The third-order algebraic diagrammatic construction method (ADC(3)) for the polarization propagator for closed-shell molecules: Efficient implementation and benchmarking

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The third-order algebraic diagrammatic construction method (ADC(3)) for the polarization propagator for closed-shell molecules: Efficient implementation and benchmarking[a)]

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The implementation of an efficient program of the algebraic diagrammatic construction method for the polarisation propagator in third-order perturbation theory (ADC(3)) for the computation of excited states is reported. The accuracies of ADC(2) and ADC(3) schemes have been investigated with respect to Thiel's recently established benchmark set for excitation energies and oscillator strengths. The calculation of 141 vertical excited singlet and 71 triplet states of 28 small to medium-sized organic molecules has revealed that ADC(3) exhibits mean error and standard deviation of 0.12 ± 0.28 eV for singlet states and -0.18 ± 0.16 eV for triplet states when the provided theoretical best estimates are used as benchmark. Accordingly, the ADC(2)-s and ADC(2)-x calculations revealed accuracies of 0.22 ± 0.38 eV and -0.70 ± 0.37 eV for singlets and 0.12 ± 0.16 eV and -0.55 ± 0.20 eV for triplets, respectively. For a comparison of CC3 and ADC(3), only non-CC3 benchmark values were considered, which comprise 84 singlet states and 19 triplet states. For these singlet states CC3 exhibits an accuracy of 0.23 ± 0.21 eV and ADC(3) an accuracy of 0.08 ± 0.27 eV, and accordingly for the triplet states of 0.12 ± 0.10 eV and -0.10 ± 0.13 eV, respectively. Hence, based on the quality of the existing benchmark set it is practically not possible to judge whether ADC(3) or CC3 is more accurate, however, ADC(3) has a much larger range of applicability due to its more favourable scaling of $O(N^6)$ with system size. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4892418]

I. INTRODUCTION

The accurate and predictive theoretical description of the photochemistry of large molecules with more than say 25 atoms of the second row of the Periodic Table is one of the greatest challenges of contemporary electronic structure theory.[1–5] Although several quantum chemical approaches exist already for the calculation of excited states, their accuracy and hence reliability and predictive power vanishes quickly with increasing level of approximation. On the other hand, feasibility and tractable molecular size increase with level of approximation. Hence, for the computation of excited states of large molecules in reasonable time, it is necessary to find a compromise between accuracy and feasibility, or in other words, a theoretical method, that is computationally efficient and at the same time accurate enough to deliver a conclusive solution to the investigated photochemical problem. For excited states of large molecules this is particularly difficult, because the excited states are usually close in energy but possess very different electronic structures, e.g., $\pi\pi^*$, $n\pi^*$, charge transfer, Rydberg or doubly excited, which require all a balanced theoretical description. In most cases it is thus not possible to identify a single quantum chemical method to describe all these states properly, and one is forced to focus only on those relevant for the investigated problem.

Today, several methods exist which are employed to calculate excited states of medium-sized to large molecules on a routine basis,[2] for example, semi-empirical approaches like INDO/S[6,7] or OM2/MRCI,[8,9] density functional theory (DFT)-based methods like TDDFT[10–12] or DFT/MRCI,[13–15] as well as *ab initio* wavefunction-based approaches CASSCF,[16,17] CC2[18–20] or EOM-/LR-CCSD,[21–24] for instance. Most recently also propagator-based approaches have gained more attention, the second-order polarization propagator approximation (SOPPA)[25–27] and most notably the second-order algebraic diagrammatic construction method (ADC(2)).[28–31] Although together these methods exhibit a wide range of applicability, every single one exhibits problems for certain classes of electronic states inevitably leading to an unbalanced description of different excited states.[1,2,4]

This strongly underpins the necessity to thoroughly benchmark quantum chemical excited-state methods prior to any computational investigation of photochemistry, which for larger molecules is, at present, practically limited to second-order approaches such as CC2 or ADC(2), because higher-order and more accurate approaches such as CC3[32,33] or CASPT2[34] are often no longer applicable to larger molecules. Hence it is important to undertake effort to provide new accurate excited-state methods and the corresponding efficient computer programs to provide a computational platform for thorough and more reliable benchmarking. One step in that direction is provided by the algebraic-diagrammatic construction method for the polarization propagator in third order of perturbation theory (ADC(3)), which aims at a more accurate

description of excited state energies and their properties.[31] The ADC(3) scheme offers the advantage of being size-consistent and hermitian. In addition, it is the most compact method for the consistent description of singly-excited, so-called primary particle-hole (p-h) states, in third-order perturbation theory, as the ADC(3) matrix representation extends only over the p-h and 2p-2h spaces. In contrast, also the 3p-3h space is in general required in CC approaches to achieve the same level of perturbation theory for the p-h states. Recently, non-iterative schemes have been developed based on the EOM-CCSD approach to include the contributions of the 3p-3h block, for example, EOM-CCSD(T),[35] or the completely renormalized (CR)-EOM-CCSD(T)[36] and CCSDR(3),[37,38] which reduce the computational effort from the evaluation of the 3p-3h block contribution at each iteration of the solution of the CC equations to a single perturbation theoretical evaluation.

Until today, only a pilot implementation of ADC(3) has been employed to test its accuracy against full configuration interaction (FCI) and CC3.[39] A test set of 41 singlet and triplet excited states of Ne, BH, CH2, HF, N$_2$, CO, H$_2$O has been used. It was found that ADC(3) deviates by less than 0.2 eV, however, it does not reach the accuracy of CC3 for these small molecules, but the accuracy is substantially better than the one of ADC(2) and CC2. It is also important to recognize that the computation time of ADC(3) scales formally as $O(N^6)$, while the one of CC3 increases with $O(N^7)$, which limits the latter to small molecule applications. For larger molecules, one can expect ADC(3) to perform even better, since small molecules often exhibit degeneracies due to symmetry and quasi-open-shell character, as, for example, CH$_2$ and BH do, which is usually not the case for typical medium-sized and large organic molecules. Here, we employ the efficient implementation of the ADC(3) method into a quantum chemical program package which has already been mentioned before.[40] It allows for the first time for a thorough benchmarking of the accuracy of ADC(3) in the calculation of excitation energies and transition moments of medium-sized organic molecules of Thiel's benchmark set.[41,42] Although the focus lies on the ADC(3) approach, for completeness, also results for the corresponding second-order ADC(2) schemes, so-called strict ADC(2)-s and extended ADC(2)-x are presented.

In Sec. II, the basic mathematical concept of ADC and the fundamental equations are presented as well as the gist of their implementation into an efficient computer programme is outlined. Computational details are given in Sec. III.

II. THEORY AND IMPLEMENTATION

The algebraic-diagrammatic construction scheme for electronically excited states is based on diagrammatic many-body Green's function theory.[28] In this framework electronic excitations are described by the polarisation propagator whose spectral representation consists of two parts

$$\Pi_{pq,rs}(\omega) = \Pi^+_{pq,rs}(\omega) + \Pi^-_{pq,rs}(\omega)$$

which both contain the same physical information and are related by $\Pi^-_{pq,rs}(\omega) = \Pi^+_{qp,sr}(-\omega)$. The Π^+ part can be

expressed as

$$\Pi^+_{pq,rs}(\omega) = \mathbf{f}^\dagger_{pq} (\omega \mathbf{1} - \mathbf{M} + \iota\eta)^{-1} \mathbf{f}_{rs}, \qquad (1)$$

where $\mathbf{M}$ is the energy shifted Hamiltonian matrix with matrix elements

$$M_{IJ} = \langle \Phi_I | \hat{H} - E_0 | \Phi_J \rangle,$$

while $\mathbf{f}_{pq}$ are the spectral amplitude vectors given by

$$f_{pq,I} = \langle \Phi_I | \hat{c}^\dagger_p \hat{c}_q | \Psi_0 \rangle.$$

Here, E_0 and $|\Psi_0\rangle$ refer to the ground state energy and wave function of the Hamiltonian, and $\hat{c}^\dagger_p$ and $\hat{c}_q$ are the usual one-particle creation and annihilation operators. In general, the states $|\Phi_I\rangle$ are the excited eigenstates of the Hamiltonian for which the representation of $\mathbf{M}$ becomes diagonal. However, in principle, any set of N-particle states can be used which in combination with $|\Psi_0\rangle$ forms an orthonormal basis, i.e., $\langle \Psi_0 | \Phi_I \rangle = 0$ and $\langle \Phi_I | \Phi_J \rangle = \delta_{IJ}$.

The ADC scheme employs the diagrammatic perturbation expansion of the polarisation propagator in terms of Feynman or Goldstone diagrams to derive representations for $\mathbf{M}$ and $\mathbf{f}_{pq}$ which are consistent to arbitrary order in perturbation theory

$$\mathbf{M}^{[n]} = \sum_{i=0}^{n} \mathbf{M}^{(i)} \qquad \text{and} \qquad \mathbf{f}^{[n]}_{pq} = \sum_{i=0}^{n} \mathbf{f}^{(i)}_{pq}, \qquad (2)$$

where the superscripts $^{(i)}$ refer to contributions entering at ith order. An equivalent derivation of the expressions for $\mathbf{M}^{[n]}$ and $\mathbf{f}^{[n]}_{pq}$ proceeds via the so-called intermediate states (IS).[43] The latter are constructed starting from the Møller-Plesset (MP) perturbation expansion of the ground state. Excitation operators for particle-hole (p-h), 2p-2h, and higher excitations

$$\hat{C}_I \in \left\{ \hat{c}^\dagger_a \hat{c}_i; \ \hat{c}^\dagger_a \hat{c}^\dagger_b \hat{c}_i \hat{c}_j, a < b, i < j; \ \dots \right\}$$

with $i, j, \dots$ referring to occupied and $a, b, \dots$ to unoccupied orbitals, are applied to the MP ground state, and the resulting precursor states are subsequently orthogonalised with respect to the ground state and to each other. Inserting the MP ground state energy and wave function, as well as the IS as $|\Phi_I\rangle$ into the general equations for $\mathbf{M}$ and $\mathbf{f}_{pq}$, and collecting terms according to their order in perturbation theory yields again the ADC representation of $\mathbf{M}^{[n]}$ and $\mathbf{f}^{[n]}_{pq}$.

