Theor Chem Acc (2011) 129:15–30
DOI 10.1007/s00214-010-0872-x

ORIGINAL PAPER

The effect of local approximations on first-order properties from expectation-value coupled cluster theory

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Received: 10 July 2010 / Accepted: 30 November 2010 / Published online: 24 December 2010

Abstract The accuracy of local approximations has been studied for expectation-value coupled cluster theory restricted to single and double excitations (XCCSD), applied to first-order one-electron molecular properties, such as dipole and quadrupole moments. The analysis has been performed separately for each component of the XCCSD expression, which allows to gauge the sensitivity of various parts of the formula to the localization conditions. The varying impact of local approximations is explained by examining the most important terms in the Møller-Plesset expansion of the first-order XCCSD property formula. It has been found that the contribution from the singly excited cluster operator plays a dominant role in the correlation part of the property, and that the common local settings, which consist in including only strong orbital pairs in the CCSD residual equations, lead to significant errors in the local multipole moments. Fortunately, the Møller-Plesset analysis of the XCCSD method allows to formulate a modified set of local approximations, which is better suited for a description of first-order properties. The new options involve the inclusion of close pairs into the CCSD residual equations and the extension of the strong-pair domains, which considerably improves the agreement of the singles-dependent part of the property with the nonlocal reference value. Additionally, for an accurate description of the part of the XCCSD expression containing the doubly excited cluster operator, it is necessary to include close and weak pairs from local MP2 theory. The mean absolute percent error of the correlation part of the dipole moment for the test set of 31 molecules in the cc-pVDZ basis amounts to 16% with the standard local settings, but can be reduced to only 5%, if the new set of local approximations is utilized instead. The existence of local approximations that are appropriate for local XCCSD opens a possibility to calculate first-order properties for large molecules on the coupled cluster level, without a need to solve an additional expensive set of equations for the zeroth-order Lagrangian multipliers from response coupled cluster theory.

Keywords Local correlation · Molecular properties · Expectation-value coupled cluster theory · Dipole moment

1 Introduction

In the last thirty years, coupled cluster (CC) theory became one of the most popular post-Hartree-Fock methods in the contemporary quantum chemistry. Its success can be explained by the facts that it offers a similar accuracy in comparison to e.g., configuration interaction theory for a comparable computational cost, being by virtue of construction size-extensive independently of the truncation level of the so-called cluster excitation operator T [1]. Soon after the introduction of CC theory into quantum chemistry [2], first attempts to treat molecular properties other than the energy were reported (see e.g., Ref. [3]). The nonvariational character of CC theory makes a very definition of properties somewhat problematic: as the Hellmann-Feynman theorem is not fulfilled in this case, one can define first-order properties either as energy derivatives (gradient or response CC theory), or as expectation values with the approximate CC wave function (expectation-value CC theory). In the literature, the former approach has been almost exclusively pursued most of the time. After the

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adaptation of a powerful Lagrangian technique to nonvariational methods of quantum chemistry and its generalization to the time-dependent case, the derivation of static and dynamic molecular properties of an arbitrarily high order turned out to be manageable (see e.g., Refs. [4–7] and Ref. [8] for a review). In particular, the orbital-unrelaxed first-order property from response CC theory for an operator X is defined by the formula,

$$\overline{X}^{\text{resp.}} = \left\langle 1 + \Lambda | e^{-T} X e^{T} \right\rangle, \tag{1}$$

where amplitudes of the excitation operator Λ are zeroth-order Lagrange multipliers (for a convenience the scalar product notation: $\langle X \rangle = \langle \Phi | X\Phi \rangle$ and $\langle X|Y \rangle = \langle X\Phi | Y\Phi \rangle$, where Φ is the reference determinant, will be used in the following). The derivation and implementation of the first-order properties and/or gradients have been reported for several CC models by many authors, see e.g., Refs. [9–23].

Another way of developing CC properties is based on employing the CC ansatz in property formulae derived originally for exact wave functions, e.g., the first-order property is just defined as an expectation value with the normalized CC wave function (see Refs. [24–32]). Unfortunately, the progress in this direction has been hampered for a long time by difficulties arising from the presence of the deexcitation operator $T^{\dagger}$ in the expression for the expectation-value CC property,

$$\overline{X} = \frac{\langle e^{T} | X e^{T} \rangle}{\langle e^{T} | e^{T} \rangle}. \tag{2}$$

An elegant solution of this problem has been proposed some time ago by Jeziorski and Moszynski [29] (see Sect. 2). The approach presented in Ref. [29] has an important practical advantage over response CC theory: the first-order properties can be obtained whenever the T operator is known, while Eq. 1 requires an additional calculation of the Λ operator, which is as expensive as the cluster operator T in terms of the CPU time. It should be stressed that both response and expectation-value CC methods converge to the same FCI (full configuration interaction) limit if increasingly higher excitations are allowed in T.

In spite of a stable popularity of CC theory in computational chemistry, its applicability to large molecules is severely limited by the steep scaling of the computer resources with the molecular size $\mathcal{N}$. For instance, the CPU time for CC theory limited to single and double excitations (CCSD) grows as $\mathcal{O}(\mathcal{N}^{6})$, and an inclusion of the cheapest version of the triple excitations, as it is done in the CCSD(T) approach [33], increases this scaling to $\mathcal{O}(\mathcal{N}^{7})$. The problem of the high scaling of CC theory can be circumvented if local approximations to the CC wave function are applied. The justification for the local treatment is based on a finding that the pair correlation is a short-range effect decreasing with the sixth inverse power of a distance (like the dispersion energy of intermolecular interactions). The first general and really successful local approach has been proposed by Pulay [34] and Pulay and Sæbø [35] and generalized to CC theory by Werner et al. (see e.g., Refs. [36–39]). Recently, the remaining obstacle of the high scaling with respect to the size of the orbital basis has been alleviated by combining local methods with density-fitting and explicit-correlation approaches (see e.g., Refs. [40–43]). Most of the available local methods in the MOLPRO suite of codes [44] scale linearly with the increasing molecular size.

The local character of the electron correlation in molecules has been also exploited by other research groups who proposed several post-Hartree-Fock methods with a lower scaling of the computational resources with respect to $\mathcal{N}$ than the respective conventional theories. Among these alternative approaches to the local electron correlation, one can list the AO-based and di- and triatomic-in-molecules methods [45–49], the cluster-in-molecule, the related divide-and-conquer and similar approaches [50–56], the incremental method [57–60], the natural-linear-scaling [52, 61], and the very recent local pair-natural-orbital CEPA model [62, 63]. Only for some of these methods, an attempt to calculate molecular properties other than the energy has been undertaken so far, what can be explained by the fact that an extension of the local approach allowing for an accurate description of effects caused by an external perturbation is highly nontrivial. It can be anticipated that different parts of the wave function can be responsible for a correct description of properties other than the energy, and therefore the argumentation about the spatial extent of the pair correlation energy does not transfer automatically to the new cases. Nevertheless, local approximations have been already investigated for gradients and other first- and second-order properties within the framework of response CC theory [64–71]. Additionally, low-lying electronic excited states can now be treated within the local equation-of-motion CCSD (LEOM-CCSD) [72, 73] and local CC2 (LCC2) models [74–78]. In nearly all applications of the local CC or Møller-Plesset (MP) methods to the molecular properties, some augmentation of the local configuration space was necessary in order to achieve satisfactory results. In a particular case of LCC2, the locality concepts are confined to the doubly excited space only, while single excitations remain nonlocal.

In this contribution, the effect of local approximations will be systematically examined for the first-order properties obtained from expectation-value CCSD theory. A detailed analysis of the property formula will be performed in order to find necessary modifications of local parameters. The conclusions from this theoretical analysis will be confronted with the numerical results for a test set of medium-sized molecules. Finally, new local settings suitable for the first-order property calculations will be proposed and discussed.

