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A Mountaineering Strategy to Excited States: Revising Reference Values with EOM-CC4

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Abstract

In the framework of the computational determination of highly-accurate vertical excitation energies in small organic compounds, we explore the possibilities offered by the equation-of-motion formalism relying on the approximate fourth-order coupled-cluster (CC) method, CC4. We demonstrate, using an extended set of more than 200 reference values based on CC including up to quadruples excitations (CCSDTQ), that CC4 is an excellent approximation to CCSDTQ for excited states with a dominant contribution from single excitations with an average deviation as small as 0.003 eV. We next assess the accuracy of several additive basis set correction schemes, in which vertical excitation energies obtained with a compact basis set and a high-order CC method are corrected with lower-order CC calculations performed in larger basis sets. Such strategies are found to be overall very beneficial, though their accuracy depend significantly on the actual scheme. Finally, CC4 is employed to improve several theoretical best estimates of the QUEST database for molecules containing between four and six (non-hydrogen) atoms, for which previous estimates were computed at the CCSDT level.

1. INTRODUCTION

Defining sets of high-quality reference values that can be employed to reliably assess the *pros* and *cons* of lower-cost theoretical methods is a very popular and useful research line in quantum chemistry.^{1–11} Although experimental values may constitute natural references for some properties (e.g., thermodynamical and kinetic data),^{12–16} it is often welcome to rely on state-of-the-art electronic structure methods to produce reference values for other properties. Of course, this latter approach is intrinsically limited by the computational cost of these high-accuracy models. However, it has the undeniable advantage to allow well-grounded comparisons within a unique, well-defined set of parameters.^{17–20} Indeed, one can perform comparisons with exactly the same geometries, basis set, solvent model, etc. Purely theoretical reference values are especially useful for electronic excited states (ESs), as the most straightforwardly accessible theoretical values, namely, vertical transition energies (VTEs), are not directly measurable experimentally.²¹ This explains why the determination of accurate VTEs has been an active and productive avenue of research during the past three decades, with, in particular, valuable works from Roos’^{22–24} and Thiel’s^{25–27} groups.

Since 2018, our groups have made several contributions in this field,^{11,28–32} and it eventually led to the creation of the QUEST database [see https://lcpq.github.io/QUESTDB_

[website](#)], that contains a large panel of reference VTEs for molecules containing from 1 to 10 non-hydrogen atoms.³³ At the present stage, the QUEST database includes more than 500 theoretical best estimates (TBEs) for diverse ESs (singlet, doublet, and triplet; valence and Rydberg; charge transfer, singly- and doubly-excited states) that have been established with the *aug-cc-pVTZ* basis set. Typically, the TBEs contained in the QUEST database are produced using VTEs computed with the selected configuration interaction (SCI) algorithm named “*Configuration Interaction using a Perturbative Selection made Iteratively*” (CIPSI)^{34–39} to obtain near full configuration interaction (FCI) quality VTEs for systems containing from 1 to 3 non-hydrogen atoms, coupled cluster (CC) with singles, doubles, triples and, quadruples (CCSDTQ)⁴⁰ for molecules encompassing 4 non-hydrogen atoms, and CC with singles, doubles, and triples (CCSDT)^{41–45} for larger derivatives. Popular basis set correction schemes have often been applied. For example, the CCSDTQ VTEs computed with a double- ζ basis set were corrected thanks to CCSDT values obtained with a triple- ζ basis set. Most TBEs included in the QUEST database were estimated to be chemically-accurate (corresponding to 1 kcal.mol⁻¹ or 0.04 eV error), with a typical error bar of ± 0.03 eV. The reference values included in QUEST have been used by various groups, for example, to (i) assess the relative accuracies of third-order,⁴⁶ multireference,⁴⁷ and other emerging^{48–53}

methods, (ii) quantify the accuracy of local hybrids for triplet ESs,⁵⁴ (iii) determine the relative performance of several hybrid⁵⁵ or double hybrid^{56–59} functionals, and (iv) evaluate the potential of orbital-optimized density-functional theory for double excitations.^{60,61}

Despite burning an unreasonable number of CPU hours during the past four years, we could hardly “do better” than what is described above, as we rapidly hit the computational wall of both high-order CC schemes and/or large CIPSI calculations. For instance, CCSDTQ formally scales as $O(N^{10})$ (where N is the number of basis functions) and determining VTEs in molecules like furan or thiophene is nearly impossible even in a double- ζ basis set. In an effort to go one step further we explored very recently, and for the first time, the performance of the approximate fourth-order CC model, CC4,⁶² in the context of ESs.⁶³ From a theoretical point of view, CC4 can be viewed as an approximation of CCSDTQ that still includes iterative quadruples, but neglects the calculation of the most expensive components (and avoids the storage of the higher-excitation amplitudes), allowing to reduce the formal scaling by one order of magnitude to $O(N^9)$.⁶² In our first investigation,⁶³ we considered very small systems (BH, BF, CO, HCl, H₂O, H₂S, N₂, and NH₃) for which well-converged CIPSI calculations were achievable for 25 ESs. This preliminary study indicates that CC4 indeed provides highly competitive VTEs, as it allows to significantly reduce the CCSDT error as compared to FCI, with final deviations — for ESs with a dominant single excitation character — only slightly larger than their CCSDTQ counterparts.

In the present contribution, which is only the second work presenting CC4 calculations for ESs, we build on our previous study,⁶³ and we aim at (i) evaluating the performance of CC4 for a more significant set of molecules and a larger variety of ESs, (ii) assessing the accuracy of additive basis set correction procedures based on CC4, and (iii) providing improved TBEs for many ESs included in the QUEST database.

2. COMPUTATIONAL DETAILS

All calculations presented here rely on the frozen-core approximation and the high-quality ground-state geometries extracted from the QUEST database.³³ For the sake of reproducibility, cartesian coordinates for all systems displayed in Figure 1 are reproduced in the supporting information (SI). Note that, below, we do not specify the equation-of-motion (EOM) prefix for the CC calculations, although all ES calculations are performed using this formalism.

