Supplementary Information for "QUESTDB: a database of highly-accurate excitation energies for the electronic structure community"

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1 | QUEST#5: ADDITIONAL MOLECULES

1.1 | Aza-naphthalene

In contrast to naphthalene (see below), its tetraaza counterpart (1,4,5,8-tetraazanaphthalene) has not been much investigated although it also has a D_{2h} symmetry. The vibronic couplings of one low-lying state were nevertheless well characterized theoretically by Dierksen and Grimme with TD-DFT [1] and compared to the experimental spectrum [2]. The latter work also contains some CIS and CNDO calculations and a few assignments for higher-lying states. Our CC results collected in Table 1 are therefore clearly the most advanced to date. For the singlet transitions, no $\%T_1$ is smaller than 80%, and we have obtained consistent CC3 and CCSDT values with the Pople basis set. Indeed, the two models yield values within ±0.03 eV of each other, the two exceptions (the second B_{1u} and the $^1B_{3u}$ states) being considered as "unsafe" in the database. Comparisons to experimental 0-0 energies in condensed medium and CNDO calculations can be found in the Table, but are not very helpful to assess our TBEs. To the best of our knowledge, the present work is the first to report triplet excited states, and we list in Table 1 eight valence transitions obtained at the CC3/aug-cc-pVTZ level. As we were not able to perform CCSDT calculations for the triplets, all these transition energies are labeled "unsafe" in the QUEST database. Nevertheless, given the large $\%T_1$ values, one can likely consider them accurate (for the basis set used at least).

1.2 | Benzoquinone

Benzoquinone, the simplest quinoidic dye, has been treated at several levels of theory previously, e.g., CASPT2 [3–6], SAC-CI [7–9] and various CC levels up to CC3 [5, 10], ADC(2) and ADC(3) [11, 12] as well as TD-DFT [8, 9, 13–16]. Our results and comparisons with a selection of the existing literature can be found in Table 2.

For the singlet transitions, we could obtain CCSDT/aug-cc-pVDZ values for the 10 considered excited states. For the two lowest transitions of $n \rightarrow \pi^*$ character, these agree well with the corresponding CC3 values and we can define safe TBE/aug-cc-pVTZ of 2.82 and 2.96 eV. These values are within 0.10 eV of the most recent estimates

TABLE 1 Transition energies (in eV) determined in aza-naphthalene (1,4,5,8-tetraazanaphthalene). For all transitions, we provide the single-excitation character $\%T_1$ obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3			CCSDT	Litt.	
	Nature	f	$\%T_1$	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	Th.[a]	Exp.[b]
Aza-naphthalene	$^1B_{3g}\,(n \to \pi^*)$		88.5	3.26	3.15	3.11	3.29	2.64	2.61
	$^1B_{2u}\,(\pi \to \pi^*)$	0.190	86.5	4.37	4.32	4.28	4.37	4.05	3.86
	$^1B_{1u}\,(n \to \pi^*)$	n.d.	88.5	4.47	4.39	4.34	4.47	3.32	
	$^1B_{2g}\,(n \to \pi^*)$		87.3	4.62	4.55	4.53	4.64	4.48	
	$^1B_{2g}\,(n \to \pi^*)$		84.1	5.00	4.91	4.86	5.03	4.76	
	$^1B_{1u}\,(n \to \pi^*)$	n.d.	82.6	5.31	5.17	5.13	5.42		
	$^1A_{u}\,(n \to \pi^*)$		83.1	5.47	5.40	5.34	5.47	4.51	
	$^1B_{3u}\,(\pi \to \pi^*)$	0.028	88.5	5.86	5.69	5.63	5.91	5.26	5.03
	$^1A_{g}\,(\pi \to \pi^*)$		85.3	5.96	5.87	5.81	5.95		
	$^1A_{u}\,(n \to \pi^*)$		84.8	5.97	5.90	5.89	6.00		
	$^1A_{g}\,(n \to 3s)$		90.5	6.56	6.39	6.49	6.57		
	$^3B_{3g}\,(n \to \pi^*)$		96.5	2.93	2.84	2.82			
	$^3B_{2u}\,(\pi \to \pi^*)$		97.2	3.86	3.73	3.67			
	$^3B_{3u}\,(\pi \to \pi^*)$		97.7	3.78	3.76	3.75			
	$^3B_{1u}\,(n \to \pi^*)$		97.1	3.85	3.79	3.77			
	$^3B_{2g}\,(n \to \pi^*)$		96.2	4.43	4.37	4.34			
	$^3B_{2g}\,(n \to \pi^*)$		95.3	4.71	4.63	4.61			
	$^3B_{3u}\,(\pi \to \pi^*)$		96.6	4.82	4.78	4.75			
	$^3A_{u}\,(n \to \pi^*)$		96.6	4.96	4.91	4.87			

[a] CNDO/S values from Ref. [2].

[b] 0-0 energy in solution estimated in Ref. [2]. There are other tentative assignments in that work.

of Thiel [10] and are clearly larger than older CASPT2 estimates [3, 4], which appear too low. The experimentally available data return 0-0 energies of roughly 2.5 eV for both transitions [17, 18]. These values are located 0.3–0.4 eV below our vertical estimates which is a quite reasonable difference between vertical and 0-0 energies. The next transition of A_g symmetry has a pure double excitation character so that unsurprisingly both CC3 and CCSDT yield values that are much too large. Indeed, at the NEVPT2/aug-cc-pVTZ level, we obtain a transition energy of 4.57 eV for this excitation, more than 1 eV below the CC3 estimate, yet again slightly above earlier CASPT2 estimates. Although one cannot consider this 4.57 eV estimate as chemically accurate (the error bar of NEVPT2 is typically ±0.10 eV for transitions of pure double character [19]), it is likely the most accurate value available at this stage. The next transition of $^1B_{3g}$ symmetry is the first of $\pi \to \pi^*$ character. Although its associated %T_1 value is rather large, there is substantial difference between CC3 and CCSDT, making our TBE of 4.58 eV falling in the "unsafe" category, though it is obviously more accurate than previous CASPT2 values that are too close from the experimental 0-0 energies to be trustworthy. For the next strongly-allowed transition ($^1B_{1u}$), one also notices small yet non-negligible differences between CC3 and CCSDT. Our TBE of 5.62 eV is slightly larger than Thiel's one (5.47 eV obtained using CC3) [6], It is objectively hard to determined which one is the most accurate, and if the difference in the ground-state geometries (CC3 here *vs* MP2 in Thiel's work) also plays a significant role in this discrepancy. The situation is similar for the B_{3u} transition, although in that case the present TBE of 5.79 eV is close to Thiel's CC3 value of 5.71 eV. Note that Thiel selected a CASPT2 value of 5.55 eV as TBE due to the rather small %T_1 value for that state. However, this value is likely slightly too low as the agreement between CC3 and CCSDT is rather good. For the higher-lying singlet transitions, we note that: i) we could produce "safe" TBEs for the two B_{2g} excited states that both show minimal changes between CC3 and CCSDT, although %T_1 is small for the lowest transition of that symmetry; ii) for the (second) ^1A_u transition, the differences are too large between CC3 and CCSDT to provide trustworthy estimates; iii) for the (second) $^1B_{1g}$ excitation, these differences are less marked and although we rated our TBE (6.38 eV) as "unsafe", it is likely the best estimate proposed to date in the literature.

For the triplets, we considered the four lowest transitions, two of $n \to \pi^*$ character ($^3B_{1g}$ and ^3A_u) and two of $\pi \to \pi^*$ character ($^3B_{1u}$ and $^3B_{3g}$), see Table 2. For all fours excited states, there is a very nice match between the CC3 and CCSDT transition energies obtained with Pople's basis set, and the single-excitation characters are very large, so that we are confident that our TBEs are trustworthy. For the $^3B_{1g}$ and ^3A_u transitions, our energies are very slightly larger than Thiel's extrapolated CC3 ones, and again ca. 0.3–0.4 eV above the experimental 0-0 energies. As for the singlet transitions, the early CASPT2 values are too low. For the two $\pi \to \pi^*$ excitations, exactly the same trends are found, but no experimental measurements exist to our knowledge.

TABLE 2 Transition energies (in eV) determined in *p*-benzoquinone. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

| | Transition | | | CC3 | | | CCSDT | | Litt. | | | | | | |
	Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	aug-cc-pVDZ	Th.[a]	Th.[b]	Th.[c]	Exp.[d]	Exp.[e]	Exp.[f]	Exp.[g]
Benzoquinone	$^1B_{1g}$ ($n \rightarrow \pi^*$)		85.3	2.85	2.81	2.79	2.87	2.84	2.50	2.39	2.74			2.52	2.49
	^1A_u ($n \rightarrow \pi^*$)		84.1	2.99	2.95	2.94	3.01	2.97	2.50	2.43	2.86			2.49	2.48
	^1A_g ($n,n \rightarrow \pi^*,\pi^*$)		0.0	5.92	5.94	6.02	5.79	5.84	4.41	4.36					
	$^1B_{3g}$ ($\pi \rightarrow \pi^*$)		88.6	4.66	4.58	4.53	4.71	4.63	4.19	4.01	4.44	4.3	4.09	4.07	
	$^1B_{1u}$ ($\pi \rightarrow \pi^*$)		88.4	5.71	5.63	5.58	5.75	5.67	5.15	5.09	5.47	5.38–5.70	5.08	5.12	
	$^1B_{3u}$ ($n \rightarrow \pi^*$)	0.471	79.8	5.95	5.77	5.75	5.96	5.81	5.15	4.91	5.71				
	$^1B_{2g}$ ($\pi \rightarrow \pi^*$)	0.001	76.2	6.11	5.96	5.94	6.10	5.97	4.80	4.99					
	^1A_u ($n \rightarrow \pi^*$)		74.8	6.41	6.29	6.27	6.46	6.37	5.79	5.47					
	$^1B_{1g}$ ($n \rightarrow \pi^*$)		83.5	6.48	6.37	6.34	6.51	6.41	5.76	5.68					
	$^1B_{2g}$ ($n \rightarrow \pi^*$)		86.6	7.33	7.28	7.20	7.33	7.30	5.49	5.62					
	$^3B_{1g}$ ($n \rightarrow \pi^*$)		96.0	2.61	2.56	2.56	2.63		2.17	2.16	2.50			2.31	2.31
	^3A_u ($n \rightarrow \pi^*$)		95.6	2.76	2.71	2.71	2.77		2.27	2.22	2.61			2.35	2.31
	$^3B_{1u}$ ($\pi \rightarrow \pi^*$)		97.7	3.13	3.16	3.14	3.11		2.91	2.57	3.02				
	$^3B_{3g}$ ($\pi \rightarrow \pi^*$)		97.9	3.46	3.46	3.44	3.48		3.19	3.09	3.37				

[a] CASPT2 values from Ref. [3].
[b] CASPT2 values from Ref. [4].
[c] CC3 (extrapolated to aug-cc-pVTZ) values from Ref. [6].
[d] EELS from Ref. [16].
[e] Absorption spectroscopy (0-0 energies) from Ref. [20].
[f] Absorption spectroscopy (0-0 energies) from Ref. [17] (gas-phase and pure crystals).
[g] Absorption spectroscopy (0-0 energies) from Ref. [18].

