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We propose an explicitly correlated local LCCSD-F12 method in which the basis set incompleteness error as well as the error caused by truncating the virtual orbital space to pair-specific local domains are strongly reduced. This is made possible by including explicitly correlated terms that are orthogonalized only to the pair-specific configuration space. Thus, the contributions of excitations outside the domains are implicitly accounted for by the explicitly correlated terms. It is demonstrated for a set of 54 reactions that the reaction energies computed with the new LCCSD-F12 method and triple-zeta basis sets deviate by at most 2.5 kJ/mol from conventional CCSD complete basis set results (RMS: 0.6 kJ/mol). The local approximations should make it possible to achieve linear scaling of the computational cost with molecular size. © *2009 American Institute of Physics.*
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Standard *ab initio* electronic structure calculations suffer from two major problems: The very steep scaling of the computational cost with increasing molecular size, and the extremely slow convergence of the correlation energy with basis set size. These two problems can be much alleviated by local and explicit correlation methods, respectively.

Local methods[1–3] exploit the short-range character of electron correlation, and using appropriate local orbital basis sets and approximations linear cost scaling can be achieved.[4–7] This has made it possible to perform accurate local coupled-cluster calculations with single and double excitations and a perturbative treatment of triple excitations [LCCSD(T)] for much larger molecules than with the conventional CCSD(T) method. For example, some enzyme reactions have recently been studied using quantum mechanical (QM) and classical molecular mechanics hybrid methods with LCCSD(T) used in the QM part for up to 49 atoms.[8,9] Unfortunately, the local approximations introduce some errors.[10] These are not always easy to control and may affect energy differences such as reaction energies or barrier heights. Therefore, local correlation methods have not yet become widely used standard tools in quantum chemistry.

Explicit correlation methods[11–25] introduce extra terms into the wave function that depend on the interelectronic distance r_{12} and thus allow to describe the wave function cusp for $r_{12} \rightarrow 0$ appropriately. The most successful form of these terms is a simple Slater function, $\hat{F}_{12} = -\gamma^{-1} \exp(-\gamma r_{12})$.[15–17] This leads to a dramatic reduction in the basis set incompleteness errors, and it has recently been demonstrated for many different molecular properties that with such so-called F12 methods highly accurate results can be obtained already with double- or triple-zeta basis sets.[18,23–28]

Recently, we have proposed an explicitly correlated LMP2-F12 method (local second-order Møller–Plesset per-turbation theory) in which the two ideas were combined.[29–31] It was demonstrated that despite the complications due to the explicitly correlated terms nearly linear scaling of the computational cost as a function of molecular size can be achieved.[31] In addition, the explicitly correlated terms not only reduce the basis set incompleteness errors, but for reasons that will be discussed below also eliminate to a large extent the errors caused by the local approximations.[30,31] Thus, the local explicitly correlated LMP2-F12 calculations yielded virtually the same results as the much more expensive canonical MP2-F12 calculations.

In the current work, we extend this approach to the more accurate explicitly correlated LCCSD-F12 method. It will be demonstrated that despite local approximations the same accuracy as with conventional CCSD-F12 methods can be obtained.

In the following, we will first summarize the ansatz for the LCCSD-F12 wave function and briefly outline the local approximations. Currently, the method is simulated by adapting a conventional CCSD-F12 program, in order to see whether the much more tedious fully local implementation is worthwhile. The benchmark calculations presented in the second part of this communication strongly militate in favor of such an implementation.

The LCCSD-F12 wave function is defined as

$$\Psi_{\text{LCCSD-F12}} = \exp(\hat{T}_1 + \hat{T}_2 + \hat{\mathcal{T}}_2)\Phi_{\text{HF}}, \tag{1}$$

where $\hat{T}_1$, $\hat{T}_2$, and $\hat{\mathcal{T}}_2$ are defined as

$$\hat{T}_1 = \sum_i \sum_{a \in [i]} t_a^i \hat{E}_{ai}, \tag{2}$$

$$\hat{T}_2 = \frac{1}{2} \sum_{ij \in P_s} \sum_{a,b \in [ij]} T_{ab}^{ij} \hat{E}_{ai} \hat{E}_{bj}, \tag{3}$$

