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ABSTRACT

An *ad hoc* modification of the algebraic-diagrammatic construction (ADC) scheme for the polarization propagator is presented. Within this approach, all first-order Møller–Plesset correlation coefficients occurring in the second-order ADC secular matrix are replaced by amplitudes obtained from a coupled cluster doubles (CCD) calculation. This new hybrid method, denoted CCD-ADC(2), has been tested on a series of small diatomic and triatomic molecules and benchmarked with respect to Thiel's benchmark set of medium-sized organic molecules. For the latter, the calculation of 134 singlet and 71 triplet states has shown that CCD-ADC(2) exhibits a mean error and standard deviation of 0.15 ± 0.34 eV for singlet states and 0.0 ± 0.17 eV for triplet states with respect to the provided theoretical best estimates, whereas standard ADC(2) has a mean error and standard deviation of 0.22 ± 0.30 eV for singlet and 0.12 ± 0.16 eV for triplet states. The corresponding extended second-order schemes ADC(2)-x and CCD-ADC(2)-x revealed accuracies of -0.70 ± 0.32 eV and -0.76 ± 0.33 eV for singlet states and -0.55 ± 0.20 eV and -0.67 ± 0.22 eV for triplet states, respectively. Furthermore, the investigation of excited-state potential energy curves along the dissociation of the N₂ molecule has shown that the higher reliability of the ground-state CCD method as compared to MP2 is also inherent to the excited states. While the curves obtained at the ADC(2) level break down at around 2 Å, the ones obtained at CCD-ADC(2) remain reasonable up to about 3.5 Å.

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I. INTRODUCTION

Since experimental optical spectra of molecular systems generally provide only indirect information on molecular structure or dynamics and their interpretation is in many cases not straightforward, an adequate theoretical description is indispensable for a comprehensive understanding of photophysical and photochemical processes. While theoretical methods available for the electronic ground state are highly advanced and yield satisfying results for most cases, the corresponding description of electronically excited states lags somewhat behind, and further improvements and theoretical methodologies are needed.

A prominent approach for obtaining excitation energies is the use of (linear) response theory,^{1,2} where the excitation energies are

obtained as eigenvalues of linear response eigenvalue equations. The simplest method is the random-phase approximation (RPA), which describes energies and transition moments up to first order of perturbation theory.^{3–6} Most notable examples for methods of higher-order in perturbation theory are the second-order polarization propagator approximation (SOPPA)^{7–9} and the algebraic-diagrammatic construction (ADC) method for the polarization propagator of second order, ADC(2).^{6,10} In these methods, the excitation energies and transition moments are determined directly and have the property of being size-consistent (or size-intensive).

Another family of methods to be mentioned here is based on coupled-cluster (CC) theory,^{11–13} which has been successfully developed and employed during the past decades. All these methods are based on the CC parameterization of the ground state and can

be divided into linear-response coupled cluster (LR-CC),^{14–16} the essentially equivalent equation-of-motion coupled cluster (EOM-CC),^{17–19} and the symmetry-adapted cluster configuration interaction (SAC-CI)^{20–22} approximations. Within the CC framework, a hierarchy of successively more accurate computational schemes can be established, including coupled cluster singles (CCS), CC2, coupled cluster singles and doubles (CCSD), CC3, and coupled cluster singles and doubles triple (CCSDT), for example. In these acronyms, S, D, and T stand for single, double, and triple excitations, respectively, considered in the configuration space with respect to the Hartree–Fock (HF) reference determinant.

Both CC and ADC approaches stand out with their high accuracy and reliability and can thus be used as “black-box methods,” but on the other hand, they are computationally expensive when it comes to highly accurate calculations, and the CC eigenvalue equation is not Hermitian. Furthermore, while ADC methods are fully size-consistent, this is not true for EOM-CC transition moments. To rigorously calculate excited-state properties, the CC equations thus have to be solved twice, once for the left-hand and once for the right-hand eigenvectors. ADC methods, on the other hand, are Hermitian and computationally generally less demanding;^{23,24} however, the results obtained with ADC(2) are often only of modest accuracy. The largest limitation of ADC schemes is the ground-state description since they are all built upon Møller–Plesset (MP) perturbation theory.^{25,26} ADC(n) is thus clear to give reasonable results only when the ground state is well described by the corresponding MP n method.²⁴ Hence, all systems with a strong multireference character in the ground state, for example transition metal complexes or open-shell singlets, but also the case of bond dissociation cannot be reasonably well described by standard ADC methods. One possible way to overcome this deficiency is, for example, by using spin-flip (SF) approaches,^{27–33} which will be discussed a little bit more in detail later.

In this work, however, we aim at improving the ground-state description by something similar to what has been done before for the related SOPPA method.^{34–38} Geertsen and Oddershede developed a variant of SOPPA called the coupled-cluster polarization propagator approximation (CCPPA) where they essentially replaced Rayleigh–Schrödinger (RS) correlation coefficients by CC amplitudes.^{34,37} With this and similar modifications of SOPPA, significantly improved results for excitation energies, polarizabilities, and other properties in systems such as Li[−], Be, BH, and CH⁺ among others were obtained.^{34,39–45} Due to the similarity of SOPPA and ADC(2), we follow the same idea and try to exploit the advantages of both ADC and CC: the reliability of CC for the ground state and the low computational cost of the ADC scheme for the polarization propagator. To be more precise, the Hermitian ADC(2) secular equation including a CC ground-state description shall be solved. This means we construct the ADC(2) scheme for the polarization propagator from a CC reference function and not from an MP one. In summary, the CC doubles amplitudes are used instead of the MP correlation coefficients in the Hermitian ADC(2) matrix and the secular equation shall be solved for excitation energies. The most logical choice for that is coupled cluster doubles (CCD) since the equation for the correlation energy of MP2 and CCD is formally identical and the difference lies in the definition of the so-called T_2 amplitudes (see Sec. II). In CCD, the ground state is solved iteratively in contrast to MP2. Hence, CCD is expected to be generally more

reliable.¹³ The question is whether this will have positive effects on the description of excited electronic states via ADC(2) as well, in particular when MP2 yields only a poor description of the ground state.

These new methods, where the MP amplitudes are replaced by CCD ones in the second-order ADC scheme, denoted CCD-ADC(2), are tested on a first set of small atomic and molecular systems and compared to standard ADC(2) calculations and full configuration interaction (FCI) or experiment. Furthermore, the new ADC variants are benchmarked with respect to the test set established by Thiel and co-workers^{46–48} and tested for the dissociation of diatomic molecules, where MP (and hence also standard ADC) is known to fail.

This paper is organized as follows: first, the underlying theory of the algebraic-diagrammatic construction scheme for the polarization propagator and coupled cluster shall be summarized briefly. Then, the implementation is described shortly and details for the subsequent calculations are given. In Sec. IV, we first present results obtained for a set of small test systems, then the new ADC variants are benchmarked with respect to Thiel’s benchmark set, and finally, the excited-state dissociation curves of the N₂ molecule are presented. The paper concludes with a brief summary and outlook.

II. THEORETICAL DETAILS

In the following, we give a brief review of ground-state CC methods and the ADC scheme for the polarization propagator and describe the relation between standard ADC(2) and with the CC-based one. While standard ADC(2) can be rigorously derived based on the MP ground state, an intermediate-state representation (ISR) formulation based on coupled cluster requires additional approximations to the ground state (*vide infra*). Thus, the scheme presented here corresponds more to an *ad hoc* modification of the original scheme.

A. Coupled-cluster theory

In coupled-cluster (CC) theory,^{11,12,49–51} the ground-state wave function $|\Psi_0\rangle$ is parameterized as

$$|\Psi_0\rangle = e^{\hat{T}}|\Phi_0\rangle, \quad (1)$$

where the so-called cluster operator \hat{T} is a sum of excitation operators

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \dots + \hat{T}_N \quad (2)$$

that create single, double, etc., substitutions from the reference $|\Phi_0\rangle$, usually the Hartree–Fock (HF) wave function, and N is the number of electrons in the system. If the cluster operator is not truncated, the exact result within the given one-electron basis set is obtained. In practice, it is truncated, giving rise to a hierarchy of coupled-cluster schemes. For double excitations only, $\hat{T} = \hat{T}_2$, this is referred to as coupled cluster doubles (CCD),^{52,53} if singles are included, $\hat{T} = \hat{T}_1 + \hat{T}_2$, the coupled cluster singles and doubles (CCSD) model is obtained,⁵⁴ and so on. In the formalism of second quantization, these excitation operators are given as

$$\hat{T}_1 = \sum_{ia} t_i^a \hat{a}_a^\dagger \hat{a}_i, \quad (3)$$

$$\hat{T}_2 = \frac{1}{4} \sum_{ijab} t_{ij}^{ab} \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i, \quad (4)$$

with the CC amplitudes $t_i^a, t_{ij}^{ab}, \dots$ that have to be determined. Here and in the following, the indices i, j, \dots are used to refer to occupied orbitals in the reference and a, b, \dots denote unoccupied (virtual) ones, while p, q, \dots is used for the general case. Following the standard procedure, the CC amplitudes are not obtained via the variational principle but rather by projection techniques. For that, the ansatz for the wave function (1) is plugged into the electronic Schrödinger equation, multiplied by $\exp(-\hat{T})$ from the left and projected onto the excited determinant manifold, e.g.,

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \quad (5)$$

yielding the equation for t_{ij}^{ab} , where $|\Phi_{ij}^{ab}\rangle$ is a doubly excited determinant. The CC ground-state energy is obtained by projection onto the HF determinant

$$E_0^{\text{CC}} = \langle \Phi_0 | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle, \quad (6)$$

where \hat{H} is the electronic Hamiltonian. Since the amplitude equations are coupled and nonlinear, they have to be solved in an iterative manner.

