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ABSTRACT

The modification of the algebraic-diagrammatic construction (ADC) scheme for the polarization propagator using ground-state coupled-cluster (CC) instead of Møller–Plesset (MP) amplitudes, referred to as CC-ADC, is extended to the calculation of molecular properties, in particular, dipole polarizabilities. Furthermore, in addition to CC with double excitations (CCD), CC with single and double excitations (CCSD) amplitudes can be used, also in the second-order transition moments of the ADC(3/2) method. In the second-order CC-ADC(2) variants, the MP correlation coefficients occurring in ADC are replaced by either CCD or CCSD amplitudes, while in the F/CC-ADC(2) and F/CC-ADC(3/2) variants, they are replaced only in the second-order modified transition moments. These newly implemented variants are used to calculate the static dipole polarizability of several small- to medium-sized molecules, and the results are compared to the ones obtained by full configuration interaction or experiment. It is shown that the results are consistently improved by the use of CC amplitudes, in particular, for aromatic systems such as benzene or pyridine, which have proven to be difficult cases for standard ADC approaches. In this case, the second-order CC-ADC(2) and F/CC-ADC(2) variants yield significantly better results than the standard third-order ADC(3/2) method, at a computational cost amounting to only about 1% of the latter.

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I. INTRODUCTION

The algebraic-diagrammatic construction (ADC) scheme for the polarization propagator^{1–4} has become a versatile and reliable tool for the calculation of excitation energies and transition moments^{1,5–10} and has also been applied successfully to static and dynamic polarizabilities,^{11,12} X-ray absorption spectroscopy,^{13–15} two-photon absorption,¹⁶ and C_6 dispersion coefficients,¹² particularly exploiting the formalism of the intermediate state representation (ISR).^{3,11} In a recent work on static polarizabilities and C_6 dispersion coefficients,¹² aromatic systems such as benzene have proven to be a difficult case for standard ADC approaches, yielding

rather poor results compared to other theoretical approaches or experiment. We extended the previous implementation of second-order ADC with ground-state coupled-cluster (CC) amplitudes¹⁷ in a development version of the Q-CHEM program package¹⁸ to the calculation of molecular properties and tested its performance on static polarizabilities of several small- to medium-sized molecules. This approach has been inspired by similar works on the related second-order polarization propagator approximation (SOPPA) method by Geertsen, Oddershede, and Sauer.^{19,20} Furthermore, a variant of the implementation relevant for molecular properties has been made by replacing the amplitudes in the transition moment vectors only, but not in the ADC secular matrix itself. This variant has also been

implemented for the ADC(3/2) method in which the eigenvectors (and response vectors) of the third-order ADC matrix are used to calculate properties with second-order dipole matrices. The current implementation allows for the use of CC with double excitations (CCD) as an underlying coupled-cluster model as well as CC with single and double excitations (CCSD), where the singles amplitudes replace a part of the second-order density-matrix correction as described in Sec. II.

Experimentally, static polarizabilities can, for instance, be obtained by considering the relative dielectric permittivity or the refractive index.²¹ Here, we would like to refer to the comprehensive work of Hohm²² in which experimental data for 174 molecules are compiled. Alternatively, static polarizabilities and other properties such as inelastic scattering cross sections of charged particles, Lamb shifts, or dipole-dipole dispersion coefficients can be estimated using the so-called dipole oscillator strength distribution (DOSD), which is constructed using various pieces of experimental information such as photoabsorption spectra, refractivity, and electron scattering as well as constraints from quantum mechanics.^{12,23,24}

As first example of the performance of the new CC-ADC variants on molecular properties, static dipole polarizabilities of several small- to medium-sized atomic and molecular systems are reinvestigated. In general, care has to be taken when comparing with experiment, in particular, due to vibrational or environmental effects. For example, the compilation of Hohm²² often includes estimates of vibrational contributions to the static polarizability, but such effects are not considered in the present computational study.^{25,26} DOSD estimates, on the other hand, often include zero-point vibrational effects, and a previous study on methane reported an increase in its static polarizability by about 5% when including zero-point vibrational averaging (ZPVA).²⁷ While, in the static limit, pure vibrational contributions can be of the same order of magnitude as the electronic contributions for some molecules, ZPVA has been observed to change polarizabilities, in general, by only a few percent.^{25,28}

II. THEORETICAL METHODOLOGY AND IMPLEMENTATION

The underlying theory and the ADC formalism for calculating polarizabilities has been discussed in detail elsewhere.^{11,12} Here, only a brief outline of the basic equations and principles for the calculation of dipole polarizabilities within the intermediate state representation shall be given.

