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Communication: Improved pair approximations in local coupled-cluster methods

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In local coupled cluster treatments the electron pairs can be classified according to the magnitude of their energy contributions or distances into strong, close, weak, and distant pairs. Different approximations are introduced for the latter three classes. In this communication, an improved simplified treatment of close and weak pairs is proposed, which is based on long-range cancellations of individually slowly decaying contributions in the amplitude equations. Benchmark calculations for correlation, reaction, and activation energies demonstrate that these approximations work extremely well, while pair approximations based on local second-order Møller-Plesset theory can lead to errors that are 1-2 orders of magnitude larger. © *2015 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4916316]

The applicability of local coupled-cluster methods[1–14] to large molecular systems relies on *domain* and *pair* approximations.[1] The domain approximation means that excitations from localized Hartree-Fock (HF) orbitals ϕ_i, ϕ_j are restricted to a spatially close subspace of local virtual orbitals, while the pair approximations introduce simplifications for distant orbital pairs that have only small contributions to the correlation energy. For a long time, it was believed that the domain approximation is most critical. The errors caused by weak pair approximations were assumed to be small since the pair correlation energies decay as r_{ij}^{-6} with the distance r_{ij} between the charge centroids of the local orbitals ϕ_i and ϕ_j. However, this situation has changed, since with modern pair natural orbital (PNO) approaches,[8–25] the domain error can be systematically controlled and made very small (<1 kJ mol^{-1} for relative energies), in particular when explicitly correlated terms are included.[5,12,25,26] On the other hand, we demonstrate in the current work that pair approximations based on local second-order Møller-Plesset theory (LMP2) can lead to very large errors (up to ≈40 kJ mol^{-1} in the present examples) for reaction and activation energies of complex chemical reactions.

Pair approximations are also implicit in fragmentation approaches,[27–37] in which (overlapping) groups of orbitals are correlated independently. These methods rely on the assumption that the contribution of amplitudes that are not included in a fragment has a negligible effect on the computed pair energies.

The problem of pair approximations in local coupled cluster methods is particularly severe if intermolecular interactions are computed. Improved approximations for this case have recently been described by Schütz and co-workers, using a PAO-LCCSD(T) (projected atomic orbital based local coupled-cluster with single, double, and perturbative triple excitations) method.[38,39] Here, we propose similar approximations for a newly developed PNO-LCCSD program and apply them to compute reaction and activation energies of systems in which strong long-range dispersion contributions can be expected. We will demonstrate that with these approximations the errors of reaction and activation energies are below 1 kJ mol^{-1} (relative to a corresponding calculation without pair approximations), while still significant savings of central processing unit (CPU)-time and storage can be achieved.

The orbital pairs ij are divided into 4 classes: *strong*, *close*, *weak*, and *distant*. Different approximations will be applied for these classes. The pairs in each class are selected using PNO-LMP2 pair energies E_{ij}. Pairs with $E_{ij} \geq T_{\text{close}}$ are strong, those with $T_{\text{close}} > E_{ij} \geq T_{\text{weak}}$ are close, those with $T_{\text{weak}} > E_{ij} \geq T_{\text{dist}}$ are weak, and the remaining ones distant. The latter are treated using a non-iterative dipole-dipole approximation,[13,25,40] which is also used to select the pairs in this class. Throughout this work, we will use $T_{\text{dist}} = 1\ \mu$H. The effect of this threshold on correlation and reaction energies has been studied in detail earlier[13,25] and is not considered here. We note in passing that the selection of the pair classes using pair energies is preferable over using distance criteria, as applied earlier.[3,38,39] Extensive tests showed that the convergence is smoother and fewer strong and close pairs are needed to reach a certain accuracy than with distance criteria.