Most of our CC calculations have been performed with CFOUR,^{64,65} that provides an efficient implementation of high-order CC methods up to quadruples.^{66,67} For all considered systems, we performed, when technically achievable, CC2,^{68,69} CCSD,^{70–74} CC3,^{75–77} CCSDT,^{41–45} CC4,^{62,78} and CCSDTQ^{40,78} calculations using three Gaussian basis sets: 6-31+G(d), *aug-cc-pVDZ*, and *aug-cc-pVTZ*. For the sake of conciseness, these basis sets are sometimes dubbed as “Pop”, “AVDZ”, and “AVTZ” in the following.

In the statistical analysis presented below, we report the usual statistical indicators: the mean signed error (MSE), the mean absolute error (MAE), as well as largest positive and

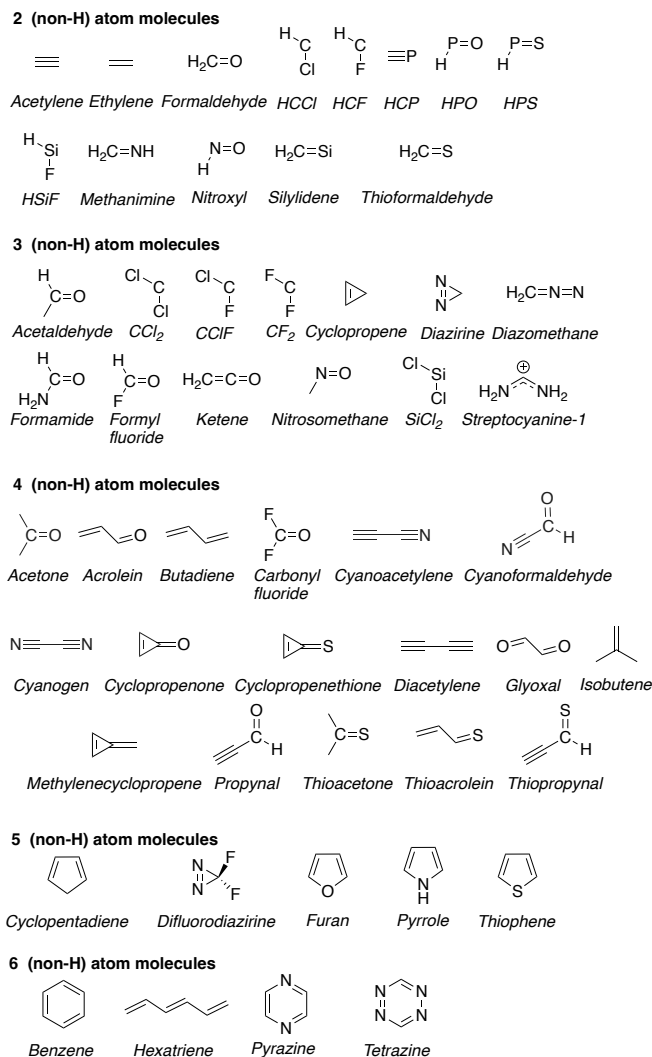


Figure 1: Representation of the systems investigated in the present study.

negative deviations [Max(+) and Max(−), respectively].

CCSDTQP/6-31+G(d) calculations have been performed with MRCC^{79,80} for the molecules encompassing two non-hydrogen atoms (see Figure 1). These values are reported in Table S1 of the SI. Considering all 32 VTEs and taking these CCSDTQP values as references, we obtain a MAE of 0.003 eV for the CCSDTQ data determined with the same basis set. Unsurprisingly, the largest error, 0.023 eV, comes from the pure $(n, n) \rightarrow (\pi^*, \pi^*)$ doubly-excited state of nitroxyl for which the CC expansion obviously converges slower. Removing this pathological case yields a MAE of 0.002 eV with all errors below 0.010 eV, clearly confirming the quality of the CCSDTQ estimates.

3. METHODOLOGICAL ASPECTS

3.1 How does CC4 compare to CCSDTQ?

Given that CC4 is an approximation of CCSDTQ, and that the accuracy of the latter is recognized as exceptional for ESs with a dominant contribution from singly-excited determinants (see above), it seems natural to assess the performance of CC4 with respect to CCSDTQ. Considering the values

Table 1: Statistical analysis obtained using various correction schemes. MSE, MAE and maximal deviations (in eV) are obtained with respect to the reference method given in the leftmost column. The number of reference ESs considered at the CCSDTQ/*aug-cc-pVTZ*, CC4/*aug-cc-pVTZ*, and CCSDT/*aug-cc-pVTZ* levels is 31, 59, and 118, respectively. In the rightmost column, we provide the number of states for which the correction provides smaller (or equal) absolute errors as compared to the non-corrected scheme (rows labeled as “no correction”).

