Supporting Information for "Approaching the basis set limit of CCSD(T) energies for large molecules with local natural orbital coupled-cluster methods"

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S1 DLPNO-CCSD(T) correlation energies

DLPNO-CCSD(T_0) and DLPNO-CCSD(T) correlation energy errors are included in Table S1 obtained with both the NormalPNO and the TightPNO settings.[1] Since the same (DF-)CCSD(T) reference was employed as in the correlation energy analysis of Sect. 5.2 of the main text, it is important to note that recovering the canonical CCSD(T) reference is not among the design goals of the DLPNO-CCSD(T_0) method, because the semi-canonical T_0 approximation remains even if all the other approximations of the DLPNO scheme are set to exact.[2] For that reason, the comparison of the DLPNO-CCSD(T_0) energies to the reference is affected by the T_0 approximation. Recently, Guo *et al.* introduced the T_0 approximation-free DLPNO-CCSD(T) scheme,[3] so we recomputed all the benchmarks with

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that improved variant as well. The data of Table S1 reveals considerable correlation energy deviations for DLPNO-CCSD(T_0) (e.g., 0.30-0.43% MAE for NormalPNO and 0.23-0.32% MAE for TightPNO), but these deviations are much decreased by the improved triples treatment of DLPNO-CCSD(T), MAEs of 0.12-0.24% and 0.04-0.10% were measured with the NormalPNO and TightPNO settings, respectively.

Table S1: Statistical measures for relative DLPNO-CCSD(T_0) and DLPNO-CCSD(T) correlation energy errors in percents for the species of the NWH, S66, and CEMS26 test sets with respect to canonical CCSD(T) reference. See section 5.2 of the main text for more details.

	DLPNO-CCSD(T_0)			DLPNO-CCSD(T)		
Threshold	MAE	MAX	STD	MAE	MAX	STD
NWH, cc-pVTZ						
NormalPNO	0.344	0.694	0.122	0.160	0.308	0.059
TightPNO	0.244	0.498	0.090	0.053	0.113	0.025
NWH, aug-cc-pVTZ						
NormalPNO	0.356	0.702	0.126	0.165	0.341	0.061
TightPNO	0.254	0.506	0.094	0.054	0.116	0.025
NWH, cc-pVQZ						
NormalPNO	0.305	0.648	0.110	0.124	0.284	0.053
TightPNO	0.229	0.467	0.082	0.037	0.088	0.022
S66, aug'-cc-pVTZ						
NormalPNO	0.321	0.534	0.114	0.141	0.312	0.070
TightPNO	0.238	0.367	0.085	0.049	0.113	0.027
CEMS26						
NormalPNO	0.434	0.698	0.127	0.236	0.430	0.082
TightPNO	0.316	0.538	0.103	0.101	0.176	0.033

The DLPNO-CCSD(T_0) correlation energy errors of Table S1 are not in contradiction to the conclusions of Ref. 1, namely that NormalPNO DLPNO-CCSD(T_0) (for smaller systems) recovers on the average 99.9% of the CCSD(T_0) reference, because the DLPNO-CCSD(T_0) results were compared with DF approximation-free CCSD(T_0) references.[1,2] Consequently, relatively higher correlation energy errors occur when benchmarking against the reference obtained without the T_0 and DF approximations. If taking into account that comparing local CCSD(T) methods exploiting DF to references without DF results in an about 0.05% cancellation of the local and DF errors, the 0.12-0.17% MAE values of NormalPNO DLPNO-

CCSD(T) obtained for the smaller NWH and S66 sets can also be interpreted as accurate to almost 99.9% when compared with a DF-error-free reference. The MAE value only grows above this mark (to about 0.24%) for the CEMS26 set, which includes significantly larger examples than the ones in the NWH and S66 sets. This point illustrates that it is important to take into account the extensivity of the local errors and test their accuracy on benchmark sets which are comparable to the size and complexity of the target systems. Regarding the TightPNO settings our calculations are also in line with Ref. 1 in the respect that TightPNO provides a significant improvement over NormalPNO for both DLPNO-CCSD(T_0) and DLPNO-CCSD(T) correlation energies, and an average accuracy of 99.9% is reached with TightPNO DLPNO-CCSD(T) for all three test compilations. It is interesting from the perspective of energy differences that, for DLPNO-CCSD(T_0), both PNO threshold sets yield a relatively consistent STD of about 0.09-0.13% for all the studied benchmarks and basis sets, while the DLPNO-CCSD(T) variant exhibits more improvement, from 0.05-0.08% to 0.02-0.03%, when switching to the TightPNO thresholds.