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$$\hat{T}_2 = \frac{1}{2} \sum_{ij \in P'_s} \sum_{\alpha,\beta} \mathcal{T}^{ij}_{\alpha\beta} \hat{E}_{\alpha i} \hat{E}_{\beta j}, \tag{4}$$

with

$$\mathcal{T}^{ij}_{\alpha\beta} = \sum_{kl} \langle \alpha\beta | \hat{Q}^{ij}_{12} \hat{F}_{12} | kl \rangle T^{ij}_{kl}, \tag{5}$$

$$\hat{F}_{12} = -\frac{1}{\gamma} \exp(-\gamma r_{12}). \tag{6}$$

The operators $\hat{T}_1$, $\hat{T}_2$ describe single and double excitations from occupied into virtual orbitals with amplitudes t^i_a and T^{ij}_{ab}, respectively. Here and in the following, the indices i,j,k,l denote correlated localized molecular orbitals (LMOs) and the indices a,b,c,d denote virtual orbitals. In local correlation methods as first proposed by Pulay and co-worker[1,2] the virtual orbital space is spanned by nonorthogonal projected atomic orbitals (PAOs). These have the property of being local, and are therefore suitable for introducing two kinds of local approximations: First, the summation over orbital pairs ij can be restricted to a list P_s of *strong pairs*, in which the LMOs i and j are spatially close. Second, the excitations into the virtual space can be restricted to subspaces of PAOs that are spatially close to i or j. Such subspaces are denoted *domains*, and $a \in [i]$ denotes a domain of PAOs for single excitations from LMO i. Similarly, the union of the orbital domains $[i]$ and $[j]$ defines a *pair domain*, denoted $[ij]$. For simplicity we will assume in the following that the orbitals a,b in each domain have been orthonormalized. The orthogonal orbitals a,b are then pair specific, but since it should always be obvious from the context to which pair they belong they will not be indexed.

Naturally, the restriction of the excitations to domains leads to a reduction in the computed correlation energy. This is usually denoted as *domain error* and amounts in conventional local correlation calculations to 1%–2% of the correlation energy obtained with the same basis set in a nonlocal calculation. Even though this relative error is rather small, it can cause significant and non-negligible errors when energy differences are computed.

The additional operator $\hat{\mathcal{T}}_2$ contains explicitly correlated terms. These formally include contracted excitations into a complete space of orbitals α,β. As will be discussed and demonstrated in the following, these excitations not only strongly reduce the basis set incompleteness error, but at the same time also eliminate the domain error to a large extent. It should be noted that the complete set of orbitals α,β never occurs in the working equations. In the derivation of the required Hamiltonian matrix elements they lead to resolutions of the identity which can mostly be replaced by new analytical integrals.

The amplitudes T^{ij}_{kl} in the explicitly correlated terms can be determined from the wave function cusp conditions.[32] It can be shown that for singlet and triplet pairs the amplitudes $T^{\pm}_{ij} = T^{ij}_{ij} \pm T^{ij}_{ji}$ should be 1/2 and 1/4, respectively, and all others should be zero. This can be combined to

$$T^{ij}_{kl} = \frac{3}{8} \delta_{ik} \delta_{jl} + \frac{1}{8} \delta_{jk} \delta_{il}. \tag{7}$$

This "fixed amplitude ansatz"[15] will be used throughout the current paper. It is size consistent, unitarily invariant, and has the advantage that no additional amplitude equations have to be solved.

$\hat{Q}^{ij}_{12}$ is a pair-specific strong orthogonality projector[30,31] that keeps the explicitly correlated terms orthogonal to the conventional part of the wave function

$$\hat{Q}^{ij}_{12} = 1 + \sum_{m,n} |mn\rangle\langle mn| - \sum_{m,\alpha} (|m\alpha\rangle\langle m\alpha| + |\alpha m\rangle\langle \alpha m|) - \sum_{c,d \in [ij]} |cd\rangle\langle cd|, \tag{8}$$

where m, c, and α run over the occupied, virtual, and complete orbital spaces, respectively. In practice, the resolution of the identity (RI), i.e., the summation over α, is approximated by the union of the orbital basis and a complementary auxiliary basis set.[16]