Approximating . . .	using . . .	and correcting with . . .	MSE	MAE	Max(+)	Max(-)	Useful?	
CCSDTQ/ <i>aug-cc-pVTZ</i>	CC4/ <i>aug-cc-pVTZ</i>	no correction	0.002	0.003	0.012	-0.003		
		+ [CCSDTQ – CC4]/ <i>aug-cc-pVDZ</i>	0.000	0.001	0.003	-0.003	22/31	
		+ [CCSDTQ – CC4]/6-31+G(d)	0.001	0.002	0.006	-0.004	19/31	
	CCSDT/ <i>aug-cc-pVTZ</i>	no correction	-0.001	0.017	0.107	-0.049		
		+ [CCSDTQ – CCCST]/ <i>aug-cc-pVDZ</i>	0.003	0.004	0.022	-0.004	27/31	
		+ [CCSDTQ – CCSDT]/6-31+G(d)	0.001	0.003	0.030	-0.005	25/31	
	CC3/ <i>aug-cc-pVTZ</i>	no correction	0.006	0.017	0.124	-0.034		
		+ [CCSDTQ – CC3]/ <i>aug-cc-pVDZ</i>	0.002	0.004	0.019	-0.003	28/31	
		+ [CCSDTQ – CC3]/6-31+G(d)	0.001	0.004	0.020	-0.008	26/31	
	CCSD/ <i>aug-cc-pVTZ</i>	no correction	0.071	0.071	0.273	-0.005		
		+ [CCSDTQ – CCSD]/ <i>aug-cc-pVDZ</i>	0.022	0.024	0.066	-0.011	26/31	
		+ [CCSDTQ – CCSD]/6-31+G(d)	0.010	0.032	0.061	-0.042	25/31	
	CC2/ <i>aug-cc-pVTZ</i>	no correction	-0.008	0.215	0.348	-0.695		
		+ [CCSDTQ – CC2]/ <i>aug-cc-pVDZ</i>	0.032	0.032	0.196	-0.001	29/31	
		+ [CCSDTQ – CC2]/6-31+G(d)	-0.005	0.051	0.108	-0.353	29/31	
CC4/ <i>aug-cc-pVTZ</i>	CCSDT/ <i>aug-cc-pVTZ</i>	no correction	0.004	0.016	0.095	-0.055		
		+ [CC4 – CCSDT]/ <i>aug-cc-pVDZ</i>	0.004	0.004	0.022	-0.005	52/59	
		+ [CC4 – CCSDT]/6-31+G(d)	0.002	0.004	0.028	-0.009	55/59	
	CC3/ <i>aug-cc-pVTZ</i>	no correction	0.006	0.016	0.112	-0.043		
		+ [CC4 – CC3]/ <i>aug-cc-pVDZ</i>	0.002	0.003	0.019	-0.005	52/59	
		+ [CC4 – CC3]/6-31+G(d)	0.000	0.004	0.018	-0.010	52/59	
	CCSD/ <i>aug-cc-pVTZ</i>	no correction	0.083	0.083	0.261	-0.009		
		+ [CC4 – CCSD]/ <i>aug-cc-pVDZ</i>	0.018	0.019	0.063	-0.009	54/59	
		+ [CC4 – CCSD]/6-31+G(d)	0.008	0.023	0.081	-0.041	51/59	
	CC2/ <i>aug-cc-pVTZ</i>	no correction	0.053	0.193	0.427	-0.701		
		+ [CC4 – CC2]/ <i>aug-cc-pVDZ</i>	0.027	0.029	0.196	-0.016	56/59	
		+ [CC4 – CC2]/6-31+G(d)	0.000	0.049	0.183	-0.352	54/59	
	CCSDT/ <i>aug-cc-pVTZ</i>	CC3/ <i>aug-cc-pVTZ</i>	no correction	0.004	0.015	0.073	-0.046	
			+ [CCSDT – CC3]/ <i>aug-cc-pVDZ</i>	-0.002	0.003	0.007	-0.016	109/118
			+ [CCSDT – CC3]/6-31+G(d)	-0.002	0.005	0.011	-0.036	102/118
CCSD/ <i>aug-cc-pVTZ</i>		no correction	0.114	0.114	0.539	0.010		
		+ [CCSDT – CCSD]/ <i>aug-cc-pVDZ</i>	0.022	0.025	0.073	-0.015	115/118	
		+ [CCSDT – CCSD]/6-31+G(d)	0.012	0.027	0.071	-0.044	112/118	
CC2/ <i>aug-cc-pVTZ</i>		no correction	-0.007	0.191	0.495	-0.675		
		+ [CCSDT – CC2]/ <i>aug-cc-pVDZ</i>	0.020	0.023	0.174	-0.020	115/118	
		+ [CCSDT – CC2]/6-31+G(d)	-0.019	0.047	0.167	-0.355	106/118	

listed in the SI (with the three basis sets and all compounds), we have 220 CCSDTQ reference values at hand. Using these reference values, one obtains a MSE of 0.002 eV and a MAE as small as 0.003 eV for CC4. As one could have foreseen,⁶³ the largest deviations between CC4 and CCSDTQ originate from the genuine double excitations in nitroxyl, nitrosomethane, and glyoxal for which CC-based methods would likely not be chosen in practical applications. Removing these three states, but keeping all other cases including the 2^1A_g dark state of butadiene, leads to a MSE of 0.001 eV and a MAE of 0.003 eV for CC4. Interestingly, in our earlier work devoted to very small compounds, we obtained the same MAE of 0.003 eV for CC4 (against CCSDTQ).⁶³ Clearly, one can state that CC4 is a very good approximation of CCSDTQ for the ESs that are not dominated by doubly-excited determinants.

3.2 Is CC4 significantly more accurate than CCSDT and CC3?

The next natural question is to determine if CC4 is worth its cost. Indeed, CC4 formally scales as $O(N^9)$ which is more costly than both CCSDT and CC3 [which scale as $O(N^8)$ and $O(N^7)$, respectively]. Using again the available CCSDTQ values as references, we obtain MSE and MAE of 0.000 and 0.015 eV for CCSDT, and 0.006 and 0.018 eV for CC3, again discarding from the set the true double excitations of nitroxyl, nitrosomethane, and glyoxal. It is no surprise that, on the one hand, both CC3 and CCSDT deliver results that would be rated as accurate enough for many applications, and, on the other hand, CC3 is an excellent approximation of CCSDT.^{33,81,82} The most valuable observation for our purposes is that CC4 indeed lowers the CCSDT and CC3 deviations by a factor of five, which we consider a very significant improvement when one aims at producing highly-accurate reference values.

3.3 Are CC4 basis set effects transferable?

When defining values for benchmarking purposes, it is obvious from the discussion above that one can safely employ CC4/*aug-cc-pVTZ* as reference when neither well-converged CIPSI/*aug-cc-pVTZ* nor CCSDTQ/*aug-cc-pVTZ* calculations are technically achievable. As detailed below, this is the case, for example, for some of the molecules encompassing four non-hydrogen atoms. However, as customary in the field,^{31,32,56,78,83–89} one can employ a double- ζ VTE computed with a CC model including quadruples in order to correct a triple- ζ VTE obtained with a quadruple-free CC method.

To test such strategies, we report in Table 1 the statistical analysis obtained with various correction schemes. We consider as reference the actual results obtained with the target method (leftmost column of Table 1). These reference values are available in Tables S3, S6, and S9 of the SI. In the rightmost column, we provide the number of states for which the correction yields smaller (or equal) absolute errors as compared to the non-corrected scheme (rows labeled as “no correction”).