B. Algebraic-diagrammatic construction for the polarization propagator

In the intermediate state representation (ISR) of the algebraic-diagrammatic construction scheme,^{24,55–58} the Hamiltonian in the standard MP splitting, $\hat{H} = \hat{H}_0 + \hat{H}_1$, shifted by the ground-state energy E_0 is represented within the orthonormal basis of the so-called intermediate states (ISs)

$$M_{IJ} = \langle \tilde{\Psi}_I | \hat{H} - E_0 | \tilde{\Psi}_J \rangle, \quad (7)$$

which leads to the Hermitian eigenvalue problem

$$\mathbf{M}\mathbf{X} = \mathbf{X}\mathbf{\Omega}, \quad \mathbf{X}^\dagger \mathbf{X} = \mathbf{1}, \quad (8)$$

where \mathbf{X} is the matrix of eigenvectors and $\mathbf{\Omega}$ is the diagonal matrix of eigenvalues that correspond to the excitation energies $\omega_n = E_n - E_0$. Spectral intensities of a transition operator $\hat{\mu}$ are obtained from the eigenvectors and the so-called modified transition moments \mathbf{F} with

$$F_I = \langle \tilde{\Psi}_I | \hat{\mu} | \Psi_0 \rangle. \quad (9)$$

The ISs $|\tilde{\Psi}_I\rangle$ are constructed from the so-called correlated excited states

$$|\Psi_I^0\rangle = \hat{C}_I |\Psi_0\rangle, \quad (10)$$

where $\{\hat{C}_I\} = \{\hat{a}_a^\dagger \hat{a}_i; \hat{a}_a^\dagger \hat{a}_b^\dagger \hat{a}_j \hat{a}_i; a < b, i < j; \dots\}$ denote physical excitation operators of particle-hole (p - h), $2p$ - $2h$, \dots type and $|\Psi_0\rangle$ is the formally exact ground state. The correlated excited states are successively orthonormalized with respect to the ground state and among each other in a Gram–Schmidt-like (GS) procedure which yields the IS

$$|\Psi_I^0\rangle = \hat{C}_I |\Psi_0\rangle \xrightarrow{\text{GS}} |\tilde{\Psi}_I\rangle. \quad (11)$$

Since the exact ground state $|\Psi_0\rangle$ is not known, an approximation has to be employed. In the standard derivation of ADC,^{24,58} it is expanded in a Møller–Plesset series^{25,26} according to

$$|\Psi_0\rangle = |\Phi_0\rangle + |\Psi_0^{(1)}\rangle + |\Psi_0^{(2)}\rangle + \dots, \quad (12)$$

and thus, also the secular matrix is expanded in a series, $\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \dots$. In principle, also a parameterization according to Eq. (1) truncated at some order could be employed.

Both the standard and the CC-based ADC(2) scheme for excitation energies can formally be derived by using the ansatz

$$|\Psi_0\rangle = |\Phi_0\rangle + \hat{T}_2 |\Phi_0\rangle + \mathcal{O}(2) \quad (13)$$

for the ground-state wave function in Eq. (10), where second- and higher-order contributions do not enter the derivation of $M_{ia,jb}^{(0-2)}$. This ansatz has also been the basis of the CCPA method by Geertsen and Oddershede,^{34,37} which is motivated by the requirement that in the first iteration of the CCD equations, the original SOPPA or in this case ADC(2) method is obtained. This results in the different definition of the \hat{T}_2 operator, which for CC-ADC(2) is given by Eq. (4), whereas for the standard ADC variant instead of the CC doubles amplitudes t_{ij}^{ab} , the first-order doubles amplitudes κ_{ij}^{ab} from MP perturbation theory are used, which are given as

$$\kappa_{ij}^{ab} = \frac{\langle ab || ij \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (14)$$

where $\langle ab || ij \rangle$ is an antisymmetrized two-electron integral and ε_p are HF orbital energies, thus yielding the first-order MP correction $|\Psi_0^{(1)}\rangle$ to the ground-state wave function. However, a full derivation of the CC-ADC(2) equations is beyond the scope of the present work; just the meaning and implications relevant here shall be discussed briefly. Yet, it is important to note that the truncation of Eq. (13) only applies to the propagator or ADC(2) calculation, and the t_{ij}^{ab} amplitudes themselves are determined as discussed in Sec. II A.

In a second-order ADC calculation, all terms in \mathbf{M} through second order in the fluctuation potential are included, but the κ_{ij}^{ab} amplitudes appear only in the p - h/p - h block of the ADC(2) matrix. In particular, they arise from the $\langle \Psi_0^{(1)} | \hat{a}_i^\dagger \hat{a}_a \hat{H}_0 \hat{a}_b^\dagger \hat{a}_j | \Psi_0^{(1)} \rangle$, $\langle \Phi_0 | \hat{a}_i^\dagger \hat{a}_a \hat{H}_1 \hat{a}_b^\dagger \hat{a}_j | \Psi_0^{(1)} \rangle$, and $\langle \Psi_0^{(1)} | \hat{a}_i^\dagger \hat{a}_a \hat{H}_1 \hat{a}_b^\dagger \hat{a}_j | \Phi_0 \rangle$ terms. The CCD-ADC(2) method presented here is thus obtained by replacing the κ_{ij}^{ab} of Eq. (14) by the converged CCD t_{ij}^{ab} amplitudes in the final $\mathbf{M}^{(2)}$ matrix equations,⁵⁹ as implemented in the `adcmn` module⁶⁰ of the Q-CHEM program package.⁶¹ In this way, the standard ADC(2) method is recovered in the first cluster iteration.

Comparing the expressions for the MP2 and CCD correlation energy,

$$E_0^{(2)} = -\frac{1}{4} \sum_{ijab} \kappa_{ij}^{ab} \langle ij || ab \rangle, \quad (15)$$

$$E_0^{\text{CCD}} = -\frac{1}{4} \sum_{ijab} t_{ij}^{ab} \langle ij || ab \rangle, \quad (16)$$

replacing the first-order MP correlation coefficients by coupled-cluster doubles amplitudes corresponds to additionally including double excitations to infinite order in the ground-state energy. In a similar way, particle-hole self-energy diagrams from double substitutions are now in principle included through infinite order for matrix elements of the form that appear in the p - h / p - h block of $\mathbf{M}^{(2)}$.^{37,41,49,62} An analogous rigorous order analysis is only possible for the matrix elements of the ADC matrix,⁵⁵ while for the excitation energies obtained after diagonalization, this is generally not unambiguously possible.

From a CC point of view, in standard ADC(2), we are thus constructing \mathbf{M} (and \mathbf{F}) using the doubles amplitudes of the first CC (either CCD or CCSD) iteration, whereas the converged amplitudes are used in CC-ADC(2). However, we want to emphasize that the CCD-ADC(2) and CCSD-ADC(2) methods obtained in this way are still second-order approximations to the polarization propagator.

In principle, the single substitution coefficients κ_i^a from the second-order wave-function correction $|\Psi_0^{(2)}\rangle$ are needed as well for a consistent second-order ADC scheme. However, the single excitations do not contribute to \mathbf{M} but only to the modified transition moments \mathbf{F} [Eq. (9)] which are needed for (transition) properties. The effect of the amplitudes on the transition moments will be studied in Paper II.⁶³ Thus, even though CCSD is in general a more reliable method than CCD,¹³ the focus in this paper will be on the ADC(2) variant with CCD amplitudes since the CCSD singles amplitudes would not be used in the calculation of excitation energies, which in our opinion would make the approach more inconsistent. The difference between CCD and CCSD amplitudes in ADC will be studied in more detail in Paper II.⁶³

C. Implementation

The implementation was carried out within a development version of the Q-CHEM program,⁶¹ which contains the necessary functions to perform CC and ADC calculations in the *ccman2* and *adcmn* modules, respectively.⁶⁰ Hence, prior to the ADC(2) calculation, a CC calculation is carried out, and the results for the energy and amplitudes are saved and used within the diagonalization of the ADC(2) matrix via the Davidson algorithm,⁶⁴ in which the MP amplitudes are replaced by the CC ones.