2 Theory

2.1 Expectation-value CC first-order properties

The main formula for expectation-value CC theory (XCC, with X coming from the second letter in the word *expectation*) of first-order molecular properties represented by some operator X was derived by Jeziorski and Moszynski [29] from Eq. 2 and is given by the expression,

$$\overline{X} = \langle e^S | e^{-T} X e^T \rangle = \langle e^{S^\dagger} e^{-T} X e^T e^{-S^\dagger} \rangle, \tag{3}$$

where an auxiliary excitation operator S ($S = S_1 + S_2 + \cdots$) is defined by the equation [29, 79]

$$e^S \Phi = \frac{e^{T^\dagger} e^T \Phi}{\langle e^T | e^T \rangle}. \tag{4}$$

It turns out that the S operator is connected (since it can be expressed through commutators of connected quantities) [29, 79], which together with the nested-commutator expansion,

$$e^{-Y} Z e^Y = Z + [Z, Y] + \frac{1}{2!}[[Z, Y], Y] + \ldots, \tag{5}$$

(applied either for $Z = e^{-T} X e^T$ and $Y = -S^\dagger$, or for $Z = X$ and $Y = T$) makes it easy to demonstrate that Eq. 3 is connected, and therefore size-extensive for any connected operator X. (Note parenthetically that second-order properties can be defined in a similar spirit [80].) An expansion of Eq. 3 resulting from the application of Eq. 5 and formulae for S (see Ref. [29]) are quite complicated on the one side and are known to contain many negligible terms on the other. Therefore, they can be truncated for practical reasons without affecting the accuracy of the results. These truncated forms are still size-extensive as long as the whole commutators only are removed from the original expanded expression. Moszynski et al. [80] proposed to include the expansion of S in T and $T^\dagger$ operators up to terms containing at most n Ts and $T^\dagger$s (the contribution to S containing exactly n such operators will be denoted as $S^{[n]}$). Additionally, some surviving terms can be removed if they are of a high order of the W operator, where W is the usual fluctuation operator of MP theory. In Ref. [81], a derivation and implementation of the expectation-value coupled cluster model for CCSD theory has been reported for a one-electron operator X, where the full form of Eq. 3 has been used, and the only truncations involve the S operator (the terms with at most three T or $T^\dagger$ operators were included). The numerical analysis of the importance of the XCCSD terms confirmed that most of them give only small or negligible contributions to the dipole moment, although also some exceptions—the BeO molecule being the most prominent example—have been found. Because of truncations within the S operator, the XCCSD density matrix from Ref. [81] shows a slight asymmetry (note that the response CC density matrix from Eq. 1 has the same feature), which however is never a problem, since property operators are usually symmetric, anyway.

Since the available studies of the local first-order properties within response theory, like local MP to the second-order (LMP2) [67], local quadratic configuration interaction theory (LQCISD) [66], local CCSD (LCCSD) [68, 71], and LCC2 [75], showed that reliable local results can be obtained with a considerably reduced computational cost, a similar examination of XCCSD theory is now in order. It should be stressed that the XCC approach does not include the orbital relaxation, which may play a quite important role in the local properties [68], so it is interesting to examine how the absence of explicit orbital-relaxation terms affects the accuracy of the local XCCSD scheme.

Most of the terms in the XCCSD expression [81] give smaller contributions than the intrinsic accuracy of the CCSD-type properties, which is limited due to the neglect of the T_3 and higher excitation operators. To this end, a simplified XCCSD model has been utilized for the local analysis presented in this paper. This model is still obtained by employing the full T operator from CCSD theory, but with only terms of order $\mathcal{O}(T^2)$ preserved in the expanded form of Eq. 3, which leads—after skipping a small $\left\langle \left[S_1^{[1]\dagger}, [X, T_1]\right] \right\rangle$ term—to the following expression,

$$\begin{aligned}\overline{X} = \langle X \rangle &+ \left\langle \left[S_1^{[1]\dagger}, X\right] \right\rangle + \left\langle \left[S_1^{[2]\dagger}, X\right] \right\rangle + \langle [X, T_1] \rangle \\ &+ \left\langle \left[S_2^{[1]\dagger}, [X, T_2]\right] \right\rangle + \left\langle \left[S_1^{[1]\dagger}, [X, T_2]\right] \right\rangle. \end{aligned} \tag{6}$$

The $S^{[n]}$ operators appearing in Eq. 6 are defined as [80],

$$\begin{aligned} S_1^{[1]} &= T_1, \\ S_2^{[1]} &= T_2, \\ S_1^{[2]} &= \widehat{\mathscr{P}}_1([T_1^\dagger, T_2]), \end{aligned} \tag{7}$$

where the superoperator $\widehat{\mathscr{P}}_n$ projects an operator Z to the subspace of n-tuply excited operators,

$$\widehat{\mathscr{P}}_{n(Z)} = (n!)^{-2} \sum_{i_1 \ldots i_n} \sum_{a_1 \ldots a_n} \langle e^{i_1}_{a_1} \ldots e^{i_n}_{a_n} Z \rangle e^{a_1}_{i_1} \ldots e^{a_n}_{i_n}, \tag{8}$$

with e^p_q denoting the spinorbital substitution operator [82] (here a and i label virtual and occupied spinorbitals, respectively). In this place, it is convenient to define a similar superoperator $\widehat{\mathscr{R}}_n$, which differs from $\widehat{\mathscr{P}}_n$ by multiplying of each term in the sum of the r.h.s. of Eq. 8 by the energy denominator $(\Delta_{i_1a_1} + \cdots + \Delta_{i_na_n})^{-1}$, where $\Delta_{ia} = \varepsilon_i - \varepsilon_a$ and ε_p is the orbital energy for an orbital ϕ_p. An examination of Eq. 6 reveals that this expression can be still simplified for a one-electron Hermitian operator X, since in this case: (1) the second and the fourth terms and (2) the third and the sixth terms of its r.h.s. are complex conjugates of each other. Taking this into account, Eq. 6 can be rewritten to the following final form,

$$\overline{X} = \langle X \rangle + 2\mathrm{Re}\langle X|T_1\rangle + \langle T_2|XT_2\rangle + 2\mathrm{Re}\langle X|\widehat{\mathscr{P}}_1(T_1^{\dagger}T_2)\rangle. \tag{9}$$

From the point of view of MP theory, Eq. 6 (and Eq. 9) contains all third-order MP terms, which appear in Eq. 3 if $T = T_1 + T_2$ from CCSD theory is applied, therefore this approach will be denoted as the XCCSD(3) model. The formula presented in Eq. 9 has been implemented into the MOLPRO suite of codes [44] for both conventional and local T operators.

2.2 Local approximations

Details of the local method proposed by Pulay et al. and extended to the CC case by Werner et al. are given elsewhere (see e.g., Refs. [34–39]), and therefore only a summary of applied local approximations will be presented here for the sake of completeness. In the first step toward a local method, localized molecular orbitals (LMOs) are created from occupied Hartree-Fock (HF) orbitals by the Pipek-Mezey procedure [83], while projected atomic orbitals (PAOs) are utilized for the virtual space [84]. The PAOs are well localized by construction, so they can be unanimously attributed to a particular atom. Single and double excitations of the local T operator are restricted to subsets of all PAOs. Single excitations from the LMOs are allowed only to the PAOs close (in a spatial sense) to the LMO, from which the excitation has occurred. A set of the PAOs specific to a given LMO ϕ_i is denoted an orbital domain $[i]$. All PAOs centered on a selected atom are always added, so the domain choice is limited to the selection of atoms, which in turn is performed by the Boughton-Pulay (BP) procedure [85]. Double excitations from a pair of LMOs ϕ_i and ϕ_j are allowed to a pair domain $[ij]$ being a union of orbital domains. Finally, the LMO pairs, from which double excitations are permitted, are also restricted to the pairs of LMOs spatially close to each other. As a measure of the closeness of two LMOs, the number of chemical bonds separating two LMOs ϕ_i and ϕ_j is utilized, which will be in the following denoted as a separation index b_{ij}. In this work, strong, close, and weak pairs are distinguished (a class of very distant pairs is not used here). Usually, two LMOs form a strong pair if they share at least one atom (i.e., are "separated" by zero bonds). Close pairs are separated by 1 or 2 bonds, while all other pairs are treated as weak. Among these three pair classes, only strong pairs are treated on the CCSD level, while both close and weak pairs used in the calculation of the correlation energy are taken from LMP2 theory. Close-pair amplitudes are additionally utilized in the CCSD residual equations as constant terms. Although they are not updated themselves, their presence modifies the resulting local CCSD amplitudes. If necessary, some domains (usually those of strong pairs) can be extended by the PAOs located on atoms separated from the original set of atoms (established by the BP procedure) by one or more chemical bonds. For single excitations from the LMO ϕ_i, the diagonal pair domains $[ii]$ are utilized (i.e., there is always $[i] \equiv [ii]$), so if the pair domains are extended, single excitations are allowed to a larger configurational space too. It should be noted that the division into strong, close, and weak pairs is always performed by the analysis of the original domains from the Boughton-Pulay procedure. (It should be noted parenthetically that so far, the only possibility to treat single excitations differently from diagonal double excitations is offered by the local simulation within the conventional CCSD program in MOLPRO, where it is allowed to use full domains for T_1 and usual local restrictions for T_2).

