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Assessment of DLPNO-CCSD(T)-F12 and its use for the formulation of the low-cost and reliable L-W1X composite method

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Abstract

In the present study, we have investigated the performance of RIJCOSX DLPNO-CCSD(T)-F12 methods for a wide range of systems. Calculations with a high-accuracy option ["DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12"] extrapolated to the complete-basis-set limit using the maug-cc-pV[D+d,T+d]Z basis sets provides fairly good agreements with the canonical CCSD(T)/CBS reference for a diverse set of thermo-chemical and kinetic properties [with mean absolute deviations (MADs) of ~1–2 kJ mol^{-1} except for atomization energies]. On the other hand, the low-cost "RIJCOSX DLPNO-CCSD(T)-F12D" option leads to substantial deviations for certain properties, notably atomization energies (MADs of up to tens of kJ mol^{-1}). With the high-accuracy CBS approach, we have formulated the L-W1X method, which further includes a low-cost core–valence plus scalar-relativistic term. It shows generally good accuracy. For improved accuracies in specific cases, we advise replacing maug-cc-pV(n+d)Z with jun-cc-pV(n+d)Z for the calculation of electron affinities, and using well-constructed isodesmic-type reactions to obtain atomization energies. For medium-sized systems, DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12 calculations are several times faster than the corresponding canonical computation; the use of the local approximations (RIJCOSX and DLPNO) leads to a better scaling than that for the canonical calculation (from ~6–7 down to ~2–4 for our test systems). Thus, the DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12 method, and the L-W1X protocol that based on it, represent a useful means for obtaining accurate thermochemical quantities for larger systems.

KEYWORDS
DLPNO-CCSD(T)-F12, thermochemistry, W1X composite protocol

1 | INTRODUCTION

The CCSD(T) method[1] at the complete-basis-set (CBS) limit has long been the "gold standard" of computational chemistry owing to its consistently achievable chemical accuracy (1 kcal mol^{-1}, i.e., ~4.2 kJ mol^{-1}) for many typical systems that are of practical interest.[2] Nonetheless, it requires substantial computational resources, and thus, to this day, its direct application is restricted to relatively small systems.

Various approaches have been used to approximate CCSD(T)/CBS. The CBS limit can be estimated by extrapolation with multiple small basis sets.[3,4] In relation to CBS extrapolation, the basis-set convergence behaviors for different components within CCSD(T), for example, the HF, CCSD correlation, and (T) correlation energies, are different. This further enables the use of optimally sized basis sets for extrapolating the various components in a layered approach, yielding computationally efficient

composite protocols such as Wn,[2,5] ccCA,[6] Gn,[7] and CBS[8] families of procedures.

In recent times, several other techniques have been developed to lower the computational cost of the CCSD(T) method. The inclusion of explicit correlation in F12-type methods has lessened the demand in the basis set;[9] this has led to substantially more efficient variants of established composite methods. Local-correlation approaches (e.g., DLPNO-CCSD(T),[10] LNO-CCSD(T),[11] PNO-LCCSD(T)[12]) automatically divide a large system into small quasi-independent fragments, which at best would essentially linearize the formally N^7-scaled CCSD(T) method. In addition, both the F12 and local-correlation approaches incorporate density fitting (DF), which further leads to more than an order of magnitude improvement in efficiency.

Among the many approaches for lowering the requirements in CCSD(T) computations, layered extrapolation is of sufficient accuracy such that the most rigorous CCSD(T)-based composite methods such as W2[13] can be considered essentially equivalent to CCSD(T)/CBS. Similarly, the F12 and the associated DF approximations are highly accurate; the F12 variants of Wn (i.e., WnX[14–16] and Wn-F12[5,17]) have been shown to deliver the substantial gain in efficiency with minimal loss in accuracy (by less than ~1 kJ mol^{-1}).

In comparison, local-correlation methods are still under active development, and their general accuracies has yet to be firmly established. Among the different approaches, the recently proposed DLPNO-CCSD(T)-F12 method,[18] as implemented in the ORCA 5[19,20] program, has several desirable features in terms of usability. It is currently implemented for both closed- and open-shell systems;[21] the ORCA program has the RIJCOSX method[22] that can (essentially) linearize the HF component of the CCSD(T) calculation; last but not the least, it has implemented the automatic generation of all the necessary DF basis sets.[23] Thus, the current implementation of DLPNO-CCSD(T)-F12 is virtually a black-box method like CCSD(T), and it can be directly used with any arbitrary basis sets.

The DLPNO-CCSD(T)-F12 method has been assessed for the reaction energies for a set of small molecules, and non-covalent interactions for some medium-sized systems,[18] while the parent DLPNO-CCSD(T) method has been tested more thoroughly.[24–29] With the lessened requirement on the basis set, we are optimistic about the prospect for the DLPNO-CCSD(T)-F12 method to achieve chemical accuracy using triple- or even double-ζ basis sets. Thus, in the present study, we evaluate the performance of DLPNO-CCSD(T)-F12 for a more diverse set of systems and properties, to contribution to establishing its general applicability.