Our goal is to develop a highly accurate PNO-LCCSD(T)-F12 program that can be applied to large molecular systems of chemical interest. However, in the current work, we restrict our discussion and benchmark calculations to local coupled-cluster with doubles (LCCD), since this clearly separates the pair effects from further contributions and approximations involving single and triple excitations. LCCD includes all terms that are of 3rd-order in the energy (within the

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Møller-Plesset partitioning), and if a noticeable error due to the pair approximation would occur already at this level, there would be no chance to obtain good accuracy within the higher-order LCCSD or LCCSD(T) treatments.

Occupied (internal) orbitals will be denoted by indices i,j,k,l and virtual (external) orbitals by a,b,c,d. In the following discussion, all orbitals are assumed to be local and orthonormal. In practice, non-orthogonal virtual orbitals [projected atomic orbitals (PAOs),[1–4] orbital specific virtuals (OSVs),[41–43] or PNOs[8–25]] are used, which leads to additional contractions with overlap matrices, but the general arguments are not affected.

In the LCCD amplitude equations only 0-external integrals $(ik|lj)$, two-external integrals $(kl|ab)$ and $(ak|lb)$, and four-external integrals $(ab|cd)$ occur. The contributions of the exchange integrals $(ak|lb)$ are not affected by the following discussion and therefore not explicitly shown. The contributions of the other three integral classes to a coupled-cluster with doubles (CCD) residual R^{ij}_{ab} are

$$R^{ij}_{ab} = \sum_{cd}(ac|bd)T^{ij}_{cd} + \sum_{kl}(ik|lj)T^{kl}_{ab} - \sum_{kc}\Big[T^{kj}_{ac}(cb|ik) + (ac|kj)T^{ik}_{cb} + (ac|ik)T^{kj}_{cb} + T^{ik}_{ac}(cb|kj)\Big] + \cdots. \tag{1}$$

Let us first consider the 4-external term $(ac|bd)T^{ij}_{cd}$ and assume that i and j are distant. From simple perturbative considerations and multipole expansions of the integrals it follows that a,c must then be close to i, while b,d must be close to j. The amplitudes T^{ij}_{cd} decay with r_{ij}^{-3}. Furthermore, unless $a = c$ or $b = d$, the integrals $(ac|bd)$ also decay with r_{ij}^{-3}, since the density $\rho_{ac}(\mathbf{r}) = \phi_a(\mathbf{r})\phi_c(\mathbf{r})$ carries no charge and only dipole-dipole interactions contribute in lowest order. Thus, the whole contribution to the residual decays with r_{ij}^{-6}, unless $a = c$ and/or $b = d$. The corresponding energy contribution decays approximately with r_{ij}^{-9}.

Exceptions to this very fast decay are the cases $a = c$ and/or $b = d$. The dominant contribution will be $(aa|bb)T^{ij}_{ab}$. This contribution decays much more slowly with r_{ij}^{-4}, since the densities ρ_{aa} and ρ_{bb} each carry a unit charge. The next important contributions are $\sum_{d\neq b}(aa|bd)T^{ij}_{ad} + \sum_{c\neq a}(ac|bb)T^{ij}_{cb}$, which decay asymptotically with r_{ij}^{-5}.

The asymptotic decay properties of the other terms in the residual (1) can be determined similarly. If we separate out the "diagonal" contributions of T^{ij}_{ab}, we get

$$R^{ij}_{ab} = T^{ij}_{ab}\,[(aa|bb) + (ii|jj) - (aa|jj) - (ii|bb) - (aa|ii) - (bb|jj)] \ldots. \tag{2}$$