From the procedure to construct the IS it is clear that the ADC matrix $\mathbf{M}^{[n]}$ possesses the usual CI-like block structure of singles (p-h), doubles (2p-2h), ... excited configurations, but without the ground state (see Figure 1). Table I shows that in zeroth and first order the [p-h,p-h] block of the ADC matrix is the only non-zero block, while in second and third order the matrix also comprises the [p-h,2p-2h], [2p-2h,p-h], and [2p-2h,2p-2h] blocks. Any blocks with triple excited configurations enter in fourth order. Explicit equations for $\mathbf{M}^{[n]}$ up to third order and for $\mathbf{f}^{[n]}_{pq}$ up to second order have been published before and the reader is referred to the original literature.[28,31] It should only be mentioned that direct couplings between 2p-2h excited configurations enter consistently at the level of ADC(3). They are also included in the ADC(2)-x method, but only as an *ad hoc* extension to ADC(2).
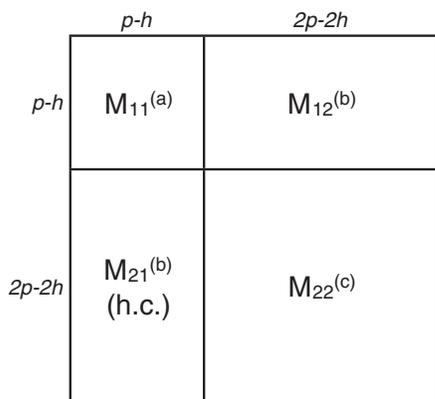
FIG. 1. Block structure of the ADC secular matrix $\mathbf{M}$. The letters in brackets indicate the perturbative expansion order of terms which have to be considered for the respective ADC schemes and are shown in Table I.

The ADC matrix $\mathbf{M}^{[n]}$ allows for the computation of consistent nth order approximations to excitation energies and excited states by solving the Hermitian eigenvalue problem

$$\mathbf{M}^{[n]}\mathbf{X} = \mathbf{X}\,\Omega, \qquad \mathbf{X}^\dagger\mathbf{X} = \mathbf{1} \qquad (3)$$

which yields the excitation energies as eigenvalues $\Omega_I = E_I^{[n]} - E_0^{[n]}$ and excited states as eigenvectors $\mathbf{x}_I$. The latter are given in the basis of intermediate states and can be combined with the spectral amplitude vector $\mathbf{f}_{pq}^{[n]}$ to obtain the one-particle transition density matrices

$$\gamma_{pq}^{I \leftarrow 0} = \langle \Psi_I | \hat{c}_p^\dagger \hat{c}_q | \Psi_0 \rangle = \mathbf{x}_I^\dagger \mathbf{f}_{pq}^{[n]}, \qquad (4)$$

and thus any one-particle transition property from ground to excited state. In addition, one-particle state density matrices and state-to-state transition density matrices can be computed using the eigenvectors according to

$$\gamma_{pq}^I = \mathbf{x}_I^\dagger \mathbf{D}_{pq}^{[n]} \mathbf{x}_I \qquad \text{and} \qquad \gamma_{pq}^{I \leftarrow J} = \mathbf{x}_I^\dagger \mathbf{D}_{pq}^{[n]} \mathbf{x}_J,$$

where $\mathbf{D}_{pq}^{[n]}$ is the nth order ADC approximation to the matrix $\mathbf{D}_{pq}$ with matrix elements

$$D_{pq,IJ} = \langle \Phi_I | \hat{c}_p^\dagger \hat{c}_q | \Phi_J \rangle.$$

Again, explicit equations for $\mathbf{D}_{pq}^{[n]}$ up to second order in perturbation theory can be found in Ref. 44.

The above derivation shows the close relation between the treatment of electronically excited states with ADC and the MP treatment of the ground state, i.e., the ADC(2) method corresponds to the MP(2) ground state, ADC(3) to MP(3), etc.[29,31,39] Thus, similar to MP, ADC is size-consistent with the ADC matrix being always separable for a system of two

$$w_{ijab} = -\frac{1}{2}\sum_k v_{kb}\left(\langle ij||ka\rangle + \sum_{lc} \langle kl||jc\rangle t_{ilac} \right.$$
$$\left. - \sum_{lc} \langle kl||ic\rangle t_{jlac} - \frac{1}{2}\sum_{cd} t_{ijcd}\langle ka||cd\rangle \right) - (a \leftrightarrow b)$$

```
w(i|j|a|b) = asymm(a, b,
    -0.5 * contract(k, v(k|b), i_ooov(i|j|k|a)
      + asymm(i, j, contract(l|c, t2(i|l|a|c), i_ooov(k|l|j|c)))
      - 0.5 * contract(c|d, t2(i|j|c|d), i_ovvv(k|a|c|d))))
```

FIG. 2. Small sample of the ADC(3) equations and its translation into code using the user-friendly interface of `libtensor`.

non-interacting parts, and local excitations being strictly decoupled. At the same time, the use of perturbation theory also limits the applicability of ADC. Whenever large static correlations are present in a system, ADC will fail, but this is of course true for essentially all single reference methods.

The parallel implementation of ADC(3) into the Q-Chem program package[45] which is presented here is based on the open-source C++ library `libtensor` to perform tensor algebra.[46] As object-oriented template library, `libtensor` has been designed to handle tensors of arbitrary rank, size, and symmetry. Therefore, tensor data are split into smaller blocks of the same rank as the original tensor by dividing every dimension into several parts. The blocks are stored individually in memory or on disk as applicable, if they are non-zero and non-duplicate due to symmetry. Tensor operations are parallelised in a shared memory environment by distributing the block operations onto multiple cores. Spin and point-group symmetry are supported directly. The user-friendly interface of `libtensor` allows for the straightforward implementation of the ADC(3) equations (see Fig. 2). The Davidson algorithm[47] is employed to solve the ADC(3) eigenvalue problem for a limited number of small excitation energies. Hence, the ADC(3) equations are implemented as product of the ADC(3) matrix with an arbitrary vector. The eigenvectors are used further to compute oscillator strengths and other transition properties, as well as excited state properties, such as dipole moments via the intermediate state representation approach.[44] Basic benchmarks on the efficiency of the ADC implementation can be found in Ref. 40.

III. COMPUTATIONAL DETAILS

The ground-state equilibrium geometries of all molecules in the benchmark set were originally optimized using restricted Møller-Plesset second-order perturbation theory (MP2)[48] in combination with the 6-31G* basis set.[41] Unfortunately, some of the in the literature available optimized geometries do not exhibit the desired molecular point-group symmetry, which were therefore re-optimized following the same protocol. At these geometries, vertical excited singlet as well as triplet states have been computed with the strict and extended versions of second-order ADC (ADC(2)-s and ADC(2)-x) and third-order ADC(3) using the TZVP basis set. Also, the corresponding transition dipole moments and oscillator strengths were calculated for the singlet excited state using ADC(2)-s, ADC(2)-x, and ADC(3/2). In ADC(3/2) transition density matrices and transition dipole moments are

TABLE I. Order of perturbative expansion of the ADC-matrix elements (see Figure 1) for the schemes up to ADC(3).

	a	b	c
CIS/ADC(1)	0-1	...	...
ADC(2)-s	0-2	1	0
ADC(2)-x	0-2	1	0-1
ADC(3)	0-3	1-2	0-1

Unsaturated Aliphatic Hydrocarbons

Ethene   E-Butadiene   all-E-Hexatriene   all-E-Octatetraene   Cyclopropene Cyclopentadiene   Nornbornadiene

Aromatic Hydrocarbons and Heterocycles

Benzene   Furan   Pyrrole   Imidazole   Pyridine   s-Tetrazine   Pyrazine   Pyrimidine   Pyridazine
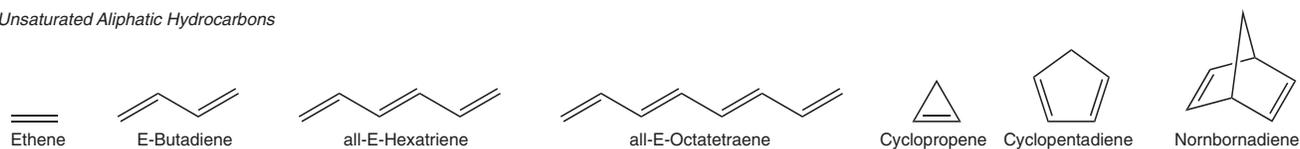
Aldehydes, Ketons and Amides

Formaldehyde   Acetone   p-Benzoquinone   Formamide   Acetamide   Propanamide

Nucleobases

Cytosine   Thymine   Uracil   Adenine
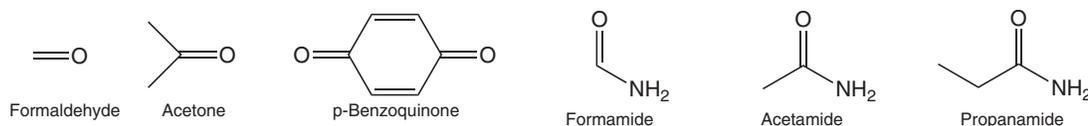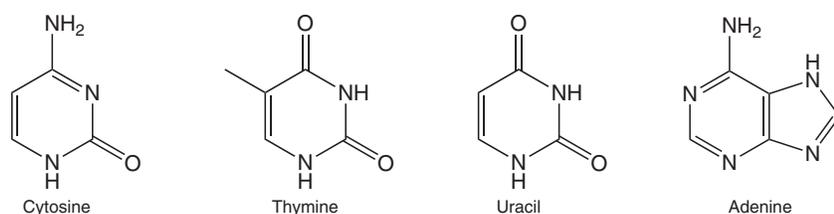
FIG. 3. Benchmark set of molecules considered for testing ADC(3).

evaluated using the ADC(3) excited state vector $\mathbf{x}^I$ and the IS representation of the spectral amplitudes in second order $\mathbf{f}_{pq}^{[2]}$ (see Eq. (4)). The transition dipole moments are then combined with the ADC(3) excitation energies to yield the oscillator strengths. All calculations were performed with a development version of adcman included in the Q-Chem 4.2 program package.[45]

IV. RESULTS AND DISCUSSION

Benchmarking being common practice for ground-state methods, established molecular benchmark sets covering a variety of ground state properties exist exhibiting a large number of small and medium-sized molecules. Only very recently, a corresponding benchmark set for excitation energies and oscillator strengths was presented.[41,42] It comprises 28 medium-sized chromophores which are typical representatives for organic photochemistry. More precisely, it includes unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and heterocycles, carbonyl compounds and nucleobases (Figure 3). For the generation of the reference data, literature data in combination with CASPT2, CC2, CCSD, and CC3 calculations have been taken into consideration. For consistency, all geometries had been optimized at the MP2/6-31G* level of theory and the standard TZVP basis set had been used.[41] Since this standard TZVP basis set does not contain diffuse functions,[49] it is clear that excited states which are spatially extended, exhibiting Rydberg character, for example, are not well described.[41] An example is the 1 ^1B_u state of small linear polyenes, the excitation energy of which strongly depends on the basis set

size and in particular the augmentation with diffuse functions. However, the focus of the benchmark set lies on the provision of a reference data set for direct comparison and in general not on the most accurate description of the individual excited states of the molecules. The electronic structure as well as the symmetries and the assignments of the individual transitions of the molecules in the benchmark set were already discussed in detail before and will hence not be done again.[41] Overall the benchmark set consists of 28 molecules with 104 benchmarked excitation energies of singlet states and 63 benchmarked excitation energies of triplet states. Due to the computational efficiency of the ADC(3) method, we have compute 141 singlet states and 71 triplet states at all applied levels of ADC theory.