It is important to compare the correlation energy errors of LNO-CCSD(T) and DLPNO-CCSD(T) against the same reference (see Tables 2 of the main text and S1) so that one can learn about the relation of the different local approximations and composite threshold combinations of the two schemes. One relatively general trend is that for all the test sets, except for the cc-pVQZ NWH one, the Loose LNO-CCSD(T) deviations are noticeably smaller than those with NormalPNO DLPNO-CCSD(T) for all three measures. Except for the MAX value of the CEMS26 set, the Loose LNO-CCSD(T) MAE and MAX errors are at least twice smaller than the corresponding NormalPNO DLPNO-CCSD(T) numbers. Again, with the exception of NWH/cc-pVQZ, the Normal LNO-CCSD(T) correlation energies are systematically better than the TightPNO DLPNO-CCSD(T) ones. For NWH/cc-pVQZ NormalPNO is about halfway between our Loose and Normal values, while TightPNO is almost as accurate as our Tight combination.

S2 Basis set dependence of reaction energies

Reaction energy deviations obtained for the NWH[4] set using the aug-cc-pVTZ and the cc-pVQZ basis sets are shown in Fig. S1 and analyzed in the discussion of Sect. 5.3 of the main text.

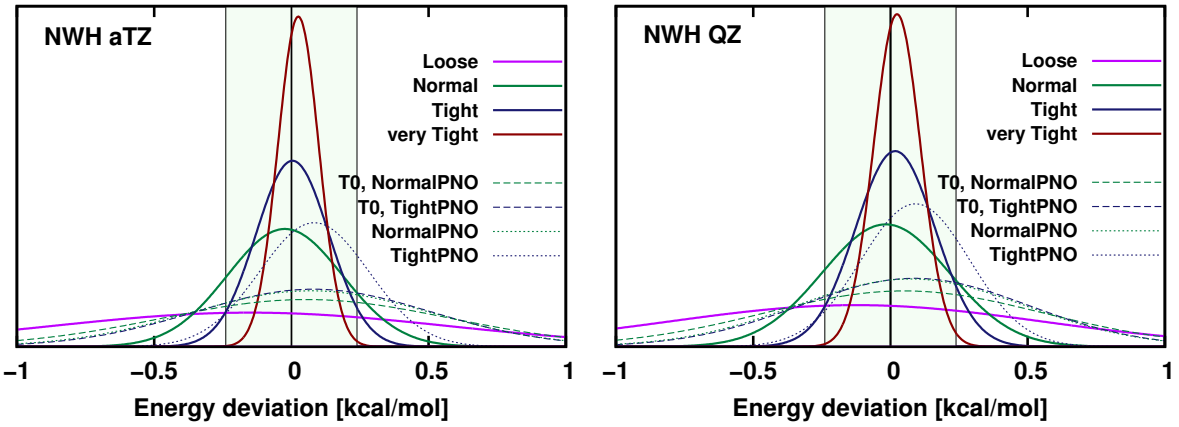

Figure S1: Normal distribution of the LNO-CCSD(T), DLPNO-CCSD(T_0), and DLPNO-CCSD(T) deviations from the reference CCSD(T) energy differences in kcal/mol for the NWH[4] set using the aug-cc-pVTZ and the cc-pVQZ basis sets. The ± 1 kJ/mol error region is highlighted in the middle. See Sect. 5.3 of the main text for more details.