This practical approach has been applied to both ADC(2) and its extended version ADC(2)-x. The latter variant is obtained by expanding the $2p$ - $2h$ / $2p$ - $2h$ block of the ADC matrix through

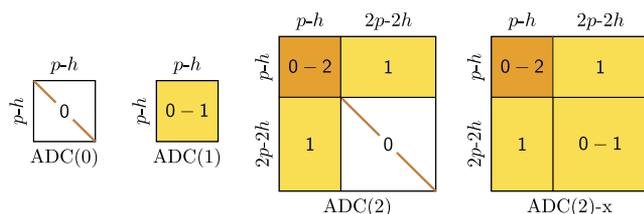


FIG. 1. Structure of the ADC matrix in zeroth, first, and second and extended second-order schemes ADC(2) and ADC(2)-x, respectively. For the individual blocks, the levels of perturbation theory are given (white: zeroth order, yellow: first order, and orange: second order).

first order in an *ad hoc* fashion (Fig. 1). It should be noted that the purpose of ADC(2)-x is not to improve the description of p - h excited states but rather as a diagnostic for $2p$ - $2h$ admixtures. These new hybrid methods are denoted CCD-ADC(2) and CCD-ADC(2)-x, respectively, if CCD doubles amplitudes are used and correspondingly CCSD-ADC(2) if the CCSD ones are used.

III. COMPUTATIONAL DETAILS

In the present study, the following atoms and small molecules have been considered at first: H₂O, HF, Ne, N₂, CH₂, and BH. Results for the ground state and some of the lowest vertical excitation energies of these systems at the levels of FCI, CC, and standard ADC methods employing modified cc-pVDZ basis sets augmented with diffuse functions are available (see below).^{23,65-68} For comparison, the same input data as in the FCI work was used.⁶⁵⁻⁶⁸ In practice, this means that for HF, BH, and N₂, the internuclear distances are 1.732 879 5 a_0 , 2.3289 a_0 , and 2.068 a_0 , respectively. For the triatomic molecules, C_{2v} symmetry was used with the following coordinates (in a_0): O(0, 0, 0) and H(0, ±1.429 937 284, -1.107 175 113) for water and for methylene C(0, 0, 0) and H(±1.644 403, 0, 1.322 13) for the *singlet* excitations and C(0, 0, 0) and H(±1.644 403, 0, 1.323 13) for the *triplet* excitations. For the Ne, BH, and CH₂ singlet excitations, the entire molecular orbital space was used in the correlated calculations, whereas for all other cases, the 1s orbitals of the first-row elements were kept frozen. For N₂, Dunning's cc-pVDZ basis set⁶⁹ was used. For the *singlet* excitations of Ne, one *s* function with exponent 0.04 and one *p* function with exponent 0.03 was added. For BH, two *s*, two *p*, and two *d* functions with exponents of 0.031 05, 0.009 244, 0.023 78, 0.005 129, 0.0904, and 0.023 83, respectively, were added to the standard cc-pVDZ basis of B, respectively.⁶⁵ For H, two *s* and two *p* functions were added with exponents 0.0297, 0.007 25, 0.141, and 0.027 35. For CH₂, the basis of C was augmented with one *s* function of exponent 0.015, and for H, one *s* function with exponent 0.025 was added. For H₂O, the oxygen basis was augmented with one *s* function of exponent 0.078 96 and one *p* function of exponent 0.068 56, and for H, one *s* function with exponent 0.029 74 was added. For HF and the *triplet* excitations of Ne, the aug-cc-pVDZ basis set was used.⁶⁷

The consistency of our input data with the ones used in previous FCI calculations was checked by comparing the HF, MP2, and CCSD ground-state energies, as well as the EOM-CCSD, ADC(1), and ADC(2) excitation energies as far as they were available.²³ For HF and the Ne and BH triplets, the configuration interaction singles (CIS) energies were compared.⁶⁷ We could not reproduce the Hartree-Fock ground-state energy of -38.884 254 E_h reported in Ref. 68 but obtained the same value as in Ref. 23 (-38.884 244 E_h). All calculations have been carried out with the Q-CHEM program package⁶¹ interfaced to a development version of the *adcmn* module. Also the standard-ADC excitation energies have been calculated again, where sometimes discrepancies in the order of 0.01 eV compared to literature²³ occur, which we account to round-off errors.

In order to check the performance of CCD-ADC(2) on unsaturated organic molecules, vertical excitation energies of the benchmark set established by Thiel and co-workers⁴⁶⁻⁴⁸ were calculated using the standard valence triple-zeta polarization (TZVP) basis set

and geometries from the literature (optimized at the MP2/6-31G* level of theory) employing Abelian point-group symmetry.

IV. RESULTS AND DISCUSSION

A. Small diatomic and triatomic molecules

In Table I, we compare ADC(1), ADC(2), CCD-ADC(2), ADC(2)-x, and CCD-ADC(2)-x results for the lowest excited singlet and triplet excited states of H₂O, HF, Ne, N₂, CH₂, and BH with full configuration interaction (FCI) results. For a comparison of ADC methods with coupled cluster results or with experiment, the reader is referred to Refs. 23, 65, 66, and 68 and references therein. In this work, we focus on the difference between the standard ADC(2) methods with the hybrid CCD-ADC(2) ones.

The ten-electron systems H₂O, HF, and Ne have in common that the weight of the Hartree-Fock determinant in the FCI wave function is larger than 90%.^{65,67} Electron correlation is almost purely dynamic in nature, and MP2 already recovers a large amount of it.^{65,66} In total, the first half of Table I comprises 34 transitions, all of which are considered in the statistical error evaluation.

The excitation energies obtained at the ADC(1) level are identical to the ones of configuration interaction singles (CIS) or also coupled cluster singles (CCS) and are of rather poor quality compared to FCI. The mean absolute error considering all 34 transitions amounts to 1.25 eV with an absolute maximum deviation of 3.73 eV for the 3¹S state of Ne. We here note a confusion in Ref. 23, where the maximum deviation of ADC(1) was indicated as 2.51 eV (the 1¹Π_u state of N₂). Either the deviation of the 3¹S state of Ne has been overlooked, or this state and not the 2¹S state was exempted, as stated at the bottom of Table II in Ref. 23.

Going to the second-order ADC levels, the description of the excitation energies becomes significantly better.²³ For the ten-electron systems H₂O, HF, and Ne, no significant change in the mean absolute errors is observed when using CCD amplitudes within ADC(2) or ADC(2)-x. The improvement of both CCD-ADC(2) schemes over standard ADC(2) is merely 0.02 and 0.03 eV for water in the standard and extended versions, respectively. For hydrogen fluoride, a minor deterioration of 0.01 eV and for neon, an improvement of the same magnitude are observed for both CCD-ADC(2) and CCD-ADC(2)-x variants. This indicates that the ground state is already sufficiently well described at the MP2 level and no major improvement is achieved by CCD, as perhaps expected. Furthermore, it is important to note that both ADC(2) variants consistently underestimate the excitation energies of these three systems. Still, ADC(2)-x and CCD-ADC(2)-x excitation energies are worse than the ones of the standard ADC(2) versions. This is due to the *ad hoc* extension of the 2*p*-2*h*/2*p*-2*h* block to first order, which improves the description of double excitations at the cost of a less balanced description of singly excited states, leading to a large underestimation of excitation energies.²⁴ Thus, an extension to higher orders of perturbation theory in some parts does not necessarily always lead to an improved description.

Taking a closer look at the different types of excited states, one can observe that the mean absolute error $\bar{\Delta}_{\text{abs}}$ is always smaller for triplet than for singlet states. As discussed in Ref. 67, triplet states have, in general, a more single-excitation character than the

corresponding excited singlet states and are therefore usually better described at a second-order level. For instance, the mean absolute error for the singlet states of neon is 0.83 and 0.81 eV for ADC(2) and CCD-ADC(2), respectively, and for triplet states, it is 0.68 and 0.67 eV. The change in the excitation energies when using CCD instead of MP2 amplitudes, however, is the same for both singlet and triplet states.

In the second half of Table I, the results for N₂, CH₂, and BH are presented. The 14-electron system N₂ differs from the previous systems since it has a π-bond and slightly larger static correlation.⁶⁷ While for the first three systems in Table I, ADC(1) overestimates the excitation energies for all considered states and both ADC(2) variants underestimate them, for N₂, it is the opposite: ADC(1) underestimates most excitation energies quite strongly, and ADC(2) overestimates all excitation energies, on average by 0.4 eV. Employing CCD amplitudes within ADC(2) improves it slightly, reducing $\bar{\Delta}_{\text{abs}}$ to 0.36 eV. ADC(2)-x, on the other hand, underestimates all excitation energies with the exception of the 3³Σ_u⁺ state, on average by 0.41 eV. The use of CCD amplitudes within ADC(2)-x gives a similar minor improvement of 0.03 eV.