Apart from the original derivation of the ADC equations with the propagator approach,¹⁷ an alternative exists via the so-called intermediate state representation (ISR).^{3,4,29,30} The ISR not only gives direct access to excited states and transition properties but also offers a straightforward way to transform expressions from time-dependent response theory into closed-form matrix expressions.^{11,16} The components of the frequency-dependent molecular dipole polarizability $\alpha_{AB}(\omega)$ (with $A, B \in \{x, y, z\}$) are given as

$$\alpha_{AB}(\omega) = -\langle \Psi_0 | \hat{\mu}_A (\hbar\omega - \hat{H} + E_0)^{-1} \hat{\mu}_B | \Psi_0 \rangle + \langle \Psi_0 | \hat{\mu}_B (\hbar\omega + \hat{H} - E_0)^{-1} \hat{\mu}_A | \Psi_0 \rangle, \quad (1)$$

with the electric dipole operator $\hat{\mu} = \sum_{pq} \mu_{pq} \hat{a}_p^\dagger \hat{a}_q$. The exact sum-over-states expression is obtained by inserting the resolution of the identity of *exact* states, $\mathbf{1} = \sum_n |\Psi_n\rangle \langle \Psi_n|$.¹¹ If instead the resolution of the identity of *intermediate* states, $\mathbf{1} = |\Psi_0\rangle \langle \Psi_0| + \sum_I |\tilde{\Psi}_I\rangle \langle \tilde{\Psi}_I|$ is inserted, one arrives at the ADC formulation of the polarizability.¹² For a static perturbation ($\omega = 0$), it is given by

$$\alpha_{AB}(0) = \mathbf{F}_A^\dagger \mathbf{M}^{-1} \mathbf{F}_B + \mathbf{F}_B^\dagger \mathbf{M}^{-1} \mathbf{F}_A, \quad (2)$$

where we introduced vectors of modified transition moments \mathbf{F} with elements

$$F_I = \langle \tilde{\Psi}_I | \hat{\mu} | \Psi_0 \rangle = \sum_{pq} \mu_{pq} \langle \tilde{\Psi}_I | \hat{a}_p^\dagger \hat{a}_q | \Psi_0 \rangle = \sum_{pq} \mu_{pq} f_{pq}^I \quad (3)$$

and used the definition of the modified transition amplitudes, $f_{pq}^I = \langle \tilde{\Psi}_I | \hat{a}_p^\dagger \hat{a}_q | \Psi_0 \rangle$. In order to obtain ADC expressions, the intermediate states are constructed as described in the literature^{3,30} and the exact ground-state wave function and energy are replaced by the Møller-Plesset (MP) perturbation series expansions³¹

$$|\Psi_0\rangle = |\Psi_0^{(0)}\rangle + |\Psi_0^{(1)}\rangle + |\Psi_0^{(2)}\rangle + \dots, \quad (4)$$

$$E_0 = E_0^{(0)} + E_0^{(1)} + E_0^{(2)} + \dots \quad (5)$$

Algebraic expressions are obtained by using the MP-partitioning of the molecular Hamiltonian and by collecting terms for the ADC matrix up to a given order n . When both the secular matrix and the transition moments are described consistently up to a certain order, this is then referred to as ADC(n).

The second-order scheme ADC(2) formally depends on the MP wave-function and energy correction up to second order and describes single excitations correct in second order of perturbation theory. The ADC(3) scheme depends on the MP energy up to third order and describes single excitations consistent in third order and double excitations consistent in first order of perturbation theory. However, for both ADC(2) and ADC(3), the excitation space is limited to single and double excitations, i.e., the ADC matrix \mathbf{M} is of the same size as the configuration interaction singles and doubles (CISD) matrix. Currently, the modified transition amplitudes are only available up to second order. Combining the second-order modified transition amplitudes with the third-order ADC matrix yields the so-called ADC(3/2) model.¹⁶ The first-order MP doubles amplitudes which are defined as

$$t_{ij}^{ab} = \frac{\langle ab || ij \rangle}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j}, \quad (6)$$

where $\langle ab || ij \rangle$ is an antisymmetrized two-electron integral and the ε_p are HF orbital energies, occur for the first time in the second-order contribution to the p - h/p - h block of the ADC matrix.¹ They have already been replaced here for the calculation of excitation energies by CC doubles amplitudes,¹⁷ which are calculated in an iterative manner according to the CC amplitude equations³² for the doubles

$$\langle \Phi_{ij}^{ab} | e^{-\hat{T}} \hat{H} e^{\hat{T}} | \Phi_0 \rangle = 0, \quad (7)$$

where $|\Phi_0\rangle$ is the Hartree–Fock reference determinant, \hat{T} is the cluster operator that is either approximated as $\hat{T} = \hat{T}_2$ for CCD or $\hat{T} = \hat{T}_1 + \hat{T}_2$ for CCSD, and $|\Phi_{ij}^{ab}\rangle$ is a doubly excited determinant.