S3 DLPNO-CCSD(T) reaction and interaction energies

We have also collected DLPNO-CCSD(T_0) and DLPNO-CCSD(T) reaction, conformation, and interaction energy deviations for the investigated three test sets in Table S2. One can observe that the performance of NormalPNO, at least the MAE and STD, is almost the same for the (T_0) and the iterative (T) models, and the MAX error differ only for the NWH test set. A closer inspection reveals that the DLPNO-CCSD(T_0) and DLPNO-CCSD(T) reaction energies in the NWH set are mostly within 1 kJ/mol from each other, supporting the notion that the error of the T_0 approximation often cancels when energy differences are formed.[3,5] The 1,2,3,4,5,6-heptahexane to hepta-1,3,5-triyne isomerization is again an outlier here, where about 0.9 kcal/mol improvement is found when switching to the DLPNO-CCSD(T) variant.

If we compare the NormalPNO and the TightPNO values of DLPNO-CCSD(T_0), except for the interaction energies of the S66 set, somewhat unexpectedly there is a small improvement in the MAE and STD values. The closest independent DLPNO-CCSD(T_0) reaction energy benchmark which compares NormalPNO and TightPNO results was published in Ref. 1 for the test set of Friedrich and Hänchen (FH set),[6] for which CCSD(T_0)/cc-pVTZ reference was employed.[1] The FH set, as the NWH set, also collects reactions and isomerizations of relatively small organic species containing in average (maximally) 14.7 (29) atoms. The NormalPNO DLPNO-CCSD(T_0) MAE value of 0.31 kcal/mol for the FH/cc-pVTZ set is in good agreement with the 0.28-0.30 kcal/mol MAE obtained for the NWH set, however, MAEs of 0.13 and 0.22-0.26 kcal/mol were found for the FH/cc-pVTZ and the NWH tests, respectively, with the TightPNO settings. The TightPNO DLPNO-CCSD(T) MAE values are in the 0.12-0.14 kcal/mol range, which is comparable to the 0.13 kcal/mol MAE obtained for the FH/cc-pVTZ set, where, however, the CCSD(T_0) reference was employed.[1] Additionally, for the CEMS26 set the MAE and especially the MAX errors are also noticeably improved with the TightPNO DLPNO-CCSD(T) scheme compared to DLPNO-CCSD(T_0). These observations show that, at least for the studied test and basis sets, the (T_0) approximation is limiting, the intrinsic accuracy of the TightPNO threshold set can only be fully exploited with the iterative triples algorithm of DLPNO-CCSD(T). Since this behavior seems to be unexplained in the literature it would be instructive to study the background and the generality of these findings on a wider range of systems.

For the interaction energies of the S66 set the (T_0) and iterative (T) variants behave almost identically, and the computed 0.27 (0.13-0.17) kcal/mol NormalPNO (TightPNO) MAE values are in excellent agreement with the S66/cc-pVTZ benchmark of Ref. 1. These trends are also apparent from the normal distribution curves of Fig. 4 of the main text and Fig. S1. For the NWH and CEMS26 sets the "T0, NormalPNO" and "NormalPNO" curves are hardly distinguishable, and the "T0, TightPNO" curves are also very close to those two. As also illustrated by the numbers of Table S2 and of Ref. 1, for the S66 set both the "T0,

TightPNO" and "TightPNO" curves of Fig. 4 have significantly smaller widths than those of the corresponding NormalPNO curves.

Table S2: Statistical measures for DLPNO-CCSD, DLPNO-CCSD(T_0), and DLPNO-CCSD(T) deviations in kcal/mol for the reaction energies of the NWH,[4] the interaction energies of the S66,[7] and the reaction and conformation energies in the CEMS26[8] test sets with respect to canonical CCSD(T) reference. See Sect. 5.3 of the main text for more details.