The first four terms decay individually with r_{ij}^{-4}, the last two even more slowly with r_{ij}^{-3}. However, the first four integrals, which can also be written as $(aa - ii|bb - jj)$, cancel approximately.[38] This happens because the charge centroids of ρ_{aa} and ρ_{ii} will be close together, and those of ρ_{bb} and ρ_{jj} as well. Each of these distributions carries a unit charge, but since the charges of $\rho_{aa} - \rho_{ii}$ and $\rho_{bb} - \rho_{jj}$ are zero, the integral $(aa - ii|bb - jj)$ decays with r_{ij}^{-3} and the whole contribution $T^{ij}_{ab}(aa - ii|bb - jj)$ with r_{ij}^{-6}. These considerations can be extended to the 4-external integral contributions that decay individually with r_{ij}^{-5}. These again cancel approximately with 2-external terms, and the total contribution of

$$\sum_{c\neq b} T^{ij}_{ac}[(aa|cb) - (ii|cb)] + \sum_{c\neq a}[(ac|bb) - (ac|jj)]T^{ij}_{cb} \tag{3}$$

then also decays as r_{ij}^{-6}. A similar asymptotic cancellation occurs between the 0-external and 2-external contributions

$$\sum_{l\neq j} T^{il}_{ab}[(ii|lj) - (aa|lj)] + \sum_{k\neq i}[(ik|jj) - (ik|bb)]T^{kj}_{ab}. \tag{4}$$

In summary,

$$T^{ij}_{ab}(ii|jj) + \sum_{cd} T^{ij}_{cd}(ac|db) - \sum_{d} T^{ij}_{ad}(ii|db) - \sum_{c}(ac|jj)T^{ij}_{cb} \tag{5}$$

decays with r_{ij}^{-6} and will therefore be neglected for close and weak pairs. Similarly,

$$\sum_{kl\neq ij}\Big[T^{kl}_{ab}(ik|jl) - \sum_{d}\delta_{lj}T^{kl}_{ad}(ik|bd) - \sum_{c}\delta_{ik}(ac|jl)T^{kl}_{cb}\Big] \tag{6}$$

decays asymptotically with r_{kl}^{-6}. Since the integrals decay exponentially with the distances r_{ik}, r_{jl}, r_{ac}, and r_{bd}, Eq. (6) also decays with r_{ij}^{-6}. This means that the first four terms of Eq. (1) can be neglected entirely unless the involved residual and amplitude matrices correspond to strong pairs. Altogether, this causes a small error in the energy that decays very quickly with r_{ij}^{-9}. If the close pairs are treated by LMP2 as in previous methods, the error is larger and decreases much more slowly with r_{ij}^{-6}. This is partly due to the last two terms in Eqs. (1) and (2), which should be fully included.[38]

In the following, we will demonstrate the effect of these approximations on the dissociation energy of a gold(I)-aminonitrene complex ($AuC_{41}H_{45}N_4P$, denoted AuAmin, see Fig. 1). This reaction is taken from Ref. 44 and plays an important role in catalytic aziridination and insertion reactions. The AuAmin molecule has three phenyl and three mesityl groups and therefore strong long-range dispersion interactions are expected. The calculations have been carried out using the VDZ-F12 basis set,[45] which is of augmented triple-zeta quality for the valence s and p orbitals and has a double polarization d-shell. For the gold atom, the ECP60MDF effective core

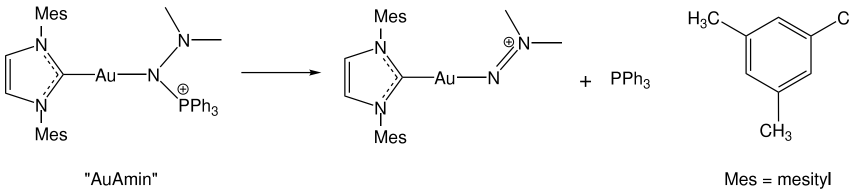

FIG. 1. The gold reaction studied in this paper.