A. Singlet excited states

The computed vertical excitation energies of the singlet states of the benchmark set are compiled in Table II at the theoretical levels of ADC(2)-s, ADC(2)-x, and ADC(3). The values are compared with previous calculations at CC2, CCSD, and CC3 level of theory, and most importantly, with the theoretical best estimates (TBE). At the ADC levels, also the amount of doubly excited configurations (%R_2) contained in the ADC excitation vectors is given as sum of squared amplitudes.

Prior to a general discussion of the accuracies of the different theoretical approaches it is useful to have a brief look at the performance of the methods for different substance classes. For *unsaturated aliphatic hydrocarbons* it can

TABLE II. Vertical excitation energies in eV of the lowest excited singlet states of the considered molecules in the benchmark set (Fig. 3) at the theoretical levels of CC2, EOM-CCSD, CC3[41] and ADC(2)-s, ADC(2)-x, and ADC(3) in comparison with the theoretical best estimates (TBE). For analysis, also the amount of double excited configurations (%R_2) in the ADC excitation vectors is given.

Molecule	State	CC2[a]	CCSD[a]	CC3[a]	TBE[a]	ADC(2)-s	%R_2	ADC(2)-x	%R_2	ADC(3)	%R_2
Ethene	$1\,^1B_{1u}$	8.40	8.51	8.37	7.80	8.36	3	8.00	5	8.14	4
E-Butadiene	$1\,^1B_u$	6.49	6.72	6.58	6.18	6.43	6	5.93	9	6.36	7
	$2\,^1A_g$	7.63	7.42	6.77	6.55	7.68	10	5.12	59	5.77	68
all-E-Hexatriene	$1\,^1B_u$	5.41	5.72	5.58	5.10	5.35	7	4.85	11	5.35	8
	$2\,^1A_g$	6.67	6.61	5.72	5.09	6.72	12	4.02	66	4.52	77
all-E-Octatetraene	$2\,^1A_g$	5.87	5.99	4.97	4.47	5.93	13	3.30	70	3.73	80
	$1\,^1B_u$	4.72	5.07	4.94	4.66	4.66	8	4.17	12	4.70	9
Cyclopropene	$1\,^1B_1$	6.96	6.96	6.90	6.76	6.97	5	6.21	10	6.75	8
	$1\,^1B_2$	7.17	7.24	7.10	7.06	7.14	4	6.60	8	6.91	6
Cyclopentadiene	$1\,^1B_2$	5.69	5.87	5.73	5.55	5.66	6	5.15	9	5.52	6
	$2\,^1A_1$	7.05	7.05	6.61	6.31	7.08	10	5.11	53	5.81	67
	$3\,^1A_1$	8.86	8.95	6.69		8.85	5	7.45	61	7.79	48
Norbornadiene	$1\,^1A_2$	5.57	5.80	5.64	5.34	5.57	7	4.97	11	5.48	8
	$1\,^1B_2$	6.37	6.69	6.49	6.11	6.39	8	5.70	13	6.45	10
	$2\,^1B_2$	7.65	7.87	7.64		7.63	6	7.08	10	7.54	7
	$2\,^1A_2$	7.66	7.87	7.71		7.67	7	7.07	11	7.63	8
Benzene	$1\,^1B_{2u}$	5.27	5.19	5.07	5.08	5.27	9	4.22	18	4.99	14
	$1\,^1B_{1u}$	6.68	6.74	6.68	6.54	6.64	6	6.20	9	6.47	6
	$1\,^1E_{1u}$	7.44	7.65	7.45	7.13	7.43	8	6.77	13	7.35	9
	$2\,^1E_{2g}$	9.03	9.21	8.43	8.41	9.06	15	7.12	40	8.58	44
Naphthalene	$1\,^1B_{3u}$	4.45	4.41	4.27	4.24	4.45	10	3.45	20	4.14	16
	$1\,^1B_{2u}$	4.96	5.21	5.03	4.77	4.93	9	4.33	15	4.90	10
	$2\,^1A_g$	6.22	6.23	5.98	5.9	6.22	11	4.94	38	5.54	67
	$1\,^1B_{1g}$	6.21	6.53	6.07	6.00	6.23	12	5.08	30	6.06	29
	$2\,^1B_{3u}$	6.25	6.55	6.33	6.07	6.23	10	5.59	15	6.26	11
	$2\,^1B_{2u}$	6.57	6.77	6.57	6.33	6.55	9	5.92	14	6.47	11
	$2\,^1B_{1g}$	6.82	6.97	6.79	6.48	6.80	8	6.22	12	6.63	12
	$3\,^1A_g$	7.34	7.77	6.90	6.71	7.38	16	5.67	43	6.41	49
Furan	$1\,^1B_2$	6.75	6.80	6.60	6.32	6.76	6	6.16	10	6.39	8
	$2\,^1A_1$	6.87	6.89	6.62	6.57	6.85	10	5.52	28	6.48	26
	$3\,^1A_1$	8.78	8.83	8.53	8.13	8.73	6	7.68	34	8.23	35
Pyrrole	$2\,^1A_1$	6.61	6.61	6.40	6.37	6.60	10	5.46	21	6.38	17
	$1\,^1B_2$	6.83	6.87	6.71	6.57	6.89	6	6.20	13	6.53	10
	$3\,^1A_1$	8.44	8.44	8.17	7.91	8.43	6	7.41	25	7.92	23
Imidazole	$2\,^1A'$	6.73	6.80	6.58	6.19	6.73	9	5.67	21	6.49	14
	$1\,^1A''$	6.86	7.01	6.82	6.81	6.74	7	6.05	13	6.46	10
	$3\,^1A'$	7.28	7.27	7.10	6.93	7.26	7	6.46	14	6.98	13
	$2\,^1A''$	8.00	8.15	7.93		7.80	8	7.14	14	7.72	11
	$4\,^1A'$	8.62	8.70	8.45		8.60	8	7.64	22	8.12	21
Pyridine	$1\,^1B_1$	5.12	5.25	5.05	4.59	5.10	9	4.21	18	5.05	14
	$1\,^1B_2$	5.32	5.27	5.15	4.85	5.32	10	4.28	18	5.06	14
	$2\,^1A_2$	5.39	5.73	5.50	5.11	5.37	11	4.45	17	5.80	13
	$2\,^1A_1$	6.88	6.94	6.85	6.26	6.83	6	6.29	12	6.58	9
	$3\,^1A_1$	7.72	7.94	7.70	7.18	7.70	8	7.00	14	7.59	11
	$2\,^1B_2$	7.61	7.81	7.59	7.27	7.59	8	6.75	20	7.46	13
	$4\,^1A_1$	9.00	9.45	8.68		7.99	12	7.28	33	8.73	37
	$3\,^1B_2$	9.37	9.64	8.77		8.84	12	7.53	35	8.99	50
Pyrazine	$1\,^1B_{3u}$	4.26	4.42	4.24	3.95	4.29	9	3.45	16	4.21	11
	$1\,^1B_{2u}$	5.13	5.14	5.02	4.64	5.16	10	4.10	18	4.88	14
	$1\,^1A_u$	4.95	5.29	5.05	4.81	4.97	10	4.06	17	5.28	12
	$1\,^1B_{2g}$	5.92	6.02	5.74	5.56	5.93	9	4.78	23	5.65	21
	$1\,^1B_{1u}$	7.10	7.18	7.07	6.58	7.06	6	6.60	16	6.85	6

TABLE II. (*Continued.*)

Molecule	State	CC2[a]	CCSD[a]	CC3[a]	TBE[a]	ADC(2)-s	%R_2	ADC(2)-x	%R_2	ADC(3)	%R_2
	$1\,^1B_{1g}$	6.70	7.13	6.75	6.60	6.70	12	5.54	16	7.18	22
	$2\,^1B_{2u}$	8.07	8.29	8.05	7.60	8.06	9	7.27	16	8.02	11
	$2\,^1B_{1u}$	8.13	8.34	8.06	7.72	8.11	8	7.40	16	7.95	10
	$1\,^1B_{3g}$	9.42	9.75	8.77		9.39	11	7.39	44	8.75	71
	$2\,^1A_g$	9.26	9.55	8.69		8.11	11	7.19	42	7.52	100
Pyrimidine	$1\,^1B_1$	4.49	4.70	4.50	4.55	4.45	10	3.59	16	4.57	13
	$1\,^1A_2$	4.84	5.12	4.93	4.91	4.80	10	3.92	16	5.10	12
	$1\,^1B_2$	5.51	5.49	5.36	5.44	5.49	10	4.46	18	5.30	14
	$2\,^1A_1$	7.12	7.17	7.06	6.95	7.03	7	6.38	15	6.66	13
	$2\,^1B_2$	8.08	8.24	8.01		7.89	10	7.20	16	7.90	12
	$3\,^1A_1$	7.79	7.97	7.74		7.70	9	6.82	20	7.53	16
Pyridazine	$1\,^1B_1$	3.90	4.11	3.92	3.78	3.91	10	3.02	17	3.92	12
	$1\,^1A_2$	4.40	4.76	4.49	4.32	4.41	11	3.40	19	4.68	15
	$2\,^1A_1$	5.37	5.35	5.22	5.18	5.37	10	4.25	20	5.10	16
	$2\,^1A_2$	5.81	6.00	5.74	5.77	5.83	10	4.72	24	5.70	21
	$2\,^1B_1$	6.40	6.70	6.41		6.40	11	5.33	21	6.64	15
	$1\,^1B_2$	7.00	7.09	6.93		6.97	7	6.27	19	6.73	8
	$2\,^1B_2$	7.57	7.79	7.55		7.58	14	6.82	19	7.43	11
	$3\,^1A_1$	7.90	8.11	7.82		7.89	8	7.03	21	7.64	20
s-Triazine	$1\,^1A_1''$	4.70	4.96	4.78	4.60	4.62	10	3.72	15	5.03	13
	$1\,^1A_2''$	4.80	4.98	4.76	4.66	4.73	10	3.86	16	4.79	13
	$1\,^1E''$	4.77	5.01	4.81	4.71	4.70	10	3.84	16	4.95	12
	$1\,^1A_2'$	5.82	5.84	5.71	5.79	5.76	10	4.76	18	5.71	14
	$2\,^1A_1'$	7.52	7.51	7.41		7.34	8	6.58	17	6.86	16
	$2\,^1E''$	8.04	8.19	7.80		7.96	11	6.71	24	7.86	19
	$1\,^1E'$	8.06	8.28	8.04		7.92	9	7.07	19	8.05	14
	$2\,^1E'$	9.93	10.24	9.44		8.64	10	8.03	15	9.31	10
s-Tetrazine	$1\,^1B_{3u}$	2.47	2.71	2.53	2.24	2.52	10	1.63	16	2.48	11
	$1\,^1A_u$	3.67	4.07	3.79	3.48	3.72	11	2.71	19	3.96	14
	$1\,^1B_{1g}$	5.10	5.32	4.97	4.73	5.13	11	3.80	27	5.00	18
	$1\,^1B_{2u}$	5.20	5.27	5.12	4.91	5.20	11	4.06	20	4.98	16
	$1\,^1B_{2g}$	5.53	5.70	5.34	5.18	5.57	11	4.11	35	4.95	40
	$2\,^1A_u$	5.50	5.70	5.46	5.47	5.54	10	4.49	21	5.39	15
	$1\,^1B_{3g}$				5.79	7.84	10	6.72	48	6.48	100
	$2\,^1B_{2g}$	6.32	6.76	6.23		6.34	12	4.87	30	6.56	29
	$2\,^1B_{1g}$	6.91	7.25	6.87		6.93	12	5.50	39	6.57	85
	$2\,^1B_{3u}$	6.70	6.99	6.67		6.73	11	5.62	21	6.82	16
	$3\,^1B_{1g}$	7.64	8.36	7.08		7.71	14	5.93	34	7.13	21
	$1\,^1B_{1u}$	7.60	7.66	7.45		7.54	7	6.92	16	7.18	9
	$2\,^1B_{1u}$	7.75	8.06	7.79		7.76	9	7.05	10	7.66	12
	$2\,^1B_{3g}$	8.97	9.44	8.47		8.85	12	7.16	16	8.25	50
	$2\,^1B_{2u}$	8.65	8.88	8.51		8.59	11	7.64	62	7.77	96
Formaldehyde	$1\,^1A_2$	4.09	3.97	3.95	3.88	3.91	6	3.10	11	3.85	9
	$1\,^1B_1$	9.35	9.26	9.18	9.10	7.67	10	7.24	13	8.96	9
	$2\,^1A_1$	10.34	10.54	10.45	9.30	9.37	9	8.71	20	9.09	32
Acetone	$1\,^1A_2$	4.52	4.43	4.40	4.40	4.30	7	3.54	11	4.38	9
	$1\,^1B_1$	9.29	9.26	9.17	9.10	9.12	7	8.41	11	9.14	9
	$2\,^1A_1$	9.74	9.87	9.65	9.40	9.44	8	8.70	15	9.96	12
p-Benzoquinone	$1\,^1B_{1g}$	2.81	3.07	2.75	2.78	2.67	10	1.74	21	2.83	18
	$1\,^1A_u$	2.92	3.19	2.85	2.80	2.76	11	1.81	22	2.98	20
	$1\,^1B_{3g}$	4.69	4.93	4.59	4.25	4.80	9	3.73	24	4.29	17
	$1\,^1B_{1u}$	5.59	5.89	5.62	5.29	5.42	10	4.68	16	5.43	14
	$1\,^1B_{3u}$	5.69	6.55	5.82	5.60	5.62	14	4.40	45	5.33	91
	$2\,^1B_{3g}$	7.36	7.62	7.27	6.98	7.25	10	5.15	41	6.94	49