	DLPNO-CCSD			DLPNO-CCSD(T_0)			DLPNO-CCSD(T)		
Threshold	MAE	MAX	STD	MAE	MAX	STD	MAE	MAX	STD
	NWH, cc-pVTZ								
NormalPNO	0.25	2.28	0.53	0.28	1.83	0.50	0.31	1.03	0.47
TightPNO	0.08	0.46	0.15	0.22	1.10	0.34	0.14	0.74	0.22
	NWH, aug-cc-pVTZ								
NormalPNO	0.24	2.29	0.52	0.30	1.85	0.53	0.29	1.15	0.44
TightPNO	0.05	0.21	0.06	0.27	1.35	0.43	0.12	0.77	0.20
	NWH, cc-pVQZ								
NormalPNO	0.24	2.36	0.54	0.30	1.85	0.51	0.30	0.98	0.42
TightPNO	0.05	0.14	0.06	0.26	1.31	0.41	0.13	0.73	0.20
	S66, aug'-cc-pVTZ								
NormalPNO	0.39	1.61	0.41	0.27	0.97	0.23	0.27	1.00	0.24
TightPNO	0.05	0.16	0.03	0.17	0.54	0.10	0.13	0.41	0.08
	CEMS26								
NormalPNO	0.83	2.36	0.91	0.63	1.60	0.51	0.74	1.60	0.45
TightPNO	0.18	0.46	0.14	0.56	1.35	0.40	0.49	0.77	0.23

Regarding the normal distribution plots (Fig. 4 of the main text and Fig. S1), in contrast to the case of correlation energies, Loose LNO-CCSD(T) energy differences are found to be less accurate than the corresponding NormalPNO DLPNO-CCSD(T) values for these test sets. According to Table 3 of the main text and Table S2, the NormalPNO errors with both (T) variants are about halfway between our Loose and Normal deviations for all the investigated test sets. Since the accuracy of TightPNO DLPNO-CCSD(T_0) is limited by the T_0 approximation for the NWH and CEMS26 sets, for those cases our Normal curves are better even than the "T0, TightPNO" ones, and only the "TightPNO" distributions have widths comparable to our Normal curves. For the S66 set, both TightPNO curves are better than our Normal one, and especially TightPNO with the iterative triples term is closer to Tight LNO-CCSD(T). Another difference is that, in all the cases, the DLPNO variants

are found to be noticeably further from the 0 kcal/mol mean signed error mark, and this deviation is almost 0.4 kcal/mol for the hardest CEMS26 set. This characteristic is, however, probably less relevant than the width of the distribution if differences of energy differences are of interest.

S4 CBS extrapolated DLPNO-CCSD(T) reaction and interaction energies

CBS extrapolated DLPNO-CCSD(T_0) and DLPNO-CCSD(T) reaction and interaction energy deviations are collected in Table S3. See the discussion of Sect. 5.4 of the main text for further details.

Table S3: Statistical measures for CBS extrapolated DLPNO-CCSD(T_0) and DLPNO-CCSD(T) deviations in kcal/mol. References: canonical CCSD(T)/(T,Q)Z for the reaction energies of the NWH[4] set and the "SILVER" reference value of Martin and co-workers[9] most accurate to date for the interaction energies of the S66[7] set.

	DLPNO-CCSD(T_0)			DLPNO-CCSD(T)		
Threshold	MAE	MAX	STD	MAE	MAX	STD
NWH, CBS (T,Q)Z						
NormalPNO	0.34	1.87	0.40	0.29	0.97	0.28
TightPNO	0.31	1.89	0.43	0.13	0.72	0.16
S66, CBS (a'T,a'Q)Z						
NormalPNO	0.24	0.85	0.21	0.27	1.15	0.27
TightPNO	0.10	0.29	0.06	0.07	0.25	0.04

S5 Comparison of local CCSD(T) methods: S66 set

The most recent PNO-CCSD(T)-F12 study of Ma and Werner provides detailed benchmark data on the S66 set.[10] Looking at the comparison with the local approximation free, canonical CCSD(T)-F12 reference first, a MAE (MAX) of 0.14 (0.43) kcal/mol was reported for the PNO-CCSD(T)-F12 method with the default settings and the aDZ-F12 basis set.[10] The

analogous value is not available for the entire S66 set with the aTZ-F12 basis set, but the trends shown in Table 7 of Ref. 10 suggest that the local errors are about 10 % smaller with the larger basis set. These results indicate that, at least for the S66 set, the local errors of the default PNO-CCSD(T)-F12 method are between our Normal and Tight settings, somewhat closer to the Normal values (cf. Table 3). Tighter PNO-CCSD(T)-F12 settings yielded 0.03 (0.11) kcal/mol MAE (MAX) errors with the aDZ-F12 basis set, and the trends in Ref. 10 suggest that a MAE (MAX) of about 0.02-0.03 (0.05-0.08) kcal/mol is expected due to the local error with the aTZ-F12 basis set. This accuracy is better than what is achieved with our Tight LNO-CCSD(T) on the S66 set, it is comparable to the accuracy level of our vTight thresholds.