2 | COMPUTATIONAL DETAILS

Standard computational chemistry calculations were carried out with ORCA 5[19,20] and Molpro 2020.[30] Geometries were obtained from previous studies. Specifically, those presented in Table 1 were from refs 31 (E0s), 32 (P34s), 33 (MB13), 34 (BH28), 35 (ZGLY), 36 (plat-AE and plat-CBH3), and 37 (PAH-BS and PAH-RO). Those for the G2/97 set[38,39] were taken from ref 40, while the geometries for the BSR-alkane and BSR-alkene sets of Table 5 were taken from refs 41 and 42, respectively. High-level reference energies were obtained primarily from the same literature, namely refs 32 (E0s), 34 (BH28), 35 (ZGLY), 36 (plat-AE and plat-CBH3), 37 (PAH-BS and PAH-RO), 40 (G2/97), 41 (BSR-alkane), and 42 (BSR-alkene). In some cases, we obtained improved reference values in the present study, as detailed in Results and Discussion. Technical options used in the single-point energy calculations were also discussed below, mainly in the options used in the calculations sub-section. Examples for carrying out calculations with some of the methods introduced in the present study are given in the ref 43, along with additional brief discussions. Relative energies in the text are reported in kJ mol^{-1}.

3 | RESULTS AND DISCUSSION

3.1 | The primary test sets

To assess the accuracy of a CCSD(T)-type method, we perceive that the reference data should be of at least similar quality. On the other hand, as we are interested in DLPNO-CCSD(T)-F12 as an approximation to CCSD(T), the inclusion of post-CCSD(T) effects would not be relevant. Thus, we use Wn-type approximations to CCSD(T)/CBS as our benchmark. For the most part of the present study, we focus on valence CCSD(T) without the incorporation of core-correlation effects, as this is often the only practical choice for large-scale applications.

The systems that we use in this pilot study are main-group species because CCSD(T) itself is often inadequate for transition metals owing to multi-reference characters for many of these species. For instance, we have shown that the CrO, CrO_2 and CrO_3 species necessitate the use of at least CCSDTQ(5) for a proper description.[44] The challenge is also evident from the analysis of a wide range of diagnostics for a large set of transition-metal molecules.[45,46] Alas, economical computation of post-CCSD(T) effects remains difficult.

We have in the past examined some transition-metal systems that can be expected to be described reasonably by CCSD(T).[47] However, many of these employ DLPNO-CCSD(T) values as reference, making these datasets inadequate for the assessment of the DLPNO-CCSD(T)-F12 method. The test sets of the present study are shown in Table 1. They either have existing reference values that are of W1- or W2-type quality, or the size of their constituent species are sufficiently small such that data of such quality can be readily obtained.

The E0s set is derived from the E0 set[31] of atomization energies, barrier heights, hydrogen bond energies, and dispersion interactions, which we used in the development of G4(MP2)- and Wn-type composite protocols.[48,49] It contains 22 energies from the E0 set, and the data points were chosen by a statistical method that we used to derive small data sets from larger ones.[50] The P34s set[32] comprise fundamental thermochemical properties of heavy-main-group species (up to the element I). The MB13 set[33,50] contains artificially created species for "stress-testing" theoretical methods. Likewise, BH28 are a

Set	#	Ref level[a]	Description
E0s	22	W2X	atomization energies, barriers, hydrogen bond energies, and dispersion interactions for light-main-group species
P34s	6	W1-P34	atomization energies, ionization energies, and electron affinities for heavy-main-group species
MB13	13	W2X	reaction energies for artificially created species
BH28	28	W1-F12	barriers for pericyclic, cycloaddition, cycloreversion, and proton-exchange reactions
ZGLY	20	W1X-2	complexation energies of zwitterionic glycine with 5-water clusters
plat-AE	6	W1-F12	atomization energies for platonic hydrocarbons
plat-CBH3	6	W1-F12	connectivity-based-hierarchy (level 3) isodesmic-type reaction energies for platonic hydrocarbons
PAH-BS	18	W1-F12	reaction energies for bond-separation-isodesmic-type reactions for polycyclic aromatic hydrocarbons
PAH-RO	13	W1-F12	reaction energies for ring-overlap-isodesmic-type reactions for polycyclic aromatic hydrocarbons

[a]Valence CCSD(T)/CBS components of these composite methods.

collection of barrier heights that may represent notable challenges.[34] The ZGLY data set[35] contains interactions of zwitterionic glycine with a cluster of five surrounding water molecules. For these energies, we have previously found that the DLPNO-CCSD(T_0) method (of ORCA 4) shows deviations on the order of 1–5 kJ mol^{-1} that grow rapidly with system size.

The above test sets contain thermochemical properties that are calculated directly. For some properties such as atomization energies, the deviations for direct calculations often scale with the system size, such that large species are often associated with large deviations. In such cases, the use of isodesmic-type reactions can usually reduce the deviations by error cancellation,[51] such that reasonably accurate atomization energies can be obtained for, for example, medium-sized fullerenes.[52–54] In the present study, we examined two sets of systems, namely platonic hydrocarbons[36] and polycyclic aromatic hydrocarbons;[37] for each of these, we use two different approaches to investigate how the use of isodesmic-type reactions influence the accuracy in the DLPNO-CCSD(T)-F12 computations.

