, W. Kutzelnigg, W. Klopper, Chem. Phys. Lett. 199 (1992) 497.
- [13] J. Noga, W. Kutzelnigg, J. Chem. Phys. 101 (1994) 7738.
- [14] J. Noga, W. Kutzelnigg, W. Klopper, in: R.J. Bartlett (Ed.), Recent Advances in Computational Chemistry, vol. 3, World Scientific, Singapore, 1997, p. 1.
- [15] R.J. Gdanitz, Chem. Phys. Lett. 210 (1993) 253.
- [16] R.J. Gdanitz, R. Röhse, Int. J. Quantum Chem. 55 (1995) 147.
- [17] W. Kutzelnigg, W. Klopper, J. Chem. Phys. 94 (1991) 1985.
- [18] W. Klopper, C.C.M. Samson, J. Chem. Phys. 116 (2002) 6397.
- [19] F.R. Manby, J. Chem. Phys. 119 (2003) 4607.
- [20] S. Ten-no, F.R. Manby, J. Chem. Phys. 119 (2003) 5358.
- [21] W. Klopper, J. Chem. Phys. 120 (2004) 10890.
- [22] E.F. Valeev, C.L. Janssen, J. Chem. Phys. 121 (2004) 1214.
- [23] A.J. May, F.R. Manby, J. Chem. Phys. 121 (2004) 4479.
- [24] E.F. Valeev, Chem. Phys. Lett. 395 (2004) 190.
- [25] S. Ten-no, Chem. Phys. Lett. 398 (2004) 56.
- [26] H. Fliegl, W. Klopper, C. Hattig, J. Chem. Phys. 122 (2005) 084107.
- [27] D.P. Tew, W. Klopper, J. Chem. Phys. 123 (2005) 074101.
- [28] S. Kedžuch, M. Milko, J. Noga, Int. J. Quantum Chem. 105 (2005) 929.
- [29] C. Neiss, C. Haettig, W. Klopper, J. Chem. Phys. 124 (2006) 044112.
- [30] H.-J. Werner, F.R. Manby, J. Chem. Phys. 124 (2006) 054114.
- [31] E.F. Valiev, J. Chem. Phys. 125 (2006) 244106.
- [32] W. Klopper, F.R. Manby, S. Ten-no, E.F. Valeev, Int. Rev. Phys. Chem. 25 (2006) 427.
- [33] E. Kordel, C. Villani, W. Klopper, Mol. Phys. 105 (2007) 19.
- [34] S. Ten-no, J. Chem. Phys. 126 (2007) 014108.
- [35] H.-J. Werner, T.B. Adler, F.R. Manby, J. Chem. Phys. 126 (2007) 164101.
- [36] J. Noga, S. Kedžuch, J. Šimunek, J. Chem. Phys. 127 (2007) 034106.
- [37] T.B. Adler, G. Knizia, H.-J. Werner, J. Chem. Phys. 127 (2007) 221106.
- [38] S. Ten-no, Chem. Phys. Lett. 447 (2007) 175.
- [39] D.P. Tew, W. Klopper, C. Hattig, Chem. Phys. Lett. 452 (2008) 326.
- [40] J. Noga, S. Kedžuch, J. Šimunek, S. Ten-no, J. Chem. Phys. 128 (2008) 174103.
- [41] E.F. Valeev, Phys. Chem. Chem. Phys. 10 (2008) 106.
- [42] D. Bokhan, S. Ten-no, J. Noga, Phys. Chem. Chem. Phys. 10 (2008) 3320.
- [43] T. Shiozaki, M. Kamiya, S. Hirata, E.F. Valeev, Phys. Chem. Chem. Phys. 10 (2008) 3358.
- [44] T. Shiozaki, M. Kamiya, S. Hirata, E.F. Valeev, J. Chem. Phys. 129 (2008) 071101.
- [45] G. Knizia, H.-J. Werner, J. Chem. Phys. 128 (2008) 154103.
- [46] E.F. Valeev, T.D. Crawford, J. Chem. Phys. 128 (2008) 244113.
- [47] J. Noga, S. Kedžuch, in: E.A.G. Armour, J. Franz, J. Tennyson (Eds.), Explicitly correlated wave functions, CCP2, Daresbury Laboratory, Warrington, 2006, p. 76.
- [48] D.J. Thouless, Nucl. Phys. 21 (1960) 225.
- [49] K. Wolinski, P. Pulay, J. Chem. Phys. 118 (2003) 9497.
- [50] N.C. Handy, J.A. Pople, M. Head-Gordon, K. Raghavachari, G.W. Trucks, Chem. Phys. Lett. 164 (1989) 185.
- [51] T.H. Dunning Jr., J. Chem. Phys. 90 (1989) 1007.
- [52] R.A. Kendall, T.H. Dunning Jr., R.J. Harrison, J. Chem. Phys. 96 (1992) 6796.
- [53] K.A. Peterson, T.H. Dunning Jr., J. Chem. Phys. 117 (2002) 10548.
- [54] R.A. Bachorz, W. Klopper, J. Chem. Phys. 126 (2007) 85101.