The "SILVER" reference was also employed in the benchmark study of Ma and Werner,[10] so the two local methods can also be compared in this respect. Unfortunately this comparison cannot completely separate the BSIE and the local errors of the two methods as well as in the case of the comparison with the DLPNO methods. The better converged ("GOLD") values of Martin and co-workers[9] and the deviation of the "SILVER" reference and the tighter PNO-CCSD(T)-F12 results obtained with the aTZ-F12 and aQZ-F12 basis sets suggest that the uncertainty of the "SILVER" reference is on the average about 0.01-0.02 kcal/mol. This level of accuracy is not yet achieved either by the Tight LNO-CCSD(T)/(a'T,a'Q)Z [0.05 (0.19) kcal/mol MAE (MAX)] or the default PNO-CCSD(T)-F12/aQZ-F12 [0.09 (0.23) kcal/mol MAE (MAX)] methods. As noted above, the (a'T,a'Q)Z results are limited by a noticeable (on the average about 0.02 kcal/mol) BSIE, hence the vTight LNO-CCSD(T) results are not much closer to the "SILVER" reference than the Tight ones, while tight PNO-CCSD(T)-F12/aQZ-F12 results can convincingly approach the "SILVER" reference within its uncertainty.[9] This is in agreement with the general notion that explicitly correlated CCSD(T) variants, especially with the aTZ-F12 and aQZ-F12 basis sets, are expected to be closer to the CBS limit than (a'T,a'Q)Z extrapolated conventional CCSD(T).[11]

This comparison, analogously to that with the DLPNO methods, reveals that there are

differences in the accuracy levels (default or tighter) of the currently available near linear-scaling CCSD(T) methods due to the different design goals of the methods. An additional factor in these comparisons is the efficiency of the implementations, which is again a complicated feature to assess fairly and generally. For instance, Ref. 10 reports that, for the uracil dimer of S66, the tighter PNO-CCSD(T)-F12/aTZ-F12 calculations took 4.0 h using a 20-core, dual CPU machine, while the default calculations are about 1.5-2.0 h long. In comparison, using a different hardware environment but almost identical processors and 20 cores, the LNO-CCSD(T)/a'TZ calculation for the uracil dimer took 0.38 and 1.5 h using the Normal and Tight settings, respectively. Additionally, the LNO-CCSD(T)/a'QZ calculation for the same dimer with the above two threshold sets required 1.0 and 3.3 h runtime, respectively. Thus the performance of Normal LNO-CCSD(T)/(a'T,a'Q)Z and default PNO-CCSD(T)-F12/aTZ-F12 or Tight LNO-CCSD(T)/(a'T,a'Q)Z and PNO-CCSD(T)-F12/aTZ-F12 with tighter domain settings are close both in terms of computation time and accuracy, at least on the example of the uracil dimer interaction energy.

S6 Comparison of local CCSD energies

Statistical measures for LNO-CCSD reaction, interaction, and conformation energies collected in Table S4 are obtained according to the following expression:

$$E^{\mathrm{LNO-CCSD}} = \sum_{i'} \left[\delta E_{i'}^{\mathrm{CCSD}}(P_{i'}) + f_{\mathrm{CCSD}}\, \Delta E_{i'}^{\mathrm{MP2}} \right], \tag{1}$$

where the $\Delta E_{i'}^{\mathrm{MP2}}$ corrections are computed as defined in Eq. (5) of the main text. If $f_{\mathrm{CCSD}} = 1$ the entire $\Delta E_{i'}^{\mathrm{MP2}}$ correction is added to the CCSD term, while (T) is left uncorrected. Since we have found that the MP2 correction systematically overcorrects the CCSD correlation enegies,[8,12] it is also interesting to redistribute the MP2 correction between the CCSD and (T) terms. Brief investigation of the CCSD correlation enegy error function revealed a shallow minimium around $f_{\mathrm{CCSD}} = 0.5$. As shown in Table S4, this choice leads

to a significant imporvement over $f_{\mathrm{CCSD}} = 1$, thus if the CCSD and (T) contributions are of interest separately, the equal distribution of the MP2 correction is recommended via the $f_{\mathrm{CCSD}} = 0.5$ choice.