3.2 | Options used in the calculations

We now turn our attention to the DLPNO-CCSD(T)-F12 methods that we will assess in the present study. As noted earlier, it can be used in conjunction with the RIJCOSX method, such that both the correlation component and the underlying HF component can at best be linearized. In the present study, we will combine both features and use RIJCOSX DLPNO-CCSD(T)-F12 throughout.

The two cost-saving methods are associated with adjustable options for achieving various level of accuracies. For RIJCOSX, a key option is the sizes of the integration grids that it uses. In ORCA 5,

three conveniently defined sizes can be chosen with the keywords DefGrid1 (smallest), DefGrid2 (medium), and DefGrid3 (largest); the default is DefGrid2. For DLPNO, a major parameter is the set of PNO cut-offs, which can be straightforwardly set by the documented LoosePNO, NormalPNO, and TightPNO keywords. For DLPNO-CCSD (T)-F12, the default is TightPNO, which, among these three options, offers the best predefined accuracy that is required for F12 calculations. In addition, a VeryTightPNO keyword is also available, but its use incurs significantly higher cost.

There are also options associated with the (T) and the F12 parts of the method. By default, the perturbative triplets in DLPNO-CCSD (T)-F12 refers to the (T_0) variant.[18] A theoretically more rigorous method can be chosen by the "DLPNO-CCSD(T1)-F12" keyword.[55] For the F12 component, there is a lower-cost F12D alternative. Overall, the various options in the RIJCOSX, DLPNO, (T) and F12 components would lead to many combinations. In the present study, we simply investigate the two ends of the spectrum. At the low-cost end, we use the "RIJCOSX DLPNO-CCSD(T)-F12D" keywords, and we use the "DefGrid3 RIJCOSX DLPNO-CCSD(T1)-F12" keywords at the high-accuracy end.

Let us now consider the basis sets to be used in the RIJCOSX DLPNO-CCSD(T)-F12 calculations. The primary function for the inclusion of the F12 term is to accelerate the basis set convergence. Indeed, modest double-ζ (DZ) and triple-ζ (TZ) basis sets are used in our W1X methods[56] that have comparable accuracy to the W1 method on which they are based, but the W1 method employs up to QZ-type basis sets.

In the present study, we use mainly the maug-cc-pV(D+d)Z and maug-cc-pV(T+d)Z basis sets,[57] which incorporate minimal sets of diffuse functions that we deem sufficient for the treatment of most properties. For Ga–Kr and In–Xe for which the inner-valence electrons are also correlated in the reference valence W1-P34[32]

calculations, we use the maug-cc-pWCVDZ-PP and maug-cc-pWCVTZ-PP basis sets.[58] For the "plat" and "PAH" sets, cc-pVDZ and cc-pVTZ are used for carbon; the use of nonaugmented basis sets is of little thermochemical consequence for neutral hydrocarbons,[2,13] but it alleviates difficulties associated with linear-dependency issues.

In addition to the conventional orbital basis sets, several DF sets are also required. They are the Coulomb, correlation-energy, and complementary auxiliary basis correction (CABS) fitting sets, as defined by the AuxJ, AuxC, and CABS options, respectively. While the two key orbital basis sets have predefined fitting sets for many elements, there are cases in which some fitting sets are not available. In those case, one may use fitting sets designed for other orbital basis sets, but this would not be ideal and is somewhat arbitrary. Instead, we use the AutoAux option to generate all the required fitting sets, which maintains a level of consistency, as well as ensuring a fully black-box operation.

The use of a DZ and a TZ basis sets would enable extrapolation to the complete-basis-set (CBS) limit, which would be analogous to the W1X methods. In the present study, we use the same formula for the CBS extrapolation, that is, $E_L = E_{CBS} + AL^{-\alpha}$, where L is the cardinal number of the basis set (2 for DZ and 3 for TZ) and α is often treated as a numerical parameter.[3] The HF, ΔCCSD [i.e., $E_{CCSD} - E_{HF}$], and the Δ(T) [$E_{CCSD(T)} - E_{CCSD}$] components are extrapolated separately.

For HF, the α value is asymptotically 5. For conventional CCSD(T) calculations, a typical α value for both the ΔCCSD and Δ(T) components is 3, though a value of 6 has been put forward in recent studies for the correlation energy to approach the asymptote in the F12 ansätze.[59–61] With CCSD(T)-F12 computations in our W1X-2 procedure, we find values of 4.74 [ΔCCSD] and 2.09 [Δ(T)] to be optimal. For the sake of consistency, we use these for the similar DLPNO-CCSD(T)-F12 methods. In passing, we also note several alternative approaches for CBS extrapolation that have been proposed recently;[59–61] their use would be of interest in future studies.

3.3 | Results for the main test set

Let us now look at the performance of the RIJCOSX DLPNO-CCSD(T)-F12 method with our chosen options for the main test set introduced above. At the lowest-cost-end of the spectrum, the method corresponds to RIJCOSX DLPNO-CCSD(T)-F12D/DZ. It performs reasonably for the E0s set that comprises light main-group species. The mean absolute deviation (MAD) is 5.5 kJ mol^{-1} (Table 2). Similarly, reasonable MADs are also found for the BH28 set of barriers (5.9 kJ mol^{-1}), the ZGLY set of zwitterionic-glycine–5-water interaction energies (6.1 kJ mol^{-1}), and the PAH-RO set of ring-separation-type isodesmic reaction of polycyclic aromatic hydrocarbons (3.7 kJ mol^{-1}).