2.3 Assessment of the importance of various terms in the XCCSD(3) formula

The expected importance of various parts in Eq. 9 can be estimated a priori by performing their analysis in terms of the MP orders and by a subsequent examination of lowest-order MP contributions. Single and double excitation cluster operators appear for the first time in the second and the first orders of MP theory, respectively, and therefore the second and the third term in Eq. 9 are of the second W leading order [i.e., in the MP expansion the first non-vanishing term is of order $\mathcal{O}(W^2)$], while the last term is of the third W leading order. Based on W orders, it can be anticipated that the two former terms are more important for the correlation part the first-order property than the last term. However, as we will see later, the second and the fourth terms probe the occupied-virtual (OV) part of the X operator and the third term—the occupied-occupied (OO) and virtual-virtual (VV) parts, so one can only definitely say that the fourth term should be an order of magnitude smaller than the second term. The relative importance of the second and the third terms is dependent on the 'weight' of the OV, OO, and VV parts of the X operator. For the dipole and quadrupole moments, the numerical experience shows that usually, the contribution to the XCCSD(3) property originating from the OV part of X constitutes the major part of the post-HF part of the multipole moment. Summarizing, from the point of view of MP theory, the T_1 and T_2 operators play an equally important role in the description of molecular properties. This feature of the first-order properties, which is quite different from the behavior of the correlation energy, should be taken into account when devising local approximations appropriate for this case.

The T_1 and T_2 operators in a spin-free form are represented by the following formulae,

$$\begin{aligned} T_1 &= \sum_{ia} t_a^i E_i^a, \\ T_2 &= \frac{1}{2}\sum_{ijab} t_{ab}^{ij} E_i^a E_j^b, \end{aligned} \tag{10}$$

where $E_k^c = e_{k\alpha}^{c\alpha} + e_{k\beta}^{c\beta}$ are orbital substitution operators [82] and where the convention of labeling occupied orbitals by letters $i, j, k, \ldots$ and virtual orbitals by letters $a, b, c, \ldots$ is used in Eq. 10 and in the following. The amplitudes t_a^i and t_{ab}^{ij} of CCSD theory are obtained from the set of nonlinear equations for all different singlet excitations, which can be produced by the action of E_i^a or $E_i^a E_j^b$ on the reference determinant Φ,

$$\begin{aligned} 0 &= \langle E_i^a | e^{-T} H e^T \rangle, \\ 0 &= \langle E_i^a E_j^b | e^{-T} H e^T \rangle. \end{aligned} \tag{11}$$

For the following analysis, it is more convenient to use an iterative formula for the T operator of CC theory [86],

$$T_n = \widehat{\mathscr{R}}_n (e^{-T} W e^T), \tag{12}$$

which allows to obtain an order-by-order expansion in terms of powers of the W operator. It is easy to see that the first nonvanishing contributions for the T_2 and T_1 CCSD operators are the following,

$$\begin{aligned} T_2 &= \widehat{\mathscr{R}}_2 (e^{-T} W e^T) = \widehat{\mathscr{R}}_2 (W) + \ldots \\ &= \frac{1}{2}\sum_{ijab} (\Delta_{ia} + \Delta_{jb})^{-1} \bar{w}_{ab}^{ij} E_i^a E_j^b + \ldots, \end{aligned} \tag{13}$$

$$\begin{aligned} T_1 &= \widehat{\mathscr{R}}_1 (e^{-T} W e^T) = \widehat{\mathscr{R}}_1 (W T_2) + \ldots \\ &= \sum_{ia} \Delta_{ia}^{-1} \left(\sum_{jbc} w_{aj}^{cb} \bar{t}_{cb}^{ij} - \sum_{jbk} w_{kj}^{ib} \bar{t}_{ab}^{kj} \right) E_i^a + \cdots, \end{aligned} \tag{14}$$

where $\bar{x}_{ab}^{ij} = 2x_{ab}^{ij} - x_{ba}^{ij}$ and $w_{rs}^{pq} = \int \phi_p(\mathbf{r}_1)\phi_q(\mathbf{r}_2) r_{12}^{-1} \phi_r(\mathbf{r}_1)\phi_s(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$. In Eqs. 13 and 14 one can recognize the well-known contributions of the W^1 and W^2 orders for doubly and singly excited cluster operators from MP theory, respectively. The algebraic expressions for the correlation part γ of the XCCSD(3) one-electron reduced density matrix can be derived from Eq. 9 if the E_q^p operator is inserted as X. For OV, OO, and VV parts of γ one obtains respectively,

$$\gamma_a^i = 2\left(t_a^i + \sum_{jb} t_b^j \bar{t}_{ab}^{ij} \right), \tag{15}$$

$$\gamma_i^k = -\sum_{jab} t_{ab}^{ij} \bar{t}_{ab}^{kj}, \tag{16}$$

$$\gamma_c^a = \sum_{ijb} t_{ab}^{ij} \bar{t}_{cb}^{ij}. \tag{17}$$

The components of the first-order property represented by various terms from Eqs. 15–17 will be denoted as the S and SD parts for the left and right parts of the r.h.s. of Eq. 15 and as the D part for both Eqs. 16 and 17. If the PAOs are used instead of the canonical virtual orbitals, the PAO overlap matrix will appear in Eqs. 15–17 (one for each summation over virtual orbitals) because of the nonorthogonality of the PAOs. Additionally, in Eqs. 13–14, the energy denominators will be then replaced by the inverse matrices of the Fock operator projected on the double and single excitation space, respectively. Apart from these technical complications, the explicit introduction of PAOs and LMOs does not change the line of reasoning presented below, so it has been decided to skip the local variants of Eqs. 13–17 for the sake of conciseness.

For a comparison, let us examine the expression for the CC correlation energy. The part involving the double amplitudes is given below,

$$E_{\mathrm{corr}} = \sum_{ijab} w_{ab}^{ij} \bar{t}_{ab}^{ij} + \mathcal{O}(W^5). \tag{18}$$

An important question arises of how ‘local’ are the expressions from Eqs. 13–18. For the case of Eq. 18, the numerical experience tells us that if the summation over occupied orbitals is restricted to strong pairs, about 90–95% of the nonlocal correlation energy is recovered. In order to achieve the accuracy of 98–99% also close and weak pairs approximated by the doubles, amplitudes from LMP2 theory should be included in Eq. 18. The extension of the pair domains has in this case a secondary effect only. This ‘hybrid’ LCCSD|LMP2 approach is utilized routinely for the local CCSD correlation energy [36]. Since Eqs. 16–17 resemble closely Eq. 18 (which is especially well appreciated if the diagrams corresponding to these terms are compared), a similar dependence on the pair list and domain restrictions can be also expected for the part D of the property expression. Summarizing, one can anticipate that in order to achieve a one-digit percent error, the inclusion of some non-strong pairs in Eqs. 16–17 will be necessary, while the extension of the domains by the next shells of atoms should have a secondary effect in this case.

Let us examine the effect of local truncations within T_1 on the first-order property (see Eq. 15). As already mentioned, the S part of the one-electron density matrix is characterized by the same leading MP order as the D part. It is therefore tempting just to enlarge singles' domains, even at cost of keeping the separate domains for single excitations, which inevitably leads to a more complicated computational algorithm. For instance, since the second term of Eq. 9 in a strict W^2 order can be trivially rewritten as