Globally, the data listed in Table 1 are quite appealing and one notices three general trends. First, adding corrections for higher-order excitations systematically decrease the MAE

and improves the (vast) majority of the estimates. For example, while CC2/*aug-cc-pVTZ* returns a MAE of 0.215 eV as compared to CCSDTQ/*aug-cc-pVTZ*, correcting them with the differences between the VTEs computed with these two models but with the much smaller 6-31+G(d) basis set allows reducing the error to 0.051 eV and improves 29 of the 31 VTEs. Second, the more refined the starting point, the more accurate the final estimate. For example, using the same approach as above but starting from CC3/*aug-cc-pVTZ* rather than CC2/*aug-cc-pVTZ* would cut down the MAE from 0.051 eV to 0.004 eV. Third, performing the correction with *aug-cc-pVDZ* typically yields smaller statistical deviations than with 6-31+G(d), though the difference between the two approaches is small.

Given that CC4 is such a stunning approximation of CCSDTQ for ESs with a single excitation character, it is particularly relevant to investigate CC4/*aug-cc-pVTZ* estimates based on CCSDT and CC3, i.e.,

$$\Delta\tilde{E}_{AVTZ}^{CC4} \simeq \Delta E_{AVTZ}^{CCSDT} + [\Delta E_{AVDZ}^{CC4} - \Delta E_{AVDZ}^{CCSDT}], \quad (1a)$$

$$\Delta\tilde{E}_{AVTZ}^{CC4} \simeq \Delta E_{AVTZ}^{CCSDT} + [\Delta E_{Pop}^{CC4} - \Delta E_{Pop}^{CCSDT}], \quad (1b)$$

$$\Delta\tilde{E}_{AVTZ}^{CC4} \simeq \Delta E_{AVTZ}^{CC3} + [\Delta E_{AVDZ}^{CC4} - \Delta E_{AVDZ}^{CC3}], \quad (1c)$$

$$\Delta\tilde{E}_{AVTZ}^{CC4} \simeq \Delta E_{AVTZ}^{CC3} + [\Delta E_{Pop}^{CC4} - \Delta E_{Pop}^{CC3}]. \quad (1d)$$

Looking at Table 1, one notices that all four approaches deliver very comparable error patterns, with MAE not larger than 0.004 eV, and global improvement over the uncorrected CCSDT/*aug-cc-pVTZ* and CC3/*aug-cc-pVTZ* data, the errors being cut down by a factor of three. Of course, as can be deduced from the last column, not all values are more accurate when adding corrections obtained with smaller basis sets, but improvements are observed for the vast majority of the cases.

Additionally, although this is not the focus of the present work, we stress that the following expressions

$$\Delta\tilde{E}_{AVTZ}^{CCSDT} \simeq \Delta E_{AVTZ}^{CC3} + [\Delta E_{AVDZ}^{CCSDT} - \Delta E_{AVDZ}^{CC3}], \quad (2a)$$

$$\Delta\tilde{E}_{AVTZ}^{CCSDT} \simeq \Delta E_{AVTZ}^{CC3} + [\Delta E_{Pop}^{CCSDT} - \Delta E_{Pop}^{CC3}], \quad (2b)$$

are extremely effective with MAE of 0.003 and 0.005 eV and small maximal deviations as compared to the true CCSDT/*aug-cc-pVTZ* transition energies. The fact that these two approximations are very accurate, is certainly valuable, as both CC3/*aug-cc-pVTZ* and CCSDT/6-31+G(d) calculations are technically achievable on systems with up to approximately 10–12 non-hydrogen atoms, allowing to significantly expand the number of TBEs based on CCSDT/*aug-cc-pVTZ* that are included in the QUEST database for larger systems.

The take-home message of this Section is that, while these correction schemes (which are widespread in the CC community) are generally valuable to produce accurate VTEs, their overall accuracy depends ultimately on the quality of the starting point.

4. REFINED THEORETICAL BEST ESTIMATES

Given the above observations, it is worth reexamining our previous TBEs with the additional accuracy provided by CC4.

4.1 Linear systems

The QUEST database includes three linear systems encompassing four non-hydrogen atoms: cyanoacetylene, cyanogen, and diacetylene.^{11,33} For these three systems CC4/*aug-cc-pVTZ* calculations could be performed, whereas CCSDTQ/*aug-cc-pVTZ* calculations remain beyond reach (see Table S9 in the SI for raw data). We have, therefore, computed new TBEs on the basis of these CC4 data, applying the very trustworthy basis set correction (see top lines of Table 1)

$$\Delta E_{\text{AVTZ}}^{\text{TBE}} = \Delta E_{\text{AVTZ}}^{\text{CC4}} + \left[\Delta E_{\text{AVDZ}}^{\text{CCSDTQ}} - \Delta E_{\text{AVDZ}}^{\text{CC4}} \right]. \quad (3)$$

The results for seven ESs of these three linear molecules are listed in Table 2. It can be seen that the variations are negligible, with three TBEs unchanged, and four decreasing by 0.01 eV.

Table 2: TBE/*aug-cc-pVTZ* (in eV) established for the linear systems encompassing four non-hydrogen atoms.^a

Molecule	Transition	Nature	TBEs		
			New	Prev.	Diff.
Cyanoacetylene	$^1\Sigma^- (\pi \rightarrow \pi^*)$	Val	5.79	5.80	-0.01
	$^1\Delta (\pi \rightarrow \pi^*)$	Val	6.07	6.07	0.00
Cyanogen	$^1\Sigma_u^- (\pi \rightarrow \pi^*)$	Val	6.38	6.39	-0.01
	$^1\Delta_u (\pi \rightarrow \pi^*)$	Val	6.65	6.66	-0.01
Diacetylene	$^1\Sigma_u^- (\pi \rightarrow \pi^*)[\text{F}]^b$	Val	5.04	5.05	-0.01
	$^1\Sigma_u (\pi \rightarrow \pi^*)$	Val	5.33	5.33	0.00
	$^1\Delta_u (\pi \rightarrow \pi^*)$	Val	5.61	5.61	0.00

^a“Val” stands for valence ESs. TBEs obtained with Eq. (3) using data from the SI. The previous TBEs taken from Ref. 11 are given for comparison. ^bFluorescence from the optimized excited-state geometry.