Larger MADs are obtained for the other sets, namely, the MB13 set of artificially created species (9.4 kJ mol^{-1}), the level-3 connectivity-based-hierarchy[62] isodesmic-type reaction energies for platonic hydrocarbons (the plat-CBH3 set, 11.5 kJ mol^{-1}), and the bond-

TABLE 2 Mean absolute deviations (kJ Mol^{-1}) for the main test sets of Table 1 obtained with RIJCOSX DLPNO-CCSD(T)-F12 with the low-cost and high-accuracy settings chosen for the present study

Set	Low-cost[a]			High-accuracy[b]		
	DZ	TZ	CBS	DZ	TZ	CBS
E0s	5.5	2.2	2.0	5.5	1.9	1.0
P34s	37.3	23.4	19.1	31.0	7.1	4.2
MB13	9.4	11.2	11.8	9.8	4.1	3.6
BH28	5.9	3.6	2.9	4.0	1.8	1.6
ZGLY	6.1	1.3	1.6	10.7	2.8	1.5
plat-AE	62.8	45.8	20.1	29.7	9.4	5.1
plat-CBH3	11.5	2.1	1.0	5.5	1.9	4.8
PAH-BS	13.4	3.2	5.8	4.1	0.7	1.0
PAH-RO	3.7	1.3	1.9	1.2	0.5	0.4

[a]Correspond to the "RIJCOSX DLPNO-CCSD(T)-F12D" keyword in ORCA 5.0.1.
[b]"DefGrid3 RIJCOSX DLPNO-CCSD(T1)-F12."

separation-type reaction energies for polycyclic-aromatic hydrocarbons (the PAB-BS set, 13.4 kJ mol^{-1}). Furthermore, exceptionally large MADs are obtained for the P34s set of heavy-main-group species (37.3 kJ mol^{-1}) and plat-AE set of atomization energies for platonic hydrocarbons (62.8 kJ mol^{-1}). Thus, overall, the performance of RIJCOSX DLPNO-CCSD(T)-F12D/DZ is inconsistent, and it is not advisable to use it for the computation of reference thermochemical values in arbitrary cases.

From this point, we can use larger basis sets, or improve the treatment in the method, or do both. If we use larger TZ basis sets, we see generally smaller MADs. In some cases, significantly better accuracies are achieved. However, for the P34s and the plat-AE sets, the improvements from 37.3 to 23.4 kJ mol^{-1} (P34s) and from 62.8 to 45.8 kJ mol^{-1} (plat-AE) are far from being sufficient. If we further extrapolate the RIJCOSX DLPNO-CCSD(T)-F12D energies to the CBS limit, we find further improvements for most sets, but the accuracies for the P34s (19.1 kJ mol^{-1}) and plat-AE (20.1 kJ mol^{-1}) sets remain inadequate.

What about the use of the more rigorous "DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12" method? With the DZ basis sets, we see general improvements over RIJCOSX DLPNO-CCSD(T)-F12D especially for the test sets with significant deviations (P34s, from 37.3 to 31.0 kJ mol^{-1}, and plat-AE, from 62.8 to 29.7 kJ mol^{-1}). Overall, the improvements provided by the improved method are of similar degree to that resulted from the use of TZ basis sets. Both changes alone do not lead to a sufficiently consistent method for the calculation of accurate reference thermochemical values.

When we apply both the more rigorous method and larger basis sets, that is, DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/TZ, we see that the MADs for all test sets are lowered to less than 10 kJ mol^{-1}. If we further extrapolate the results to the CBS limit, we now arrive at MADs that are ~5 kJ mol^{-1} or less for all test sets.

We note that, for the E0s, MB13, and BH28 sets, the reference values are obtained with the W2X or W3 methods that are equivalent to at least the CCSD(T)-F12/[T,Q]Z level, which is closer to the CBS than the [D,T] extrapolation for the DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12 calculations. For these sets, we have obtained values with the W1X-2 method, which is a composite CCSD(T)-F12/[D,T]Z method without local approximation. The MADs are 0.5 (E0s) and 1.7 (MB13) kJ mol^{-1}. Thus, for these two sets, the accuracies of this DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/[D,T]Z protocol is just slightly less well than those for the canonical CCSD(T) method.

For the other test sets, the reference values correspond roughly to conventional CCSD(T)-F12/[D,T]Z, and they can be expected to have general uncertainties in the vicinity of 3–5 kJ mol^{-1}. Thus, the MADs for the DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/[D,T]Z protocol are consistent with the perceived achievable accuracy, and this is attained with local approximations that may enable the application to significantly larger systems.

In passing, it is noteworthy that the comparison between the plat-AE and PAH-BS sets on the one hand, and the plat-CBH3 and PAH-RO sets on the other hand, illustrates the utility of well-constructed isodesmic-type reactions for obtaining accurate relative energies with low-cost methods. In the case of PAH-RO set of carefully formulated ring-overlap isodesmic-type reactions, even the lowest-cost method achieves chemical accuracy (3.7 kJ mol^{-1}). In comparison, the corresponding PAH-BS set of bond-separation-type reactions, which benefit less from error cancellation, has a significant MAD of 13.4 kJ mol^{-1}.