Table S4: Statistical measures for LNO-CCSD deviations with $f_{\mathrm{CCSD}} = 1$ (left) and $f_{\mathrm{CCSD}} = 0.5$ (right) correction factors of Eq. (1) in kcal/mol for the reaction energies of the NWH,[4] the interaction energies of the S66,[7] and the reaction and conformation energies in the CEMS26[8] test sets with respect to canonical CCSD reference.

	full MP2 correction			half MP2 correction		
Threshold	MAE	MAX	STD	MAE	MAX	STD
NWH, cc-pVTZ						
Loose	0.72	5.06	1.18	0.22	0.92	0.22
Normal	0.36	2.10	0.62	0.13	0.62	0.20
Tight	0.15	0.94	0.24	0.07	0.25	0.07
vTight	0.09	0.53	0.14	0.05	0.22	0.05
NWH, aug-cc-pVTZ						
Loose	0.73	4.99	1.15	0.22	0.71	0.19
Normal	0.37	2.21	0.66	0.13	0.40	0.18
Tight	0.18	1.05	0.26	0.07	0.23	0.08
vTight	0.10	0.59	0.15	0.05	0.24	0.07
NWH, cc-pVQZ						
Loose	0.72	4.91	1.14	0.23	0.85	0.25
Normal	0.40	2.31	0.69	0.14	0.51	0.20
Tight	0.20	1.04	0.27	0.07	0.31	0.08
vTight	0.12	0.64	0.16	0.06	0.26	0.07
S66, aug'-cc-pVTZ						
Loose	0.79	2.85	0.62	0.69	1.71	0.41
Normal	0.48	1.72	0.35	0.22	0.76	0.19
Tight	0.23	0.74	0.15	0.04	0.23	0.05
vTight	0.14	0.43	0.08	0.04	0.15	0.04
CEMS26						
Loose	2.37	5.09	1.85	2.84	4.31	1.15
Normal	1.24	2.30	0.85	0.48	2.42	0.63
Tight	0.61	1.05	0.38	0.22	1.17	0.31
vTight	0.36	0.64	0.21	0.16	0.35	0.10

The closer inspection of the LNO-CCSD energy deviations of Table S4 indicates that with $f_{\mathrm{CCSD}} = 1$ the LNO-CCSD energy differences converge slower towards the canonical reference than the same measures of LNO-CCSD(T). Nevertheless, the convergence with the Loose, Normal, etc. hierarchy of composite thresholds is again monotonic, and about one

step tighter threshold set is needed for LNO-CCSD if comparable accuracy is required to that of LNO-CCSD(T). For instance, Normal LNO-CCSD(T) and Tight LNO-CCSD exhibit comparable energy deviations. On the other hand, there is a dramatic improvement in the LNO-CCSD correlation energies when using $f_{\mathrm{CCSD}} = 0.5$. Comparing the right columns of Table S4 with the corresponding LNO-CCSD(T) numbers of Table 3 of the main text one finds the two schemes almost identically accurate. The LNO-CCSD results are even better for the NWH test set, especially for the cases of the Loose settings or for the maximum errors. For the non-covalent interactions of the S66 set and for the most challeging examples in the CEMS26 collection the LNO-CCSD(T) results are noticeably, but not much better than LNO-CCSD with $f_{\mathrm{CCSD}} = 0.5$.