TABLE II. (*Continued.*)

Molecule	State	CC2[a]	CCSD[a]	CC3[a]	TBE[a]	ADC(2)-s	%R_2	ADC(2)-x	%R_2	ADC(3)	%R_2
Formamide	$1\,^1A''$	5.76	5.66	5.65	5.63	5.46	7	4.77	11	5.69	9
	$2\,^1A'$	8.15	4.52	8.27	7.44	7.82	10	7.26	14	7.48	12
	$3\,^1A'$	11.24	11.34	10.93		7.98	11	7.46	15	8.83	13
Acetamide	$1\,^1A''$	5.77	5.71	5.69	5.80	5.48	7	4.80	11	5.78	9
	$2\,^1A'$	7.66	7.85	7.67	7.27	7.47	9	6.81	13	7.59	12
	$3\,^1A'$	10.71	10.77	10.50		8.33	8	7.76	16	8.09	11
Propanamide	$1\,^1A''$	5.78	5.74	5.72	5.72	5.49	7	4.82	11	5.81	9
	$2\,^1A''$	7.56	7.80	7.62	7.20	7.39	9	6.75	13	7.58	11
	$3\,^1A'$	10.33	10.34	10.06		7.94	11	7.44	15	8.09	11
Cytosine	$2\,^1A'$	4.80	4.98		4.66	4.60	11	3.83	18	4.83	14
	$1\,^1A''$	5.13	5.45		4.87	4.81	14	4.14	18	5.42	12
	$2\,^1A''$	5.01	5.99		5.26	5.24	12	4.47	19	6.16	10
	$3\,^1A'$	5.71	5.95		5.62	5.56	11	4.67	20	5.76	18
	$4\,^1A'$	6.65	6.81			6.43	10	5.73	15	6.64	12
Thymine	$1\,^1A''$	4.94	5.14		4.82	4.67	10	3.93	16	5.22	13
	$2\,^1A'$	5.39	5.60		5.20	5.30	9	4.64	14	5.35	12
	$2\,^1A''$	6.33	6.57		6.16	6.09	10	5.46	14	6.52	10
	$3\,^1A'$	6.46	6.78		6.27	6.29	12	5.33	24	6.57	22
	$4\,^1A'$	6.80	7.05		6.53	6.72	10	5.97	16	6.80	14
	$3\,^1A''$	6.73	7.67			6.58	14	5.93	21	6.76	10
	$4\,^1A''$	7.18	7.87			6.74	8	6.13	12	7.74	9
Uracil	$1\,^1A''$	4.91	5.11		4.80	4.64	10	3.88	17	5.19	13
	$2\,^1A'$	5.52	5.70		5.35	5.41	9	4.71	15	5.44	13
	$2\,^1A''$	6.73	7.68		6.10	6.01	10	5.37	14	6.68	10
	$3\,^1A'$	6.43	6.76		6.26	6.26	12	5.28	24	6.53	22
	$3\,^1A''$	6.26	6.50		6.56	6.59	15	5.90	21	6.71	10
	$4\,^1A'$	6.96	7.19		6.70	6.89	10	6.10	16	6.94	14
	$4\,^1A''$	7.12	7.74			6.95	7	6.32	17	7.85	25
	$5\,^1A'$	7.66	7.81			7.40	11	6.69	15	7.76	13
Adenine	$1\,^1A''$	5.27	5.58		5.12	5.19	11	4.43	16	5.56	12
	$2\,^1A'$	5.28	5.37		5.25	5.20	11	4.38	18	5.19	14
	$3\,^1A'$	5.42	5.61		5.25	5.33	10	4.65	15	5.30	12
	$2\,^1A''$	5.91	6.19		5.75	5.84	10	5.07	16	6.13	12
	$4\,^1A'$	6.58	6.83			6.49	11	5.67	19	6.56	19
	$5\,^1A'$	6.93	7.17			6.81	11	5.80	25	6.60	20

[a]Taken from literature.[41]

generally be noted that the ADC(3) results for ^1B single excitations are close to the best estimated values (usually by less than 0.2 eV) and they are often closer than the CC3 values. ADC(2)-s usually overestimates the excitation energies slightly more than ADC(3), while ADC(2)-x tends to underestimate the excitation energies strongly. As has been noticed earlier, ADC(2)-s and CC2 exhibit very similar values for the excitation energies.[20]

However, generally most difficult is the description of states with large double excitation character, as the ^1A_g states of polyenes typically have. This can be seen at the large (%$R2$) values in the ADC excitation vectors at ADC(2)-x and ADC(3) (Table II). Compared to the TBE values, ADC(3) seems to underestimate their excitation energies slightly, while CC3 has a tendency to overestimate them. The second order methods CC2 and ADC(2)-s cannot capture the double excitation character, since the 2p-2h blocks M_{22} of their corresponding matrices are expanded only in zeroth order of perturbation theory. As a result, excitation energies of pre-

dominantly doubly excited states are grossly overestimated. The *ad hoc* expansion of these matrix elements in ADC(2)-x up to first order leads to an improved description of the double excitation character at the expense of a balanced description of singly and doubly excited states. ADC(2)-x can thus serve more as a diagnostic tool for pronounced double excitation character than as a balanced excited state methods.

Going to *aromatic hydrocarbons and heterocycles*, the calculated vertical excitation energies of the $\pi\pi*$ excited states in the seven molecules are in reasonable agreement with the TBE values at the ADC(3) level. While the excitation energies of hydrocarbons are slightly underestimated at ADC(3) level, the lowest excitation energies of heterocycles seem to be generally overestimated by at most 0.1–0.3 eV can be observed. $n\pi*$ excitations exhibit larger deviations of, in the worst case, up to 0.69 eV for the $2\,^1A_1$ state of pyridine for example. However, this seems to be an outlier in the benchmark set, because also the excitation energies computed at CC3 level exhibit unusually large deviations. One source of

TABLE III. Statistical error analysis of the calculated excitation energies of the singlet excited states of the benchmark set at CC2, ADC(2)-s, ADC(2)-x, CC3, and ADC(3) levels of theory. The theoretical best estimates (TBE) have been used as reference data as well as the ones obtained at CC3 and ADC(3).

	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
TBE as reference						
Count[a]	103	103	84	104	104	104
Min	−0.30	−2.92	−0.11	−1.43	−1.86	−0.78
Max	1.58	1.58	1.15	2.05	0.93	0.90
Mean	0.29	0.43	0.23	0.22	−0.70	0.12
Std. dev	0.28	0.44	0.21	0.38	0.37	0.28
Abs. mean	0.30	0.49	0.24	0.29	0.72	0.24
CC3 as reference						
Count[a]	114	114	…	114	114	114
Min	−0.22	−3.75	…	−2.95	−3.47	−2.41
Max	2.17	2.26	…	2.16	0.76	1.10
Mean	0.14	0.27	…	−0.03	−0.99	−0.20
Std. dev	0.29	0.48	…	0.54	0.48	0.46
Abs. mean	0.17	0.34	…	0.27	1.00	0.29
ADC3 as reference						
Count[a]	141	141	114	141	141	…
Min	−1.15	−2.96	−1.10	−1.29	−1.80	…
Max	2.62	2.68	2.41	2.19	0.24	…
Mean	0.24	0.41	0.20	0.08	−0.83	…
Std. dev.	0.55	0.59	0.46	0.50	0.38	…
Abs. mean	0.36	0.47	0.29	0.34	0.84	…

[a]Total number of considered states.

error may be a potential multi-reference character, which is not captured neither by ADC nor CC approaches, however, it may be also worthwhile to revisit the excited states of pyridine at higher level of theory to challenge the existing data. CC2 and the ADC(2)-s and -x approaches exhibit the same trends and tendencies compared to the CC3 and ADC(3) value as has been denoted for the previous class of unsaturated aliphatic hydrocarbons.