4.2 Four non-hydrogen compounds

For most non-linear compounds encompassing four non-hydrogen nuclei, the TBEs of the QUEST database were obtained with CCSDT/*aug-cc-pVTZ* corrected using CCSDTQ/6-31+G(d) to take into account the quadruples contribution.^{11,33} Given the results gathered in Table 1, it is not clear that applying CC4/*aug-cc-pVDZ* corrections would improve significantly these original estimates. However, for a few compounds, the QUEST TBEs do not include corrections from the quadruples as they were computed at the CCSDT/*aug-cc-pVTZ* level “only”. Hence, we have considered these derivatives and employed Eq. (1a) to determine new TBEs. The results are listed in Table 3 and compared to the previous estimates.

Although the differences listed in the rightmost column of Table 3 have different signs, the impact of CC4 is typically a small decrease of the previous estimates, hinting that CCSDT tends to overestimate the VTEs. This is consistent with the 0.003 eV MSE reported in Table 1 for CCSDT as compared to CC4. For the 13 states listed in Table 3, the average correction is -0.011 eV and the average absolute change is 0.022 eV only. More importantly, for the vast majority of cases, the changes are not larger than ± 0.03 eV which was the estimated error bar in Ref. 11.

Table 3: TBE/*aug-cc-pVTZ* (in eV) established for non-linear systems containing four non-hydrogen atoms obtained using Eq. (1a).^a

Molecule	Transition	Nature	TBEs		
			New	Prev.	Diff.
Acrolein	$^1A'' (n \rightarrow \pi^*)$	Val	3.72	3.78 ^b	-0.06
	$^1A' (\pi \rightarrow \pi^*)$	Val	6.67	6.69	-0.02
	$^1A'' (n \rightarrow \pi^*)$	Val	6.69	6.72 ^c	-0.03
	$^1A' (n \rightarrow 3s)$	Ryd	7.11	7.08	+0.03
Carbonylfluoride	$^1A' (\pi \rightarrow \pi^*)$	Val ^d	7.93	7.87 ^b	+0.06
	$^1A_2 (n \rightarrow \pi^*)$	Val	7.29	7.31 ^e	-0.02
Cyanoformaldehyde	$^1A'' (n \rightarrow \pi^*)$	Val	3.82	3.81	+0.01
	$^1A'' (\pi \rightarrow \pi^*)$	Val	6.43	6.46	-0.03
Isobutene	$^1B_1 (\pi \rightarrow 3s)$	Ryd	6.48	6.46	+0.02
	$^1A_1 (\pi \rightarrow 3p)$	Ryd	7.01	7.01	0.00
Propynal	$^1A'' (n \rightarrow \pi^*)$	Val	3.81	3.80	+0.01
	$^1A'' (\pi \rightarrow \pi^*)$	Val	5.51	5.54	-0.03
Thioacrolein	$^1A'' (n \rightarrow \pi^*)$	Val	2.10	2.11	-0.01
Thiopropynal	$^1A'' (n \rightarrow \pi^*)$	Val	2.02	2.03	-0.01

^a“Val” and “Ryd” stand for valence and Rydberg ESs. Raw data are given in the SI. The previous TBE/*aug-cc-pVTZ* values taken from Refs. 29, 11, 30, and 33 are given for comparison. ^bTBEs obtained from a basis set corrected CIPSI/6-31+G(d) estimate. The CCSDT/*aug-cc-pVTZ* value for this particular state is 3.73 eV. ^cConsidered as *unsafe* in Ref. 11. ^dES with a significant double excitation character. ^eTBE obtained from a basis set corrected CIPSI/6-31+G(d) estimate.

Nevertheless, a molecule worth discussing is acrolein. For its lowest hallmark $n \rightarrow \pi^*$ transition, the CCSD, CC3, and CCSDT VTEs obtained with *aug-cc-pVTZ* are 3.913, 3.743, and 3.725 eV. The new TBE, 3.72 eV, is consistent with this trend, but is significantly smaller than the original CIPSI-based estimate of 3.78 eV. It is likely that the CIPSI extrapolation error bar was underestimated previously, and we believe that our current TBE is more accurate. Indeed, CC4/6-31+G(d) and CCSDTQ/6-31+G(d) values are very consistent (see Table S7). The second ES, a strongly dipole-allowed $^1A' (\pi \rightarrow \pi^*)$ transition, was slightly blueshifted in our original work, but the error, -0.02 eV, remains low, a statement also holding for the higher-lying Rydberg ES of the same symmetry. The original estimate for the second $^1A'' (n \rightarrow \pi^*)$ transition, 6.72 eV, was labeled as *unsafe* in Ref. 11 due to its significant double excitation character. Indeed, its percentage of single excitations ($\%T_1$) is only 79.4% according to CC3/*aug-cc-pVTZ*. Nevertheless, the CC4 correction obtained with *aug-cc-pVDZ* is not very large and one can likely claim that the new TBE of 6.69 eV stands as the most trustworthy estimate published to date for this particular ES. The higher-lying $^1A' (\pi \rightarrow \pi^*)$ transition of acrolein has a nature similar to the famous A_g state of butadiene with a $\%T_1$ of 75%. At the CIPSI/6-31+G(d) level, a value of 8.00 ± 0.03 eV was obtained previously,²⁹ and our CC4 value obtained with the same basis set is consistent with this result: 8.035 eV (see Table S7 in the SI). Based on CC4/*aug-cc-pVDZ*, *i.e.*, using Eq. (1a) the new TBE is 7.93 eV, upshifted by 0.06 eV as compared to the original one. Given that for the similar transition in butadiene, the changes between CC4 and CCSDTQ

are trifling (Table S7), we consider this new TBE as more trustworthy than the original one, though giving a reliable error bar is not straightforward. Finally, one can also note that, for carbonylfluoride, the current TBE is 0.02 eV smaller than the original CIPSI-based one, for which the estimated extrapolation error bar was 0.02 eV.¹¹

4.3 Larger systems

Table 4: TBE/*aug-cc-pVTZ* (in eV) established for systems containing five non-hydrogen atoms.^a