3.4 | Further validation and the assessment of a "local-W1X" method

Let us now further scrutinize the accuracy of the local-CCSD(T) method for the computation of thermochemical properties. Specifically, we examine just the DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/[D,T]Z method because, between the methods shown in Table 2, it is the only one that achieves (essentially) chemical accuracy for all test sets.

Among the test sets in Table 2, the worst performances can be seen for the plat-AE set of atomization energies (MAD = 5.1 kJ mol^{-1}), the corresponding plat-CBH3 isodesmic-type reactions (4.8 kJ mol^{-1}), and the P34s set of atomization energies, ionization energies, and electron affinities for heavy-main-group species (4.2 kJ mol^{-1}). Thus, such "fundamental chemical properties" appear to be more challenging than typical reaction energies, barriers, and noncovalent interactions. We therefore focus on such quantities, and we use the G2/97 test set for the assessment, which contains a wide range of prototypical chemical systems.

For the G2/97 set, we have previously obtained high-level W3X-L[40] (i.e., W2X + post-CCSD(T) effects) reference energies. We will use the valence W2X component as the benchmark for validating the valence DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/[D,T]Z energies. In addition, for fundamental chemical properties, core–valence

TABLE 3 Mean absolute deviations (kJ mol^{-1}) from W2X reference values for the G2/97 set and its subsets [atomization energy (AE), ionization energy (IE), electron affinity (EA), and proton affinity (PA)] obtained with the W1X-2 and "local-W1X" protocols

Method	G2/97	AE	IE	EA	PA
valence[a]					
W1X-2	1.7	2.6	0.9	0.7	0.8
L-W1X (maug)	3.7	4.5	1.4	5.4	0.8
L-W1X (jun)	2.9	4.3	1.7	1.5	1.5
ΔCV+SR[b]					
W1X-2	1.7	3.1	0.4	0.2	0.7
L-W1X (maug)	1.4	2.0	0.9	0.7	0.7
L-W1X (jun)	"	"	"	"	"
Combined					
W1X-2	1.4	1.8	1.0	0.8	1.4
L-W1X (maug)	4.5	6.1	1.6	5.5	1.2
L-W1X (jun)	3.9	5.9	2.2	1.6	2.2

[a]L-W1X (maug) values obtained as DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/maug-cc-pV[D+d,T+d]Z energies, and L-W1X (jun) uses jun-cc-pV[D+d,T+d]Z.
[b]Core–valence plus scalar-relativistic contributions obtained, for L-W1X, as all-electron DKH DefGrid3 RIJCOSX DLPNO-MP2/cc-pWCVTZ energy minus the corresponding non-relativistic frozen-core value.

correlation effects represent a non-negligible contribution. We thus also examine the prospect of using a local-correlation method for the calculation of such effects.

In W2X, a combined core–valence plus scalar-relativistic (CV+SR) component is obtained in a composite manner [MP2/TZ+ΔCCSD(T)/DZ]. We will use these values as our reference. In the lower-cost W1X-2 method, the corresponding term is obtained with just the MP2 calculations. In the present study, because we aim to assess the performance of a low-cost option for obtaining reliable energies, we will base our CV+SR calculations on MP2. Specifically, we use the "DKH DefGrid3 RIJCOSX DLPNO-MP2/cc-pWCVTZ method", that is, ΔCV+SR = all-electron DKH DefGrid3 RIJCOSX DLPNO-MP2/cc-pWCVTZ minus frozen-core DefGrid3 RIJCOSX DLPNO-MP2/cc-pWCVTZ. We do not use the DLPNO-MP2-F12 method as the support for open-shell systems is yet to be implemented.

Table 3 shows the results of the assessment for the valence RIJCOSX DLPNO-CCSD(T$_1$)-F12 energies, the RIJCOSX DLPNO-MP2 ΔCV+SR contributions, and the total composite energies. To provide a baseline for comparison, we have also obtained the corresponding W1X-2 values. At the W1X-2 level, the MADs for the G2/97 set and its subsets are all within the chemical accuracy of 4.2 kJ mol^{-1} for the valence component, the ΔCV+SR component, and the combined composite energies.

For the valence RIJCOSX DLPNO-CCSD(T$_1$)-F12 relative energies calculated with the extrapolated maug-cc-pV[D+d,T+d]Z basis sets, that is, the high-accuracy CBS method of Table 2, we find reasonable accuracies for the ionization energies (IEs) and proton affinities (PAs),

TABLE 4 Mean absolute deviations (kJ Mol^{-1}) and mean deviations for the G2/97 set and its subsets for DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/Jun-cc-pV[D+d,T+d]Z and its underlying HF, ΔCCSD, and Δ(T) components against benchmark values of W2X

Component	G2/97	AE	IE	EA	PA
Mean absolute deviation					
CCSD(T)	2.9	4.3	1.7	1.5	1.5
HF	16.2	29.2	3.6	4.5	0.2
ΔCC	12.7	21.5	4.1	5.2	0.5
Δ(T)	4.1	6.4	1.8	2.0	1.2
Mean deviation					
CCSD(T)	−1.5	−4.2	1.5	1.0	−1.5
HF	−14.1	−28.9	0.3	−0.4	0.2
ΔCC	8.6	18.2	−0.6	−0.6	−0.5
Δ(T)	4.0	6.4	1.8	2.0	−1.2

with MADs of 1.4 and 0.8 kJ mol^{-1}, respectively. However, the MADs for the atomization energies (AEs, 4.5 kJ mol^{-1}) and electron affinities (EAs, 5.4 kJ mol^{-1}) are quite significant.