The *aldehydes, ketones, and amides* contained in the benchmark set possess excited states with different electronic structures, which can be classified as $\pi\pi^*$, $n\pi^*$, and $\sigma\pi^*$ excited states. The excitation energies of these states calculated at ADC(3) level of theory exhibit a similar deviation from the TBE values as the ones of the previously studied molecular classes. The same holds for ADC(2)-s and ADC(2)-x.

To demonstrate the computational efficiency of the ADC(3) approach, the vertical excited states of the *nucleobases* cytosine, thymine, uracil, and adenine have also been computed. These calculations are not feasible at the more expensive CC3 level of theory.[41] Obviously, the excitation energies obtained at ADC(3) level partially differ from the TBE values and, in most cases, CC2 and ADC(2)-s results are much closer, although they are at formally lower theoretical level. This owes to the fact that these TBE values were derived also taking CC2 values into consideration. This casts some doubts at the quality of the TBE values for the nucleobases and a further detailed investigation of their energetically low-lying excited states may be advised. However, this demonstrates once more the difficulty to derive high-quality benchmark data for excited states of medium-sized

molecules like those of the nucleobases, and that their development is an ongoing processes requiring repeated revisions and improvement.[50]

The *statistical analysis* of the data is presented in Table III and Figure 4. As a first step, the excitation energies computed at the ADC levels are compared against the TBE values. While ADC(2)-s exhibits a mean error of 0.22 eV with a standard deviation of 0.38 eV, ADC(3) is a substantial improvement decreasing the mean error to 0.12 eV with a standard deviation of 0.28 eV. The analysis of the ADC(2)-x excitation energies, on the other hand, clearly reveals that the *ad hoc* extension of the 2p-2h block to first-order leads to a pronounced underestimation of the excitation energies, i.e., a mean error of −0.7 eV with a standard deviation of 0.37 eV. Comparing ADC(2)-s with CC2, it is seen that the first exhibits a smaller mean error of 0.22 eV compared to 0.29 eV, but a larger standard deviation of 0.38 eV compared to 0.28 eV, respectively. Comparing Figures 4(a) and 4(d), this is readily apparent through the position and width of the gaussian distribution function.

For a fair comparison of the accuracy of ADC(3) and CC3, the CC3 excitation energies have been analyzed only with respect to TBE values that are not CC3 values. This gives a smaller number of only 84 counts for CC3 than for ADC(3). Following this procedure, CC3 exhibits a slightly larger mean error of 0.23 eV compared to 0.12 eV of ADC(3), but a smaller standard deviation of 0.21 eV compared to 0.28 eV, respectively. However, if only the same 84 states are considered in the statistical analysis of the ADC(3) results as well, the mean error of ADC(3) decreases further to 0.08 eV
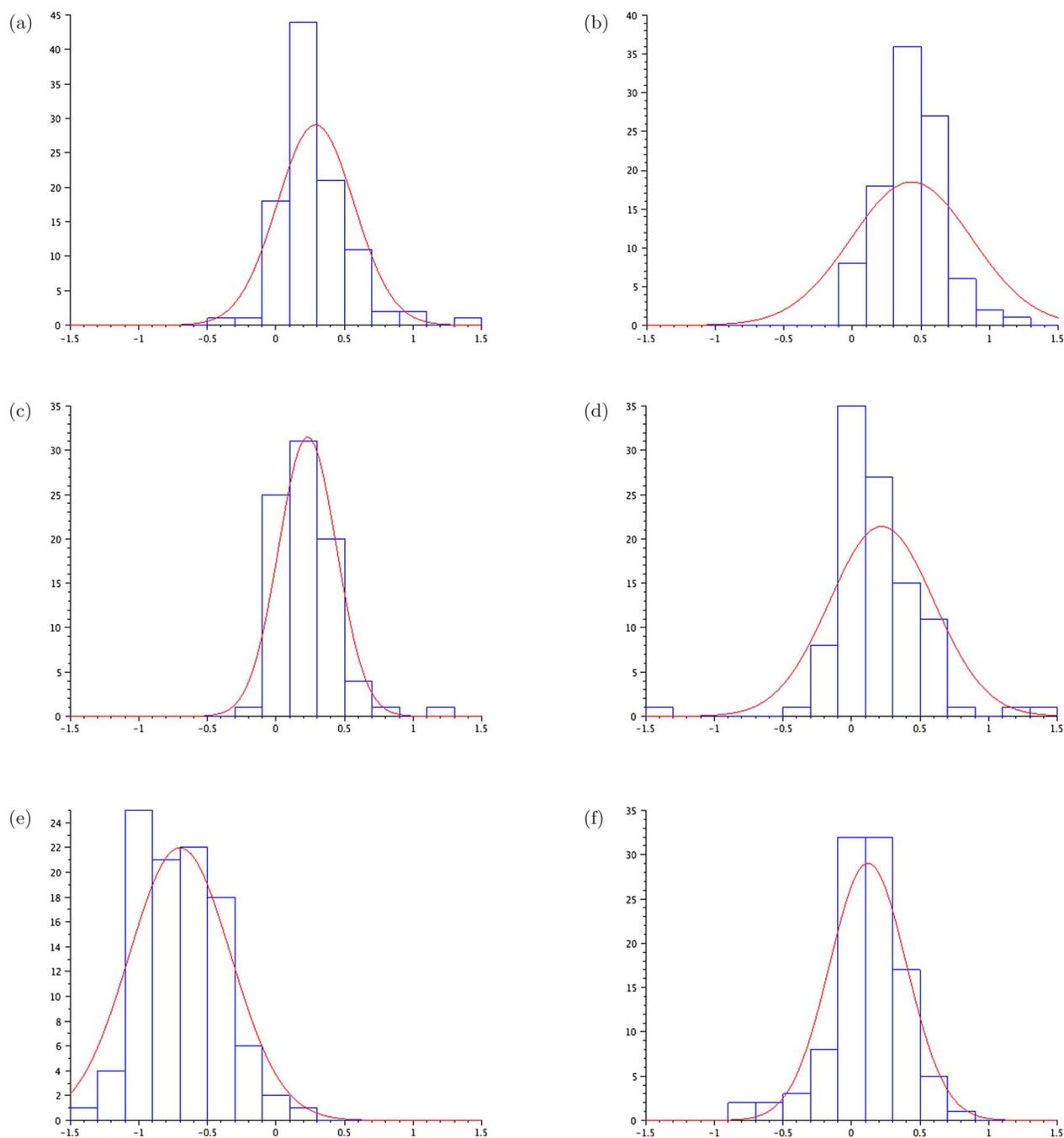
FIG. 4. Histograms of the distribution of deviations of all calculated singlet excited states with respect to the best estimates at the theoretical levels of (a) CC2, (b) CCSD, (c) CC3, (d) ADC(2)-s, (e) ADC(2)-x, and (f) ADC(3).

while the standard deviation amount to 0.27 eV. The minimal error is −0.78, while the maximal error is 0.69 eV for the considered 84 excited states at ADC(3) level. Another important aspect in the analysis is the span of the minimal and maximal errors of the methods. While CC2 spans a range from −0.3 eV to 1.58 eV, it is strongly decreased to −0.11 to 1.15 eV at CC3 level. The same is true for the transition from ADC(2)-s to ADC(3), where the span is reduced from −1.43 to 2.05 eV at ADC(2)-s level to −0.78 to 0.90 eV at ADC(3) level.

In conclusion, ADC(3) exhibits a smaller mean deviation from the TBE values of the considered singlet states

than CC3 but a slightly larger standard deviation. In other words, the error distribution is slightly broader at ADC(3) level than at CC3 level, but the error distribution is more symmetrically localized around zero (Figures 4(c) and 4(f)). The same trend holds for ADC(2)-s compared to CC2, however, owing to the broader error distribution and the much larger span of the minimal and maximal errors of the second order methods, ADC(3) and CC3 exhibit a much larger predictive power. Based on this statistical analysis it is impossible to judge whether CC3 or ADC(3) is the more accurate method for singlet excited states of medium-sized organic molecules.

However, it is clear that ADC(3) exhibits a much larger range of applicability due to its fortunate scaling of only $O(N^6)$ with system size compared to the one of $O(N^7)$ of CC3.

Since ADC(3) and CC3 exhibit similar accuracies, it is worthwhile to statistically analyze the excitation energies further. Assuming that CC3 and ADC(3) are valuable benchmark methods, the excitation energies have been analyzed also with respect to the CC3 values and the ADC(3) values only (Table III). Of course the details of the analysis changes slightly, although the general trend remains the same. One remarkable aspect, though, are the different results of the analyses of ADC(2) and CC2 depending on the choice of benchmark. When CC3 is chosen as benchmark, the mean deviation of CC2 is only 0.14 eV with a comfortable standard deviation of only 0.29 eV. On the contrary, the mean deviation of ADC(2)-s is only −0.03 eV with very broad standard deviation of 0.54 eV. Using the ADC(3) values as reference, the ADC(2)-s performance remains more or less the same with, but CC2 exhibits a larger mean error of 0.24 eV now and a much broader standard deviation of 0.55 eV. In summary one can state, using the CC3 values as reference favours CC2, while ADC(3) benchmarks favor ADC(2)-s.

B. Triplet excited states

For the evaluation of the accuracy of the ADC methods, 71 triplet excited states of 20 molecules of the benchmark set (Figure 3) have been computed and compared to the available TBE and CC2, CCSD, and CC3 values. In comparison to the evaluation of the singlet states, no benchmark data are available for the triplet states of the molecules pyrazine, pyrimidine, pyridazine, s-tetrazine, and the nucleobases cytosine, thymine, uracil, adenine. It is also important to realize that most of the TBE values correspond to CC3 values, i.e., only 19 values are non-CC3 values. The results for all investigated triplet states are compiled in Table IV.

Since the accuracy of the ADC methods is very similar for the triplet states of all different substance classes, it is not particular insightful to go into an individual analysis as has been done for the singlet states. Instead, the statistical analysis of the overall errors of the ADC methods is instructive, the results of which are compiled in Table V and displayed in Figure 5. As a first step, the excitation energies are evaluated against the TBE values. It can generally be noted that the mean errors of all considered methods, i.e., CC2, EOM-CCSD, CC3, ADC(2)-s, ADC(2)-x, and ADC(3) are smaller for the triplet states than for the singlet states. ADC(3) exhibits a mean error of −0.18 eV and a standard deviation of 0.16 eV, while ADC(2)-s exhibits an error of only 0.12 eV and a standard deviation of 0.16 eV. As already observed for the singlet states, ADC(2)-x largely underestimates the excitation energies by a mean error of −0.55 eV, however quite consistently as the small standard deviation of 0.2 eV indicates. CC2 and EOM-CCSD perform extremely well compared to the TBE values, as they exhibit mean errors of only 0.17 and 0.06 eV with very small standard deviations of 0.13 and 0.14 eV. In general, it is surprising that all second-order methods, except ADC(2)-x, perform slightly better than ADC(3) in the description of the triplet excitation energies. However,

this may have an origin in the choice of the TBE values, as a comparison of ADC(3) and CC3 below may reveal.