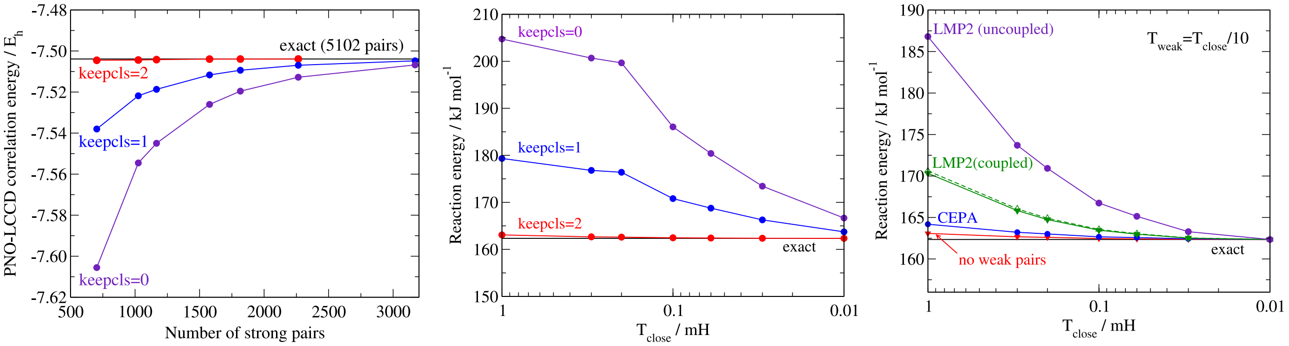

FIG. 2. Correlation energies for AuAmin (left panel) and reaction energies (middle panel) using various close-pair approximations as a function of the number of strong pairs. The values of T_{close} for the 7 points were (in mH) 1.0, 0.3, 0.2, 0.1, 0.06, 0.03, and 0.01. Right panel: reaction energies using in addition various weak pair approximations (see text).

potential[46] for the inner 60 electrons along with the cc-pVDZ-PP basis set[47] was used. All molecular structures and other computational details can be found in the supplementary material.[48] Additional results for correlation, reaction, and activation energies of three further reactions are presented therein as well.

Fig. 2 shows the PNO-LCCD correlation energies for AuAmin (left panel) and the reaction energy (middle panel) as a function of the number of strong pairs, using three different close-pair approximations. No weak pair approximations were employed here, i.e., $T_{\text{weak}} = T_{\text{dist}}$. The black horizontal bar corresponds to the correlation and reaction energies obtained with the PNO-LCCD method without any close pair approximations (cf. Table I in the supplementary material[48]). With `keepcls` = 0, the close pair energies are taken from the preceding LMP2 calculation, and only the strong pairs are optimized in the LCCD calculation. Hence, the strong and close pairs are entirely decoupled. This can be considered as the simplest close or weak pair approximation. It has been used in early PNO-LCCSD methods,[2,3] as well as in the LPNO-CCSD (local PNO-CCSD) method of Riplinger and Neese[13] (however, in their program, the weak pair energy is obtained using a semi-canonical MP2 approximation, which can introduce additional errors). Fig. 2 shows that the `keepcls` = 0 approximation leads to a strong overestimation of the correlation energies. For the largest threshold (1 mH), this error amounts to 102 mH for the correlation energy of the AuAmin molecule. For `keepcls` = 1, the close-pair amplitudes and energies are still taken from the preceding LMP2, but the amplitudes are included in the LCCD equations for the strong pairs. This approximation has been applied in Refs. 4 and 5. It leads to a significant improvement, but nevertheless the errors of the correlation energy stay rather large (34 mH) and decay only slowly with an increasing number of strong pairs. Note that the difference of the correlation energies for `keepcls` = 0 and `keepcls` = 1 solely arises from the strong pairs, since in both cases all remaining pair energies are taken from the preceding LMP2 calculation. Finally, the new approximation (`keepcls` = 2) leads to a dramatic improvement. The largest error of the correlation energy is now reduced to 0.6 mH and hardly visible on the scale of the figure. Note that in this case the close-pair amplitudes are fully optimized, but without the terms in Eqs. (5) and (6). These findings are qualitatively similar for all other molecules studied in this work, though the absolute errors for the other systems are smaller.[48]