Molecule	Transition	Nature	TBEs		
			New	Prev.	Diff.
Cyclopentadiene	$^1B_2 (\pi \rightarrow \pi^*)$	Val	5.54	5.56 ^b	-0.02
	$^1A_2 (\pi \rightarrow 3s)$	Ryd	5.78	5.78	0.00
	$^1B_1 (\pi \rightarrow 3p)$	Ryd	6.41	6.41	0.00
	$^1A_2 (\pi \rightarrow 3p)$	Ryd	6.45	6.46	-0.01
	$^1B_2 (\pi \rightarrow 3p)$	Ryd	6.56	6.56	0.00
	$^1A_1 (\pi \rightarrow \pi^*)$	Val	6.45	6.52 ^c	-0.07
Difluorodiazirine	$^1B_1 (n \rightarrow \pi^*)$	Val	3.73	3.74	-0.01
	$^1A_2 (\pi \rightarrow \pi^*)$	Val	6.99	7.00	-0.01
	1B_2 (n.d.) ^d	Ryd	8.50	8.52	-0.02
Furan	$^1A_2 (\pi \rightarrow 3s)$	Ryd	6.08	6.09	-0.01
	$^1B_2 (\pi \rightarrow \pi^*)$	Val	6.34	6.37	-0.03
	$^1A_1 (\pi \rightarrow \pi^*)$	Val	6.53	6.56	-0.03
	$^1B_1 (\pi \rightarrow 3p)$	Ryd	6.66	6.64	+0.02
	$^1A_2 (\pi \rightarrow 3p)$	Ryd	6.81	6.81	0.00
Pyrrole	$^1B_2 (\pi \rightarrow 3p)$	Ryd	7.23	7.24	-0.01
	$^1A_2 (\pi \rightarrow 3s)$	Ryd	5.23	5.24	-0.01
	1B_1 (n.d.)	Ryd	5.97	6.00	-0.03
	$^1A_2 (\pi \rightarrow 3p)$	Ryd	6.01	6.00	+0.01
	1B_1 (n.d.) ^e	Ryd	6.09		
	$^1B_2 (\pi \rightarrow \pi^*)$	Val	6.24	6.26	-0.02
	$^1A_1 (\pi \rightarrow \pi^*)$	Val	6.27	6.30	-0.03
Thiophene	$^1B_2 (\pi \rightarrow 3p)$	Ryd	6.82	6.83	-0.01
	$^1A_1 (\pi \rightarrow \pi^*)$	Val	5.62	5.64	-0.02
	$^1B_2 (\pi \rightarrow \pi^*)$	Val	5.94	5.98	-0.04
	$^1A_2 (\pi \rightarrow 3s)$	Ryd	6.13	6.14	-0.01
	$^1B_1 (\pi \rightarrow 3p)$	Ryd	6.12	6.14	-0.02
	$^1A_2 (\pi \rightarrow 3p)$	Ryd	6.23	6.21	+0.02
	$^1B_1 (\pi \rightarrow 3s)$	Ryd	6.49	6.49	0.00
	$^1B_2 (\pi \rightarrow 3p)$ ^f	Ryd	7.27	7.29	-0.02
$^1A_1 (\pi \rightarrow \pi^*)$ ^f	Val	7.30	7.31 ^c	-0.01	

^a “Val” and “Ryd” stand for valence and Rydberg ESs. TBEs established with Eq. (1b), except for difluorodiazirine for which Eq. (1a) is used. Raw data are given in Table S10 in the SI. The previous TBEs taken from Refs. 11 and 30 are also listed. ^bThe most recent TBE, based on a basis set corrected CIPSI/6-31+G(d) value, is 5.54 eV, see Ref. 33. ^cConsidered as *unsafe* in Ref. 11. ^dIncorrectly labeled as valence in Ref. 30. ^eNot considered previously. ^fNon-negligible valence/Rydberg mixing.

For the largest systems of Figure 1, CC4 has the advantage to provide a systematic path towards high-accuracy for systems that are beyond reach at the CCSDTQ level. Let us first illustrate this with a set of 30 ESs extracted from systems with five (non-hydrogen) atom (Table 4). To the best of our knowledge, for all five molecules, our results provide the first VTEs including quadruples corrections. As one can see, the differences with the previous TBEs are small, and

are typically slightly negative, confirming the outcome of the previous section showing that CCSDT/*aug-cc-pVTZ* yields slightly too large VTEs. The average absolute correction for the data of Table 4 is nonetheless very small, 0.02 eV, which confirms that quality of the original TBEs from the QUEST database.

Let us now take a look at the most problematic cases. Unsurprisingly, the $^1A_1 (\pi \rightarrow \pi^*)$ transition of cyclopentadiene is significantly redshifted by the CC4 correction (−0.07 eV). This transition was previously classified as *unsafe*,¹¹ due to its $\%T_1$ value of 78.9% and its similar nature to the famous 1A_g ES of butadiene. For the latter compound, the difference between the CIPSI/6-31+G(d) and CCSDT/6-31+G(d) estimates is −0.08 eV,²⁹ which suggests that the CC4 correction of −0.07 eV for the 1A_1 ES of cyclopentadiene is very reasonable. The lowest B_2 ES of thiophene is subject to a −0.04 eV shift despite having also a very large single excitation character ($\%T_1 = 91.5\%$). All other ESs are even less affected by the CC4 corrections with variations of ± 0.03 eV at most.

We now consider three highly-symmetric six-membered rings, namely benzene, pyrazine, and tetrazine, for which CC4/6-31+G(d) calculations are still doable. The results obtained for a large number of ESs are listed in Table 5. For these three compounds, this Table is, as far as we are aware of, the first to propose CC-based VTEs including corrections from iterative quadruples.

For benzene, we consider three valence and four Rydberg ESs. These ESs have a very strong single excitation character with $\%T_1 > 92\%$, except for the lowest $^1B_{2u}$ transition ($\%T_1 = 86\%$). In all cases, one finds, as most of the five-membered cycles, that CC4/6-31+G(d) provides small negative or null corrections, with a maximal amplitude of −0.02 eV, even for the lowest-energy transition.