The last two systems considered here are yet different from the previous ones since CH₂ and BH can be considered as *quasi-open-shell* systems, which means that they possess only a small energy gap between occupied and virtual orbitals.²³ This is reflected by unusually low excitation energies. As noted by Trofimov and co-workers,²³ the second-order results for the single excitation energies with ADC(2) and CC2 are surprisingly good, both having mean errors below 0.15 eV, but the irregularity is noted at the ADC(3) level, where the mean absolute errors are significantly higher. Similar to this previous study,²³ for the ADC(2) versions, no results for excited states with a dominant double excitation character are given since they are treated only in zeroth order in ADC(2), and they are also always exempted from the statistical error evaluation.

Concerning the CH₂ molecule, ADC(2) underestimates essentially all excitation energies (except for the 1¹A₂ one) but has a surprisingly small mean absolute error of 0.12 eV. As expected, the use of CCD amplitudes instead of MP ones has a significantly larger influence here than for the previous systems. In general, it can be observed that the excitation energies increase by about 0.3–0.4 eV on average, which leads to a systematic overestimation with a mean (absolute) error of 0.23 eV. Furthermore, it is important to notice that due to the choice of the 1¹A₁ reference state, the true ground state 1³B₁ has a negative excitation energy.²³ This is also reflected in all given methods, except CCD-ADC(2) which raises its excitation energy to a positive value. The ADC(2)-x scheme again systematically underestimates all excitation energies, by 0.62 eV on average (considering only dominant singly excited states), which is even more pronounced for the doubly excited states, where the maximum absolute deviation goes up to 1.14 eV. The effect of using CCD amplitudes in ADC(2)-x is the same for singly excited states as in ADC(2), meaning that it raises the excitation energy by about 0.3–0.4 eV. However, in this case, this corresponds to a systematic improvement to a mean absolute error of only 0.3 eV, which is thus 0.32 eV smaller than for standard ADC(2)-x.

The difference in the excitation energies with MP or CCD amplitudes in ADC(2) and ADC(2)-x can most likely be explained

TABLE I. FCI, ADC, and CCD-ADC results for vertical excitation energies (in eV) of H₂O, HF, Ne, N₂, CH₂, and BH. The last two lines for each system give the mean absolute error ($\overline{\Delta}_{\text{abs}}$) and the maximum absolute error (Δ_{max}) in electron volt, respectively, relative to FCI. "(2)" indicates a dominant double-excitation character. These transitions were excluded in the statistical error evaluation.

Transition	FCI ^a	ADC(1)	ADC(2)	CCD-ADC(2)	ADC(2)-x	CCD-ADC(2)-x
H ₂ O 1 ¹ A ₁ →						
2 ¹ A ₁	9.87	10.98	9.37	9.42	9.11	9.16
1 ¹ B ₁	7.45	8.67	6.95	6.98	6.68	6.71
1 ¹ B ₂	11.61	12.64	10.97	11.01	10.83	10.86
1 ¹ A ₂	9.21	10.36	8.58	8.60	8.42	8.44
1 ³ B ₁	7.06	8.00	6.61	6.64	6.32	6.35
1 ³ A ₂	9.04	10.03	8.46	8.48	8.29	8.30
1 ³ A ₁	9.44	10.15	9.00	9.05	8.73	8.77
2 ³ A ₁	10.83	11.43	10.47	10.46	10.18	10.17
2 ³ B ₁	11.05	11.98	10.57	10.58	10.34	10.35
1 ³ B ₂	11.32	11.89	10.77	10.80	10.60	10.63
$\overline{\Delta}_{\text{abs}}$		0.92	0.51	0.49	0.74	0.71
Δ_{max}		1.22	0.64	0.61	0.79	0.77
HF 1 ¹ Σ ⁺ →						
1 ¹ Π	10.44	11.76	9.63	9.64	9.48	9.49
2 ¹ Π	14.21	15.48	13.35	13.35	13.27	13.28
2 ¹ Σ ⁺	14.58	15.42	13.91	13.94	13.78	13.80
1 ¹ Δ	15.2	16.37	14.46	14.44	14.29	14.28
1 ¹ Σ ⁻	15.28	16.36	14.54	14.52	14.36	14.34
3 ¹ Π	15.77	17.24	14.92	14.92	14.79	14.79
3 ¹ Σ ⁺	16.43	17.84	15.32	15.34	15.33	15.36
1 ³ Π	10.04	11.07	9.30	9.30	9.12	9.13
1 ³ Σ ⁺	13.54	13.59	13.05	13.06	12.87	12.88
2 ³ Π	14.01	15.18	13.14	13.14	13.09	13.08
2 ³ Σ ⁺	14.46	15.24	13.80	13.76	13.59	13.56
1 ³ Δ	14.93	15.89	14.22	14.20	14.03	14.01
1 ³ Σ ⁻	15.25	16.36	14.52	14.50	14.34	14.32
3 ³ Π	15.57	16.91	14.72	14.72	14.60	14.59
$\overline{\Delta}_{\text{abs}}$		1.07	0.77	0.78	0.91	0.92
Δ_{max}		1.47	1.11	1.08	1.10	1.07
Ne 1 ¹ S →						
1 ¹ P	16.40	18.09	15.62	15.64	15.54	15.56
1 ¹ D	18.21	19.95	17.30	17.31	17.34	17.31
2 ¹ P	18.26	19.98	17.34	17.35	17.38	17.39
2 ¹ S	18.48	20.42	17.43	17.45	17.55	17.57
3 ¹ S	44.05	47.78	43.57	43.60	43.15	43.19
1 ³ P	18.70	19.94	17.99	18.00	17.78	17.79
1 ³ S	19.96	20.90	19.22	19.20	19.09	19.07
1 ³ D	20.62	21.80	19.83	19.83	19.72	19.72
2 ³ P	20.97	22.27	20.15	20.15	20.05	20.05
2 ³ S	45.43	48.47	45.11	45.13	44.46	44.49
$\overline{\Delta}_{\text{abs}}$		1.85	0.75	0.74	0.90	0.89
Δ_{max}		3.73	1.05	1.03	0.97	0.94
N ₂ 1 ¹ Σ _g ⁺ →						
1 ¹ Π _g	9.58	10.07	9.76	9.77	8.89	8.90
1 ¹ Σ _u ⁻	10.33	8.65	10.62	10.61	10.23	10.22
1 ¹ Δ _u	10.72	9.23	11.17	11.16	10.67	10.66
1 ¹ Π _u	13.61	16.12	14.56	14.64	12.35	12.41

TABLE I. (Continued.)

Transition	FCI ^a	ADC(1)	ADC(2)	CCD-ADC(2)	ADC(2)-x	CCD-ADC(2)-x
$1^3\Sigma_u^+$	7.90	6.37	8.31	8.01	7.97	7.68
$1^3\Pi_g$	8.16	8.05	8.33	8.34	7.61	7.62
$1^3\Delta_u$	9.19	7.48	9.52	9.39	9.16	9.04
$1^3\Sigma_u^-$	10.00	8.65	10.54	10.47	9.99	9.92
$1^3\Pi_u$	11.44	12.04	11.73	11.81	10.51	10.58
$\bar{\Delta}_{\text{abs}}$		1.27	0.40	0.36	0.41	0.38
Δ_{max}		2.51	0.95	1.02	1.26	1.20
$\text{CH}_2 1^1A_1 \rightarrow$						
$2^1A_1(2)$	4.66				3.55	3.55
3^1A_1	6.51	6.95	6.43	6.74	5.87	6.18
4^1A_1	8.48	8.86	8.28	8.59	7.84	8.14
1^1B_2	7.70	8.12	7.59	7.90	7.16	7.43
$2^1B_2(2)$	8.02				6.88	6.92
1^1B_1	1.79	1.65	1.65	2.07	1.20	1.61
$2^1B_1(2)$	8.91				8.30	8.30
$3^1B_1(2)$	10.55				10.01	10.01
1^1A_2	5.85	6.07	5.89	6.31	5.19	5.61
$2^1A_2(2)$	9.41				8.91	8.91
1^3A_1	6.39	6.69	6.27	6.59	5.74	6.04
2^3A_1	8.23	8.12	8.06	8.37	7.65	7.95
3^3A_1	9.84	10.18	9.73	10.04	9.20	9.50
$1^3B_2(2)$	6.41				5.27	5.28
2^3B_2	7.70	7...87	7.52	7.83	7.06	7.37
1^3B_1	-0.01	-0.49	-0.17	0.21	-0.59	-0.22
2^3B_1	8.38	8.77	8.30	8.60	7.71	7.93
1^3A_2	4.79	4.66	4.79	4.94	4.14	4.53
$\bar{\Delta}_{\text{abs}}$		0.29	0.12	0.23	0.62	0.30
Δ_{max}		0.48	0.20	0.46	1.14	1.13
$\text{BH } 1^1\Sigma^+ \rightarrow$						
$1^1\Pi$	2.94	2.84	2.85	3.36	2.34	2.83
$1^1\Delta(2)$	5.88				4.68	4.69
$2^1\Sigma^+$	6.38	6.37	6.30	6.73	5.85	6.26
$3^1\Sigma^+(2)$	7.00				5.45	5.47
$2^1\Pi$	7.47	7.37	7.35	7.79	6.89	7.30
$4^1\Sigma^+$	7.56	7.40	7.36	7.80	6.98	7.39
$3^1\Pi$	8.24	8.12	8.11	8.54	7.67	8.08
$1^3\Pi$	1.31	0.55	1.02	1.53	0.71	1.21
$1^3\Sigma^-(2)$	4.69				3.50	3.50
$1^3\Sigma^+$	6.26	6.02	6.14	6.57	5.69	6.11
$2^3\Sigma^+$	7.20	6.85	7.00	7.44	6.65	7.08
$2^3\Pi$	7.43	7.21	7.26	7.69	6.85	7.27
$3^3\Sigma^+$	7.62	7.40	7.54	7.97	7.06	7.46
$3^3\Pi$	7.92	7.77	7.92	8.33	7.38	7.71
$\bar{\Delta}_{\text{abs}}$		0.22	0.13	0.25	0.57	0.15
Δ_{max}		0.76	0.29	0.42	1.55	1.53