The effect of the `keepcls` = 0 and `keepcls` = 1 approximations on the reaction energies is drastic. The errors for the largest threshold of 1 mH amount to 42 and 17 kJ mol^{-1}, respectively. The error for `keepcls` = 0 and a threshold of 0.1 mH still amounts to 24 kJ mol^{-1}. This corresponds to the threshold used by default in the LPNO-CCSD method of Riplinger and Neese.[13] In a very recent paper,[16] Liakos *et al.* recommended a tighter threshold of 0.01 mH for highly accurate LPNO-CCSD calculations. But even with this threshold the error still amounts to 4.3 kJ mol^{-1} (1 kcal/mol). For our new method (`keepcls` = 2), the error of the reaction energy is reduced to 0.6 kJ mol^{-1} already for the largest threshold of 1 mH. The error quickly converges to zero with smaller thresholds. For T_{close} = 0.1 mH it amounts to only 0.1 kJ mol^{-1}. Similar results are obtained for the other three systems.[48]

The computed reaction energy can be compared to an experimental gas-phase value[44] of 196.5 ± 11.2 kJ/mol (this value is obtained by subtracting the PW91/cc-pVTZ-pp zero-point correction[44] of −8.2 kJ/mol from the measured value and can therefore be compared directly to computed energy differences without ZPE). The PNO-LMP2-F12 reaction energies for the basis sets VDZ-F12 and VTZ-F12 are 250.0 and 250.5 kJ/mol, respectively (including the CABS singles corrections for the errors of the HF energies[48]). Based on previous benchmarks,[25] we believe that the VTZ-F12 result should be close to the MP2/CBS value. Adding the PNO-LCCD/VDZ-F12 correction of −56.2 kJ/mol yields 194.3 kJ/mol, which is already well within the experimental error bounds. It can be expected that this value will increase if the singles and triples contributions are added.

From a practical point of view, the advantage of the close pair approximation is twofold: first, removing the terms in Eq. (5) for close and weak pairs substantially reduces the number of 4-external integrals, which are expensive to compute. In the AuAmin calculation, 5102 non-distant pairs are included in the PNO-LCCD calculation, but for T_{close} = 1 mH, the 4-external integrals have to be computed only for the 702 strong pairs, i.e., for 14% of all pairs. For each pair ij, a distinct set of 4-external integrals $(a^{ij}c^{ij}|b^{ij}d^{ij})$ is needed (a^{ij} denotes a PNO belonging to pair ij). The total number of these integrals is reduced from 7.3×10^9 to 3.7×10^9. This is less than expected from the number of pairs because the domains for weak pair are much smaller than those for strong pairs. However, in the density fitting algorithm, the 3-index integrals are first computed in the PAO basis, in which the domains are of similar size for all pairs. The number of these integrals is reduced by a factor of 9, and the overall computation time for the 4-external integrals is reduced by a factor of about 6.

Second, neglecting Eq. (6) for close and weak pairs reduces the number of required 0-external integrals from 50.8×10^6 to 0.8×10^6 and the number of overlap integrals from 25.2×10^9 to 3.8×10^9. The latter reduction occurs because in the PNO case the 0-external contributions to R^{ij}_{ab} are $\sum_{kl} \sum_{cd} (ik|jl) \langle a^{ij}|c^{kl}\rangle T^{kl}_{cd} \langle d^{kl}|b^{ij}\rangle$, and the overlap matrix elements $\langle a^{ij}|c^{kl}\rangle$ are then only needed if ij and kl are strong (but further overlap matrix elements of this type are required for other terms).

Even if the contributions $T^{kl}_{ab}(ik|jl)$ are only included for strong pairs ij and kl as discussed above, the remaining number of these terms still scales quadratically with the molecular size. This can be avoided by realizing that the integrals $(ik|jl)$ decay exponentially with the distances r_{ik} and r_{jl}. One can therefore neglect these terms unless ik and jl or jk and il are strong pairs [integrals $(ik|jl)$ and $(il|jk)$ are always treated together]. This reduces the number of 0-external integrals by another order of magnitude to only 0.07×10^6, but the reaction energy is affected by only 0.1 kJ mol^{-1}. Similar approximations are possible for other terms in the PNO-LCCSD equations, but a detailed discussion is beyond the scope of this communication.