It is also iteresting to compare this behavior to alternative local correlation methods. Thus the same error measures were also evaluated for DLPNO-CCSD (see Table S2). For NormalPNO setting one finds DLPNO-CCSD and DLPNO-CCSD(T) average errors comparable to each other (DLPNO-CCSD is slightly better than DLPNO-CCSD(T) for NWH and somewhat worse for S66 and CEMS26). In terms of the maximum errors, DLPNO-CCSD(T) performs clearly better, especially, with the iterative (T) algorithm the errors are smaller by a factor of 1.5–2.4. This indicates some compensation of the CCSD and (T) errors in this case. Compared to the case of the NormalPNO settings, TightPNO DLPNO-CCSD average deviations are highly, by about a factor of 3-5 times more accurate, which errors are consequently also significantly better than the ones with TightPNO DLPNO-CCSD(T). In comparison to the LNO results, NormalPNO DLPNO-CCSD is very close, within about 0.2 kcal/mol to Normal LNO-CCSD with $f_{\mathrm{CCSD}} = 1$, while TightPNO DLPNO-CCSD is practically as good as Tight LNO-CCSD with $f_{\mathrm{CCSD}} = 0.5$.

S7 LMP2 and LNO-CCSD(T) reaction and interaction energies of larger examples

DF-HF, LMP2,[13] and LNO-CCSD(T) reaction and interaction energies, which are displayed on the convergence plots of Figs. 7-10 of the main text, are collected in the following tables.

Table S5: DF-HF and LNO-CCSD(T) reaction energies (in kcal/mol) for the formation of androstendione from its precursor corresponding to Fig. 7 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	-0.73	-1.29	-1.44			
Loose	7.54	5.85	4.88			
Normal	7.60	5.91	4.93	7.62±0.03	5.93±0.03	4.96±0.03
Tight	7.79	5.99	4.94	7.88±0.09	6.04±0.04	4.95±0.01
vTight	7.91	5.98	4.83	7.97±0.06	5.97±0.01	4.88±0.06

Table S6: DF-HF and LNO-CCSD(T) reaction energies (in kcal/mol) for the ISOL4 reaction corresponding to Fig. 8 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	19.29	18.79	18.65			
Loose	78.52	73.26	69.66			
Normal	76.85	71.75	68.26	76.02±0.83	70.99±0.76	67.56±0.70
Tight	76.20	71.07	67.56	75.87±0.33	70.73±0.34	67.21±0.35
vTight	76.06	70.89	67.35	75.99±0.07	70.80±0.09	67.24±0.11

Table S7: DF-HF and LNO-CCSD(T) reaction energies (in kcal/mol) for the AuAmin reaction corresponding to Fig. 8 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	22.08	21.92	21.88			
Loose	54.31	52.02	50.43			
Normal	53.17	50.59	48.77	52.60±0.57	49.87±0.72	47.94±0.83
Tight	52.66	49.94	48.03	52.41±0.26	49.62±0.32	47.66±0.37
vTight	52.45	49.60	47.59	52.34±0.11	49.43±0.17	47.37±0.22

Table S8: DF-HF and LNO-CCSD(T) interaction energies (in kcal/mol) for the dimer of the GC complex corresponding to Fig. 9 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	11.28	12.06	12.28			
Loose	-22.83	-19.22	-16.95			
Normal	-21.49	-17.76	-15.40	-20.82±0.67	-17.03±0.73	-14.62±0.77
Tight	-20.41	-16.48	-13.98	-19.86±0.54	-15.84±0.64	-13.27±0.71
vTight	-20.13	-16.07	-13.47	-19.99±0.14	-15.86±0.21	-13.21±0.26
vvTight	-20.13	-16.07	-13.47	-20.13±0.00	-16.07±0.00	-13.47±0.00

Table S9: DF-HF and LNO-CCSD(T) interaction energies (in kcal/mol) for the coronene dimer corresponding to Fig. 9 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	14.84	15.72	15.96			
Loose	-39.44	-33.01	-28.71			
Normal	-33.84	-27.58	-23.42	-31.04±2.80	-24.87±2.71	-20.78±2.65
Tight	-30.76	-24.57	-20.46	-29.22±1.54	-23.07±1.51	-18.98±1.48
vTight	-29.68	-23.49	-19.37	-29.14±0.54	-22.94±0.54	-18.83±0.54
vvTight	-29.34	-23.15	-19.04	-29.18±0.17	-22.99±0.17	-18.87±0.17