1.3 | Cyclopentadienone and cyclopentadienethione

This two five-membered rings with an external (thio)ketone moiety have been investigated theoretically by Serrano-Andrés and coworkers in 2002 [21] who used the best method available at the time, namely CASPT2 (without IPEA). Our results are compared to these earlier estimates in Table 3. For both structures and both spin symmetries, the two lowest singlet transitions are of $A_2(n \to \pi^*)$ and $B_2(\pi \to \pi^*)$ spatial symmetries. There is a good to excellent agreement between the CC3 and CCSDT values for both the 6-31+G(d) and the aug-cc-pVDZ basis sets for these eight excited states, consistent with the large single excitation character. Thus, one can likely trust the obtained TBEs as these transitions are unproblematic. Experimentally, a tBu substituted cyclopentadienone shows a weakly-allowed band peaking at 3.22 eV in vapour [22], which is likely the $^1B_2$ state. For the lowest triplet state of cyclopentadienone, the experimental triplet energy was (indirectly) estimated experimentally to be 1.50 ± 0.02 eV [23], but this value corresponds to the triplet lowest-energy geometry, so that direct comparisons with our data is unreasonable. This 2014 work also contains CCSD(T) estimates of the adiabatic electron affinities for the two lowest triplet states.

In the singlet manifold of this molecule, one next finds one dark transition of purely double $(n, \pi) \to (\pi^*, \pi^*)$ character, for which CC theory is not well suited, as clearly illustrated by the huge difference between CC3 and CCSDT. Using a minimal active space (π space and lone pairs), we obtained with NEVPT2 value of 5.02 eV, i.e., 0.7 eV below the CCSDT estimate and roughly half an eV higher than the earlier CASPT2 values. This 5.02 eV estimate although not chemically accurate is likely the best available today. The fourth singlet state is an interesting yet challenging $(pi, \pi) \to (\pi^*, \pi^*)$ showing a %T_1 of 49.9 %. For this particular state, the NEVPT2 value is 6.02 eV, which is likely again the most realistic value available. The fifth transition shows a butadiene-A_g-like character, that is a totally-symmetric $\pi \to \pi^*$ transition with a significant double excitation character around 25%. For this transition, we based our TBE on the CCSDT estimate, but it might be too large by roughly 0.10 eV. The experimental spectrum of the related compounds shows a strong peak at 5.93 eV [22], likely corresponding to the overlap between these two $^1A_1$ transitions. In cyclopentadienone, the third triplet is an unproblematic $\pi \to \pi^*$ transition, for which there is a remarkable consistency between our CC estimates, again significantly above the previous CASPT2 data [21]. Finally, the highest triplet considered has originally a highly dominant multi-excitation character and our best estimate of 4.91 eV was obtained with NEVPT2, the CC values being too large.

For the singlet manifold of cyclopentadienethione, on finds again a $^1B_1(n, \pi \to \pi^*, \pi^*)$ purely double transition and a 50/50 single/double $^1A_1(\pi, \pi) \to (\pi^*, \pi^*)$ transition. The methodological trends are similar to those noted for the oxygen-derivatives, and the TBE listed in the QUEST database are obtained with NEVPT2: 3.16 eV and 5.43 eV. For the latter, it should be noted that there are several transitions of mixed character close in energy, so that definitive attribution is challenging. In contrast to cyclopentadienone, the $^1A_1(\pi \to \pi^*)$ transition shows a very large %T_1 value and small differences between CC3 and CCSDT, so that we have been able to define a "safe" TBE of 4.96 eV. For the records, our NEVPT2 estimate for that state is consistent, 4.90 eV. For the triplets of cyclopentadienethione, the trends are totally similar to those of the oxygen structure. For the fourth triplet of double character, our TBE is 3.13 eV, a value again obtained with NEVPT2.

1.4 | Diazirine

This compact molecule is the diazo equivalent of cyclopropene, and it has been introduced in our latest work [24]. It is a rather elusive compound experimentally so that the most complete study of its transitions energies are theoretical and have been performed at the MCQDPT2 [25] and EOM-CCSD [26] levels. For the eight considered transitions (Table 4), the %T_1 values are larger than 90% and the differences between the CC3, CCSDT, and CCSDTQ values are

TABLE 3 Transition energies (in eV) determined in cyclopentadienone and cyclopentadienethione. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3				CCSDT		Litt.
	Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	6-31+G(d)	aug-cc-pVDZ	Th.[a]
Cyclopentadienone	$^1A_2(n \rightarrow \pi^*)$		88.5	3.03	2.95	2.94	2.95	3.03	2.95	2.48
	$^1B_2(\pi \rightarrow \pi^*)$	0.004	91.2	3.69	3.57	3.54	3.53	3.72	3.61	3.00
	$^1B_1(n, \pi \rightarrow \pi^*, \pi^*)$	0.000	3.1	6.06	6.07	6.12	6.12	5.67	5.69	4.49
	$^1A_1(\pi, \pi \rightarrow \pi^*, \pi^*)$	0.131	49.9	7.20	7.12	7.10	7.08	7.07	6.95	5.42
	$^1A_1(\pi \rightarrow \pi^*)$	0.090	73.6	6.26	6.23	6.21	6.20	6.12	6.11	5.98
	$^3B_2(\pi \rightarrow \pi^*)$		98.0	2.30	2.29	2.28	2.28	2.32	2.30	1.97
	$^3A_2(n \rightarrow \pi^*)$		96.9	2.72	2.63	2.64	2.65	2.72	2.64	2.51
	$^3A_1(\pi \rightarrow \pi^*)$		98.2	4.21	4.20	4.19	4.20	4.20	4.20	3.78
	$^3B_1(n, \pi \rightarrow \pi^*, \pi^*)$		10.0	5.98	5.99	6.05	6.04	5.55		4.46
Cyclopentadienethione	$^1A_2(n \rightarrow \pi^*)$		87.2	1.76	1.74	1.71	1.72	1.74	1.73	1.43
	$^1B_2(\pi \rightarrow \pi^*)$	0.000	85.3	2.71	2.66	2.62	2.61	2.71	2.67	1.99
	$^1B_1(n, \pi \rightarrow \pi^*, \pi^*)$	0.000	1.1	4.27	4.35	4.40	4.39	3.84	3.93	2.89
	$^1A_1(\pi \rightarrow \pi^*)$	0.378	89.2	5.13	5.01	4.94	4.93	5.14	5.03	4.42
	$^1A_1(\pi, \pi \rightarrow \pi^*, \pi^*)$	0.003	51.7	5.86	5.90	5.89	5.88	5.68		4.84
	$^3A_2(n \rightarrow \pi^*)$		97.0	1.50	1.47	1.47	1.48	1.49	1.47	1.26
	$^3B_2(\pi \rightarrow \pi^*)$		97.1	1.91	1.90	1.88	1.88	1.91	1.90	1.61
	$^3A_1(\pi \rightarrow \pi^*)$		98.1	2.51	2.55	2.52	2.53	2.50	2.54	2.41
	$^3B_1(n, \pi \rightarrow \pi^*, \pi^*)$		4.2	4.25	4.34	4.39	4.37	3.81	3.90	2.88

[a] CASPT2 values from Ref. [21].

at most 0.02 eV. In addition, except possibly for the $^1B_2$ transition, the basis set effects are rather limited. In short, one can be very confident that the TBEs/aug-cc-pVTZ given in the database are chemically accurate at least for the selected geometry and basis set. If we compare to the previously published values, one notes that the MCQDPT2 results are likely slightly off target, whereas there is quite a good agreement with the EOM-CCSD values of Krylov and coworkers [26]. This latter work used a very diffuse basis set, so that one cannot be definitive that the remaining differences are purely related to the level of theory. Finally, we are aware of only one experimental data: the 0-0 energy of the lowest singlet state at 3.87 eV [27], a value slightly smaller than the computed vertical transition energy, as it should.

TABLE 4 Transition energies (in eV) determined in diazirine with CC3, CCSDT, and CCSDTQ. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

Transition			CC3				CCSDT			CCSDTQ		Litt.	
Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	aug-cc-pVDZ	Th.[a]	Th.[b]
Diazirine $^1B_1(n \to \pi^*)$	0.002	92.5	4.20	4.16	4.11	4.11	4.18	4.15	4.10	4.17	4.14	4.01	4.27
$^1A_2(\sigma \to \pi^*)$		90.9	7.43	7.40	7.31	7.29	7.40	7.37	7.28	7.39	7.36	7.79	7.61
$^1B_2(n \to 3s)$	0.000	93.5	7.62	7.36	7.45	7.48	7.62	7.35	7.44		7.35	7.16	7.32
$^1A_1(n \to 3p)$	0.132	93.8	8.05	7.97	8.04	8.05	8.03	7.95	8.03	8.02	7.95	9.91	7.86
$^3B_1(n \to \pi^*)$		98.2	3.56	3.53	3.51	3.51	3.55	3.53	3.50	3.54		3.37	
$^3B_2(\pi \to \pi^*)$		98.8	5.08	5.06	5.05	5.05	5.08	5.06	5.05	5.09		5.46	
$^3A_2(n \to \pi^*)$		98.3	6.20	6.15	6.13	6.13	6.18	6.14	6.12	6.18		5.97	
$^3A_1(n \to 3p)$		98.4	6.87	6.82	6.83	6.85	6.85	6.80	6.81	6.85		6.57	

[a] MCQDPT2 values from Ref. [25].
[b] EOM-CCSD energies from Ref. [26].