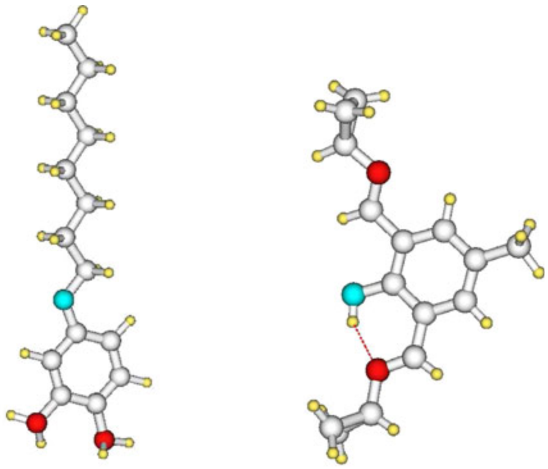
$$\begin{aligned}\langle X|T_1^{(2)}\rangle &= \langle X|\widehat{\mathscr{R}}_1([W,T_2^{(1)}])\rangle = \langle\widehat{\mathscr{R}}_1(X)|[W,T_2^{(1)}]\rangle \\ &= \langle C_1^{(0)}(X)|[W,T_2^{(1)}]\rangle, \qquad (19)\end{aligned}$$

where $C_1^{(0)}(X)$ is a singly excited operator being a solution of the uncoupled perturbed HF (UCHF) equations with the perturbation X, one could think of a construction of the orbital domains from the analysis of the solution of the UCHF (or coupled HF) equations (as a matter of fact, this idea has already been pursued in a different context, see Refs. [69, 75]). However, the analysis of the main term in the MP expansion of the T_1 operator (see Eq. 14) shows clearly that such a solution does not touch the essence of the problem. The crucial step in a construction of the local T_1 operator is the assembly of the singly excited operator $\widehat{\mathscr{P}}_1(WT_2)$ with a sufficient accuracy by performing the summations given in the parenthesis of Eq. 15. Let us assume that the LMOs are spread over at most two atoms (this corresponds to a typical LMO describing one chemical bond) and let us estimate which pairs should be included in the summation over jkb in Eq. 14 in this case. First, it can be seen from Eq. 14 that the orbital ϕ_a should belong simultaneously to the domains $[ii]$ and $[jk]$. One can also assume that for the localized occupied orbitals ϕ_i and ϕ_k, a large value of w_{kj}^{ib} occurs for the strong pair (ik). Even if the pairs (ik) and (jk) are strong, the third pair, (ij), can be separated by one bond (i.e., it can be a close pair), so in order to assure that ϕ_a belongs to the strong-pair domain $[jk]$, such domains should be extended by PAOs localized on close atoms. In the summation over jbc in Eq. 14, the PAOs ϕ_a and ϕ_c centered on neighboring atoms may significantly overlap, giving a large contribution to the w_{aj}^{cb} integral. This means that also close pairs should enter Eq. 14 in order to reach a sufficient accuracy for T_1.

In general, the presence of 3-virtual or 3-occupied electron-repulsion integrals in the approximated terms strongly indicates that close pairs should be somehow included, and that also the extension of domains is expected to have a sizable effect on the quality of a model under consideration. It can be noted that numerical tests for the first versions of the local CCSD(T) method [38, 87] have led to similar local approximations, e.g., close pairs were found to be necessary for an accurate description of the local triple correction. The similar requirements for the first-order properties and for the triples corrections can be a posteriori explained by the fact that the approximated triply excited operator in CCSD(T) is calculated from the formula $T_3^{(2)} = \widehat{\mathscr{R}}_3(WT_2^{(1)})$ with the same WT_2 operator as for the case of the T_1 operator. Also in the LEOM-CCSD calculations, some selected weak pairs have been included to improve the quality of the single-dominated electronic excitations [72]. One can additionally note that roughly the same spatial extension of the first-order property has been reported by the incremental analysis of Friedrich et al. [71], who found that the third and possibly fourth incrementation order should be taken into account for accurate dipole and quadrupole moments.

3 Technical details

The test calculations of electric dipole and quadrupole moments were performed for a selected set of 34 molecules from Ref. [88]: 3-pentanone, 1-propanol, propionamide, 2-aminopropane, 2-nitropropane, 2-propanol, propanoic acid, 4-heptanone, 1,3,5-triborane, *N*-methylacetamide, *N*-methylformamide, acetaldehyde, acetone, pentanol, butane, 1-amino-4-nitro-tetrahydro-1,3,5-triazine, 4-amino-1-nitro-tetrahydro-1,3,5-triazine, *p*-nitroaniline, 1-amino-3-nitro-1,3,5-triborane, trifluoroethane, fluorobenzene, chloroethane, chloroformamide, cyanomethane, nitrobenzene, phenol, cyanoethane, cyanopropane, nitrobutane, *o*-dichlorobenzene, aniline, butane, benzene, and hexafluorobenzene (the last three molecules were used for the quadrupole moment only, since they have zero dipole moment). Their optimized geometries were taken from the supporting information of Ref. [88]. The same directions of the cartesian axes as in Ref. [88] are preserved; however, in some cases, the axes have been reshuffled, so that the largest (in the absolute value) diagonal component of the HF traceless quadrupole moment always corresponds to the z axis. Additionally, the second test set of polyglycines $(\text{gly})_n$, $n = 1, \ldots, 6$, was utilized to show the reduction of the computational resources in the local method. This set has been applied many times to check the scalability of e.g., LMP2 [37], LCCSD [39], and LCCSD(T) [38] correlation energies. Two orbital basis sets were employed. First, the cc-pVDZ basis [89, 90] was utilized. Although this basis is not appropriate for a quantitative description of the properties, it can nonetheless show trends that can be then checked for larger molecules and basis sets. Additionally, calculations for the test set from Ref. [88] were repeated in a larger Sadlej polarization (Sadlej-POL) basis [91], which was especially devised to describe electric properties with a good accuracy. As examples of larger molecules, two species have been used (see Fig. 1). One



4-octyloxy-1,2-diaminobenzene from Ref. [92] the model Schiff base from Ref. [93]

Fig. 1 Two large real-life molecules used in this work

of them is 4-octyloxy-1,2-diaminobenzene, which has been recently synthetized as a model liquid-crystal molecule [92]. Its geometry has been optimized on the HF level in the 6-31G(d) basis set. As the second example, a 2,6-bis(alkylimino)phenol Schiff base studied in Ref. [93] has been selected (the molecule I from Fig. 2 in this reference), and the geometry parameters from the supporting information of this reference have been used. For both these molecules, the cc-pVDZ basis has been applied. The $1s$ shell for the B,C,N,O, and F atoms and $1s2s2p$ shells for the Cl atom were frozen in the post-HF calculations. For the BP completeness check, the threshold of 0.015 was employed. All calculations have been performed with the MOLPRO program [44], with the locality simulated by the canonical code. The local results are always compared with the nonlocal XCCSD(3) values.

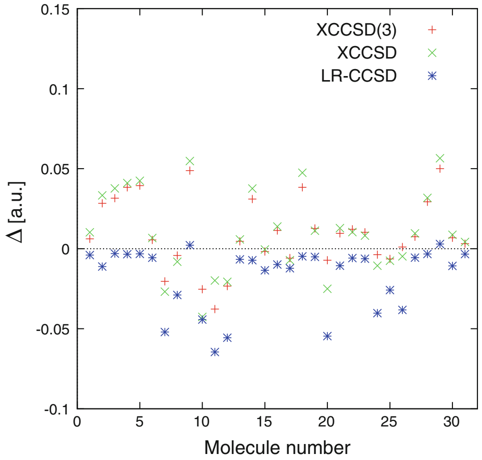


Fig. 2 Signed differences of the dipole moment, $\Delta = |\boldsymbol{\mu}^{\text{corr}}(\text{method})| - |\boldsymbol{\mu}^{\text{corr}}(\text{QCISD(T)})|$, for the test set of 31 molecules and the cc-pVDZ basis obtained with XCCSD(3), XCCSD, and orbital-nonrelaxed LR-CCSD methods with respect to the QCISD(T) results. The results are in a.u.

4 Results and discussion

In this contribution, a new nonlocal modification of the previously proposed XCCSD model [81] has been introduced. It is therefore worthwhile to compare its accuracy with other available CCSD-type methods for the calculation of the first-order properties before analyzing the local variants of this method. To this end, the differences of the lengths of the correlated part of the dipole moments of various models with respect to the triple-containing QCISD(T) [14] results, as implemented in MOLPRO [66, 94], are presented in Fig. 2 for the test set of 31 molecules and for the cc-pVDZ basis. As can be seen, the discrepancies between the new simplified XCCSD(3) model and the full XCCSD, as described in Ref. [81], are unsubstantial. Somewhat larger differences occur between XCCSD(3) and the orbital-unrelaxed linear-response (LR) CCSD method obtained from the differentiation of the ground-state Lagrangian (see Eq. 1). Figure 2 shows that usually, the LR-CCSD model gives smaller lengths than QCISD(T), while XCCSD(3) results are more evenly distributed with respect to the reference. The average percent errors of the XCCSD(3), XCCSD, and LR-CCSD with respect to QCISD(T) for the lengths for the correlated part of the dipole moment are equal to 8.6, 10.1, and 6.7%, respectively. One can note parenthetically that the error of the orbital-nonrelaxed QCISD(T) method for the same set of molecules is significantly higher (15%), reflecting the fact that the diagrams missing in the QCISD approach [95] are important for an indirect inclusion of the orbital relaxation, according to the Thouless theorem [96]. Summarizing, the presented results confirm the conclusions of Ref. [81] that both LR-CCSD and XCCSD (with its XCCSD(3) modification) give results of a comparable quality with respect to higher-level methods, so that the XCCSD(3) and XCCSD models can be used instead of LR-CCSD if only first-order properties, and not gradients, are required.