^aResults from the literature.^{23,65-68}

with the different ground-state energies. While for systems such as HF and Ne, CCD yields a ground-state energy of only about 0.06 eV lower than MP2, for CH₂ and BH, the CCD total energy is about 0.75 eV lower than the MP2 one, thus raising the excitation energies more strongly. Hence, for these systems, an iterated ground state is indeed crucial, and the good performance of standard ADC(2) seems just fortuitous. Another important point to notice is the behavior of ADC(2)-x and CCD-ADC(2)-x for excited states with a dominant double excitation character, where virtually no difference can be observed. This is due to the fact that the T_2 amplitudes occur only in the p - h block in ADC(2). Thus, pure double excitations are identical in all ADC(2) and CCD-ADC(2) schemes.

A similar picture is obtained for the BH molecule, where standard ADC(2) systematically underestimates excitation energies slightly with a small mean absolute error of 0.13 eV. CCD amplitudes again raise them by about 0.4 eV to give a mean error of 0.25 eV. ADC(2)-x again strongly underestimates excitation energies by 0.57 eV (counting only dominant single excitations), and CCD-ADC(2)-x significantly improves it to a slight underestimation of only 0.15 eV. The dominant doubly excited states remain again virtually unchanged, of course.

To summarize, no significant improvement was observed for those cases for which ADC(2) gave already surprisingly good results. However, the results did also not deteriorate when CCD amplitudes were used. In general, their influence was only marginal.

In order to further include a challenging case, we have calculated the lowest excited states of the ozone molecule, which exhibits a complicated ground-state electronic structure and has thus been used as a benchmark molecule in the development especially of multireference (MR) methodologies^{70–80} and compare the results to available experimental data.^{81,82} Improving the ground-state electronic structure by going from MP2 to CCD should thus improve the accuracy of the excitation energies. Therefore, vertical excitation energies have been calculated with ADC(2) and CCD-ADC(2) in combination with the cc-pVTZ basis set⁶⁹ using the experimental C_{2v} geometry of the 1A_1 ground state,⁸³ where the bond length and angle are 1.272 Å and 116.8°, respectively. From the results shown in Table II, it can be seen that for the first excited singlet state, 1A_2 , ADC(2) overestimates the excitation energy by more than 0.5 eV compared to experiment, whereas the CCD-ADC(2) variant is on spot. For the next state, 1B_1 , ADC(2) yields a better result than

CCD-ADC(2), but for the third excited state, 1B_2 , that is actually the only one here with a nonvanishing oscillator strength, standard ADC(2) again overestimates the excitation energy by almost 0.5 eV, whereas the CCD-ADC(2) result agrees within less than 0.1 eV with experiment. The comparison of the triplet states with experiment has to be done with care. Since they were determined via photoelectron spectroscopy of the O₃⁻ anion,⁸² they can be regarded as adiabatic excitation energies rather than vertical ones.⁷⁶ However, disregarding these issues for a moment, indeed a clear improvement can be observed when going from ADC(2) to CCD-ADC(2), especially for the lowest triplet state 3A_2 , where ADC(2) again overestimates the excitation energy significantly by more than 0.6 eV, whereas CCD-ADC(2) agrees within less than 0.1 eV with experiment.

B. Medium-sized organic molecules

In this subsection, we investigate the performance of CCD-ADC(2) and CCD-ADC(2)-x for unsaturated organic compounds, using the benchmark set introduced by Thiel and co-workers.^{46,47} The 28 molecules used for this study are shown in Fig. 2. It comprises unsaturated aliphatic hydrocarbons, aromatic hydrocarbons and heterocycles, carbonyl compounds, and nucleobases, which are all standard chromophores in organic photochemistry. An extensive comparison of standard ADC methods with CC2, CCSD, and CC3 results has been given before.⁸⁴ Here, we want to focus on the difference between standard ADC(2) variants and the hybrid CCD-ADC(2) ones and evaluate them with respect to the theoretical best estimates (TBEs).⁴⁶ Furthermore, a variety of SOPPA-based methods including SOPPA(CCSD) has been tested on the same benchmark set,⁸⁵ where it was shown that standard ADC(2) clearly outperforms standard SOPPA. For SOPPA(CCSD), a deterioration compared to its standard version could even be observed.⁸⁵

For consistency, all geometries have been optimized at the MP2/6-31G* level of theory and the standard TZVP basis set has been used for the excited-state calculations.^{46,86–88} As discussed before,^{46,84} excited states which are spatially extended, such as Rydberg states, are not well described since this basis set does not include diffuse functions.^{86,87} Both the electronic structure and the symmetries and assignments of the individual transitions of the molecules in the benchmark set have already been discussed in detail⁴⁶ and are here not given again. We have computed and compared 134 singlet and 71 triplet states at the CCD-ADC(2) and CCD-ADC(2)-x levels.

1. Singlet excited states

The calculated vertical excitation energies of singlet states of the benchmark set are compiled in Table S1 of the [supplementary material](#). The results for CCD-ADC(2) and CCD-ADC(2)-x are compared with the ones from standard ADC(2) and ADC(2)-x and, most importantly, with the theoretical best estimates (TBEs). For the different ADC(2) variants, also the amount of doubly excited configurations (% R_2) contained in the ADC excitation vector is given as the sum of the squared doubles amplitudes.

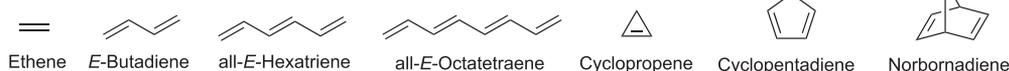
Prior to a thorough discussion of the accuracy of the (CCD-) ADC methods, a brief look at their performance for different substance classes is taken. For “unsaturated aliphatic hydrocarbons,” standard ADC(2) overestimates excitation energies on average by about 0.5 eV, whereas ADC(2)-x tends to underestimate

TABLE II. Vertical excitation energies (in eV) for the lowest excited singlet and triplet states of the O₃ molecule calculated with the cc-pVTZ basis set compared to experimental results.

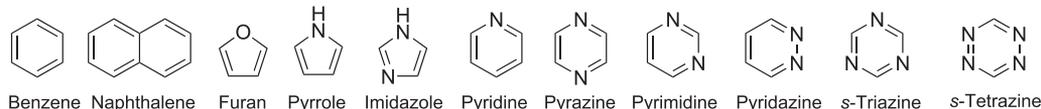
State	ADC(2)	CCD-ADC(2)	Expt. ^a
1A_2	2.14	1.59	1.6
1B_1	2.24	1.67	2.1
1B_2	5.38	4.82	4.9
3A_2	1.83	1.25	1.18
3B_2	1.73	1.13	1.30
3B_1	2.07	1.13	1.45

^aExperimental results for singlet states from Ref. 81 and for triplet states from Ref. 82.