1.5 | Hexatriene and octatetraene

Ethylene and butadiene, the two shortest members of the polyenes, have been treated in QUEST#1 and QUEST#3, respectively [28, 29]. The evolution of excited state energies in longer polyenic chains is obviously of interest and this is why we considered hexatriene and octatetraene here. It should be noted that the transition energies are rather sensitive to the bond length alternation in polyenes, so that we trust that our choice of CC3 geometries is an asset as compared to previous estimates. Our results are collected in Table 5. Let us start by the famous singlet B_u and A_g valence states. The transition to B_u is bright and has a strong single-excitation character, so that one expects CC to be an adequate methodology, and one indeed finds small differences between CC3 and CCSDT values (ca. 0.03 eV). Our TBE/aug-cc-pVTZ are 5.37 and 4.78 eV for hexatriene and octatetraene, respectively. These values are compared to selected previous theoretical estimates in Table 5 and one clearly notices quite a large spread. Experimentally, the 0-0 transition has been measured to be 4.95 eV by electron impact [30] and 4.93 eV by optical spectroscopy [31] for hexatriene, and 4.41 eV with the latter technique for the longer oligomer [32], values logically smaller than our vertical estimates. However, one clearly notices a decrease of 0.53 eV when increasing the chain length, as compared to 0.59 eV with our TBE/aug-cc-pVTZ highlighting the consistency of quantum and measured trends. The A_g transitions are known to be much more challenging: the states are dark in one-photon absorption, and it has a very significant multi-excitation character (%T_1 of roughly 65% for both compounds). On a positive note, the basis set effects are very limited for the A_g state, 6-31+G(d) being apparently sufficient. In contrast, as expected for such transition, there is a significant drop of the theoretical estimate in going from CC3 to CCSDT. From the analysis performed for double excitations in Ref. [19], it is unclear if NEVPT2 or CASPT2 would in fact outperform CCSDT for such "mixed-character" state, so that we cannot define a trustworthy TBE on this basis. However, based on our experience for butadiene [29], one can widely estimate the transition energy to be in the range 5.55–5.60 eV for hexatriene and in the range 4.80–4.85 eV for octatetraene. Interestingly the FCI value of Chien *et al.* with a small basis set for hexatriene (5.59 eV) is compatible with such an estimate. Experimentally, for hexatriene, multiphoton experiments estimate the A_g state to be slightly above the B_u transition [33], an outcome that theory reproduces.

For the two Rydberg transitions of hexatriene, the differences between CC3 and CCSDT estimates are very small, %T_1 values are large, so that CC estimates can likely be trusted. However, the basis set effects are rather large, and aug-cc-pVTZ might be insufficient to reach basis set convergence. Our values are reasonably similar to those obtained with CASPT2 almost thirty years ago [34]. The experimental 0-0 energies are 5.68 eV and 6.06 eV [35], but the assignments of Rydberg transitions is a matter of discussion [34], so that we prefer again not to use measured data as reference.

For the triplet excited states, given their very large %T_1 values, we logically trust the CC estimates. We note that, to the best of our knowledge, this work is the first to report true CC3/aug-cc-pVTZ values for these two systems. Indeed, the previous CC3 estimates provided by Thiel [6, 10] were obtained by correcting CC3/TZVP values thanks to CC2 calculations using a larger basis set. These authors nevertheless provided very close estimates to ours: 2.71, 4.33, 2.32, and 3.69 eV (going down the list of triplet excited states in Table 5). These data are within 0.04 eV of the current values. Comparatively, the previous MRMP and CASPT2 results [6, 34, 36] are therefore slightly too low for the triplet transition energies. For hexatriene (octatetraene), electron impact studies return maxima at 2.61 (2.10) and 4.11 (3.55) eV for the two lowest transitions [30] ([37]), in reasonable agreement with the values listed in the QUEST database.

TABLE 5 Transition energies (in eV) determined in hexatriene and octatetraene. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3			CCSDT		Litt.			
	Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	aug-cc-pVDZ	Th.[a]	Th.[b]	Th.[c]	Th.[d]
Hexatriene	$^1B_u(\pi \to \pi^*)$	1.115	92.2	5.54	5.37	5.34	5.56	5.40	5.01	5.37	5.74	5.59
	$^1A_g(\pi \to \pi^*)$		65.3	5.76	5.76	5.75	5.62	5.63	5.19	5.34	5.73	5.58
	$^1A_u(\pi \to 3s)$	0.009	93.6	6.04	5.71	5.78	6.05	5.72	5.84			
	$^1B_g(\pi \to 3p)$		93.5	6.05	5.84	5.92	6.07	5.86	6.12			
	$^3B_u(\pi \to \pi^*)$		97.9	2.73	2.73	2.73	2.73		2.55	2.40		
	$^3A_g(\pi \to \pi^*)$		98.3	4.37	4.37	4.36	4.37		4.12	4.15		
Octatetraene	$^1B_u(\pi \to \pi^*)$	n.d.	91.5	4.95	4.78	4.75	4.98		4.35	4.66		
	$^1A_g(\pi \to \pi^*)$		63.7	5.05	5.05	5.04	4.91		4.53	4.47		
	$^3B_u(\pi \to \pi^*)$		97.5	2.35	2.36	2.36			2.27	2.20		
	$^3A_g(\pi \to \pi^*)$		98.0	3.73	3.73	3.73			3.61	3.55		

[a] CASPT2 values from Ref. [34] (hexatriene) and Ref. [6] (octatetraene).

[b] MRMP values from Ref. [36].

[c] Cumulant values from Ref. [38].

[d] FCI/double-ζ values from Ref. [39].

1.6 | Maleimide

Maleimide was quite surprisingly much less studied theoretically than other similar compounds. We are only aware of the 2003 CASPT2 analysis of Climent and coworkers [40], a refined 2020 joint theory/experiment study using CASPT2, ADC(3), and EOM-CCSD [41], as well as two quite recent investigations focussed on the geometries of specific states [42, 43] rather than on the transition energies. Our results are listed in Table 6. For all considered singlet (triplet) transitions, we obtained %T_1 values larger than 85% (95%), and one indeed notices very consistent estimates with CC3 and CCSDT, the largest difference being 0.03 eV. All transitions can therefore be considered as rather "safe". Comparing the 2003 and 2020 CASPT2 values (see Table 6), one notices large differences between the two, and our present estimates are (much) closer from the most recent values. Nevertheless, even the 2020 CASPT2 results seem rather too low as compared to the values provided here. The experimental data are limited. Interestingly, Climent and coworkers attributed the experimental 0-0 absorption at 3.33 eV (see footnotes in Table 6) to the second transition, but given our data, we believe that it is more likely the B_1 transition, an assignment consistent with the fact that this band shows non-zero experimental intensities. The A_2 transition seems indeed significantly too high with CCSDT to be attributed to the 3.33 eV measurement. For this assignment, we therefore agree with the analysis of Ref. 41. Globally, our CCSDT values are typically bracketed by the EOM-CCSD and CASPT2 values of this recent study, which we consider a good hint of accuracy.

1.7 | Naphthalene

Naphthalene, due to its high-symmetry and significance for organic electronics, is also a popular benchmark molecule [5, 6, 10, 11, 45–48], although some studies are focussed on the lowest-energy states "only" [49, 50]. Our results are listed in Table 7. We believe that the convincing work of Fliegl and Sundholm remains the most complete analysis to date [48].

For the singlet transitions, we could obtain CCSDT, albeit only with Pople's basis set. However, these remain quite significant as none of the considered excited state (even those with Rydberg character) seems to be strongly

TABLE 6 Transition energies (in eV) determined in maleimide. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3			CCSDT		Litt.			
	Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	aug-cc-pVTZ	Th.[a]	Th.[b]	Exp[c]	Exp[d]
Maleimide	$^1B_1(n \to \pi^*)$	0.000	87.6	3.86	3.80	3.78	3.87	3.82	2.48	3.37	3.33	
	$^1A_2(n \to \pi^*)$		85.9	4.58	4.54	4.51	4.59	4.55	3.29	3.96		
	$^1B_2(\pi \to \pi^*)$	0.025	88.2	4.93	4.87	4.86	4.96	4.90	4.44	4.62	~4.4	4.72
	$^1B_2(\pi \to \pi^*)$	0.373	89.1	6.32	6.23	6.18	6.35	6.26	5.59	5.80	5.53	4.95
	$^1B_2(n \to 3s)$	0.034	89.1	7.25	7.08	7.19	7.27	7.09	5.98			
	$^3B_1(n \to \pi^*)$		96.3	3.63	3.57	3.56	3.64		2.31	3.61		
	$^3B_2(\pi \to \pi^*)$		98.4	3.72	3.75	3.73	3.73		3.49	3.32		
	$^3B_2(\pi \to \pi^*)$		96.9	4.28	4.25	4.25	4.27		3.84	3.83		
	$^3A_2(n \to \pi^*)$		96.1	4.37	4.33	4.31	4.38		3.14	4.32		

[a] CASPT2 values from Ref. [40].

[a] CASPT2 (singlet) or ADC(3) (triplet) values from Ref. [41].

[c] From Ref. 44: the 3.33 eV value is a 0-0 energy at low temperature in (frozen) EPA, the 4.4 eV value is the lowest (close from 0-0) peak observed in vapour for *N*-Me-maleimide, and the 5.53 eV value is a 0-0 energy in vapour for the N-Me-maleimide.