We note that the maug basis sets comprise diffuse s and p functions for heavy atoms for both the DZ and TZ basis sets. In comparison, the W1X-2 and the reference W2X methods employ aug' basis sets that become progressively larger (spd for DZ, $spdf$ for TZ, and $spdfg$ for QZ). To examine the degree of the (prospective) improvement of adopting such a systematic progression, we use the alternative jun-cc-pV[D+d,T+d]Z basis sets,[57] which include sp and spd diffuse functions for DZ and TZ, respectively. This yields substantial improvement for EAs (MAD = 1.5 kJ mol^{-1}), as one would expect. However, the improvement for AEs is marginal, and the accuracies for IE and PA somewhat deteriorate.

Given that the performance for AEs remains somewhat disappointing, let us now briefly examine the results in more detail. Table 4 shows the MADs and MDs for the G2/97 set and its subsets for DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/jun-cc-pV[D+d,T+d]Z against benchmark W2X values. It also shows the corresponding MAD and MD values for the underlying HF, ΔCCSD, and Δ(T) components. The most notable observation is that, for AEs, we can see substantial deviations in the HF and ΔCCSD components, which may in part be attributed to, for the atoms, the use of UHF wavefunctions versus ROHF for the benchmark. The deviations for HF and ΔCCSD generally have opposite signs, as indicated by the MD values. Thus, the results for the total composite AEs involve substantial cancellation of the deviations, but incomplete cancellations nonetheless lead to a large overall MAD for the AEs. For other properties, we also see cancellations of deviations but to much lesser degrees.

These results suggest some disparities in the treatments for (open-shell) atoms and (closed-shell) molecules. One means to address this issue is to apply corrections for atoms, in a way that is akin to those used in Gn-type methods.[7,63,64] However, this does introduce additional empiricism to the method. Alternatively, as the calculation of reaction energies of molecules appears to be quite robust, another

means is to avoid the use of atomic species but to use equivalent reactions that involves just molecules, which we will further examine in the next section.

We now turn our attention to the ΔCV+SR component. The RIJCOSX DLPNO-MP2/cc-pWCVTZ energies show good agreements with the reference W2X [i.e., MP2/TZ + ΔCCSD(T)/DZ] values, with MADs of ~2.0 kJ mol^{-1} or less. Overall, the accuracy is similar to that for the corresponding W1X-2 component; the MADs for the W1X-2 and L-W1X ΔCV+SR components are 1.7 and 1.4 kJ mol^{-1}, respectively.

When we combine the valence and the ΔCV+SR components to give the total composite energies, the "local-W1X" protocol with the jun basis sets yield an overall MAD of 3.9 kJ mol^{-1}. However, the MAD for the AEs is substantial (5.9 kJ mol^{-1}). In contrast, for the other three properties, the MADs are moderate, with values of ~2 kJ mol^{-1}. Overall, we perceive that such a local-W1X protocol would be a cost-effective means for obtaining reliable relative energies except for the calculation of AEs. We also note that the use of maug basis sets provides reasonable results except for EAs, and their use may be preferable from the perspective of computational cost.
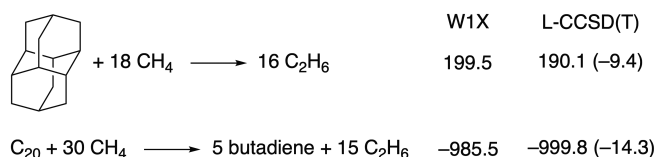
3.5 | Isodesmic-type reactions to the rescue

It is noteworthy that, from a practical point of view, AEs are equivalent to heats of formation (HOF) as a measure for thermochemical stability. In this regard, the use of isodesmic-type reactions often represents a more reliable means for obtaining HOFs. Let us now further examine the use of such an approach to close the gap in the application of RIJCOSX DLPNO-CCSD(T)-F12 methods to thermochemical stability. The isodesmic-type reactions that we use comprise bond-separation-type reactions for alkanes in the BSR36 set,[13] and those for unsaturated (often conjugated) hydrocarbons in our BSR17 set.[14] In the present study, we term them, respectively, the BSR-alkane and BSR-alkene sets for a more straightforward distinction.

For the BSR-alkene set, we have previously obtained W1X-1 reference values, which we will adopt in the present study. For the BSR-alkane set, the existing reference values correspond essentially to a composite CCSD(T)/DZ + ΔMP2/[T,Q]Z scheme. For a better consistency in the reference values within the present study, we have obtained higher-level W1X-2 energies for this set. For both BSR sets, we have assessed the performance for just the valence component, because one would generally expect it to dominate the overall errors, which is also supported by the results in Table 3. In our RIJCOSX DLPNO-CCSD(T)-F12 calculations for these hydrocarbon systems, we use the cc-pVnZ basis sets to avoid linear dependency in the corresponding AutoAux basis sets.