Before discussing the local results, it is interesting to examine the relative importance of the S, D, and SD parts of the dipole moment in comparison to the total correlated contribution. It turns out that the respective average ratios for the test set of 31 molecules are equal to 93, 20, and 13% (the contributions do not sum to 100% because these parts of the dipole moments are usually not colinear). Ratios of the same order of magnitude are observed for the quadrupole moment too. From these numbers, it is straightforward to make a conclusion that the key to the success of the local method is its ability to evaluate the T_1 operator accurately enough and that those local settings should be preferred, which treat single excitations in the best possible way.

In Tables 1, 2, 3 and 4, various statistical data are presented, like mean absolute percent errors (δ_{aver}) and maximum absolute percent errors ($\delta_{\max}$) for the length of the total dipole moment ($|\boldsymbol{\mu}|$) and the largest component of the quadrupole moment (Q_{zz}), as well as for their electron-correlated parts ($|\boldsymbol{\mu}^{\text{corr}}|$ and Q_{zz}^{corr}). The δ_{aver} values for the S, D, and SD parts of the properties are also listed in these tables. The same data are shown in a graphical form in Figs. 3 and 5. Additionally, signed errors of $|\boldsymbol{\mu}^{\text{corr}}|$ and Q_{zz} are presented for each molecule in Figs. 4 and 6. Since in the case of 2-aminopropane, the errors for the dipole moment in the Sadlej-POL basis set are much larger than average, in Table 2 also the percent errors obtained without this molecule are presented. Finally, the selected data for the polyglycine chains and two real-life molecules are given in Table 5.

In total, 10 various combinations of local options have been examined. For convenience of the discussion, these local settings are numbered according to the order of appearance in Table 1. The following variations of the local parameters were included: (1) changing of a strong-pair description from a default definition [the pair (*ij*) is strong if it has the separation index equal to zero, see $SP = 0$ in

Table 1 Statistical data for the length of the dipole moments calculated in the cc-pVDZ basis set for the test set of 31 molecules

Local options						Total		Correlated		*S*	*D*	*SD*
No.	*SP*	*CP*	*WP*	*EXS*	*EXC*	δ_{aver}	$\delta_{\max}$	δ_{aver}	$\delta_{\max}$	δ_{aver}	δ_{aver}	δ_{aver}
1	0	–	≥ 1	0	–	3.3	13.3	15.9	52.1	18.2	10.3	27.0
2	0	–	–	0	–	3.7	14.5	17.6	52.9	18.2	17.9	33.9
3	0	–	–	0 (fs)	–	3.1	13.7	15.2	46.3	16.2	17.4	35.0
4	All	–	–	0	–	1.3	5.6	6.7	47.7	7.4	5.8	11.6
5	All	–	–	1	–	0.3	1.5	1.4	13.4	1.5	1.3	1.9
6	0–1	–	≥ 2	0	–	1.8	8.6	8.8	42.8	9.9	6.8	15.8
7	0	1	≥ 2	0	0	2.0	9.1	9.7	48.5	11.0	9.3	21.5
8	0	1–2	≥ 3	1	0	1.0	3.6	5.3	26.7	6.0	6.8	15.1
9	0	1	≥ 2	1	0	1.2	5.9	6.1	27.1	7.0	6.9	15.5
10	0	1–2	≥ 3	1	1	0.8	3.1	4.4	20.9	5.0	5.7	13.3

Mean absolute percent errors ($\delta_{\text{aver}} = \frac{1}{N}\sum_{i=1}^{N}|\delta_i| \cdot 100$, where N is the number of molecules and δ_i is the percent error for the ith molecule) and maximum absolute percent errors ($\delta_{\max}$) for various local variants of the XCCSD(3) approach are presented for the total dipole moment (the column denoted as *total*), its correlation part (the column denoted as *correlated*), the *S* correlation part (the *S* column), the *D* correlation part (the *D* column), and the *SD* correlation part (the *SD* column). A hyphen means that a given pair or domain type is absent for selected local settings. The abbreviations *SP, CP, WP* denote strong, close, or weak pairs, respectively, and the numbers in these columns denote the separation index for these LMO pairs (e.g., $CP = 1$–2 means that close pairs are separated by one or two bonds). Nonzero *EXS* or *EXC* denote the extension of strong- or close-pair domains by one bond, respectively. Additionally, the abbreviation *fs* signifies that for single excitations full (i.e., unrestricted) domains are used, while for the pair domains, usual restrictions are imposed

Table 2 Statistical data for the length of the dipole moments calculated in the Sadlej-POL basis set for the test set of 31 molecules

Local options						Total		Correlated		*S*	*D*	*SD*
No.	*SP*	*CP*	*WP*	*EXS*	*EXC*	δ_{aver}	$\delta_{\max}$	δ_{aver}	$\delta_{\max}$	δ_{aver}	δ_{aver}	δ_{aver}
1	0	–	≥ 1	0	–	1.5 (1.3)	6.0 (4.6)	12.5 (9.7)	97.5 (34.1)	15.3 (11.4)	6.0 (6.0)	16.3 (15.5)
2	0	–	–	0	–	1.5 (1.4)	4.9 (4.9)	11.6 (10.0)	59.3 (27.6)	15.3 (11.4)	9.5 (9.2)	21.4 (20.2)
3	0	–	–	0 (fs)	–	1.1 (1.1)	3.1 (3.1)	8.4 (7.0)	51.4 (22.4)	11.1 (7.8)	8.7 (8.3)	21.3 (19.8)
4	All	–	–	0	–	0.9 (0.8)	3.0 (2.7)	7.1 (6.2)	34.8 (25.2)	7.8 (6.8)	4.2 (4.0)	6.7 (6.4)
5	All	–	–	1	–	0.3 (0.2)	1.7 (0.8)	2.6 (1.5)	33.7 (5.8)	3.1 (1.7)	1.8 (0.8)	1.7 (1.6)
6	0–1	–	≥ 2	0	–	1.2 (0.8)	10.5 (3.0)	8.5 (6.2)	77.2 (28.7)	10.3 (7.0)	5.6 (3.9)	9.0 (8.5)
7	0	1	≥ 2	0	0	1.2 (1.0)	9.2 (3.2)	9.8 (7.3)	86.6 (30.7)	12.0 (8.5)	6.3 (5.8)	13.5 (13.0)
8	0	1–2	≥ 3	1	0	0.6 (0.5)	4.2 (1.3)	5.6 (3.5)	67.9 (11.5)	6.8 (4.2)	6.5 (3.8)	8.7 (8.7)
9	0	1	≥ 2	1	0	0.7 (0.4)	8.3 (1.5)	6.5 (3.0)	110.5 (10.8)	8.6 (3.8)	6.3 (3.6)	9.8 (9.2)
10	0	1–2	≥ 3	1	1	0.5 (0.4)	3.9 (1.2)	4.4 (3.0)	47.6 (8.2)	5.4 (3.6)	5.0 (3.3)	8.1 (8.3)

The *numbers in parenthesis* contain the data for 30 test molecules, with 2-aminopropane excluded. For more explanations, see Table 1

Table 3 Statistical data for the Q_{zz} component of the traceless quadrupole moment calculated in the cc-pVDZ basis set for the test set of 34 molecules