[d] Vapour measurements at 315 K from Ref. [41].

affected by the basis set. Indeed, the mean absolute deviation between CC3/6-31+G(d) and CC3/aug-cc-pVTZ is 0.16 eV, the maximal discrepancy being 0.23 eV. When one compares the CCSDT and CC3 values, we note that there are only two transitions (the lowest ^1A_g and the second $^1B_{3u}$) for which changes exceeding 0.03 eV can be found between the two bases. It is also striking that for the higher-lying A_g state, both CC3 and CCSDT transition energies are the same despite %T_1 being 72% only. It therefore appears that naphthalene provides a series of well-behaved transitions for which CC theory is well suited. For the valence transition, the TBEs that we obtained are very close from the previous Thiel's CC3 values. Let us now discuss the valence transitions in more details. For the lowest $^1B_{3u}$ and $^1B_{2u}$ transitions, our TBEsaug-cc-pVTZ are 4.27 eV and 4.90 eV. On the theoretical side, these can be compared to Thiel's 4.25 eV and 4.82 eV values [6], or Fliegl and Sundholm 4.16 and 4.80 eV estimates (obtained with larger basis sets) [48]. On the experimental side, we are aware of vapour phase energy loss values of 4.0 and 4.45 eV [51] and (optical) 0-0 energies of 3.97 and 4.45 eV [52], as well as a 3.93 and 4.35 eV 0-0 energy measurement in cyclohexane [53]. The next transition is the lowest Rydberg state [$^1A_u(\pi \to 3s)$], and our TBE/aug-cc-pVTZ is 5.65 eV, which fits very well the old CASPT2 estimates of Rubio and coworkers (5.54 eV [45]), the more recent CC-derived value (5.56 eV [48]) and the only experimental value we are aware off (5.60 eV by energy loss [51]). It is also likely that the use of even large basis set than aug-cc-pVTZ would decrease a bit our estimate. Next come the valence $^1B_{1g}$ and A_g states for which our TBE/aug-cc-pVTZ are 5.84 and 5.89 eV (we recall that we labeled the second one as "unsafe"). On the theoretical side, previous calculations led 5.75 and 5.90 eV with exCC3 [6], 5.87 and 6.00 eV with RASPT2 [47], 5.64 and 5.77 eV with exCC3 [48]. On the experimental side, the measured 0-0 energies are 5.22 and 5.52 eV [54] and 5.28 and 5.50 eV, both in solution [53]. All these estimates are rather consistent with one another. Next come two $\pi \to 3p$ Rydberg transitions, for which our TBE of 6.07 and 6.09 eV are slightly larger than the CASPT2 values of Ref. [45] and the extrapolated CC2 estimates of 5.94 and 5.96 eV. To our knowledge, no experimental measurement exists for these two transitions. We estimate the next valence $^1B_{3u}$ excited state to be close to 6.19 eV with the aug-cc-pVTZ basis set. This value is consistent with recent estimates of 6.11 [6], 6.20 [47] and 6.06 eV [48]. For this bright state, there are several available experimental values: 5.55 eV (crystal) [55], 5.62/5.63 eV (solution) [55, 56] and 5.89 (vapour) eV [52], the latter value being also found by energy loss [51]. The last of the four Rydberg states considered herein, $^1B_{1u}(\pi \to 3s)$, is located by us at 6.33 eV, a value 0.3 eV above the CASPT2 value [45] but consistent with

a recent CC2 estimate (6.26 eV [48]). For the second $^1B_{2u}(\pi \to \pi^*)$ transition, our vertical best estimate is 6.42 eV, fitting Thiel's (6.36 eV) [6] and Sundholm's (6.30 eV) results [48]. The experimental values are around 6.0 eV (energy loss [51]) and 6.14 eV (optical spectroscopy) [52]. Finally, for the higher-lying $^1B_{1g}(\pi \to \pi^*)$ and $^1A_g(\pi \to \pi^*)$ states, our TBE/aug-cc-pVTZ values of 6.48 and 6.87 eV appear too high as compared to the estimates of Ref. [48] (6.19 and 6.40 eV), which is likely due to the strong basis set effects for these two excited states. The ^1A_g transition was estimated at 6.05 eV [54] by two-photon spectroscopy.

For the triplet transitions, we have investigated almost the same valence transitions as in Thiel's set [5, 6, 10]. Let us note that for all states, CC3 returns very large %T_1, and that the differences between aug-cc-pVDZ and aug-cc-pVTZ estimates is at most 0.04 eV. This clearly hints that the present estimates are trustworthy, but as we have been unable to perform CCSDT calculations, we nevertheless rate all of them as "unsafe" in the QUEST database, which is a conservative choice. The present values are also very similar to those obtained by basis set extrapolation thanks to the work of Thiel [6], except for the highest triplet transition considered here in which a significant difference of 0.2 eV is found. For most transitions, one also find a good consistency with earlier RASPT2 calculations [47]. Experimentally, the available data are typically T-T absorption, and this includes values of +2.25 eV, +2.93 eV for the two ^3A_g states [57] and 3.12 eV for the intermediate $^3B_{1g}$ transition [58], that we can compare to our +2.32, +3.22, and +3.00 eV values, respectively.

TABLE 7 Transition energies (in eV) determined in naphthalene. For all transitions, we provide the single-excitation character %T_1 obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3			CCSDT	Litt.		
	Nature	f	%T_1	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	6-31+G(d)	Th.[a]	Th.[b]	Th.[c]
Naphthalene	$^1B_{3u}(\pi \to \pi^*)$	0.000	85.8	4.36	4.33	4.30	4.33	4.03	4.25	4.23
	$^1B_{2u}(\pi \to \pi^*)$	0.067	90.3	5.10	4.91	4.87	5.13	4.56	4.82	4.61
	$^1A_u(\pi \to 3s)$		92.7	5.85	5.57	5.63	5.87	5.54		
	$^1B_{1g}(\pi \to \pi^*)$		84.7	5.99	5.85	5.83	6.00	5.53	5.75	5.87
	$^1A_g(\pi \to \pi^*)$		83.8	6.03	5.97	5.94	5.98	5.39	5.90	6.00
	$^1B_{3g}(\pi \to 3p)$		92.8	6.12	5.98	6.04	6.15	5.98		
	$^1B_{2g}(\pi \to 3p)$		92.5	6.24	6.00	6.07	6.26	5.94		
	$^1B_{3u}(\pi \to \pi^*)$	n.d.	90.6	6.30	6.19	6.15	6.34	5.54	6.11	6.20
	$^1B_{1u}(\pi \to 3s)$	n.d.	91.9	6.55	6.27	6.32	6.56	6.03		
	$^1B_{2u}(\pi \to \pi^*)$	n.d.	90.2	6.61	6.45	6.39	6.64	5.93	6.36	6.12
	$^1B_{1g}(\pi \to \pi^*)$		87.5	6.64	6.52	6.46	6.66	5.87	6.46	6.35
	$^1A_g(\pi \to \pi^*)$		71.5	6.99	6.91	6.87	6.99	6.04	6.87	6.66
	$^3B_{2u}(\pi \to \pi^*)$		97.7	3.19	3.18	3.17			3.09	3.21
	$^3B_{3u}(\pi \to \pi^*)$		96.6	4.25	4.19	4.16			4.09	4.11
	$^3B_{1g}(\pi \to \pi^*)$		97.8	4.53	4.49	4.48			4.42	4.44
	$^3B_{2u}(\pi \to \pi^*)$		96.8	4.71	4.67	4.64			4.56	4.62
	$^3B_{3u}(\pi \to \pi^*)$		97.5	5.17	4.99	4.95			4.92	4.66
	$^3A_g(\pi \to \pi^*)$		97.3	5.56	5.52	5.49			5.42	5.46
	$^3B_{1g}(\pi \to \pi^*)$		95.6	6.37	6.21	6.17			6.12	5.95
	$^3A_g(\pi \to \pi^*)$		95.2	6.52	6.42	6.39			6.17	6.25

[a] CASPT2 values from Ref. [45].
[b] exCC3 values from Ref. [6].
[c] RASPT2 values from Ref. [47].

1.8 | Nitroxyl (HNO)

In QUEST#2 [19], we treated only one excited state, of pure double-excitation character, of this compact molecule. We have used a large panel of high-level methods here, considering five excited states (see Table 8). For all transitions (except the Rydberg one), we could nicely converge FCI/aug-cc-pVTZ values that can be used a solid references. For the Rydberg transition, which is naturally more sensitive to the basis set effect, the CCSDTQ/aug-cc-pVDZ and FCIaug-cc-pVDZ also perfectly match. A previous CASPT2 work [59], reported transition energies to the lowest singlet and triplet of 0.67 eV and 1.53 eV, two values that now appear rather too low, a usual trend for CASPT2 when no IPEA shift is applied.

TABLE 8 Transition energies (in eV) determined in nitroxyl with CC3, CCSDT, CCSDTQ and FCI. For all transitions, we provide the single-excitation character $\%T_1$ obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

| | Transition | | | CC3 | | CCSDT | | CCSDTQ | FCI | |
	Nature	f	$\%T_1$	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVDZ	aug-cc-pVDZ	aug-cc-pVTZ
HNO	$^1A''(n \rightarrow \pi^*)$	0.000	93.2	1.78	1.75	1.77	1.74	1.77	1.78(1)	1.74(2)
	$^1A'(n, n \rightarrow \pi^*, \pi^*)$	0.000	0.3	5.25	5.26	4.76	4.79	4.42	4.41(1)	4.33(0)
	$^1A'$ (Ryd)	0.038	92.4	6.12	6.26	6.12	6.25	6.14	6.15(1)	
	$^3A''(n \rightarrow \pi^*)$		99.2	0.87	0.88	0.87	0.88	0.87	0.87(1)	0.88(2)
	$^3A'(\pi \rightarrow \pi^*)$		98.5	5.62	5.59	5.62	5.59	5.64		5.61 (1)

1.9 | Streptocyanines

In addition to the smallest streptocyanine treated in our earliest work [28], we have investigated here the properties of the two next members of the cationic series which contain 3 and 5 carbon atoms respectively bracketed by NH_2 groups (Table 9). These systems are of specific interest because it is well-known that there are challenging for TD-DFT [60]. We report in Table 9 the transition energies to the lowest excited states of both spin symmetries with (valence) $\pi \rightarrow \pi^*$ character. For the smallest of the two compounds treated here, we have been able to converge a CIPSI calculation with the 6-31+G(d) basis set, and it clearly gives us confidence that both CC3 and CCSDT values are accurate, the former method being actually even closer to the FCI extrapolation for that specific molecules. The detailed investigation of these compounds likely remains the one of Send, Valsson, and Filippi [61]. These authors reported for the singlet states of these two cyanines: i) exCC3 values of 4.84 and 3.65 eV; ii) DMC values of 5.03(2) and 3.83(2) eV; and iii) CASPT2 estimates of 4.69 and 3.53 eV. The present estimates better match the previous CC estimates, the DMC (CASPT2) transition energies appearing sightly too large (too low). Once more, given the results in Table 9, we believe that our TBEs are the most accurate to date, at least for the considered geometries.