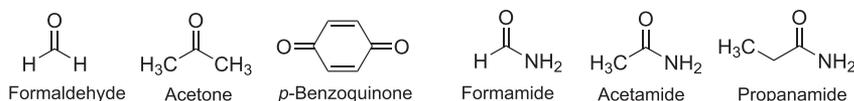
Unsaturated Aliphatic Hydrocarbons



Aromatic Hydrocarbons and Heterocycles



Carbonyl Compounds



Nucleobases

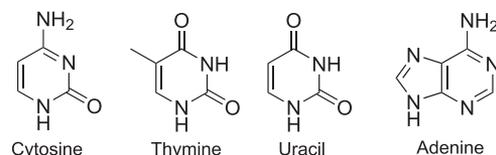


FIG. 2. Thiel's benchmark set of molecules considered for testing CCD-ADC(2) and CCD-ADC(2)-x.

them strongly (about 0.6 eV on average). Similar to what has been observed in Sec. IV A, the use of CCD amplitudes generally increases excitation energies here, thus increasing also the error for ADC(2), while for ADC(2)-x, it becomes slightly smaller. However, the description of states with a large double-excitation character

such as the 1A_g states of linear polyenes is in general difficult for single-reference methods^{84,89} because of its large % R_2 values in the ADC excitation vectors at the ADC(2)-x and CCD-ADC(2)-x levels (Table S1). For these states, both ADC(2) and ADC(2)-x have significantly larger errors compared to the TBE values than for states

TABLE III. Statistical error analysis of the calculated excitation energies (in eV) of the excited singlet states of the benchmark set at the ADC(2), CCD-ADC(2), ADC(2)-x, CCD-ADC(2)-x, and ADC(3) levels of theory.^a The theoretical best estimates (TBEs) were used as reference data as well as the ADC(3) values.

	ADC(2)	CCD-ADC(2)	ADC(2)-x	CCD-ADC(2)-x	ADC(3) ^a
TBE as reference					
Count ^b	103	103	103	103	103
Min	-0.32	-0.42	-1.83	-1.37	-0.78
Max	1.63	1.71	0.20	0.38	0.90
Mean	0.22	0.15	-0.70	-0.76	0.12
Mean absolute	0.26	0.25	0.71	0.76	0.23
Standard deviation	0.30	0.34	0.32	0.33	0.27
ADC(3) as reference					
Count ^b	134	134	134	134	...
Min	-1.00	-1.06	-1.79	-1.79	...
Max	2.20	2.28	-0.13	0.04	...
Mean	0.09	0.03	-0.83	-0.89	...
Mean absolute	0.33	0.34	0.83	0.89	...
Standard deviation	0.48	0.51	0.37	0.38	...

^aFor ADC(3) results, see Ref. 84.

^bTotal number of considered states.

with smaller $\%R_2$ fractions, however with different signs. It can also be seen that the difference between standard ADC(2) and CCD-ADC(2) becomes negligibly small for doubly excited states because the t -amplitudes occur only in the p - h block of the ADC matrix. Hence, for pure doubly excited states, both ADC(2) and CCD-ADC(2) schemes will yield exactly the same excitation energies.

Going to *aromatic hydrocarbons and heterocycles*, ADC(2) performs somewhat better, slightly overestimating excitation energies in most cases. While for aromatic systems with one heteroatom such as furan, pyrrole, or pyridine, the overestimation lies mostly in the range between 0.2 and 0.5 eV, for the six-membered rings containing two or three nitrogen atoms (with the exception of pyrazine), the error is always below 0.2 eV. ADC(2)-x shows the same trend as before, strongly underestimating excitation energies up to about 1 eV, on average between 0.3 and 0.7 eV. The use of CCD amplitudes

within ADC(2), however, now has the opposite effect as it tends to lower the excitation energies. For ADC(2), this has a positive effect and decreases the errors, whereas for ADC(2)-x, the magnitude of the error becomes somewhat bigger. Only for states where ADC(2) already slightly underestimates the TBE value, the lowering of the excitation energy in CCD-ADC(2) has a negative effect compared to the reference.

The *carbonyl compounds* in the benchmark set (aldehydes, ketones, and amides) possess different excited-state structures which can be classified as $\pi\pi^*$, $n\pi^*$, and $\sigma\pi^*$ transitions.⁸⁴ The accuracy and trends for ADC(2) and ADC(2)-x as well as CCD-ADC(2) and CCD-ADC(2)-x are very similar to the ones of the previous compound classes. The use of CCD amplitudes does not seem to have a significant impact on the results but mostly lower the excitation energies slightly.

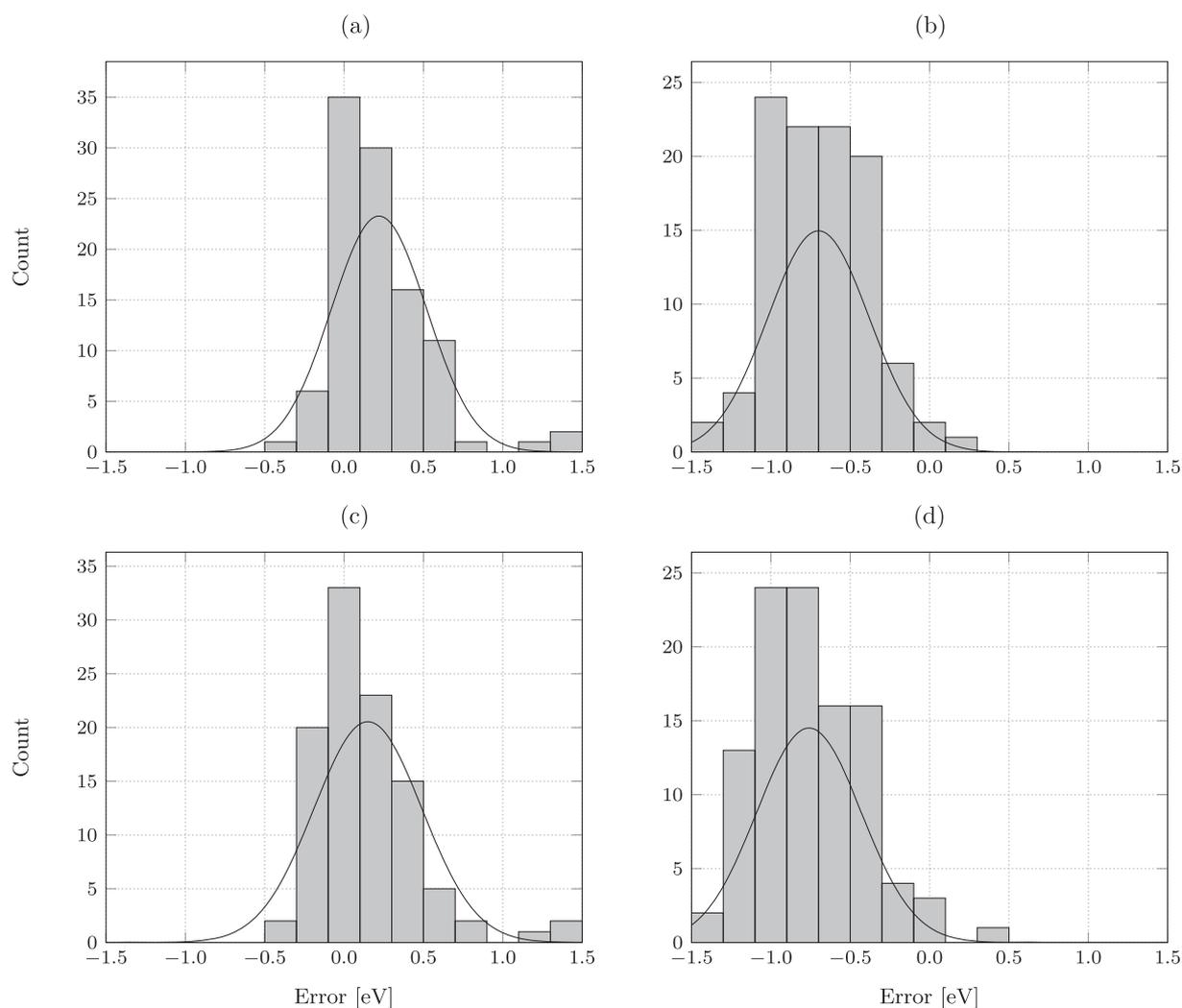


FIG. 3. Histograms of the error distribution of all calculated excited singlet states with respect to the theoretical best estimates at the theoretical levels of (a) ADC(2), (b) ADC(2)-x, (c) CCD-ADC(2), and (d) CCD-ADC(2)-x.

For the last set of molecules considered in the benchmark set, the *nucleobases*, ADC(2) shows only very small negative deviations of less than 0.1 eV on average, which is due to the fact that no CC3 values were available for these molecules, and hence, also CC2 was taken into consideration for the TBE values.^{46,84} Due to the surprisingly good results of standard ADC(2), the use of CCD amplitudes makes the error slightly larger in most cases, again by lowering the excitation energies. For ADC(2)-x and CCD-ADC(2)-x, the same conclusions hold as before.