Local options						Total		Correlated		*S*	*D*	*SD*
No.	*SP*	*CP*	*WP*	*EXS*	*EXC*	δ_{aver}	$\delta_{\max}$	δ_{aver}	$\delta_{\max}$	δ_{aver}	δ_{aver}	δ_{aver}
1	0	–	≥ 1	0	–	8.8	102.5	27.4	149.1	32.4	10.4	34.1
2	0	–	–	0	–	10.3	129.4	34.6	260.1	32.4	26.3	42.1
3	0	–	–	0 (fs)	–	7.5	67.9	50.9	818.3	40.4	26.2	43.3
4	All	–	–	0	–	4.2	73.5	21.8	467.3	14.2	6.5	12.3
5	All	–	–	1	–	0.4	4.5	5.2	132.9	2.7	1.4	2.3
6	0–1	–	≥ 2	0	–	5.8	77.8	19.9	217.4	19.0	8.6	17.1
7	0	1	≥ 2	0	0	6.1	84.1	18.2	150.8	18.8	9.2	20.8
8	0	1–2	≥ 3	1	0	1.7	17.4	5.4	25.5	5.5	5.8	11.9
9	0	1	≥ 2	1	0	3.2	36.0	39.2	957.4	25.2	6.4	15.1
10	0	1–2	≥ 3	1	1	1.2	10.1	10.3	242.2	6.8	6.2	12.5

For more explanations, see Table 1

Table 4 Statistical data for the Q_{zz} component of the traceless quadrupole moment calculated in the Sadlej-POL basis set for the test set of 34 molecules

Local options						Total		Correlated		*S*	*D*	*SD*
No.	*SP*	*CP*	*WP*	*EXS*	*EXC*	δ_{aver}	$\delta_{\max}$	δ_{aver}	$\delta_{\max}$	δ_{aver}	δ_{aver}	δ_{aver}
1	0	–	≥ 1	0	–	5.2	49.1	28.1	186.4	36.9	7.2	25.2
2	0	–	–	0	–	4.9	30.0	31.0	203.7	37.0	17.9	34.7
3	0	–	–	0 (fs)	–	4.1	27.5	28.5	209.5	36.4	17.1	36.4
4	All	–	–	0	–	1.2	7.4	6.9	27.4	8.9	4.2	7.1
5	All	–	–	1	–	0.8	20.2	2.3	31.9	2.9	2.2	1.2
6	0–1	–	≥ 2	0	–	3.9	45.3	20.0	112.2	26.3	5.3	13.8
7	0	1	≥ 2	0	0	3.8	39.0	20.0	114.9	25.6	6.6	14.4
8	0	1–2	≥ 3	1	0	1.3	11.7	6.6	49.6	7.0	4.6	8.7
9	0	1	≥ 2	1	0	2.9	23.2	16.8	131.8	21.0	5.1	12.5
10	0	1–2	≥ 3	1	1	1.3	21.0	5.5	42.5	7.5	3.3	9.3

For more explanations, see Table 1

Tables] to either setting also pairs separated by one bond as strong (*SP* = 0–1), or making all pairs strong (*SP* = All); (2) similar changes in a description of close pairs, i.e., when close pairs are used, they are either separated by one bond only (*CP* = 1), or by one or two bonds (*CP* = 1–2); (3) treating as weak pairs these orbital pairs, which are separated by *n* bonds or more ($WP \geq n$), where *n* can be equal to one, two, or three; (4) utilizing of unextended or extended by one bond strong-pair domains (*EXS* = 0 or *EXS* = 1, respectively); and (5) the same modification (*EXC* = 0 or *EXC* = 1) of close-pair domains.

4.1 Influence of local approximations on the dipole moment

The results for lengths of the dipole moments are listed in Tables 1 and 2 for the cc-pVDZ and Sadlej-POL basis sets, respectively, and additionally are shown in Figs. 3 and 4. By a simultaneous examination of Tables 1 and 2, one can notice that errors for a better Sadlej-POL basis set are generally smaller than the corresponding cc-pVDZ errors. The larger maximum absolute percent errors in Table 2 are solely due to the 2-aminopropane molecule with a very small dipole moment. It has been already observed (see e.g., Ref. [68]) that often smaller dipole moments are more sensitive to the local approximations and show therefore larger relative errors. Without taking into account this one molecule (see the second rows of Table 2), the $\delta_{\max}$ values for the Sadlej-POL basis set are significantly smaller than those from Table 1. Larger cc-pVDZ errors with respect to the nonlocal results can be simply explained by a poor quality of this basis. In the nonlocal case, the description of the electric polarization profits from the next-shell atomic orbitals, which 'mimick' to some extent missing diffuse

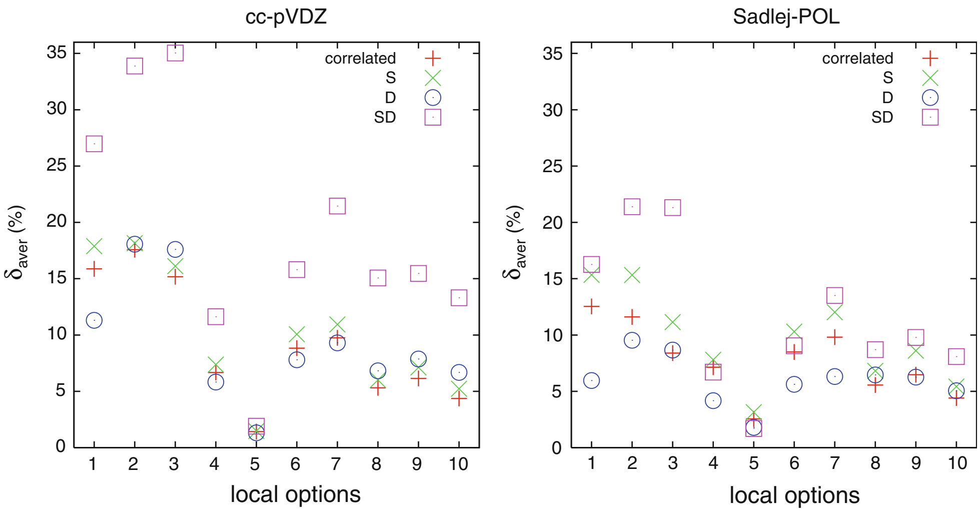


Fig. 3 The mean absolute percent error of the correlation part of the dipole moments for the test set of 31 molecules obtained with various local settings described in Table 1

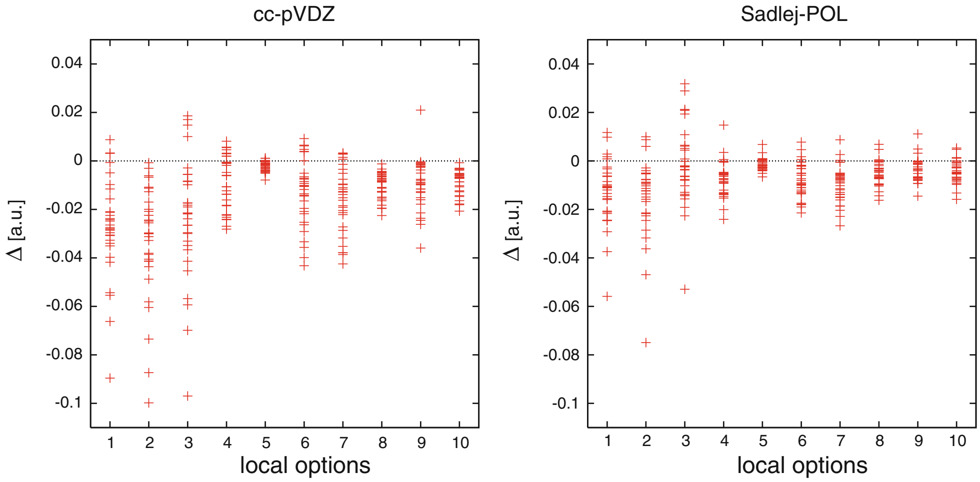


Fig. 4 Signed errors of the dipole moment, $\Delta = |\boldsymbol{\mu}^{\mathrm{corr}}(\mathrm{local})| - |\boldsymbol{\mu}^{\mathrm{corr}}(\mathrm{nonlocal})|$ for the test set of 31 molecules obtained with various local settings described in Table 1. Results are given in a.u.

and high-angular momentum AOs. This process of 'borrowing' of neighbors' AOs is disrupted in the local method by forcing excitations into domains. However, if a better basis set (like Sadlej-POL) is used, the PAOs from the domains are mostly sufficient for a description of the polarization effect, what results in smaller local errors and a weaker dependence of δ_{aver} on local approximations.

In the first row (No. 1 in Tables 1 and 2), standard local settings for the correlation energy were applied, i.e., strong pairs only were utilized in Eq. 11, and no close pairs or domain extensions were used. The average and the maximum percent errors are quite large in this case (16 and 52% for the cc-pVDZ basis set for $|\boldsymbol{\mu}^{\mathrm{corr}}|$). Predictably, even worse results are obtained if MP2 amplitudes are neglected also in the equations for the XCCSD(3) density matrix [Eqs. 15–17], although the error rises by 1.7% only in the cc-pVDZ basis set, and even less for the case of Sadlej-POL. It should be noted that the improvement in a description of the *D* part is quite significant in this case (7.6%), and the only reason for a weak effect on $|\boldsymbol{\mu}^{\mathrm{corr}}|$ is the smallness of the D part itself.