Table S10: DF-HF and LNO-CCSD(T) for the ΔG of the Michael-reaction (in kcal/mol) corresponding to Fig. 10 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	5.57	5.87	5.95			
Loose	-10.18	-8.89	-8.09			
Normal	-10.19	-8.61	-7.59	-10.19±0.01	-8.47±0.14	-7.34±0.25
Tight	-9.92	-8.27	-7.21	-9.78±0.14	-8.11±0.17	-7.02±0.19
vTight	-9.87	-8.17	-7.06	-9.84±0.02	-8.11±0.05	-6.99±0.07

Table S11: DF-HF and LNO-CCSD(T) for the barrier height of the Michael-reaction (in kcal/mol) corresponding to Fig. 10 of the main text.

Threshold	LNO-CCSD(T)			Estimate and error bar		
	aTZ	aQZ	(aT,aQ)Z	aTZ	aQZ	(aT,aQ)Z
DF-HF	60.09	60.93	61.16			
Loose	9.27	12.81	15.01			
Normal	11.02	14.79	17.16	11.89±0.87	15.78±0.99	18.23±1.07
Tight	11.14	15.19	17.77	11.21±0.06	15.40±0.20	18.07±0.31
vTight	10.87	15.11	17.82	11.01±0.14	15.15±0.04	17.85±0.03

Table S12: LMP2 and DF-MP2 reaction and interaction energies (in kcal/mol) corresponding to the discussion in Sect. 6 of the main text.

Threshold	aTZ	aQZ	(aT,aQ)Z
	Androstendione		
Loose	6.44	4.91	4.05
Normal	6.70	5.13	4.25
Tight	7.01	5.30	4.30
vTight	7.19	5.33	4.22
DF-MP2	7.34	5.47	4.27
	ISOL4		
Loose	87.04	81.80	78.19
Normal	87.84	82.68	79.13
Tight	88.12	83.09	79.65
vTight	88.15	83.17	79.77
DF-MP2	88.25	83.26	79.86
	GC–GC dimer		
Loose	-23.57	-20.17	-18.05
Normal	-24.21	-20.66	-18.43
Tight	-24.76	-21.03	-18.66
vTight	-25.03	-21.28	-18.89
vvTight	-25.12	-	-
DF-MP2	-25.13	-21.47	-19.16
	Coronene dimer		
Loose	-46.09	-39.73	-35.50
Normal	-45.95	-39.67	-35.49
Tight	-46.65	-40.52	-36.45
vTight	-46.80	-40.81	-36.84
vvTight	-46.91	-	-
DF-MP2	-46.97	-40.92	-36.91

S8 Reference results for the CEMS26 test set

A couple of typos were found in the reference CCSD(T) energy section of Table 10 of Ref. 8, which are corrected in Table S13.

Table S13: CCSD(T) reference reaction energies and conformation energies in kcal/mol units.

reaction/conformers	AO basis	$\Delta E^{\mathrm{CCSD(T)}}$
ISOL11 educt → ISOL11 product	cc-pVTZ	35.32
2 *p*-xylene → [2, 2]PCP + 2 H_2	cc-pVTZ	58.49
2 *p*-xylene → [2, 2]PCP + 2 H_2	aug-cc-pVTZ	56.35
2 *p*-xylene → [2, 2]PCP + 2 H_2	cc-pVQZ	58.52
2 2,3-dimethylbut-2-ene → OMCB	cc-pVTZ	-19.70
2 2,3-dimethylbut-2-ene → OMCB	aug-cc-pVTZ	-21.89
2 2,3-dimethylbut-2-ene → OMCB	cc-pVQZ	-18.98
porphyrin + Mg → Mg-porphyrin + H_2	cc-pVTZ	-97.28
Li^+ + 2 12-crown-4 → $[Li(crown)_2]^+$	cc-pVTZ	-125.20
melatonine aa → melatonine dw	cc-pVT'Z	9.56
$(H_2O)_{17}$ sphere → $(H_2O)_{17}$ 5525	aug-cc-pVTZ	0.71
GC-dDMP A → GC-dDMP B	6-311++G**	-1.22

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