The *statistical analysis* of the obtained data is presented in Table III and Fig. 3. In the former, both TBE and ADC(3) values (taken from Ref. 84) were taken as a reference in order to evaluate the accuracy of the CCD-ADC(2) approaches. Starting with the TBE reference, one can see that the mean error can be significantly improved by using CCD amplitudes within ADC(2). The mean error of CCD-ADC(2) is with 0.15 eV almost as good as ADC(3), which has a mean error of 0.12 eV, whereas the one of standard ADC(2) is 0.22 eV. However, the mean absolute error is very similar for all three methods, ranging from 0.23 eV for ADC(3) to 0.26 eV for ADC(2), while CCD-ADC(2) lies in between with 0.25 eV. Concerning the standard deviation, on the other hand, CCD-ADC(2) has a larger value of 0.34 eV than standard ADC(2) with 0.30 eV, indicating a slightly higher variation of the results when using CCD amplitudes. This is also indicated by the about 0.2 eV larger range between the minimal and maximal error of CCD-ADC(2) compared to ADC(2). Going to the extended version CCD-ADC(2)-x, the underestimation of excitation energies by the *ad hoc* extension of the *2p-2h* block to first order cannot be corrected by using CCD amplitudes; on the opposite, it gets slightly worse. The mean error is with -0.76 eV slightly larger than for ADC(2)-x with -0.70 eV. This underestimation, however, is very consistent since the mean absolute error has exactly the same numerical value, just the opposite sign. The

standard deviation of CCD-ADC(2)-x is with 0.33 eV almost identical to the one for ADC(2)-x with 0.32 eV. Only the range between the minimal and maximal error is slightly improved, which amounts to 2.03 eV for standard ADC(2)-x and only 1.75 eV for CCD-ADC(2)-x. Taking ADC(3) as a reference, a similar picture is obtained. The mean error of 0.09 eV of ADC(2) can be reduced by using CCD amplitudes to only 0.03 eV for CCD-ADC(2), whereas the mean absolute error stays almost the same and the standard deviation increases slightly from 0.48 eV for ADC(2) to 0.51 eV for CCD-ADC(2). The range between minimal and maximal error is again increased by about 0.14 eV. The mean (absolute) error for CCD-ADC(2)-x is again slightly larger in magnitude than for ADC(2)-x, whereas the standard deviation remains virtually unchanged. However, the range between minimal and maximal deviation becomes slightly larger in this case when CCD amplitudes are employed.

2. Triplet excited states

For a further evaluation of the accuracy of the CCD-ADC(2) methods, 71 excited triplet states of 20 molecules of the benchmark set (Fig. 2) have been calculated and compared to available TBE and ADC(2) and ADC(2)-x values. No benchmark data are available for the triplet states of the molecules pyrazine, pyrimidine, pyridazine, *s*-triazine as well as the nucleobases cytosine, thymine, uracil, and adenine. The results are compiled in Table S2 of the [supplementary material](#). Since the results are rather similar for all considered substance classes, an individual discussion is omitted at this point and the statistical analysis presented in Table IV and Fig. 4 is discussed immediately.

The error of the second-order ADC methods is generally smaller for triplet than for singlet excited states. Compared to the TBE values, standard ADC(2) has a mean error of 0.12 eV with a

TABLE IV. Statistical error analysis of the calculated excitation energies (in eV) of the excited triplet states of the benchmark set at the ADC(2), CCD-ADC(2), ADC(2)-x, CCD-ADC(2)-x, and ADC(3) levels of theory.^a The theoretical best estimates (TBEs) were used as reference data as well as the ADC(3) values.

	ADC(2)	CCD-ADC(2)	ADC(2)-x	CCD-ADC(2)-x	ADC(3) ^a
TBE as reference					
Count ^b	63	63	63	63	63
Min	-0.27	-0.38	-0.96	-1.06	-0.49
Max	0.48	0.35	-0.24	-0.23	0.44
Mean	0.12	0.00	-0.55	-0.67	-0.18
Mean absolute	0.17	0.13	0.55	0.67	0.21
Standard deviation	0.16	0.17	0.20	0.22	0.16
ADC(3) as reference					
Count ^b	71	71	71	71	...
Min	-0.38	-0.42	-1.41	-1.44	...
Max	1.52	1.32	0.08	-0.01	...
Mean	0.32	0.20	-0.40	-0.51	...
Mean absolute	0.38	0.29	0.41	0.51	...
Standard deviation	0.30	0.29	0.33	0.32	...

^aFor ADC(3) results, see Ref. 84.

^bTotal number of considered states.

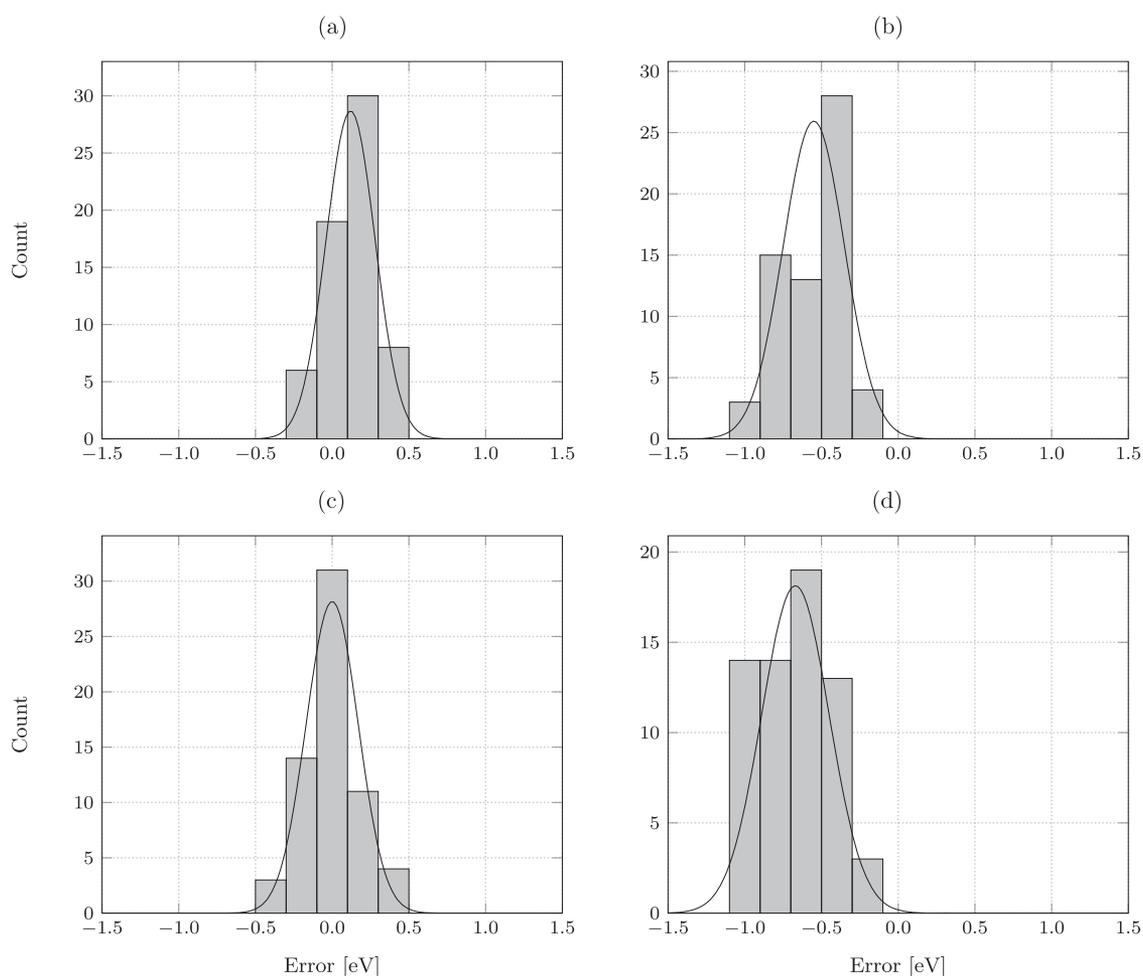


FIG. 4. Histograms of the error distribution of all calculated excited triplet states with respect to the theoretical best estimates at the theoretical levels of (a) ADC(2), (b) ADC(2)-x, (c) CCD-ADC(2), and (d) CCD-ADC(2)-x.

standard deviation of only 0.17 eV. The largest improvement, however, can be seen for the CCD-ADC(2) variant with a vanishing mean error of 0.00 eV and almost the same small standard deviation as standard ADC(2). This can be seen in the histogram in Fig. 4(c), where the Gaussian curve is centered exactly at 0.0 eV. The mean absolute error, on the other hand, is of course larger than zero, but with 0.13 eV still smaller than the one of ADC(2) with 0.17 eV.

The mean (absolute) errors of ADC(2)-x and CCD-ADC(2)-x are also smaller in magnitude for the triplet than for the singlet excited states, but both still underestimate excitation energies by more than 0.5 eV on average. The mean error of CCD-ADC(2)-x is 0.12 eV smaller than the one of the standard version, exactly the same amount as for ADC(2), although here this represents a deterioration. The lowering of the excitation energies when using CCD amplitudes in ADC(2) thus seems to be rather consistent. Yet, one has to keep in mind that these are numbers averaged

over the employed benchmark set and not rigorous trends that are valid for all individual excitation energies. Still, both the mean error and mean absolute error compared to TBE values are significantly smaller for CCD-ADC(2) than for ADC(2).