In Sect. 2.3, it has been predicted that if single excitations are allowed to the whole virtual space, but usual limitations are imposed on double excitations, only a small improvement in the description of the local T_1 operator should be observed. This conjecture is tested in the set of local approximations No. 3. As can be seen in both Tables, the errors in comparison to the settings No. 2 become smaller by only 2%, in agreement with the theoretical predictions from Sect. 2.3. Therefore, in order to obtain the

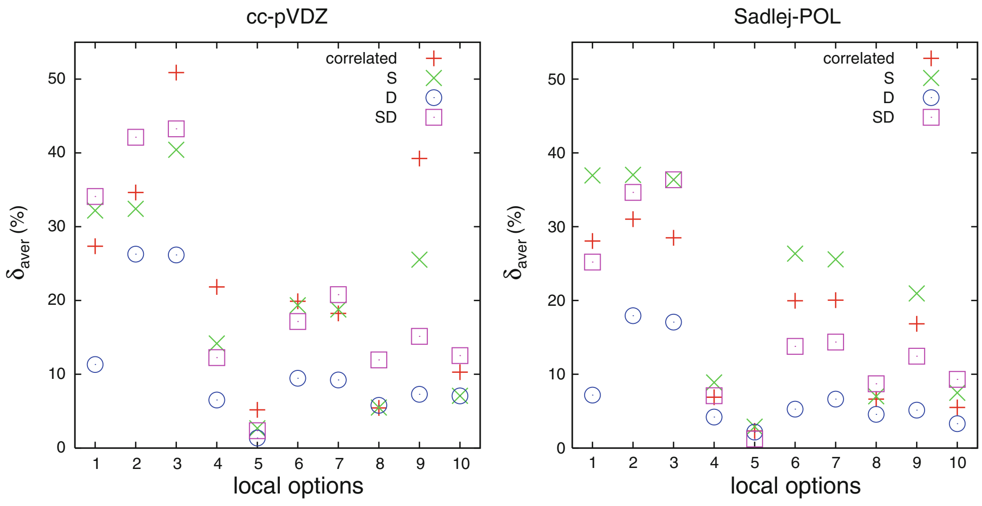


Fig. 5 The mean absolute percent error for the correlated part of the Q_{zz} component of the quadrupole moment for the test set of 34 molecules obtained with various local settings described in Table 1

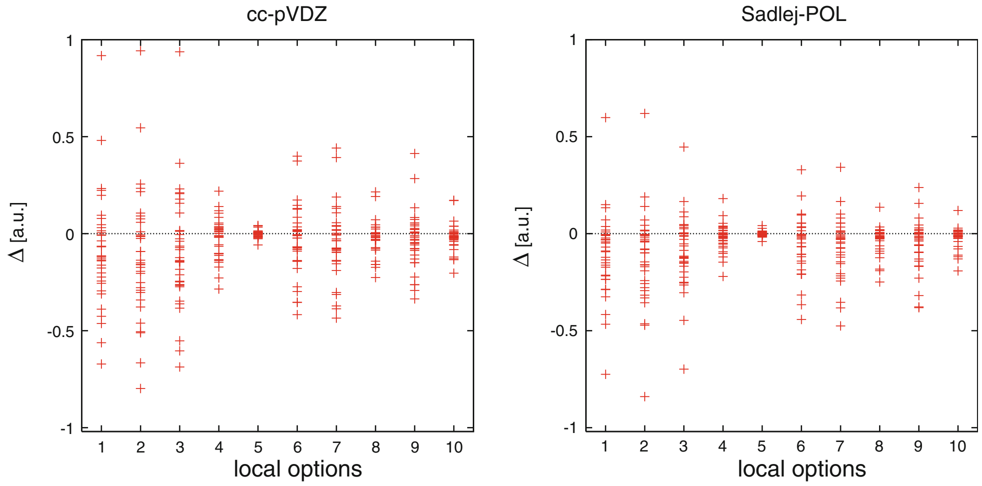


Fig. 6 Signed errors for the Q_{zz} component of the quadrupole moment, $\Delta = Q_{zz}(\text{local}) - Q_{zz}(\text{nonlocal})$ for the test set of 34 molecules obtained with various local settings described in Table 1. Results given in a.u.

local T_1 operator that is accurate enough for the first-order properties, one should rather concentrate on improving a description of the T_2 operator entering Eq. 14. An extension of the single domains alone cannot be sufficient, since possible excitations have been already truncated on the earlier stage of the calculations, i.e., by performing ‘preposterous’ approximations in the local T_2 operator.

In the next two cases, the effect of using all pairs in the local CCSD residual equations (No. 4) and additionally extending the pair domains (No. 5) is examined. In both cases, the errors are significantly reduced in comparison to the first three local settings: δ_{aver} in Table 1 becomes 2.4 times smaller if all pairs are treated as strong and even 11 times smaller if additionally domains are augmented by the next shell of PAOs. Unfortunately, the options No. 4 and 5 are completely unpractical, as they require an expensive solution of the CCSD residual equations to be performed for all orbital pairs. Therefore, in the next cases, we will gradually decrease the number of strong pairs and reduce the pair-domain dimensions in order to see to what extent the locality criteria can be relaxed for the first-order properties. To this end, in the next set of local options (No. 6), a list of strong pairs has been limited to the pairs with the separation index equal to 0 or 1. The settings No. 6 give considerably better results than No. 1 and are only slightly worse than No. 4 (note that all three approximations use the original, i.e., unextended, pair domains). The next are the settings No. 7, where pairs with the separation index equal to 1 are shifted from the strong-pair list to the close-pair list, which allows to further reduce the computational time

Table 5 Percent errors for the local XCCSD(3) dipole moment lengths for the test set of polyglycines and for two large molecules from Refs. [92] and [93] obtained with the recommended local approximations

Molecule	δ_{tot}	δ_{corr}	δ_S	δ_D	δ_{SD}	n_{strong}	n_{close}	n_{weak}	D_{strong}	D_{close}	D_{weak}	N_{AO}
$(gly)_1$	0.5	−0.8	−1.1	−3.2	−5.0	52	59	9	56	42	31	95
$(gly)_2$	−0.1	−3.0	−3.2	−7.8	−13.1	95	137	119	69	49	44	166
$(gly)_3$	−0.7	−4.4	−4.0	−4.2	−5.4	140	213	350	69	48	44	237
$(gly)_4$	−1.0	−10.1	−9.4	−11.0	−21.4	185	289	702	75	52	49	308
$(gly)_5$	−1.2	−9.6	−8.5	−7.7	−7.9	230	365	1,175	77	53	50	379
$(gly)_6$	−1.3	−12.4	−11.3	−12.7	−33.9	275	441	1,769	78	53	51	450
Ref. [92]	3.0	−10.0	−10.5	−9.0	−11.1	205	268	703	95	51	51	358
Ref. [93]	0.4	−10.5	−12.1	−8.5	−17.5	277	269	582	141	77	54	342

The domains of two latter molecules were merged whenever the original domains share at least two atoms (the `MERGEDOM=1` option in MOLPRO). N_{AO} denotes the dimension of the orbital basis, δ_{tot} (δ_{corr}) is the percent error of the total (correlation) part of the length of the local XCCSD(3) dipole moment with respect to the nonlocal value, while δ_S, δ_D, and δ_{SD} are the percent errors of the *S*, *D* and *SD* parts of the LXCCSD(3) dipole moment with respect to the nonlocal *S*, *D* and *SD* values. n_{type} and D_{type} stay for the number of pairs of a given type and the average domain dimension for this pair type, respectively

spent on Eq. 11. A comparison of settings No. 6 and No. 7 shows that the average error increases by about 1%, when these pairs are downgraded to the close-pair list.