TABLE 9 Transition energies (in eV) determined in two cyanines with CC3, CCSDT and FCI. For all transitions, we provide the single-excitation character $\%T_1$ obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

| | Transition | | | CC3 | | | | CCSDT | | FCI |
	Nature	f	$\%T_1$	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	6-31+G(d)	aug-cc-pVDZ	6-31+G(d)
Streptocyanine-3	$^1B_2(\pi \rightarrow \pi^*)$	0.755	87.2	4.83	4.83	4.82	4.82	4.80	4.81	4.83(1)
	$^3B_2(\pi \rightarrow \pi^*)$		98.0	3.45	3.45	3.44	3.44	3.44		3.45(1)
Streptocyanine-5	$^1B_2(\pi \rightarrow \pi^*)$	1.182	85.8	3.63	3.66	3.66		3.60	3.64	
	$^3B_2(\pi \rightarrow \pi^*)$		97.7	2.49	2.49	2.48		2.48		

1.10 | Thioacrolein

This heavier analog of acrolein was not much studied theoretically before, except for calculations of its 0-0 energies [62] and rather old TD-DFT calculations [63]. We report in Table 10 the transition energies to the lowest excited states of both spin symmetries, of clear valence $n \rightarrow \pi^*$ character. As one can see, there is for both excited states, a remarkable insensibility to the basis set size, and also very similar CC3 and CCSDT estimates. The experimental 0-0 energies are 1.88 eV (singlet) and 1.74 eV (triplet) [64], both slightly below our vertical estimates as it should.

TABLE 10 Transition energies (in eV) determined in thioacrolein with CC3 and CCSDT. For all transitions, we provide the single-excitation character $\%T_1$ obtained at LR-CC3/aug-cc-pVTZ level. For the dipole-allowed transitions, we provide the corresponding values of the oscillator strength at the same level of theory.

	Transition			CC3				CCSDT		
	Nature	f	$\%T_1$	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ	aug-cc-pVQZ	6-31+G(d)	aug-cc-pVDZ	aug-cc-pVTZ
Thioacrolein	$^1A''(n \rightarrow \pi^*)$	0.000	86.4	2.17	2.17	2.14	2.15	2.14	2.15	2.11
	$^3A''(n \rightarrow \pi^*)$		96.9	1.96	1.95	1.93	1.94	1.94	1.93	
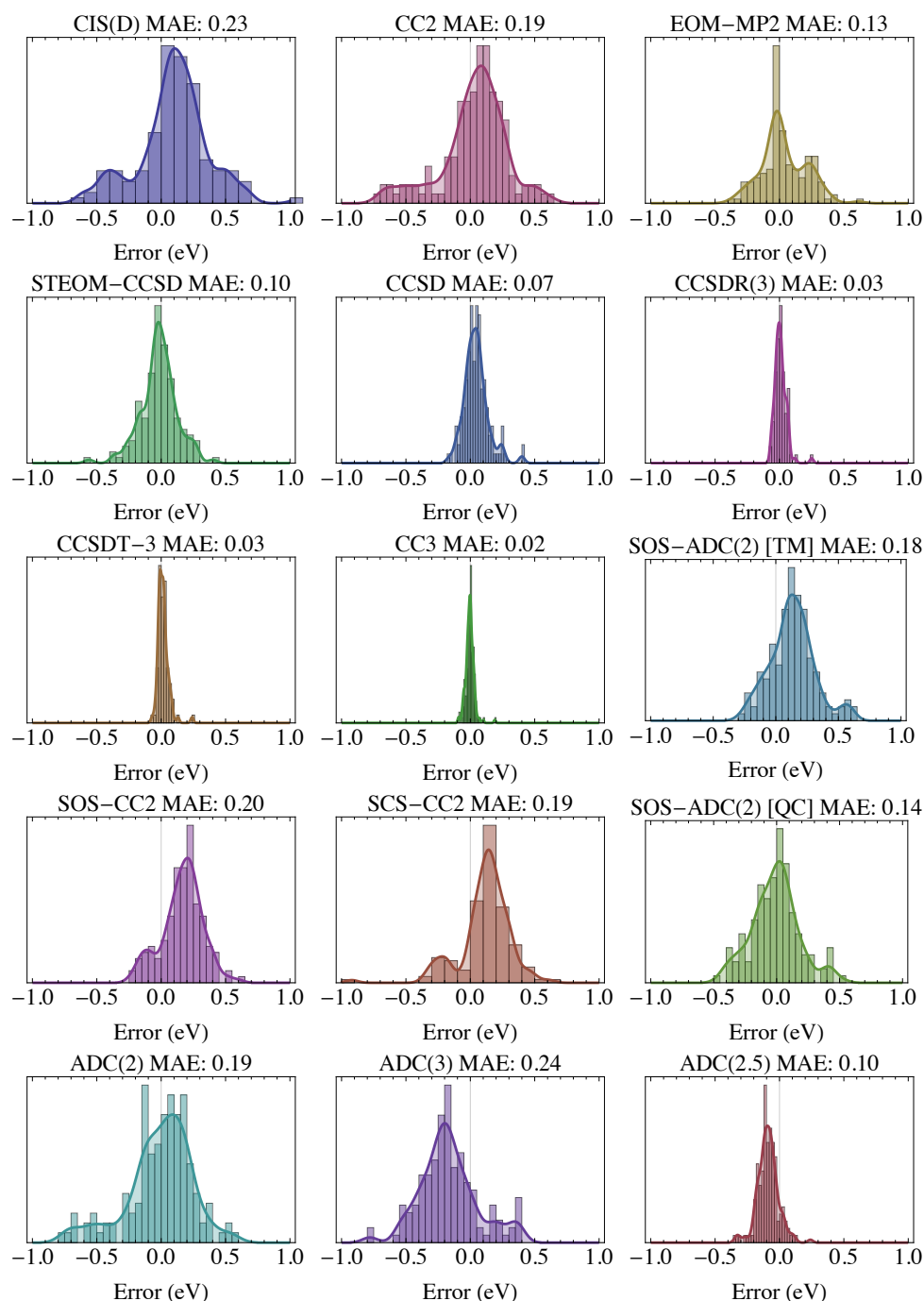
FIGURE 1 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the molecules of the QUEST database containing from one to three non-hydrogen atoms (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
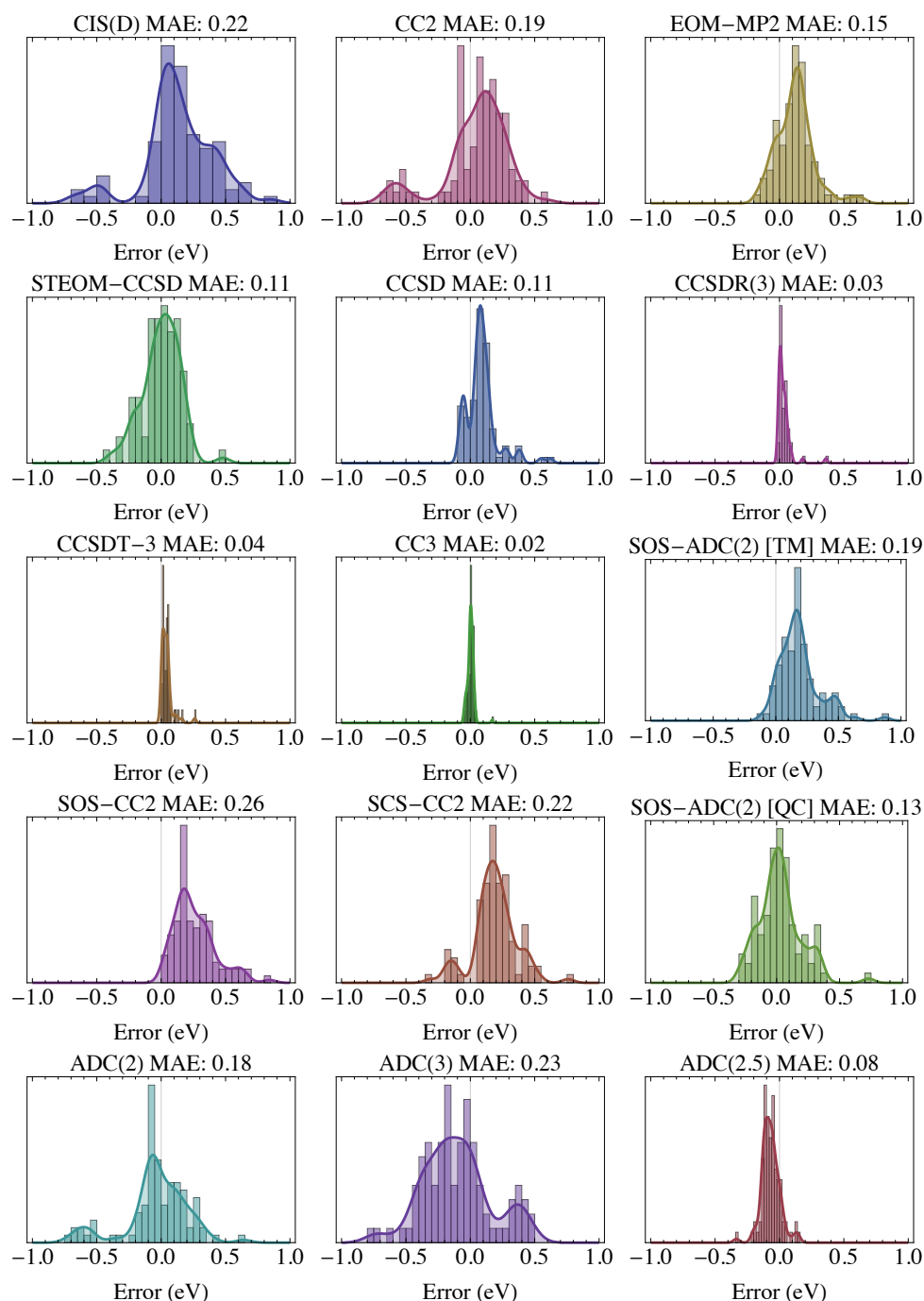
FIGURE 2 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the molecules of the QUEST database containing four non-hydrogen atoms (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
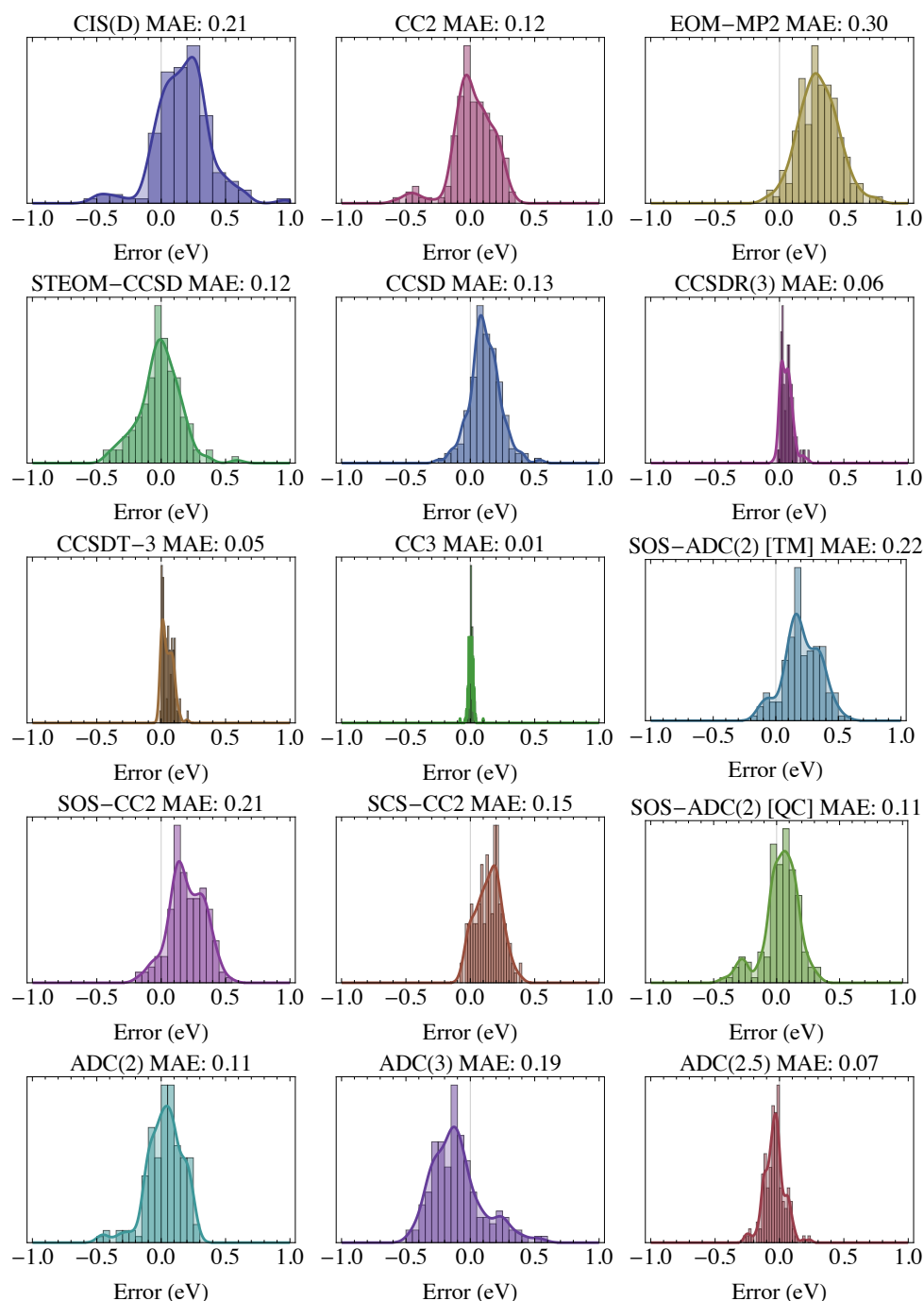
FIGURE 3 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the molecules of the QUEST database containing five or six non-hydrogen atoms (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.