The MADs for the two BSR sets are shown in Table 5. For the BSR-alkane set, the results are far from being chemically accurate when the low-cost [RIJDOSX DLPNO-CCSD(T)-F12D] option is applied (MAD = 7.9 kJ mol^{-1} for the extrapolated CBS reaction energies). The deviations are dramatically reduced with the high-accuracy setting, such that even the use of the cc-pVDZ basis set provides

TABLE 5 Mean absolute deviations (kJ Mol^{-1}) for the BSR (alkane and alkene) test sets of bond-separation-type reactions obtained with RIJCOSX DLPNO-CCSD(T)-F12D and DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12

Basis set	BSR-alkane	BSR-alkene
RIJCOSX DLPNO-CCSD(T)-F12D		
DZ	10.9	30.5
TZ	5.3	10.4
CBS	7.9	9.2
DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12		
DZ	1.1	4.6
TZ	3.1	5.4
CBS	3.3	4.5

		W1X	L-CCSD(T)
[adamantane structure] + 18 CH$_4$ ⟶ 16 C$_2$H$_6$		199.5	190.1 (−9.4)
C$_{20}$ + 30 CH$_4$ ⟶ 5 butadiene + 15 C$_2$H$_6$		−985.5	−999.8 (−14.3)

FIGURE 1 Reactions in the BSR-alkane and BSR-alkene sets for which deviations (in parentheses) of DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/CBS reaction energies from the reference valence W1X values are the largest (reaction energies and deviations in kJ mol^{-1})

chemically accurate energies. Fortuitously, its MAD of 1.1 kJ mol^{-1} is smaller than the TZ and CBS values of 3.1 and 3.3 kJ mol^{-1}, respectively.

We now turn our attention to the BSR-alkene set. We see generally larger deviations when compared with those for BSR-alkane, presumably due to a greater degree of delocalization in the BSR-alkene systems. Notably, the low-cost calculations with the DZ basis set yield an MAD of 30.5 kJ mol^{-1}. The extrapolation to CBS gives an MAD of 9.2 kJ mol^{-1}, which is comparable to (but somewhat larger than) the corresponding BSR-alkane MAD of 7.9 kJ mol^{-1}. With the high-accuracy setting [DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12], the MADs are also larger than the corresponding BSR-alkane values, but the MAD values are all ~5 kJ mol^{-1}, even with the small cc-pVDZ basis set. Overall, we again see that the use of the high-accuracy option is critical for the reliable calculation of thermochemical properties.

We have more closely examined the deviations in the BSR sets. We find that, with the high-accuracy CBS method, the significant deviations are dominated by several outlier reactions. As an example, we show the reactions with the largest deviations for the BSR-alkane and BSR-alkene sets in Figure 1. In both cases, the molecules of interest (C$_{14}$H$_{20}$ and C$_{20}$) are separated into many small constituent fragments, which also necessitate the use of a large number of CH$_4$ molecules to balance the equations. Thus, accumulation of small deviations leads to substantial total deviations.

An advantage of using small constituent molecules in an isodesmic-type reaction is that highly accurate AEs and/or HOFs are

usually available for these species, thus minimizing the deviations associated with these quantities. Nonetheless, high-accuracy composite methods such as W1X can now be routinely carried out on typical computer workstations for systems with as many as ~20 heavy atoms. This would provide a means to obtain reliable reference AEs for medium-sized species, which would facilitate the minimization of deviations associated with reaction energies obtained with lower-cost methods.

As an aside, we note that the deficiency in the DLPNO approximation may be mitigated by extrapolating to the "complete PNO space" (CPS) limit.[65] However, doing so would essentially double the computational cost due to the requirement for an additional calculation with a slightly loosened PNO cut-off (i.e., the TCutPNO parameter in the ORCA program). One possibility for the inclusion of CPS without incurring a computational penalty is to combine the CPS and CBS extrapolations by using a loosened TCutPNO for the DZ calculation. We find this to be useful for the alternative LNO-CCSD(T) method in some specific cases.[66]

In the present study, we have attempted to apply this approach to the DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12/CBS method for our test cases. We find that this, for the TCutPNO values that we have examined (between 10^{-4} and 10^{-6}), yields improvements in some cases but leads to over-corrections in others. Overall, we do not find the results compelling to recommend a simple combined CPS–CBS extrapolation scheme. Nonetheless, a more thorough tuning with additional parameters may lead to a more consistent improvement.

3.6 | Prototypical timing comparison

The primary rationale for the use of the local approximations in the RIJCOSX DLPNO-CCSD(T)-F12 method is to reduce the computational cost. Let us now briefly examine this aspect with four medium-sized systems, namely the alkanes adamantane (C$_{10}$H$_{18}$) and diadamantane (C$_{14}$H$_{20}$) and the aromatic hydrocarbons pyracyclene (C$_{14}$H$_8$) and chrysene (C$_{18}$H$_{12}$). Specifically, we compare the time consumed for the DefGrid3 RIJCOSX DLPNO-CCSD(T$_1$)-F12 and CCSD (T)-F12b[67] computations with the cc-pVTZ basis set, which are used in the L-W1X and W1X-2 protocols for these systems.