The overall reduction of errors observed when going from No. 1 to No. 7 is still not satisfactory. The theoretical analysis presented in Sect. 2 and a spectacular decrease of the δ_{aver} values caused by the extension of pair domains (see No. 5) suggest that an augmentation of some domain types might be a valuable option. In order to test this possibility, the next local approximation is utilized which adds PAOs separated by one bond to the strong-pair domains. If additionally pairs separated by two bonds are also classified as close (the settings No. 8), the error of the total dipole moment becomes only 1.0% and the error of the electron-correlated part—only 5.3% for the cc-pVDZ basis (the respective numbers for the Sadlej-POL basis are: 0.6 and 5.6% for the same set of molecules, or 0.5 and 3.5% if the 2-aminopropane molecule with a small dipole moment strongly dependent on the correlation effects is excluded from the test set). Although this result is already satisfactory, it is worth to try whether the list of close pairs can be shortened so that only LMOs pairs separated by one bond are treated as close (No. 9). Unfortunately, the numerical tests show that even if the average percent error does not rise much in this case, the absolute deviations for the settings No. 9 presented in Fig. 4 are significantly larger than for the case No. 8. The last test (No. 10) presented in Tables 1 and 2 examines the effect of improving of the settings No. 8 by an extension of the close-pair domains. This enlargement of the allowed excitation space leads to slightly better results than those obtained with the settings No. 8, but the improvement is not large enough to sacrifice even more computational time for the local calculations.

Finally, it is interesting to examine the spread of the signed errors shown in Fig. 4. One can see for instance that the largest deviations become systematically smaller for the settings No. 5, 8, and 10. It is also worth to notice that the local correlation treatment has a tendency to underestimate the length of the dipole moment resulting from the electron correlation, although this effect seems to be more pronounced for the cc-pVDZ basis set. By comparing both parts of Fig. 4, one can also observe that the errors become in general smaller for a better basis, which is a well-known effect in the local methods, already explained at the beginning of this section.

4.2 Influence of local approximation on the quadrupole moment

The percent errors for the largest diagonal component of the traceless quadrupole moment are presented in Tables 3 and 4 and in Figs. 5 and 6 for the test set of 34 molecules. The first comment is due to huge maximum percent errors (δ_{max}) in these tables. The data analysis reveals that these errors are obtained from a small subset of molecules, namely for 2-aminopropane, 2-nitropropane, and butane. For 2-aminopropane, the contribution from the electron correlation to the quadrupole moment is below 1%, and even very large relative errors result in completely insignificant errors for the total Q_{zz} component. For two other problematic molecules, large percent errors occur only for some local settings and are reduced to one-digit values if e.g., the settings No. 5, 8, or 10, selected as the best ones for the dipole moments, are utilized. However, the existence of such cases for the quadrupole moment should be noticed and will require more attention in the future. Apart from the large δ_{max} values, the examination of both tables leads to virtually the same conclusions as reached for the dipole moments. An interesting finding can be made from a comparison of the options No. 2 and 3, which clearly shows that the extension of single domains does not improve the S part of the Q_{zz} term. Interestingly, for the cc-pVDZ basis set, a presumably better option No. 9 gives worse results than No. 7, but for the better Sadlej-POL basis set, these trends are reversed back to the anticipated way (No. 9 better than No. 7). Finally, Fig. 6 shows signed Q_{zz} errors for both basis sets. Similarly, as in Fig. 4, the spread of the errors becomes smaller if the settings No. 5, 8, or 10 are employed. One can also notice smaller deviations from nonlocal references for the case of the larger Sadlej-POL basis set. Interestingly, the errors are in this case evenly scattered between the negative and the positive half of the figure, which indicates that there is a similar probability of obtaining a local quadrupole moment, which is smaller or larger than the nonlocal value. Summarizing, the quadrupole moments seem to be more sensitive to the quality of the local settings than the dipole moments, although this undesirable feature persists only for about 10% of the molecules under study. The accuracy of local Q_{zz} for other molecules is similar as for the case of the dipole moment, and it can be concluded that the same local approximations work well for both dipole and quadrupole moments.

4.3 Selection of the optimal local settings and example applications

The data collected in Tables 1, 2, 3 and 4 and in Figs. 3, 4, 5 and 6 allow to select the local criteria, which should be used for the calculation of the first-order local XCCSD properties. As already mentioned, for a cost-effective method, the classification of the orbital pairs should be preserved, which excludes the settings No. 4 and 5. From other combinations of the local options, two settings No. 8 and 10 perform the best. Since the set No. 10 leads to more expensive CCSD residual equations, No. 8 has been chosen as the optimal set of options from the point of view of predicted accuracy and estimated computational costs. Since the same local approximations work for both dipole and quadrupole moments, it is expected that these criteria are quite universal.

Table 5 lists relative errors of the dipole moments for several polyglycines, (gly)$_n$, obtained for the selected local options (No. 8 from Table 1) as well as various data, like the number of orbital pairs and the domain dimensions, which allow to estimate the potential computational gains of the local approach. In the same table, the similar data for two example real-life molecules are presented. Table 5 reveals that the number of strong and close pairs grows linearly with the number of the glycine units n, and the average sizes of all domains for (gly)$_n$ quickly become independent of the molecular size. The average domain size of the real-life molecules is larger, especially for the extended strong-pair domains, but nonetheless, it is much smaller than the total number of AOs. The percent errors for the three largest polyglycines are around 10% for the correlation part of the property. The same error can be observed for the molecules from Refs. [92, 93]. The percent error of the total dipole moment length is of order of 1% for all cases.

5 Summary

The study of the applicability of local approximations in the CCSD wave function for the calculation of first-order one-electron properties from expectation-value coupled cluster theory has been presented. The results show that the standard local approximations do not work well for properties, but the proposed modifications in the local settings allow for a threefold reduction of the average percent error (from 16 to 5%) for the electron-correlated part of the dipole moment obtained with the cc-pVDZ basis set. The new options involve the inclusion of close pairs into the residual CCSD equations, and the extension of the strong-pair domains by one shell of atoms and the utilization of LMP2 amplitudes in the expression for the XCCSD(3) reduced density matrix. It should be stressed that this reduction of errors has been achieved without an explicit inclusion of the orbital relaxation, so one can conclude that accurate local first-order CCSD properties can be obtained without accounting for the relaxation of the orbitals. The sensitivity of the results to various local restrictions has been explained by the examination of the iterative MP formulae for the T_1 and T_2 operators and the expressions for the XCCSD(3) first-order properties. From this analysis and from the numerical results, one can conclude that for the first-order properties, single excitations should be treated in a privileged way, opposite to the case of the correlation energy. Moreover, since the main contribution to the T_1 cluster operator is constructed by utilizing the single-excited part of the $[W,T_2]$ commutator, double excitations from T_2 should be also accounted for accurately enough, e.g., in order to achieve a proper description of the $\widehat{\mathscr{P}}_1(WT_2)$ operator, the range of summation indices connecting the W and T_2 operators should be extended for both occupied and virtual indices. Such an enrichment of the local excitation space can be achieved in a systematic way by adding close pairs and augmenting strong-pair domains, which affects occupied and virtual summation ranges, respectively. Additionally, the description of the virtual–virtual and occupied–occupied parts of the local XCCSD(3) density matrix should be improved by utilizing the LMP2 amplitudes in all places where the LCCSD amplitudes are not available because of the local restrictions. Summarizing, in the selected optimal local settings (1) excitations from the strong pairs utilize the domains extended by one shell of atoms, (2) the LMP2 amplitudes t_{ab}^{ij}, where the LMOs ϕ_i and ϕ_j are separated by one or two bonds, are used in local CCSD residual equations, and (3) all LMP2 pairs enter into the equations for the XCCSD(3) density matrix.

It should be noted that the proposed local settings should work as well for the response CCSD case, since both XCCSD and response CCSD formulae have the same MP expansion through order $\mathcal{O}(W^2)$. Although the new local configurational space is larger than the space utilized for the correlation energy calculations, it is nonetheless considerably smaller than the full space for single and double excitations in the nonlocal case. Since the numerical results presented in this paper show that the classification of the orbital pairs can still be utilized, the most expensive calculation of the LCCSD amplitudes can be performed for the strong pairs only, while all other pairs can be treated by the relatively cheap LMP2 method.

Summarizing, the performed study leads to the conclusion that the local approach can be applied with confidence for expectation-value CCSD theory. Since highly efficient linear-scaling algorithms for the calculation of the local *T* operator from CCSD theory are already available within the MOLPRO suite of programs, their application together with the newly developed local settings, reported in this contribution, will allow to perform calculations of local XCCSD(3) first-order properties at a fraction of cost of the original nonlocal method.

Acknowledgments The European Science Foundation and the Polish Ministry of Science and Higher Education (Grant No. 1165/ESF/2007/03) is acknowledged for financial support.

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