The only difference to the ordinary projector used in standard MP2-F12 or CCSD-F12 theory is that the summation in the last term is restricted to the pair domain $c,d \in [ij]$. This is not an additional approximation but is implied by the local ansatz in the conventional part of the wave function. This restriction means that double excitations into virtual orbitals *outside* the domain $[ij]$ are not entirely excluded as in standard local correlation methods, but for a pair ij approximated by

$$\Delta\hat{\mathcal{T}}^{ij}_2 = \sum_{a,b \notin [ij]} \bar{F}^{ij}_{ab} \hat{E}_{ai} \hat{E}_{bj}, \tag{9}$$

where $\bar{F}^{ij}_{ab} = \sum_{kl} T^{ij}_{kl} \langle kl | \hat{F}_{12} | ab \rangle$. This can be viewed as an externally contracted excitation operator, i.e., instead of fully optimized amplitudes T^{ij}_{ab} the fixed matrix elements $\bar{F}^{ij}_{ab}$ are used. In our previous work[30,31] we already demonstrated for LMP2-F12 that these terms correct to a very large extent for the domain error, and are a prerequisite for achieving linear scaling of the computational cost with molecular size.

Our LCCSD-F12 method is based on the CCSD-F12a approximation introduced recently.[24,25] Here we use ansatz 3^*A, which is simpler and more suitable for a linear scaling algorithm[29,31] than the more rigorous ansatz $3C$ which is normally used in the CCSD-F12 method. In approximation 3^*A the extended Brillouin condition is implied and certain exchange terms are neglected. Furthermore, the X-matrix is neglected (for details see Refs. 13 and 23). These approximations have a minor impact on energy differences such as reaction energies (see, e.g., Ref. 23).

The only difference in the LCCSD-F12 and LCCSD amplitude equations are the terms $\Delta R^{ij}_{ab} = \langle ab | r^{-1}_{12} \hat{Q}^{ij}_{12} \hat{F}_{12} | kl \rangle T^{ij}_{kl}$. Neglecting the contributions of the complementary auxiliary orbitals, which have a very small effect,[25] yields explicitly

TABLE I. Correlation energies ($-E_{corr}$ in mH obtained with the VTZ-F12 basis set in comparison to the extrapolated CCSD/CBS[45] values.

Molecule	CCSD	LCCSD	CCSD-F12	LCCSD-F12	CBS
C_2H_4O	611.8	609.2	658.0	658.1	650.4
CH_3CHO	606.1	603.8	651.6	651.7	643.9
C_2H_5OH	648.2	644.3	697.3	697.3	689.1
NH_2CONH_2	851.9	847.6	918.0	917.9	908.2
$HCOOCH_3$	844.7	841.1	911.7	911.7	901.7

$$\Delta R_{ab}^{ij} \approx \bar{W}_{ab}^{ij} - \sum_{m,n} \langle ab|r_{12}^{-1}|mn\rangle \bar{F}_{mn}^{ij}$$

$$- \sum_{m,c} [\langle ab|r_{12}^{-1}|mc\rangle \bar{F}_{mc}^{ij} + \langle ab|r_{12}^{-1}|cm\rangle \bar{F}_{cm}^{ij}]$$

$$- \sum_{c,d\in[ij]} \langle ab|r_{12}^{-1}|cd\rangle \bar{F}_{cd}^{ij} \text{ for } a,b \in [ij], \quad (10)$$

where $\bar{W}_{ab}^{ij} = \sum_{kl}\langle ab|r_{12}^{-1}\hat{F}_{12}|kl\rangle T_{kl}^{ij}$. The first important observation is that in the last term of Eq. (10) the use of the local projector directly leads to linear scaling of the number of two-electron integrals $\langle ab|r_{12}^{-1}|cd\rangle$ over four external orbitals. This is true because $a,b,c,d \in [ij]$ and the number of orbitals in a given domain is independent of the molecular size. In fact, exactly the same integrals are needed in standard LCCSD theory in similar contractions with the amplitudes T_{ab}^{ij}. Thus, both contractions can be done together with virtually no extra cost by forming $T_{cd}^{ij} - \bar{F}_{cd}^{ij}$. The contraction of these quantities with the integrals $\langle ab|r_{12}^{-1}|cd\rangle$ scales linearly with molecular size, without introducing any additional approximations.