In these calculations, we used the prebuilt Linux binary of ORCA 5 and Molpro 2020. They were carried out on a computer with a 10-core Intel 10900 CPU, 128 GB of memory, a 2 TB SSD scratch disk, and the Ubuntu 20 LTS operating system with Open MPI 4 for parallel computation. We carried out each calculation with 8 of the CPU cores and 12 GB of memory per core. This leaves sufficient headroom to minimize any potential impact of background processes on the performance of the calculations. In the CCSD(T)-F12b computations, we did not use symmetry, which enables a direct comparison with the RIJCOSX DLPNO-CCSD(T$_1$)-F12 calculation, in which symmetry are not exploited.

For adamantane, the total time consumed for the RIJCOSX DLPNO-CCSD(T$_1$)-F12 is 6209 s (Table 6). For the larger diadamantane, the corresponding calculation took 19,984 s. The

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TABLE 6 Total wall time (s) consumed for the DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12/cc-pVTZ, and the CCSD(T)-F12b/cc-pVTZ calculations for adamantane ($C_{10}H_{18}$), diadamantane ($C_{14}H_{20}$), pyracyclene ($C_{14}H_8$), and chrysene ($C_{18}H_{12}$), and the number of atomic orbital basis functions involved in the computations

Molecule	# AO basis	RIJCOSX DLPNO-CCSD(T_1)-F12[a]	CCSD(T)-F12b	Ratio[b]
adamantane	524	6209	23,274	3.7
diadamantane	700	19,984	152,715	7.6
pyracyclene	532	14,583	32,430	2.2
chrysene	708	32,238	192,774	6.0

[a]All calculations were carried out on the same workstation (10-core Intel 10900 CPU, 128 GB memory, 2 TB SSD scratch space) using 8 CPU cores and 12 GB of memory per core.
[b]t[CCSD(T)-F12b]/t[RIJCOSX DLPNO-CCSD(T_1)-F12].

CCSD(T)-F12b calculation for adamantane took several times longer (23,274 s) than the RIJCOSX DLPNO-CCSD(T_1)-F12 calculation, while the CCSD(T)-F12b calculation for diadamantane took 152,715 s. For the aromatic hydrocarbons, the observations on the comparisons between the different methods and between differently sized systems are similar. We note that, while the scaling of computer time with respect to the number of basis functions is super-linear for these systems for both RIJCOSX DLPNO-CCSD(T_1)-F12 and CCSD(T)-F12b, it is (expectedly) less steep for the former, which could thus provide a means for the calculation of larger systems.

4 | CONCLUDING REMARKS

In the present study, we have investigated the performance of RIJCOSX DLPNO-CCSD(T)-F12 methods as a cost-effective means to obtain accurate relative energies for a wide range of systems. Specifically, we have examined a low-cost [ORCA 5 keywords "RIJCOSX DLPNO-CCSD(T)-F12D"] and a high-accuracy ["DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12"] options in conjunction with maug-cc-pV(D+d)Z and maug-cc-pV(T+d)Z basis sets, and the corresponding [D, T] extrapolated complete-basis-set (CBS) limit. Expectedly, the high-accuracy method at the CBS limit provides the best agreement with the canonical CCSD(T)/CBS reference, with a mean absolute deviation (MAD) approaches the chemical accuracy of 1 kcal mol^{-1} (4.2 kJ mol^{-1}). On the other hand, the low-cost CBS method leads to substantial deviations for certain properties, notably atomization energies (AEs).

With the high-accuracy CBS approach, we have formulated the L-W1X method, which further includes a low-cost core–valence plus scalar-relativistic term obtained with the DefGrid3 RIJCOSX DLPNO-MP2/cc-pWCVTZ method. Testing with the G2/97 set demonstrates its good accuracy, though the calculation of electron affinities does benefit considerably by replacing the maug-cc-pV(n+d)Z basis sets with the more systematically converging jun-cc-pV(n+d)Z basis sets. The accuracy for the calculation of AEs remains just at the margin of chemical accuracy. To obtain chemically accurate AEs, we thus recommend the use of well-constructed isodesmic-type reactions, which leverages cancellation of errors to yield more accurate results.

In terms of computational efficiency, DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12 calculations are several times faster than the corresponding (canonical) CCSD(T)-F12b computation for medium-sized systems. Importantly, the use of the local approximations (RIJCOSX and DLPNO) leads to a scaling that is indeed better than that for the canonical calculation, for which the scaling is close to the formal value of N^7. Nonetheless, in our test cases, the scaling is still super-linear. Despite this caveat, the DefGrid3 RIJCOSX DLPNO-CCSD(T_1)-F12 method, and the L-W1X protocol that based on it, do represent a useful means for obtaining accurate thermochemical quantities for larger systems.

DATA AVAILABILITY STATEMENT

Examples for carrying out calculations with L-W1X using the ORCA 5 program are given in ref 43. Data available on request from the authors.

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