In order to achieve larger savings than with the approximations discussed so far, additional weak pair approximations can be introduced. The right panel of Fig. 2 shows the PNO-LCCD reaction energies using $T_{\text{weak}} = T_{\text{close}}/10$. The close-pair approximations are the same as before (`keepcls = 2`), and they are also employed for the weak pairs (where applicable). For comparison, 4 different weak approximations are shown. LMP2(uncoupled) means that the weak pair energies are taken from the preceding PNO-LMP2 calculation without change, and the weak pair amplitudes are not included in the LCCD residuals for the strong and close pairs. As already seen before, this leads to large and very slowly decaying errors. In the LMP2(coupled) cases, the weak pair amplitudes are included in the strong and close pair residuals. The open triangles (dashed line) represent values obtained using the original LMP2 amplitudes, while the full triangles (full line) are obtained with LMP2 amplitudes that are re-optimized in the LCCD calculation, using the LMP2 residual equations (which are part of the LCCD ones). This re-optimization, which includes the coupling to the strong and close pairs, has only a very small effect, and the results are still inaccurate. Better accuracy is only achieved if the weak pair amplitudes are optimized at a higher level. We used CEPA-2,[49] and for the threshold $T_{\text{close}} = 1$ mH the error then amounts to only 1.8 kJ mol^{-1} [0.6 kJ of which is due to the neglect of the terms in Eqs. (5) and (6) for close and weak pairs]. This error is quickly decaying, and for $T_{\text{close}} = 0.1$ mH it is reduced to 0.3 kJ mol^{-1}. Using linearized coupled-cluster (CEPA-0) for the weak pairs yields virtually the same results, since the CEPA-0 and CEPA-2 residuals R^{ij}_{ab} only differ by a term $-E_{ij}T^{ij}_{ab}$, and the weak-pair energies E_{ij} are very small.

We found that it is not necessary to include the weak pair amplitudes in the non-linear terms of the strong and close pairs. For the tested range of thresholds, this affects the reaction energy by at most 0.4 kJ mol^{-1}. However, if the non-linear terms in the close pairs are entirely neglected, the error of the reaction energy increases by 2.3 kJ mol^{-1}. For the other 3 studied systems,[48] the results are similar, and in all three cases the errors of the computed reaction and activation energies were below 1 kJ mol^{-1}, using $T_{\text{close}} = 1$ mH, $T_{\text{weak}} = 0.1$ mH.

In summary, this work shows that close and weak pair approximations based on LMP2 pair energies are poor and can lead to large errors of absolute and relative energies, which are very slowly decaying with increasing number of strong pairs. A large fraction of these errors stems from the neglect of the weak pair amplitudes in the residuals for the strong and close pairs. Furthermore, it is not sufficient to use LMP2 weak pair amplitudes to avoid this error. This should also affect the accuracy of fragmentation approaches[27–37] and implies that the fragments must be very large in order to obtain converged results.

We have compared and discussed various new approximations for close and weak pairs. It was shown that the calculation and processing of the 0-external and 4-external integrals can be avoided for close and weak pairs due to systematic long-range cancellations with contributions of 2-external integrals. This approximation causes only a very small and quickly decaying error in the correlation energy. In addition, the residuals for the weak pairs can be simplified by omitting the non-linear terms. Even though this means that the remaining linear (CEPA) terms in the LCCD equations should be included for all non-distant pairs, these approximations reduce the computation time and memory requirements significantly. The approximations are controlled by a single energy threshold, and in all studied cases it is easily possible to reduce the error to less than 1 kJ mol^{-1}. This is essential for the accuracy of future PNO-LCCSD(T)-F12 calculations on large chemical systems.

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