Eleven ESs of pyrazine are listed in Table 5, including four Rydberg states. The corrections to previous CCSDT-based TBEs are either positive, null or negative, but most are within the expected error bar of the original estimates. Nevertheless, for the lowest $^1B_{1g}$ ES, corresponding to a $n \rightarrow \pi^*$ excitation, a relatively large correction of −0.04 eV is noticed. This transition has a rather low $\%T_1$ value of 84%, which however does not translate into a large CC3/CCSDT difference (ca. 0.01 eV for the three basis sets, see the SI). Likewise the highest-lying $^1B_{1u}$ ES also undergoes a −0.04 eV correction, but this state was rated *unsafe* previously,^{11,33} due to an unusually large CC3/CCSDT difference. Four other ESs have their VTEs corrected by ± 0.03 eV by CC4, a shift corresponding to the expected error bar of the original TBEs.

In tetrazine, we consider 12 ESs, including two with a pure double excitation character, for which NEVPT2 was employed in the QUEST database to obtain TBEs, whereas, for the other transitions, CCSDT/*aug-cc-pVTZ* or basis set corrected CCSDT/*aug-cc-pVDZ* values were originally selected as TBEs.¹¹ All the latter were rated as *safe* as the energy differences between CCSDT and CC3 were smaller than 0.03 eV despite $\%T_1$ values often smaller than 90%.^{11,33} For several ESs, small negative CC4 corrections, −0.01 or −0.02 eV, are obtained. For the lowest $\pi \rightarrow \pi^*$ transition, the correction is only slightly larger, i.e., −0.04 eV. However, for

Table 5: TBE/*aug-cc-pVTZ* (in eV) established for benzene, pyrazine, and tetrazine.^a

Molecule	Transition	Nature	TBEs		
			New	Prev.	Diff.
Benzene	¹ B _{2u} ($\pi \rightarrow \pi^*$)	Val	5.05	5.06	-0.01
	¹ B _{1u} ($\pi \rightarrow \pi^*$)	Val	6.43	6.45	-0.02
	¹ E _{1g} ($\pi \rightarrow 3s$)	Ryd	6.52	6.52	0.00
	¹ A _{2u} ($\pi \rightarrow 3p$)	Ryd	7.08	7.08	0.00
	¹ E _{2u} ($\pi \rightarrow 3p$)	Ryd	7.15	7.15	0.00
	¹ A _{1u} ($\pi \rightarrow 3p$) ^b	Ryd	7.23		
Pyrazine	¹ E _{1u} ($\pi \rightarrow \pi^*$) ^b	Val	7.17		
	¹ B _{3u} ($n \rightarrow \pi^*$)	Val	4.14	4.15	-0.01
	¹ A _u ($n \rightarrow \pi^*$)	Val	4.97	4.98	-0.01
	¹ B _{2u} ($\pi \rightarrow \pi^*$)	Val	4.99	5.02	-0.03
	¹ B _{2g} ($n \rightarrow \pi^*$)	Val	5.68	5.71	-0.03
	¹ A _g ($n \rightarrow 3s$)	Ryd	6.66	6.65	+0.01
	¹ B _{1g} ($n \rightarrow \pi^*$)	Val	6.70	6.74	-0.04
	¹ B _{1u} ($\pi \rightarrow \pi^*$)	Val	6.85	6.88	-0.03
	¹ B _{1g} ($\pi \rightarrow 3s$)	Ryd	7.20	7.21	-0.01
	¹ B _{2u} ($n \rightarrow 3p$)	Ryd	7.27	7.24	+0.03
Tetrazine	¹ B _{1u} ($n \rightarrow 3p$)	Ryd	7.45	7.44	+0.01
	¹ B _{1u} ($\pi \rightarrow \pi^*$)	Val	7.94	7.98 ^c	-0.04
	¹ B _{3u} ($n \rightarrow \pi^*$)	Val	2.46	2.47	-0.01
	¹ A _u ($n \rightarrow \pi^*$)	Val	3.68	3.69	-0.01
	¹ A _g ($n, n \rightarrow \pi^*, \pi^*$)	Val		4.61 ^d	
	¹ B _{1g} ($n \rightarrow \pi^*$)	Val	4.87	4.93	-0.06
	¹ B _{2u} ($\pi \rightarrow \pi^*$)	Val	5.17	5.21	-0.04
	¹ B _{2g} ($n \rightarrow \pi^*$)	Val	5.50	5.45	-0.05
	¹ A _u ($n \rightarrow \pi^*$)	Val	5.51	5.53	-0.02
	¹ B _{3g} ($n, n \rightarrow \pi^*, \pi^*$)	Val		6.15 ^d	
¹ B _{2g} ($n \rightarrow \pi^*$)	Val	6.05	6.12	-0.07	
¹ B _{3g} ($n \rightarrow 3s$) ^b	Ryd	6.47			
¹ B _{3u} ($\pi \rightarrow \pi^*$) ^b	Val	6.67			
¹ B _{1g} ($n \rightarrow \pi^*$)	Val	6.89	6.91	-0.02	

^a“Val” and “Ryd” stand for valence and Rydberg ESs. TBEs established using Eq. (1b). Raw data are given in Table S11 in the SI. The previous TBEs taken from Ref. 11 are also listed. ^bNot considered previously. ^cConsidered as *unsafe* in Ref. 11. ^dGenuine doubly-excited states with TBEs obtained at the NEVPT2/*aug-cc-pVTZ* level and considered as *unsafe* in Ref. 11.

three $n \rightarrow \pi^*$ transitions (¹B_{1g}, ¹B_{2g}, and ²B_{2g}), much larger changes (−0.06, −0.05, and −0.07 eV) are induced by the inclusion of quadruples, indicating that our original assessment of the TBE quality was optimistic. Interestingly, for these three transitions, one has %*T*₁ < 85%, in contrast with the other singly-excited ESs for which %*T*₁ > 85%. This observation suggests that the 85% barrier might be the limit for which CCSDT can be considered trustworthy, irrespective of the difference between CC3 and CCSDT. For the two doubly-excited states of tetrazine listed in Tables 5 and S11, that are both characterized by %*T*₁ < 1%,¹¹ the differences between CC4/6-31+G(d) and CCSDT/6-31+G(d) are very significant, that is, −0.79 eV (*A*_g) and −0.99 eV (*B*_{3g}). These values are nonetheless typical for these challenging ESs with a dominant contribution from the doubly-excited determinants. Applying Eq. (1b) delivers VTEs of 5.17 and 6.44 eV. These two results logically remain higher in en-

ergy than the corresponding NEVPT2/*aug-cc-pVTZ* values of 4.61 and 6.15 eV, that we consider as the most accurate TBEs available to date, though with an error bar of approximately ±0.1 eV.