Unfortunately, this is not the case for the first and second summations in Eq. (10) which involve integrals over two and three external orbitals. Since these terms arise from the RI approximation they are not automatically affected by the local ansatz. However, in a local orbital basis the integrals $\bar{F}_{mn}^{ij}$, $\bar{F}_{cm}^{ij}$, and $\bar{F}_{mc}^{ij}$ will be small unless m, n, and c are spatially close to the orbitals i and j. Therefore, we can restrict the summations to domains. We have found that it is sufficient to restrict c to the pair domain $[ij]$, and to include in the summation over m,n only the LMOs whose domains overlap with the orbital domains $[i]$ or $[j]$; furthermore, it is possible to neglect the contributions of core orbitals. The errors introduced by these approximations are very small. If these approximations are made, the number of transformed two-electron integrals $\langle ab|r_{12}^{-1}|mn\rangle$ and $\langle ab|r_{12}^{-1}|mc\rangle$ and the computational effort will scale linearly with molecular size. Since the standard LCCSD method also scales linearly,[7] overall linear scaling should be possible.

The new LCCSD-F12 method was implemented in the MOLPRO package[33] of *ab initio* methods. As a first test of its accuracy, the same 21 molecules and 16 reactions as in Refs. 29 and 30 were chosen. The CCSD-F12 and LCCSD-F12 results were compared to standard CCSD calculations in which the complete basis set (CBS) limits were approximated by extrapolating the correlation energies obtained with the aug-cc-pVQZ and aug-cc-pV5Z basis sets[34] using the extrapolation formula[35,36] $E_n = E_{CBS} + An^{-3}$. For all explicitly

correlated calculations the VTZ-F12 AO-basis sets[37] along with the associated RI-basis sets[38] were used. All integrals needed in the LMP2-F12 calculation were obtained by robust density fitting[39] using the aug-cc-pVTZ/MP2FIT fitting basis sets.[40] Density fitting was not used in the Hartree–Fock and LCCSD calculations. The exponent γ of the correlation factor in the explicitly correlated treatments was set to $1.0a_0^{-1}$ throughout. In extensive benchmarks this value was found to be a good compromise for many different properties.[25,27,28]

The occupied orbitals were localized by the method of Pipek and Mezey.[41] The contribution of the most diffuse function of each angular momentum at each atom was eliminated in the localization criterion, which improves the localization.[10] The PAO domains were defined by the Boughton–Pulay procedure[3,42] using a completeness criterion of 0.985. Since the molecules treated here were relatively small, weak pair approximations were not applied. Thus, the difference between CCSD and LCCSD calculations just reflects the domain approximation.

In Table I correlation energies of five typical molecules are presented and compared to the CCSD/CBS reference values. Due to the domain approximation the CCSD and LCCSD correlation energies differ by several millihartrees, while CCSD-F12 and LCCSD-F12 energies differ at most by 0.1 mH. That means that the domain error is almost completely removed due to the implicit effect of the terms in Eq. (9). Comparing the correlation energies with the basis set limits, it can be seen that the results for the conventional methods are far from basis set convergence. The CCSD-F12 and LCCSD-F12 results are much closer to the CBS limits but somewhat overestimate them, an effect which is well known for the approximations F12a and 3*A. The results in Table I were obtained without domain approximations in the first two summations of Eq. (10). If such approximations are made as described above, the LCCSD-F12 energies change by at most 1 mH.

Table II lists the deviations of the correlation contributions to the reaction energies from the estimated CCSD basis set limits. It can be seen that due to the domain error the conventional CCSD and LCCSD results often differ by several kJ/mol (≈ 1 kcal/mol). The basis set incompleteness error of the conventional methods is of the same order of magnitude. In contrast, both kinds of errors are strongly reduced in the explicitly correlated methods: The maximum absolute deviations (MAX) for both CCSD-F12 and LCCSD-F12 are roughly 1 kJ/mol, and the mean absolute deviations (MADs) as well as the root mean square (RMS) deviations of both methods are very similar and less than 0.5 kJ/mol. Overall,

TABLE II. Deviations of the correlation contributions to reaction energies (in kJ/mol) from the CCSD/CBS[45] results. The VTZ-F12 basis set was used in all calculations.