FIGURE 4 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the molecules of the QUEST database containing from 7 and 10 non-hydrogen atoms (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.

FIGURE 5 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the $n \rightarrow \pi^*$ excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.

FIGURE 6 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the $\pi \rightarrow \pi^*$ excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
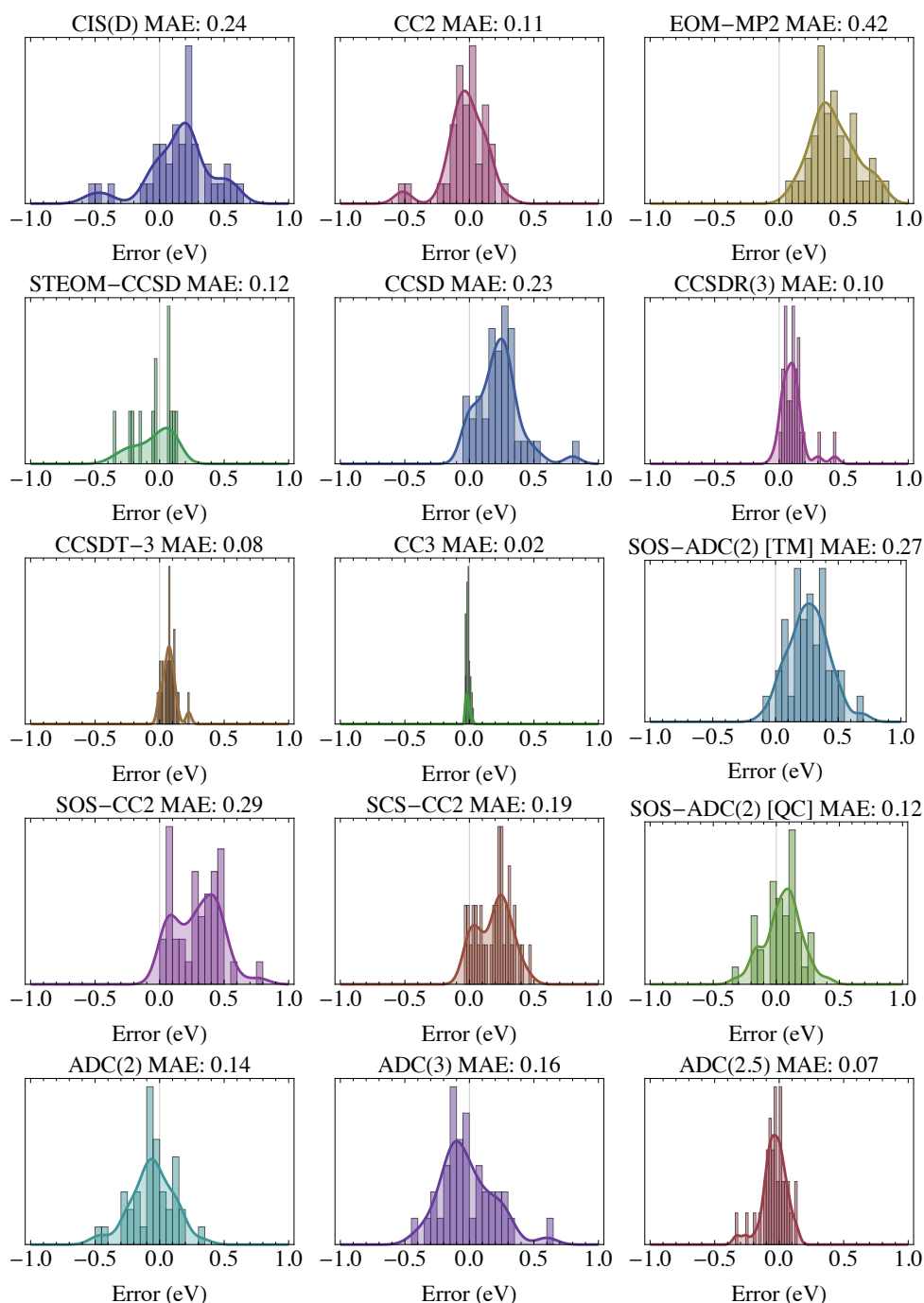