Since most of the TBE values correspond to CC3 values, it is thus not statistically relevant to evaluate the accuracy of CC3 with respect to the TBE values. A comparison of CC3 and ADC(3) is still possible to a limited extend, if only the 19 triplet states of the TBE values are considered which do not correspond to CC3 values. When statistical analyses of the CC3 and ADC(3) values with respect to these states are performed, CC3 exhibits a mean error of 0.12 eV with a standard deviation of 0.10 eV and an error span from −0.04 to 0.32 eV, while ADC(3) has a mean error of −0.10 with a standard deviation of 0.13 eV and an error span from −0.41 eV to 0.44 eV. Therefore, CC3 and ADC(3) exhibit also for these triplet states similar accuracy, CC3 slightly overestimating, ADC(3) slightly underestimating excitation energies. Overall, the same trend of CC3 and ADC(3) is found for triplet states as previously for singlet states.

In a next set of analyses, the excitation energies are compared with respect to the CC3 values and, equivalently, with respect to the ADC(3) values as benchmarks (Table V). When the reference is changed from the TBE values to only CC3 values, all second-order methods get statistically slightly better and ADC(3) gets slightly worse, however, the changes are only small. This is, of course, different when ADC(3) values are used as the reference benchmark set, then the statistical mean error of all second-order methods and CC3 increases by about 0.2 eV. In view of the finding that CC3 and ADC(3) exhibit similar accuracies when only non-CC3 benchmark values are considered, the behaviour of the statistical analyses demonstrates that the choice of the benchmark is crucial.

C. Oscillator strengths

Another important aspect in the theoretical investigation of excited states is, besides the computation of the excitation energies, also the reliable prediction of oscillator strength, i.e., transition dipole moments from the ground to the corresponding excited state, as well as of excited state properties in general. Along this line of thought, a set of literature data has been provided for the oscillator strengths of most of the excited singlet states of the benchmark set.[41] Accordingly the oscillator strengths have been computed at ADC(2)-s, ADC(2)-x, and ADC(3/2) level of theory and compared to the benchmark set and CC2 and EOM-CCSD values. These data are compiled in Table VI. Note that no oscillator strengths are available at CC3 level in Ref. 41.

In general, the hermitian structure and the corresponding ISR formulation of the ADC approaches bare some advantages over the CC methods.[51] For instance, the transition moments computed at CC2 level exhibit an error of perturbation theoretical order 2 owing to the first-order approximation used for the T2 amplitudes, while the truncation error is of perturbation theoretical order 3. Within the ADC(2)-s approach transition moments are consistently treated through 2nd order and the truncation error order is 4. For a detailed discussion, the reader is referred to Ref. 51. At ADC(3) level, algebraic expressions for the oscillator strengths consistent up to third order in perturbation theory are not available yet.

TABLE IV. Vertical excitation energies in eV of the lowest excited triplet states of the considered molecules in the benchmark set (Figure 3) at the theoretical levels of CC2, EOM-CCSD, CC3 and ADC(2)-s, ADC(2)-x, and ADC(3) in comparison with the theoretical best estimates (TBE). For analysis, also the amount of double excited configurations ($\%R_2$) in the ADC excitation vectors is given.

Molecule	State	CC2[a]	CCSD[a]	CC3[a]	Best est.[a]	ADC(2)-s	$\%R_2$	ADC(2)-x	$\%R_2$	ADC(3)	$\%R_2$
Ethene	$1\,^3B_{1u}$	4.52	4.42	4.48	4.50	4.52	2	4.16	4	4.23	3
E-Butadiene	$1\,^3B_u$	3.40	3.25	3.32	3.20	3.40	3	2.83	9	3.03	7
	$1\,^3A_g$	5.25	5.15	5.17	5.08	5.22	3	4.80	5	4.89	4
All-E-Hexatriene	$1\,^3B_u$	2.78	2.62	2.69	2.40	2.79	4	2.13	13	2.38	10
	$1\,^3A_g$	4.40	4.28	4.32	4.15	4.38	3	3.83	10	4.00	7
All-E-Octatetraene	$1\,^3B_u$	2.40	2.23	2.30	2.20	2.41	5	1.70	15	1.97	12
	$1\,^3A_g$	3.76	3.62	3.67	3.55	3.74	4	3.11	13	3.33	10
Cyclopropene	$1\,^3B_2$	4.44	4.30	4.34	4.34	4.43	3	4.01	5	4.08	4
	$1\,^3B_1$	6.65	6.66	6.62	6.62	6.66	5	5.97	9	6.45	7
Cyclopentadiene	$1\,^3B_2$	3.36	3.18	3.25	3.25	3.35	4	2.80	9	2.97	6
	$1\,^3A_1$	5.22	5.07	5.09	5.09	5.19	3	4.72	6	4.83	5
Norbornadine	$1\,^3A_2$	3.76	3.67	3.72	3.72	3.74	4	3.29	6	3.46	4
	$1\,^3B_2$	4.25	4.09	4.16	4.16	4.24	3	3.83	5	3.91	4
Benzene	$1\,^3B_{1u}$	4.31	3.94	4.12	4.15	4.30	4	3.80	7	3.88	5
	$1\,^3E_{1u}$	5.14	4.97	4.90	4.86	5.13	7	4.33	14	4.62	12
	$1\,^3B_{2u}$	6.08	6.00	6.04	5.88	6.05	5	5.42	8	5.73	6
	$1\,^3E_{2g}$	7.99	7.73	7.49	7.51	7.90	7	7.27	12	7.66	9
Naphthalene	$1\,^3B_{2u}$	3.27	2.99	3.11	3.11	3.26	6	2.66	12	2.85	8
	$1\,^3B_{3u}$	4.38	4.27	4.18	4.18	4.36	8	3.58	17	3.90	14
	$1\,^3B_{1g}$	4.64	4.44	4.47	4.47	4.63	5	4.02	11	4.21	8
	$2\,^3B_{2u}$	4.88	4.67	4.64	4.64	4.86	7	4.13	15	4.37	12
	$2\,^3B_{3u}$	5.11	5.10	5.11	5.11	5.08	7	4.46	11	4.82	8
	$1\,^3A_g$	5.76	5.57	5.52	5.52	5.74	6	5.04	13	5.24	10
	$2\,^3B_{1g}$	6.44	6.79	6.48	6.48	6.45	12	5.58	22	6.27	41
	$2\,^3A_g$	6.83	6.81	6.47	6.47	6.82	8	5.64	34	6.16	33
	$3\,^3B_{1g}$	7.23	7.04	6.76	6.76	7.24	7	5.91	38	6.49	20
	$3\,^3A_g$	6.94	6.96	6.79	6.79	6.94	9	6.12	14	6.59	12
Furan	$1\,^3B_2$	4.38	4.10	4.17	4.17	4.35	4	3.77	9	3.84	6
	$1\,^3A_1$	5.67	5.48	5.48	5.48	5.59	4	5.02	8	5.22	7
Pyrrole	$1\,^3B_2$	4.68	4.41	4.48	4.48	4.66	4	4.09	9	4.21	6
	$1\,^3A_1$	5.72	5.54	5.51	5.51	5.67	5	5.04	10	5.26	8
Imidazole	$1\,^3A'$	4.89	4.62	4.69	4.69	4.86	4	4.27	9	4.40	6
	$2\,^3A'$	6.01	5.83	5.79	5.79	5.98	5	5.33	10	5.52	8
	$1\,^3A''$	6.44	6.43	6.37	6.37	6.38	7	5.59	13	6.26	8
	$3\,^3A'$	6.74	6.56	6.55	6.55	6.71	5	6.01	10	6.29	8
	$4\,^3A'$	7.68	7.54	7.42		7.60	13	6.83	14	7.20	13
	$2\,^3A''$	7.52	7.76	7.51		7.61	8	6.97	13	7.50	10
Pyridine	$1\,^3A_1$	4.46	4.07	4.25	4.06	4.45	4	3.80	13	3.98	5
	$1\,^3B_1$	4.54	4.61	4.50	4.25	4.52	8	3.92	8	4.43	9
	$1\,^3B_2$	5.07	4.91	4.86	4.64	5.06	6	4.28	13	4.55	10
	$2\,^3A_1$	5.33	5.13	5.05	4.91	5.30	7	4.43	17	4.74	11
	$1\,^3A_2$	5.35	5.67	5.46	5.28	5.34	10	4.49	14	5.72	13
	$2\,^3B_2$	6.52	6.41	6.40	6.08	6.47	6	5.75	10	6.08	9
	$3\,^3B_2$	8.39	8.12	7.83		8.14	6	7.00	31	7.40	30
	$3\,^3A_1$	8.18	7.90	7.66		7.86	12	6.96	28	7.23	25
s-Tetrazine	$1\,^3B_{3u}$	1.86	1.99	1.89	1.89	1.89	8	1.13	13	1.75	9
	$1\,^3A_u$	3.43	3.74	3.52	3.52	3.47	10	2.56	17	3.58	11
	$1\,^3B_{1g}$	4.30	4.31	4.21	4.21	4.29	8	3.42	16	4.03	9
	$1\,^3B_{1u}$	4.62	4.05	4.33	4.33	4.60	4	4.00	9	3.93	5
	$1\,^3B_{2u}$	4.81	4.57	4.54	4.54	4.79	7	3.95	14	4.05	10
	$1\,^3B_{2g}$	5.03	5.09	4.93	4.93	5.04	8	4.05	23	4.70	20
	$2\,^3A_u$	5.05	5.20	5.03	5.03	5.08	9	4.19	16	4.98	11
	$2\,^3B_{1u}$	5.67	5.48	5.38	5.38	5.64	8	4.66	17	5.00	14

TABLE IV. (*Continued.*)

Molecule	State	CC2[a]	CCSD[a]	CC3[a]	Best est.[a]	ADC(2)-s	$\%R_2$	ADC(2)-x	$\%R_2$	ADC(3)	$\%R_2$
	$2\,^3B_{2g}$	6.05	6.51	6.04		6.09	12	4.71	28	6.12	63
	$2\,^3B_{1g}$	6.72	7.11	6.60		6.75	12	5.35	55	6.43	90
	$2\,^3B_{3u}$	6.52	6.80	6.53		6.54	10	5.52	19	6.64	14
	$2\,^3B_{2u}$	7.65	7.46	7.36		7.59	7	6.06	100	6.07	100
Formaldehyde	$1\,^3A_2$	3.57	3.52	3.55	3.50	3.41	5	2.78	8	3.43	7
	$1\,^3A_1$	6.08	5.78	5.83	5.87	5.96	5	5.54	4	5.46	3
Acetone	$1\,^3A_2$	4.08	4.03	4.05	4.05	3.88	6	3.26	9	4.00	7
	$1\,^3A_1$	6.27	5.94	6.03	6.03	6.12	3	5.64	5	5.71	4
p-Benzoquinone	$1\,^3B_{1g}$	2.47	2.71	2.51	2.51	2.35	9	1.58	17	2.57	12
	$1\,^3A_u$	2.59	2.83	2.62	2.62	2.44	9	1.67	18	2.72	13
	$1\,^3B_{1u}$	3.12	2.89	2.96	2.96	3.07	6	2.37	13	2.63	9
	$1\,^3B_{3g}$	3.50	3.42	3.41	3.41	3.52	5	2.86	11	3.06	7
Formamide	$1\,^3A''$	5.39	5.32	5.36	5.36	5.13	6	4.53	9	5.36	7
	$1\,^3A'$	5.94	5.67	5.74	5.74	5.81	5	5.21	7	5.51	6
Acetamide	$1\,^3A''$	5.42	5.39	5.42	5.42	5.16	6	4.57	9	5.46	7
	$1\,^3A'$	6.06	5.83	5.88	5.88	5.92	5	5.32	8	5.70	6
Propanamide	$1\,^3A''$	5.44	5.41	5.45	5.45	5.18	7	4.59	9	5.49	7
	$1\,^3A'$	6.07	5.84	5.90	5.90	5.92	5	5.33	8	5.73	6

[a]Taken from literature.[41]

Instead, for their computation the third-order ADC(3) excitation vector is contracted with the second-order IS expression of the spectral amplitudes resulting in the one-particle transition density matrix at the level which is generally denoted as ADC(3/2). The latter is then combined with the dipole operator and the ADC(3) excitation energies to obtain ADC(3/2) oscillator strengths.