Taking now ADC(3) values as a reference, CCD-ADC(2) still outperforms ADC(2) significantly. Both the mean error with 0.20 eV and the mean absolute error with 0.29 eV are more than 0.1 eV smaller than for ADC(2). It can thus be said that by the use of CCD instead of Møller-Plesset amplitudes, the ground-state energy is consistently lowered which may lead to the, on average, improved numerical results.

The trend for CCD-ADC(2)-x compared to standard ADC(2)-x is the same as with respect to the TBE reference; both the mean error and mean absolute error are about 0.1 eV larger in magnitude when CCD amplitudes are employed. The range between the minimal and maximal deviation from the reference, however, decreases both for CCD-ADC(2) and for CCD-ADC(2)-x with

respect to the ADC(3) reference, for CCD-ADC(2) significantly by 0.18 eV.

A subset of the molecules considered in Secs. IV A and IV B has also been calculated with the CCSD-ADC(2) variant, the results of which can be found in Table S3 of the [supplementary material](#). As can be seen there, for the small molecules, the difference in excitation energies between the variants using CCD or CCSD doubles amplitudes is usually only up to 0.02 eV. For the organic molecules, this difference is slightly larger although no improvement can be observed when using CCSD amplitudes. Rather, the results of CCSD-ADC(2) are in general closer to standard ADC(2) than the ones of CCD-ADC(2).

C. Excited-state potential energy curves along N_2 dissociation

The failure of standard perturbation theory at points away from the equilibrium geometry due to static correlation has been known for a long time.²⁶ Along a bond dissociation coordinate, any MP n model fails to give the correct asymptotic behavior. Single-reference coupled-cluster models, on the other hand, tend to be more stable and break down at a later point along the dissociation coordinate.⁹⁰ Several approaches exist which describe dissociation processes correctly, for instance multireference (MR) methods such as multireference configuration interaction (MR-CI) or multireference coupled cluster (MR-CC),^{90–92} and also the so-called spin-flip (SF) methods starting from an open-shell triplet ground state.^{27,29–33,93,94}

Here, the conceptually simple approach of CCD-ADC(2) is tested, thus staying within a closed-shell single-reference description. Since standard ADC methods can generally not be applied for cases where the MP ground-state description breaks down, it is investigated whether the higher stability of the CCD ground state can be transferred to the excited states. The potential energy curves of the HF molecule with standard ADC as well as SF-ADC were presented before.³⁰ In order to choose a different, nontrivial example, the dissociation of the triple bond in the N_2 molecule is investigated here. The MP2 curve breaks down already at about 1.7 Å, while the CCSD one, for instance, stays stable also beyond 2 Å.⁹⁰

Figure 5 shows that the increased stability of CCD along the dissociation coordinate can indeed be transferred to the ADC excited states. Exemplarily, the energy curves of the first excited singlet and triplet states of the nitrogen molecule are shown, i.e., the first $^1\Sigma_u^-$, $^1\Pi_g$, and $^3\Sigma_u^-$ states. As can be seen in Fig. 5, the energy curves obtained at the ADC(2) level start to break down at around 2 Å, similar to the MP2 curve, and eventually even become lower in energy than the ground state. The CCD-ADC(2) curves, on the other hand, do not show this unphysical behavior that early and remain reasonable throughout almost the entire range up to 3.5 Å, as shown here. As a consequence, chemical reactions in the excited state might be modeled qualitatively more correctly at the CCD-ADC(2) level and excited-state equilibrium geometries which are spatially far away from the ground-state geometry may be obtained with higher accuracy. As mentioned before, this is achievable by staying within a single-reference framework and with a closed-shell restricted HF determinant, in contrast to SF-ADC where one necessarily starts from an open-shell reference. Of course, it remains

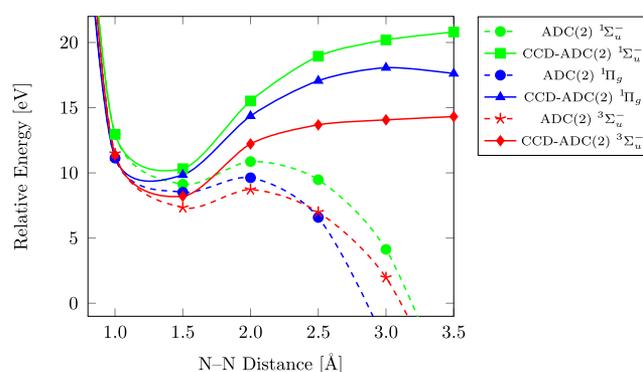


FIG. 5. Excited-state potential energy curves along the dissociation of N_2 calculated with standard ADC(2) (dashed lines) and CCD-ADC(2) (solid lines) using the cc-pVTZ basis set.

restricted to within the area of applications where single-reference coupled cluster remains stable.

V. SUMMARY AND OUTLOOK

The algebraic-diagrammatic construction scheme for the polarization propagator, which combines diagonalization of a Hermitian secular matrix with perturbation theory for the matrix elements, has the advantages of being size-intensive for both excitation energies and transition moments and its computational scaling is lower compared to similar CC approaches. However, as had been pointed out before,²³ the use of perturbation theory limits the applicability of the method since the perturbation expansion of the secular matrix elements behaves basically like the corresponding MP ground-state (energy) expansions. This means whenever the MP ground state fails, for example in the case of large nondynamical electron correlation, ADC can no longer be applied with reasonable accuracy. Standard coupled-cluster ground-state methods are also affected in such cases but usually not as strong as MP theory.

In this work, an *ad hoc* modification of the ADC scheme of second order was presented. Instead of using first-order Møller–Plesset doubles correlation coefficients, coupled-cluster doubles amplitudes were used within the ADC(2) secular matrix to compute electronically excited states. While the equation for the correlation energy of MP2 and CCD is formally identical, MP correlation coefficients are calculated in a one-shot manner and are of first order, whereas the coupled-cluster amplitudes have to be solved iteratively and are formally of infinite order. This work was motivated by a similar study on the related SOPPA method,^{34,37} where better results for excitation energies and properties were obtained in many cases. The new hybrid methods, denoted CCD-ADC(2), were tested on a set of small and medium-sized atomic and molecular systems, and the results for electronic excitation energies were compared with standard ADC(2) results and FCI, theoretical best estimates or experiment. It was also applied to the dissociation of the nitrogen molecule.

As expected, for small closed-shell systems such as HF and H_2O , where MP2 provides a good ground-state description, virtually no differences were observed for ADC(2) when CCD amplitudes

were used instead of MP ones. While some minor improvement was observed for the N_2 molecule, a deterioration in the order of 0.1 eV was observed for the CH_2 and BH molecules. These two quasi-open-shell systems are difficult to describe by means of standard perturbation theory and expectedly the use of CCD amplitudes in ADC(2) had the biggest influence in these cases. However, since standard ADC(2) gives already surprisingly good results,²³ the use of CCD amplitudes raised the excitation energies, thus deteriorating the results compared to FCI. Yet, the same effect improves the results for the extended version of second-order ADC, ADC(2)-x. The standard version of ADC(2)-x underestimates the excitation energies of CH_2 and BH strongly, while the use of CCD amplitudes again raises them, thus significantly improving the mean absolute error. For the difficult case of the ozone molecule, however, a significant improvement of the excitation energies could be observed compared to experimental values when using CCD amplitudes in ADC(2). Concerning the small- and medium-sized organic molecules of the Thiel benchmark set,⁴⁶ no significant difference could be observed in the mean signed and mean absolute errors as well as standard deviation for the investigated singlet excited states. For triplet excited states, however, the mean error and standard deviation exhibited by ADC(2) of 0.12 ± 0.16 eV could be lowered to 0.00 ± 0.17 eV for CCD-ADC(2) at the same time leading to a worse description in the (CCD)-ADC(2)-x case. These results are in contrast to SOPPA-based methods,⁸⁵ where, on the one hand, standard ADC(2) outperforms standard SOPPA and the use of coupled-cluster amplitudes such as in SOPPA(CCSD) reduced the quality of the results in the statistical analysis. On the other hand, CCD-ADC(2) did not significantly change or rather slightly improved the results.

The most impressive improvement apart from the ozone molecule, however, was observed for the excited-state potential energy curves of N_2 . Since the MP2 ground state breaks down at a distance of only about 1.7 Å, so do the excited states described by ADC(2). Using a CCD ground-state description that remains stable up to more than 3 Å of interatomic distance, also the corresponding excited states calculated with CCD-ADC(2) remain stable over this range.

In future work, the CC-ADC approach will be used not only for the calculation of excitation energies but also for properties such as dipole moments or polarizabilities.⁹⁵ Furthermore, CC-ADC will be extended in the context of the ADC(3/2) model,⁸⁴ making use of not only CCD but also CCSD singles and doubles amplitudes.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for results of vertical excitation energies of the medium-sized organic molecules calculated with CCD-ADC(2) and CCD-ADC(2)-x compared to standard ADC(2) and ADC(2)-x and the theoretical best estimates as well as results with CCSD-ADC(2) for a subset of all considered molecules.

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