FIGURE 7 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the Rydberg excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
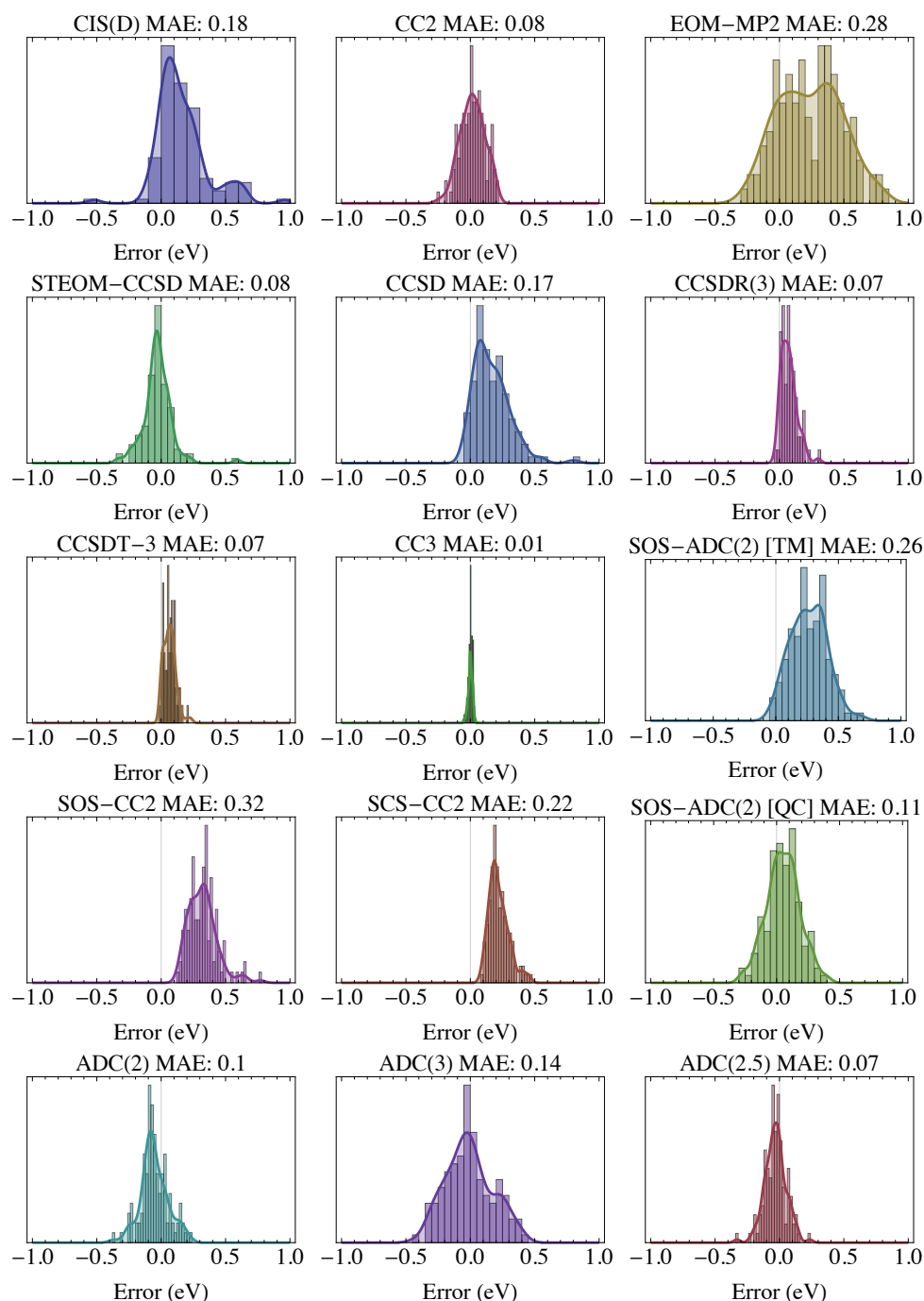
FIGURE 8 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the valence excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
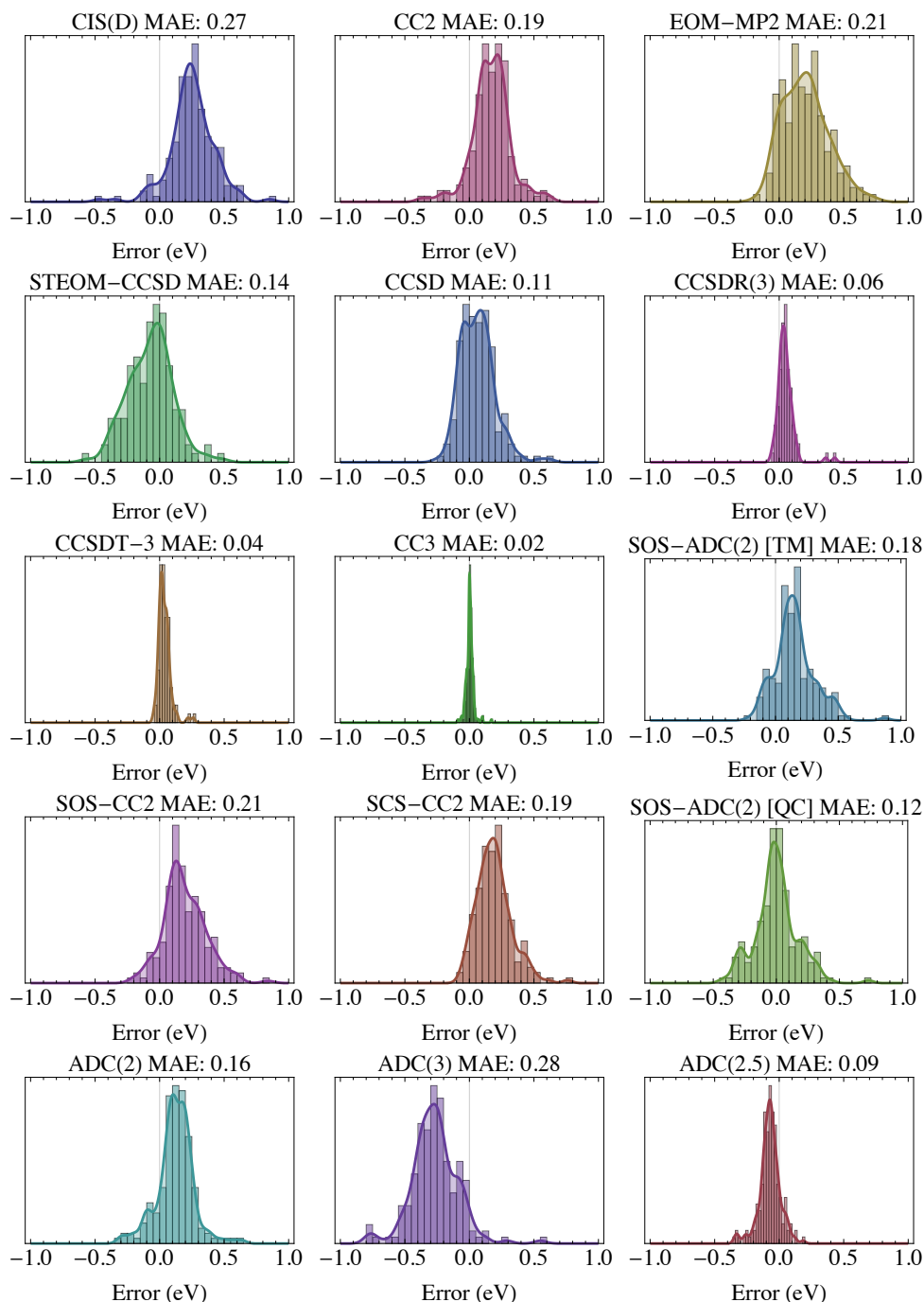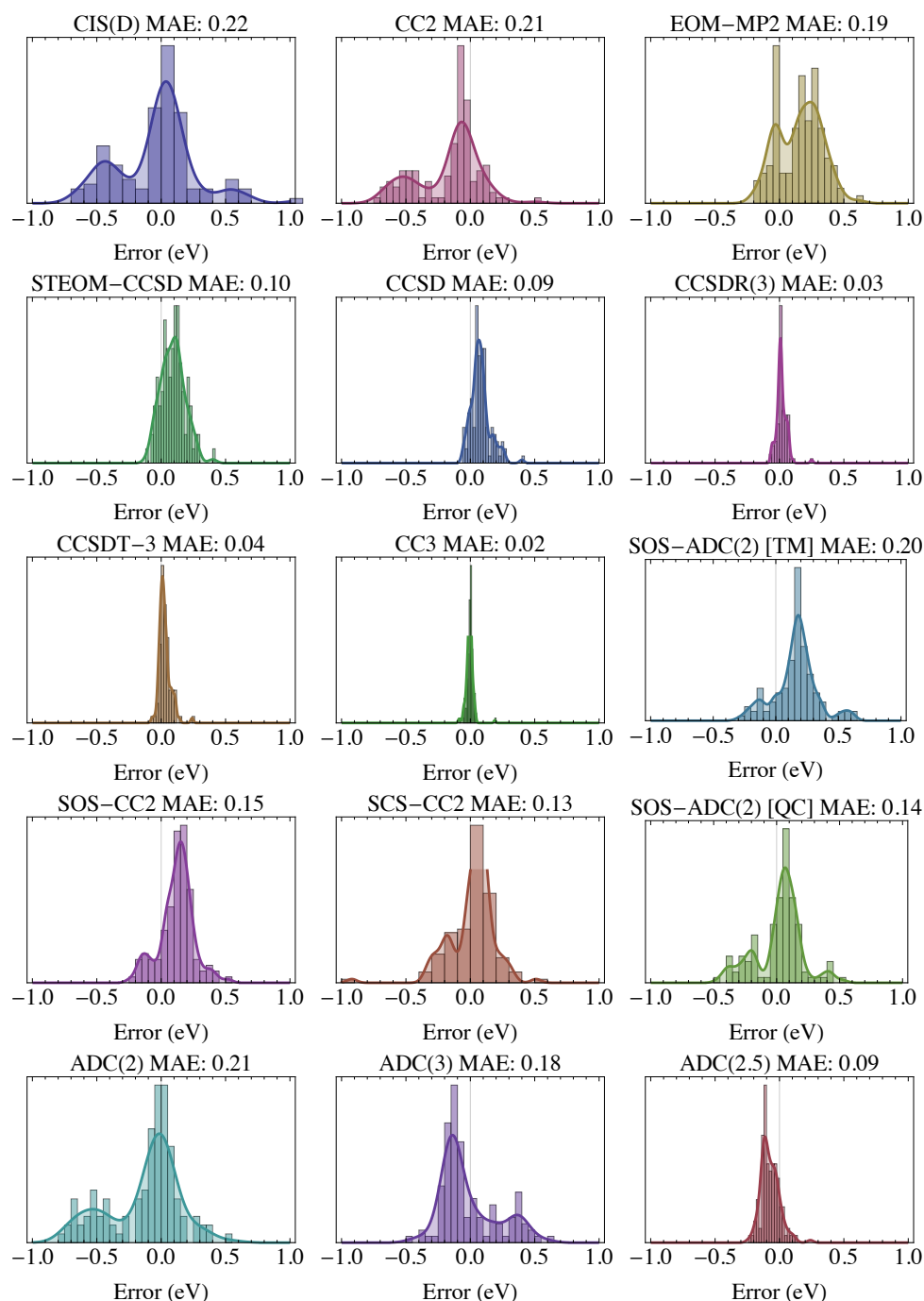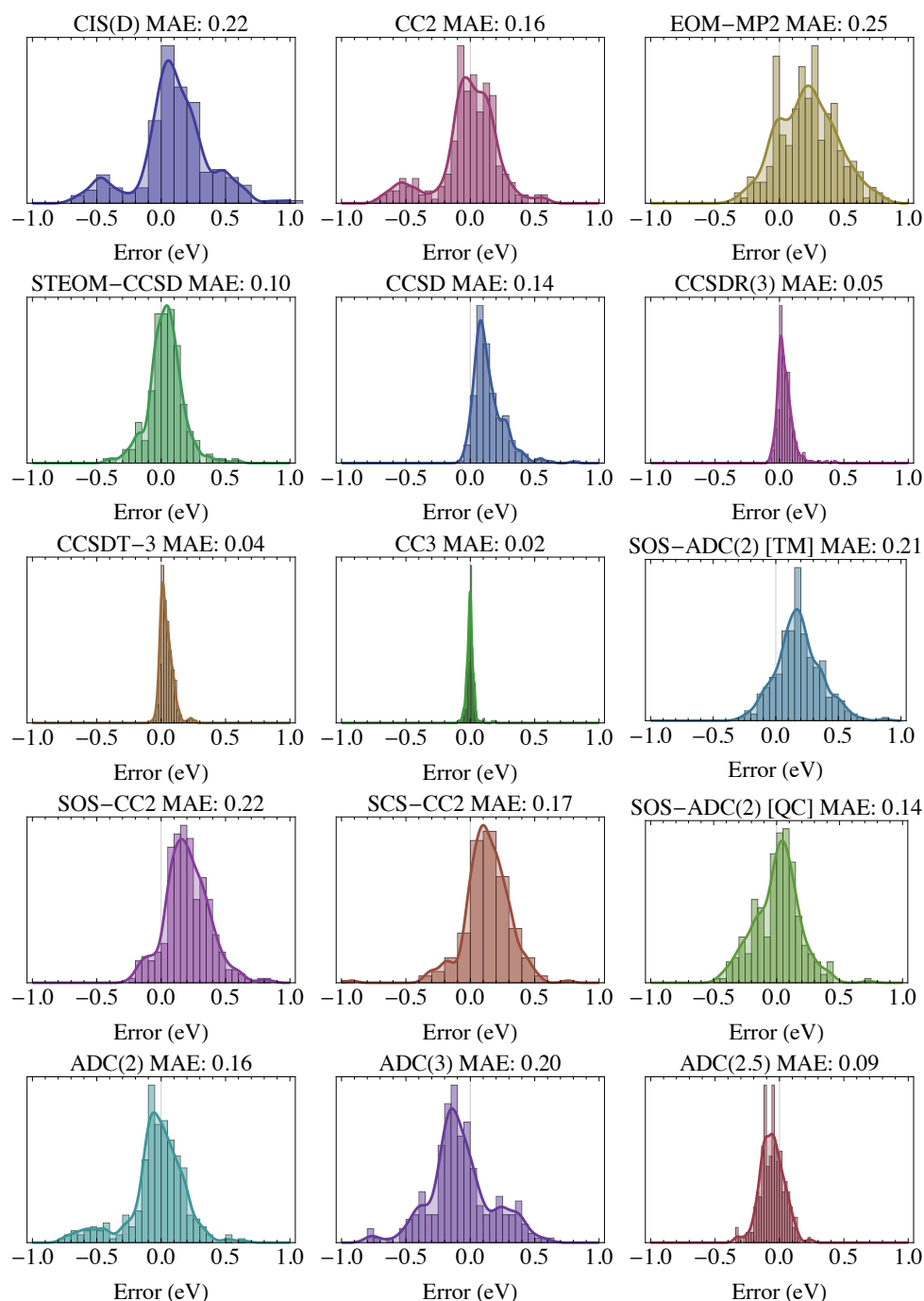
FIGURE 9 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the singlet excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
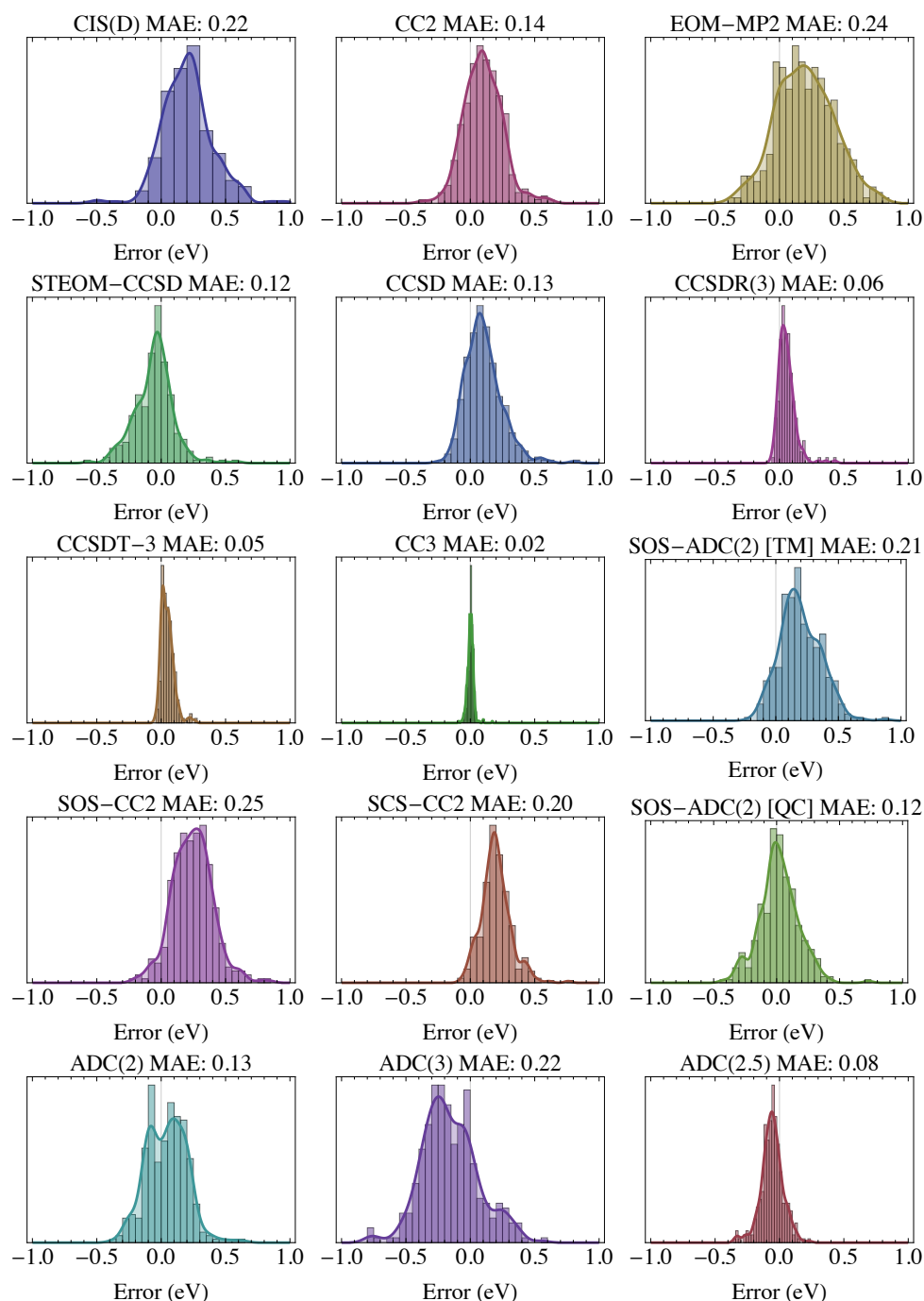