Since the literature data provide ranges for the oscillator strengths it is very difficult and not instructive to perform a detailed statistical analysis. Going through the data of

TABLE V. Statistical error analysis of the calculated excitation energies of the triplet excited states of the benchmark set at CC2, ADC(2)-s, ADC(2)-x, CC3, and ADC(3) levels of theory. The theoretical best estimates (TBE) have been used as reference data as well as the ones obtained at CC3 and ADC(3).

	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
			TBE as reference			
Count[a]	63	63	63	63	63	63
Min	-0.09	-0.28	-0.04	-0.27	-0.96	-0.49
Max	0.48	0.39	0.32	0.48	-0.24	0.44
Mean	0.17	0.06	0.04	0.12	-0.55	-0.18
Std. dev	0.13	0.14	0.08	0.16	0.20	0.16
Abs. mean	0.18	0.11	0.04	0.17	0.55	0.21
			CC3 as reference			
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[a]	71	71	…	71	71	71
Min	-0.11	-0.28	…	-0.27	-1.33	-1.29
Max	0.56	0.51	…	0.48	-0.22	0.26
Mean	0.14	0.05	…	0.09	-0.63	-0.22
Std. dev	0.14	0.15	…	0.14	0.24	0.20
Abs. mean	0.15	0.11	…	0.14	0.63	0.25
			ADC3 as reference			
	CC2	CCSD	CC3	ADC(2)-s	ADC(2)-x	ADC(3)
Count[a]	71	71	71	71	71	…
Min	-0.37	-0.96	-0.26	-0.38	-1.41	…
Max	1.58	1.39	1.29	1.53	0.08	…
Mean	0.37	0.27	0.22	0.32	-0.41	…
Std. dev.	0.29	0.21	0.20	0.30	0.33	…
Abs. mean	0.40	0.28	0.25	0.38	0.41	…

[a]Total number of considered states.

TABLE VI. Oscillator strength of a selected set of vertical excited singlet states of the benchmark set (Figure 3) at the theoretical levels of CC2, EOM-CCSD and ADC(2)-s, ADC(2)-x, and ADC(3) in comparison with the literature data.

Molecule	State	CC2[a]	CCSD[a]	Literature[a]	ADC(2)-s	ADC(2)-x	ADC(3/2)
Ethene	$1\,^1B_{1u}$	0.431	0.41	0.358–0.494	0.437	0.409	0.423
E-Butadiene	$1\,^1B_u$	0.809	0.776	0.52–0.803	0.811	0.720	0.806
All-E-Hexatriene	$1\,^1B_u$	1.272	1.213	0.655–1.154	1.253	1.100	1.257
All-E-Octatetraene	$1\,^1B_u$	1.757	1.665	1.382	1.701	1.473	1.724
Cyclopropene	$1\,^1B_1$	0.001	0.001		0.001	0.001	0.001
	$1\,^1B_2$	0.086	0.083		0.094	0.078	0.096
Cyclopentadiene	$1\,^1B_2$	0.11	0.097	0.099–0.157	0.113	0.102	0.101
	$2\,^1A_1$	0.011	0.008	0.001–0.019	0.012	0.002	0.001
	$3\,^1A_1$	0.658	0.648	0.025–0.538	0.695	0.041	0.029
Norbornadiene	$1\,^1B_2$	0.023	0.029		0.028	0.018	0.036
	$2\,^1B_2$	0.185	0.187		0.210	0.179	0.221
	$2\,^1A_1$	0	0		0	0	0
Benzene	$1\,^1E_{1u}$	0.694	0.686	0.323–1.33	0.748	0.667	0.707
Naphthalene	$1\,^1B_{3u}$	0	0	0	0	0	0
	$1\,^1B_{2u}$	0.094	0.083	0.082	0.106	0.099	0.097
	$2\,^1B_{3u}$	1.45	1.461	1.326	1.531	1.338	1.524
	$2\,^1B_{2u}$	0.272	0.294	0.268	0.313	0.248	0.299
Furan	$1\,^1B_2$	0.172	0.159	0.144–0.185	0.176	0.164	0.160
	$2\,^1A_1$	0.003	0.001	0.000–0.011	0.007	0.001	0.000
	$3\,^1A_1$	0.506	0.501	0.194–0.494	0.546	0.328	0.345
Pyrrole	$2\,^1A_1$	0.006	0.005	0.000–0.036	0.009	0.003	0.004
	$1\,^1B_2$	0.182	0.166	0.099–0.99	0.185	0.165	0.171
	$3\,^1A_1$	0.532	0.527	0.176–0.706	0.574	0.433	0.458
Imidazole	$2\,^1A'$	0.088	0.088	0.08	0.092	0.038	0.112
	$1\,^1A''$	0.003	0.005		0.000	0.000	0.000
	$3\,^1A'$	0.085	0.081	0.07	0.093	0.121	0.064
	$2\,^1A''$	0.006	0.004		0.003	0.001	0.002
	$4\,^1A'$	0.406	0.42		0.435	0.388	0.273
Pyridine	$1\,^1B_2$	0.025	0.022	0.023–0.040	0.025	0.016	0.027
	$1\,^1B_1$	0.005	0.006	0.005–0.01	0.005	0.004	0.005
	$2\,^1A_1$	0.021	0.015	0.006–0.021	0.020	0.009	0.010
	$3\,^1A_1$	0.489	0.59	0.513–0.67	0.611	0.562	0.620
	$2\,^1B_2$	0.549	0.548	0.407–0.65	0.609	0.440	0.538
Pyrazine	$1\,^1B_{3u}$	0.007	0.008	0.01	0.007	0.005	0.007
	$1\,^1B_{2u}$	0.07	0.067	0.08	0.074	0.050	0.077
	$1\,^1B_{1u}$	0.096	0.074	0.06	0.098	0.100	0.070
	$2\,^1B_{1u}$	0.424	0.458	0.37	0.505	0.446	0.496
	$2\,^1B_{2u}$	0.4	0.423	0.33	0.471	0.426	0.446
Pyrimidine	$1\,^1B_1$	0.006	0.007	0.007–0.01	0.006	0.005	0.007
	$1\,^1B_2$	0.023	0.022	0.01–0.026	0.024	0.015	0.028
	$2\,^1A_1$	0.062	0.038	0.017–0.03	0.052	0.058	0.025
	$2\,^1B_2$	0.476	0.47	0.41–0.499	0.213	0.389	0.523
	$3\,^1A_1$	0.446	0.461		0.519	0.355	0.462
Pyridazine	$1\,^1B_1$	0.006	0.007		0.006	0.004	0.007
	$2\,^1A_1$	0.014	0.014		0.016	0.011	0.019
	$2\,^1B_1$	0.005	0.005		0.005	0.004	0.005
	$1\,^1B_2$	0.009	0.006		0.007	0.040	0.012
	$2\,^1B_2$	0.489	0.459		0.544	0.376	0.492
	$3\,^1A_1$	0.444	0.494		0.541	0.407	0.466
s-Triazine	$1\,^1A_2''$	0.017	0.018	0.02–0.027	0.017	0.013	0.016
	$1\,^1E'$	0.441	0.437	0.92	0.521	0.395	0.443
	$2\,^1E'$	0	0		0.070	0.029	0.062

TABLE VI. (*Continued.*)