Reaction	CCSD	LCCSD	CCSD-F12	LCCSD-F12[a]	LCCSD-F12[b]
$C_2H_2+H_2 \rightarrow C_2H_4$	0.88	3.09	0.08	0.11	0.23
$C_2H_4+H_2 \rightarrow C_2H_6$	2.40	4.67	0.22	0.03	0.10
$C_2H_6+H_2 \rightarrow 2CH_4$	−0.03	−1.75	−0.22	−0.25	−0.48
$CO+H_2 \rightarrow HCHO$	4.40	5.65	−0.20	−0.25	−0.17
$HCHO+H_2 \rightarrow CH_3OH$	4.29	7.81	0.61	0.77	1.06
$H_2O_2+H_2 \rightarrow 2H_2O$	4.71	4.36	1.03	0.92	0.71
$C_2H_2+H_2O \rightarrow CH_3CHO$	−1.61	0.87	−0.54	−0.58	−0.16
$C_2H_4+H_2O \rightarrow C_2H_5OH$	1.27	5.74	0.05	0.22	0.64
$CH_3CHO+H_2 \rightarrow C_2H_5OH$	3.75	7.96	0.67	0.91	1.04
$CO+NH_3 \rightarrow HCONH_2$	5.63	8.03	0.18	0.16	0.48
$CO+H_2O \rightarrow CO_2+H_2$	0.95	0.22	−0.39	−0.67	−0.49
$HNCO+NH_3 \rightarrow NH_2CONH_2$	3.40	8.09	0.60	0.95	1.17
$CO+CH_3OH \rightarrow HCOOCH_3$	4.42	7.36	0.00	0.11	0.55
$HCOOH+NH_3 \rightarrow HCONH_2+H_2O$	1.09	1.42	0.21	0.29	0.30
$CO+H_2O_2 \rightarrow CO_2+H_2O$	5.67	4.58	0.64	0.25	0.22
$H_2CCO+HCHO \rightarrow C_2H_4O+CO$	−0.23	0.98	0.37	0.41	−0.05
MAX	5.67	8.09	1.03	0.95	1.17
MAD	2.80	4.53	0.38	0.43	0.49
RMS	1.88	2.76	0.27	0.31	0.34

[a]Without domain approximations in the first two summations of Eq. (10).
[b]With domain approximations in the last two summations of Eq. (10), see text.

the errors of the LCCSD-F12 values are approximately one order of magnitude smaller than the corresponding LCCSD ones. This is similar to what has been found earlier for LMP2-F12.[30] If domain approximations in the first two sums of Eq. (10) are made (see above), the MAX, MAD, and RMS values increase only slightly to 1.17, 0.49, and 0.34 kJ/mol, respectively.

In an extended investigation of 54 closed-shell reactions as defined in Ref. 25, which also involve second row atoms, the MAX, MAD, and RMS results for LCCSD-F12 (CCSD-F12) were found to be 2.5 (2.6), 0.7 (0.7), and 0.6 (0.6) kJ/mol. Again these values are not much affected by making domain approximations in the first two summations of Eq. (10): The corresponding LCCSD-F12 values are 3.7, 0.8, and 0.7 kJ/mol, respectively. The additional errors mainly arise from the approximations in the first summation in Eq. (10), and can be much reduced by extending the summation over m, n to include the next shell of neighboring LMOs. This will be investigated in more detail once a fully local implementation is available and larger molecules can be treated.

To conclude, the new LCCSD-F12 method proposed here not only strongly reduces the basis set incompleteness error but also the domain error, and thus eliminates the main problem of conventional local coupled-cluster methods. The development of a fully local implementation of the LCCSD-F12 method is currently under way in our laboratory. It is expected that near linear scaling of the computational effort with molecular size will be achieved. Furthermore, a perturbative local treatment of triple excitations as described in Refs. 5 and 6 will be included, yielding a highly efficient LCCSD(T)-F12 method that can be applied to molecules with 50–100 atoms.

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