FIGURE 10 Distribution of the error (in eV) in excitation energies (with respect to the TBE/aug-cc-pVTZ values) for various methods for the triplet excitations of the QUEST database (closed-shell compounds only). Only the "safe" TBEs are considered (see Table **??**). See Table in the main text for the values of the corresponding statistical quantities. QC and TM indicate that Q-CHEM and TURBOMOLE scaling factors are considered, respectively. The SOS-CC2 and SCS-CC2 approaches are obtained with the latter code.
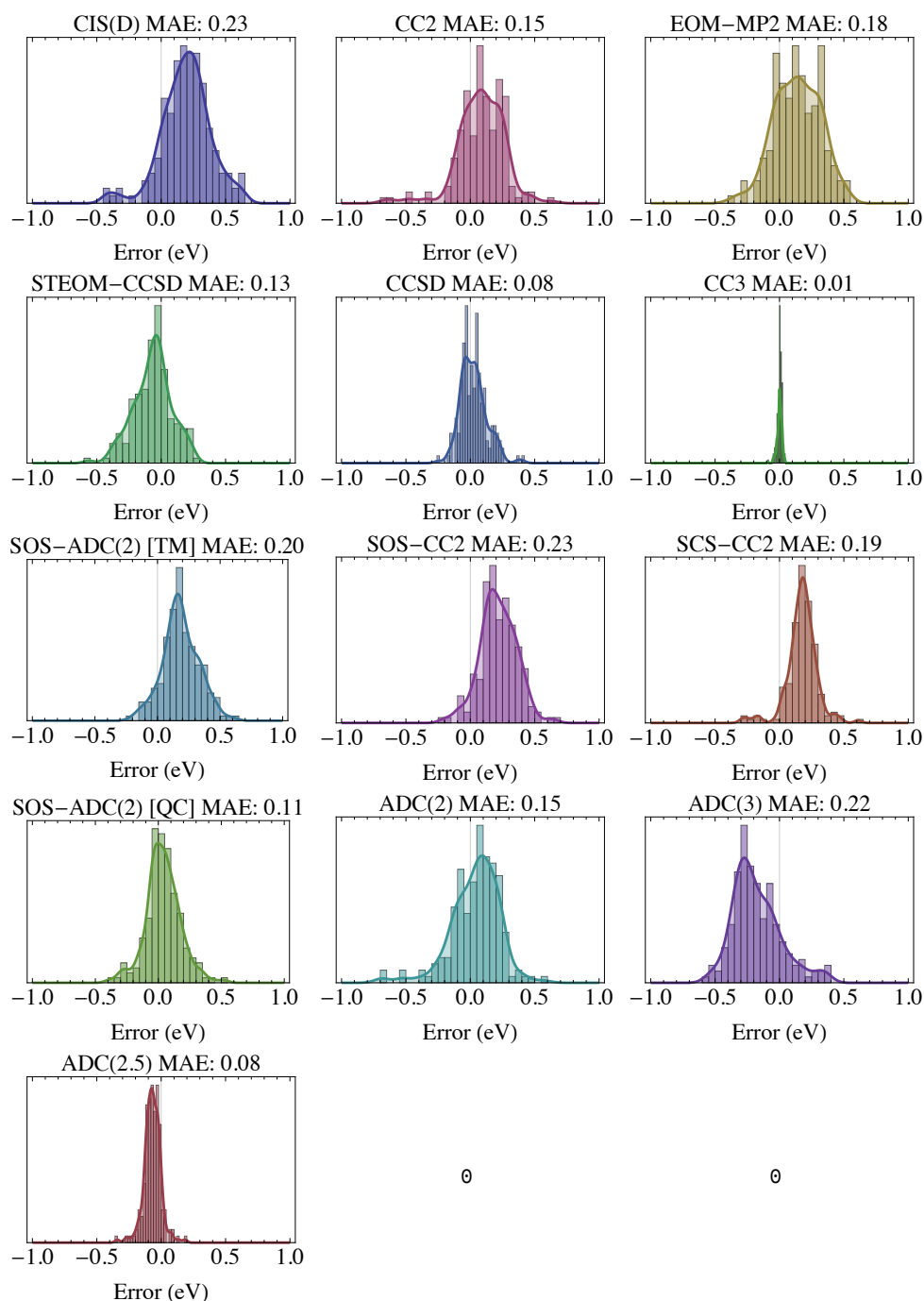
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