Molecule	State	CC2[a]	CCSD[a]	Literature[a]	ADC(2)-s	ADC(2)-x	ADC(3/2)
s-Tetrazine	$1\ ^1B_{3u}$	0.007	0.009	0.007–0.012	0.007	0.005	0.008
	$1\ ^1B_{2u}$	0.046	0.047	0.052–0.095	0.055	0.036	0.000
	$2\ ^1B_{3u}$	0.011	0.012	0.01–0.018	0.011	0.009	0.011
	$1\ ^1B_{1u}$	0.017	0.003	0.00–0.054	0.009	0.296	0.004
	$2\ ^1B_{1u}$	0.376	0.381	0.39–0.630	0.448	0.105	0.421
	$2\ ^1B_{2u}$	0.368	0.333	0.45–0.755	0.022	0.160	0.013
Formaldehyde	$1\ ^1B_1$	0.079	0.074	0.000–0.001	0.068	0.06	0.091
	$2\ ^1A_1$	0.368	0.374	0.063–0.100	0.029	0.002	0.096
Acetone	$1\ ^1B_1$	0	0	0.003	0.000	0.000	0.000
	$2\ ^1A_1$	0.298	0.256	0.255	0.401	0.311	0.134
p-Benzoquinone	$1\ ^1B_{3g}$	0	0		0	0	0
	$1\ ^1B_{1u}$	0.538	0.558	0.636–0.704	0.621	0.509	0.590
	$1\ ^1B_{3u}$	0	0.001	0	0	0	0
Formamide	$1\ ^1A''$	0.001	0.001	0.000–0.001	0.001	0.001	0.001
	$2\ ^1A'$	0.385	0.371	0.149–0.338	0.373	0.401	0.135
	$3\ ^1A'$	0.01	0.102		0.213	0.100	0.299
Acetamide	$1\ ^1A''$	0.001	0.001		0.001	0	0.001
	$2\ ^1A'$	0.199	0.223		0.235	0.222	0.132
	$3\ ^1A'$	0.279	0.299		0.281	0.059	0.145
Propanamide	$1\ ^1A''$	0	0		0	0	0
	$2\ ^1A'$	0.138	0.108		0.179	0.184	0.126
	$3\ ^1A'$	0.189	0.15		0.098	0.069	0.112
Cytosine	$2\ ^1A'$	0.049	0.058	0.052–0.080	0.046	0.034	0.071
	$1\ ^1A''$	0.001	0.002	0.001–0.002	0	0.001	0.002
	$3\ ^1A'$	0.165	0.178	0.138–0.181	0.195	0.123	0.143
	$4\ ^1A'$	0.632	0.608		0.712	0.634	0.538
	$2\ ^1A''$	0.002	0	0.001–0.003	0.002	0.001	0.000
Thymine	$1\ ^1A''$	0	0		0	0	0
	$2\ ^1A'$	0.197	0.222	0.18	0.23	0.189	0.238
	$3\ ^1A'$	0.08	0.071	0.04	0.083	0.055	0.055
	$2\ ^1A''$	0	0		0	0	0
	$4\ ^1A'$	0.25	0.285	0.18	0.284	0.198	0.242
	$3\ ^1A''$	0	0		0	0	0
	$4\ ^1A''$	0	0		0	0	0.001
Uracil	$1\ ^1A''$	0	0		0	0	0
	$2\ ^1A'$	0.197	0.224	0.18-0.26	0.235	0.2	0.242
	$3\ ^1A'$	0.058	0.061	0.04-0.05	0.059	0.023	0.04
	$2\ ^1A''$	0	0.001		0	0	0
	$3\ ^1A''$	0	0		0	0	0
	$4\ ^1A'$	0.188	0.209	0.035-0.17	0.215	0.16	0.179
	$4\ ^1A''$	0	0		0	0	0.001
	$5\ ^1A'$	0.547	0.43	0.51	0.377	0.442	0.471
Adenine	$1\ ^1A''$	0	0	0.001–0.007	0.001	0.000	0.001
	$2\ ^1A'$	0.037	0.002	0.004–0.03	0.091	0.018	0.006
	$3\ ^1A'$	0.276	0.297	0.17–0.36	0.244	0.252	0.274
	$2\ ^1A''$	0	0	0.003–0.005	0.002	0.002	0.002
	$4\ ^1A'$	0.496	0.513	0.51	0.563	0.384	0.249
	$5\ ^1A'$	0.085	0.07		0.044	0.018	0.257

[a]Taken from literature.[41]

Table VI, it is easily recognized that the computed ADC(3/2) values lie usually within the range of the literature data or are slightly larger. Overall, the agreement between the ADC(3/2) values and the literature data is excellent. Similarly, ADC(2)-s yields oscillator strengths in good agreement with the lit-erature data, but with sometimes larger deviations from the ADC(3/2) values, in particular when doubly excited config-uration are important for the description of the excited state under consideration. The same holds for CC2 and EOM-CCSD as well. ADC(2)-x underestimates oscillator strengths
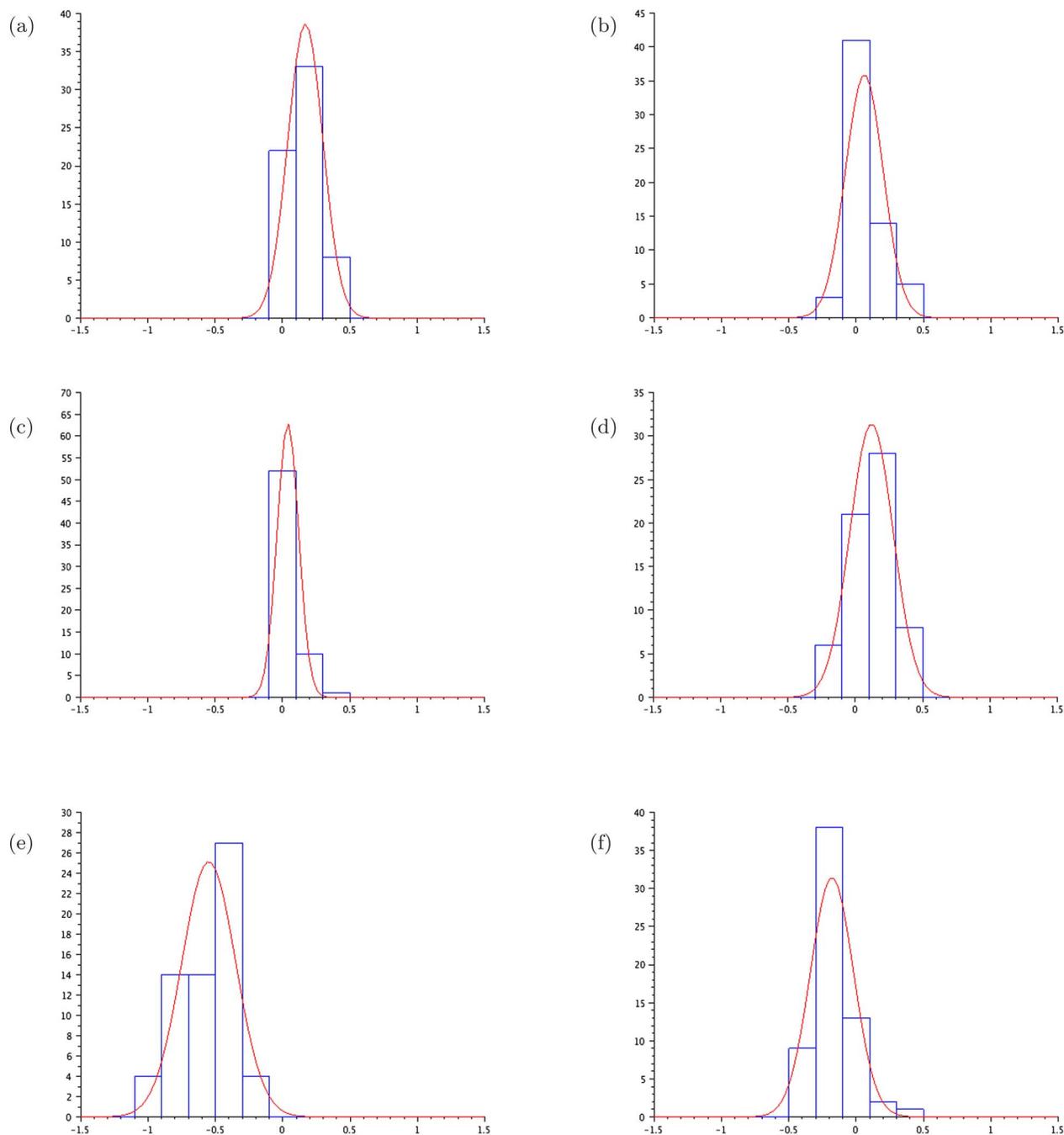
FIG. 5. Histograms of the distribution of deviations of all calculated triplet excited states with respect to the best estimates at the theoretical levels of (a) CC2, (b) CCSD, (c) CC3, (d) ADC(2)-s, (e) ADC(2)-x, and (f) ADC(3).

consistently, which certainly originates from the strong underestimation of excitation energies in general, since the excitation energies enter linearly into computation of the oscillator strengths.

V. BRIEF SUMMARY AND CONCLUSIONS

The accuracies of the algebraic diagrammatic construction schemes of the polarisation propagator (ADC) in second and third order perturbation theory for the calculation of excitation energies and oscillator strengths have been investigated

with respect to Thiel's recently established benchmark set. The calculation of 141 vertical excited singlet and 71 triplet states of 28 small to medium-sized organic molecules has revealed that ADC(3) exhibits mean error and standard deviation of 0.12 ± 0.28 eV for singlet states and -0.18 ± 0.16 eV for triplet states when the provided theoretical best estimates are used as benchmark. Accordingly, ADC(2)-s and ADC(2)-x calculations revealed accuracies of 0.22 ± 0.38 eV and -0.70 ± 0.37 for singlets and 0.12 ± 0.16 and -0.55 ± 0.20 for triplets, respectively. While the perturbation theoretical consistent methods ADC(2)-s and ADC(3) provide a

balanced description of the excited states, the *ad hoc* extension of the 2p-2h block in the ADC(2)-x matrix to first order perturbation theory leads to a drastic underestimation of the vertical excitation energies.

It is important to note, though, that some of the benchmark data have been obtained at CC3 level, which itself exhibits an error. Hence, for a comparison of CC3 and ADC(3), non-CC3 benchmark values were used, which comprise 84 singlet states and 19 triplet states. For these singlet states CC3 exhibits an accuracy of 0.23 ± 0.21 and ADC(3) an accuracy of 0.08 ± 0.27, and accordingly for the triplet states of 0.12 ± 0.10 eV and -0.10 ± 0.13 eV. Hence, based on the quality of the existing benchmark set it is difficult if not impossible to judge whether ADC(3) or CC3 is more accurate. A previous analysis of the accuracy of CC3 and ADC(3) in the description of excitation energies of atoms and diatomic molecules has yielded a slightly better accuracy of CC3. This study, however, contained pathological cases with ground-state multi-reference character for which ADC methods are known to exhibit larger problems than iterative CC ground-state schemes.

Besides the accuracy, our extensive investigation here has demonstrated the large range of applicability of the ADC(3) method. Owing to its rather favourable scaling of the computational effort with $O(N^6)$ with system size in contrast to $O(N^7)$ for CC3, it is applicable to fairly large molecules with up to 25 atoms of the second row of the Periodic Table. The specific number of atoms clearly depends on the employed basis and the available computational hardware. So far, the largest ADC(3) calculation performed with the current implementation comprised close to 450 basis functions, while the largest calculation for the present benchmark set involved 238 basis functions. Hence, we advocate ADC(3) as new benchmark method for excited states of molecules of that size, since in contrast to CC2 and ADC(2)-s it also captures double excitation character correctly. The method will be made available in one of the next releases of the Q-Chem program package.

In the future, we plan to further improve the accuracy and the computational efficiency of the ADC(3) method. For example, the MP(2) density matrix correction, that is a finite perturbation expansion to the one-particle density matrix, is not always an adequate treatment. In general, it is possible to extend the strict third-order expressions in the ADC matrix where the density matrix explicitly appears. These expressions are the so-called self-energy terms

$$\Sigma_{pq}(\infty) = \sum_{rs} \langle pq| |qs \rangle \rho_{sr}^{(i)}. \tag{5}$$

Here $\rho_{sr}^{(i)}$ is the correlation density, which is defined as the difference between the exact ground-state one-particle density matrix and the HF ground state density matrix

$$\rho^{(i)} = \rho - \rho^{(0)}. \tag{6}$$

Since zeroth- and first-order contributions vanish, only second-order corrections contribute and appear for the first time in ADC(3). For future improvement it is thus advisable to replace the MP(2) density matrix correction with the density matrix correction arising from the so-called Dyson expansion method.[52–54] The method is based on an iterative procedure

in third-order perturbation theory to the electron propagator and has proven to give better results for smaller molecular systems.[31,39]

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