Finally, let us briefly discuss the challenging case of hexatriene (Table 6). The original TBEs for this small polyene have been obtained via Eq. (2a): 5.37, 5.62, 5.79, and 5.94 eV for the lowest ¹B_u, ¹A_g, ¹A_u, and ¹B_g ESs, respectively.³³ All were considered *safe*, except the second one that has a very significant contribution from the double excitations with %*T*₁ = 65% (i.e., 10% less than in butadiene). Using Eq. (1d) to include CC4 corrections leads to improved TBEs of 5.34, 5.46, 5.79, and 5.93 eV. Only the ¹A_g VTE undergoes a significant downshift (−0.16 eV) due to the quadruples. Logically, this 5.46 eV value can be considered as an upper bound and we roughly approximate the exact value to be of the order of 5.43 eV. To support this crude estimate, we looked at the equivalent transition in the smaller polyene, butadiene. Indeed, in butadiene, the difference between the CC4/6-31+G(d) and FCI/6-31+G(d) values is −0.01 eV; the correction should be larger for hexatriene given its smaller %*T*₁ value. In addition, as can be seen in Ref. 29, the NEVPT2/6-31+G(d) value is 0.20 eV larger than the FCI/6-31+G(d) result for butadiene, and applying such rigid shift to NEVPT2/*aug-cc-pVTZ* VTE of hexatriene,²⁹ would yield an estimate of 5.44 eV. Although it would not be suited to rate this new TBE/*aug-cc-pVTZ* of 5.43 eV as *safe*, it is likely one of the most accurate estimate published to date for this dark transition.

Table 6: TBE/*aug-cc-pVTZ* (in eV) established for hexatriene.^a

Molecule	Transition	Nature	TBEs		
			New	Prev.	Diff.
Hexatriene	¹ B _u ($\pi \rightarrow \pi^*$)	Val	5.34	5.37	-0.03
	¹ A _g ($\pi \rightarrow \pi^*$)	Val	5.46/5.43 ^c	5.62 ^b	-0.16/-0.19
	¹ A _u ($\pi \rightarrow 3s$)	Ryd	5.79	5.79	0.00
	¹ B _g ($\pi \rightarrow 3p$)	Ryd	5.93	5.94	-0.01

^a“Val” and “Ryd” stand for valence and Rydberg ESs. TBEs established using Eq. (1d). Raw data are given in Table S11 in the SI. The previous TBEs taken from Ref. 33 are also listed. ^bConsidered as *unsafe* in Ref. 33. ^cSee text.

5. CONCLUSIONS AND OUTLOOK

Three main problems were tackled in the present study. Our first aim was to confirm that CC4 provides very accurate VTEs. To this end, we considered 43 molecules containing between two and four (non-hydrogen) atoms and computed their ESs with three Gaussian basis sets containing diffuse functions, i.e., 6-31+G(d), *aug-cc-pVDZ*, and *aug-cc-pVTZ*. We started by defining more than 200 CCSDTQ reference values. Excluding the few pathological pure doubly-excited states of (*n, n*) → (π^*, π^*) nature but conserving all other transitions that have a non-negligible double excitation character (²A_g in butadiene, ²A” in acrolein, etc), we showed that CC4 is an excellent approximation of CCSDTQ with a mean absolute error of 0.003 eV. This is a totally negligible deviation for the vast majority of chemical studies (< 0.1

kcal.mol⁻¹). We also showed that neither CC3 nor CCSDT could deliver the same level of accuracy for the very same set of ESs.

Second, we investigated the performance of additive basis set correction schemes in the EOM-CC context using the same set of ESs as in the first part. It appeared that these popular correction strategies indeed statistically improve the quality of the VTEs. More interestingly, such basis set corrections were found particularly powerful when starting from CC3/*aug-cc-pVTZ* or CCSDT/*aug-cc-pVTZ*, as they allowed estimating the true CC4/*aug-cc-pVTZ* or CCSDTQ/*aug-cc-pVTZ* VTEs with average errors of approximately 0.005 eV. Of course, it is essential to confirm these trends for larger compounds, but the cost of CC4/*aug-cc-pVTZ* and/or CCSDTQ/*aug-cc-pVTZ* unfortunately prevents us of doing it as of today.

Finally, CC4 was employed to improve previous CCSDT-based TBEs of the QUEST database.³³ For benzene, cyclopentadiene, difluorodiazirine, furan, hexatriene, pyrazine, pyrrole, tetrazine, and thiophene, it was possible to perform CC4/6-31+G(d) and/or CC4/*aug-cc-pVDZ* calculations whereas CCSDTQ remains beyond reach. The corrections obtained were, in most cases, smaller than the expected average error of the original TBEs (ca. ±0.03 eV). Nevertheless, most corrections were null or negative, hinting at a slight overestimation trend in our original TBEs. In addition, some of the estimates originally viewed as *unsafe* can be now considered as trustworthy (²1A'' in acrolein, ²1A₁ in cyclopentadiene, ³1A₁ in thiophene, etc) whereas a few optimistic assessments have been revised, resulting in more accurate TBEs (in particular for the valence B_{1g} and B_{2g} ESs of tetrazine).

We are currently pursuing our efforts to improve the quality, size, and diversity of the QUEST database, so as to provide the most trustworthy reference values possible to the community. We plan to publish, within a year or two, an expanded and improved version of the QUEST database.

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SUPPORTING INFORMATION AVAILABLE

Raw VTEs. Geometries.

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Graphical TOC Entry