The MP amplitudes also occur in the first- and second-order contribution to the modified transition amplitudes f_{pq}^l ,¹ where they were replaced by CCD or CCSD doubles amplitudes as well. Furthermore, in a similar spirit to the work of Sauer,²⁰ the p - h part of the second-order one-particle density matrix correction¹⁰

$$\rho_{ia}^{(2)} = -\frac{1}{2(\varepsilon_a - \varepsilon_i)} \left[\sum_{jbc} t_{ij}^{bc} \langle ja || bc \rangle + \sum_{jkb} \langle jk || ib \rangle t_{jk}^{ab} \right] \quad (8)$$

was replaced by the corresponding CCSD singles amplitudes. Since Eq. (8) corresponds precisely to the second-order contribution of \hat{T}_1 , i.e., the lowest order where the singles occur in the MP wavefunction expansion, CCSD was considered to an equal extent as CCD here, in contrast to Paper I on excitation energies.¹⁷ These singles amplitudes are not replaced when CCD is chosen as the coupled-cluster model, but $\rho_{ia}^{(2)}$ is calculated instead with the CCD T_2 amplitudes.

We would like to mention that the CC-ADC approach presented here is still size consistent (size intensive), since, on the one hand, in the ISR, the ground state is completely decoupled from the excited configurations, and, on the other hand, as described before,¹⁷ the form of the ADC equations is still the same in the CC-ADC variants, which means that local and nonlocal excitations are exactly decoupled as well.

The CCD and CCSD amplitudes were combined with ADC(2) to yield the variants termed CCD-ADC(2) and CCSD-ADC(2). Furthermore, in order to check for the importance of the amplitudes in different parts of the calculation, more variants of ADC(2) as well as ADC(3/2) have been implemented, in which the amplitudes are replaced in the modified transition moments **F**, but not in the ADC matrix **M**. These variants are then referred to as F/CC-ADC(2) and F/CC-ADC(3/2), where CC stands for either CCD or CCSD.

III. RESULTS AND DISCUSSION

In the following, static dipole polarizabilities of a series of small and medium-sized atomic and molecular systems are calculated using different ADC and CC-ADC variants and the results are compared to full configuration interaction (FCI), CC3, or experimental values. In a previous study,¹¹ it was shown that double-zeta basis sets are clearly insufficient for the calculation of polarizabilities at the wave-function correlated level. Furthermore, one set of diffuse functions is crucial, whereas adding further sets of diffuse functions seemed to be of minor importance at the triple-zeta level. Thus, a basis set like aug-cc-pVTZ represents a good compromise between basis-set size and accuracy.¹¹ Since the purpose of this study is to compare different CC-ADC variants with other methods, in particular, standard ADC, no attempt was made to optimize the employed one-particle basis set. Instead, the basis sets of previous studies were employed for comparability. Most of the geometries were taken from the literature as well.¹¹

A. Comparison with FCI

1. The case of Li^-

As a first step, we reinvestigate the case of the lithium anion, Li^- , which has been a prominent test case for the calculation of dipole polarizabilities with many correlated methods.^{33–37} Sauer chose to investigate this anion first as an “ideal test case” for the SOPPA variant referred to as SOPPA(CCSD),²⁰ where he replaced MP by CCSD amplitudes, based on earlier works by Geertsen *et al.*^{19,38} Thus, it was chosen as the first test case for the CC-ADC approaches using the same uncontracted (16s12p4d) Gaussian one-electron basis set.²⁰

The values for the static dipole polarizability calculated with different ADC- and SOPPA-based methods compared to FCI are shown in Table I. A graphical representation of the relative error defined as $\frac{\alpha(X) - \alpha(\text{FCI})}{\alpha(\text{FCI})}$, where X is the corresponding method, is depicted in Fig. 1. As can be seen, both standard second-order methods, ADC(2) and SOPPA, show only a small improvement compared to the first-order random-phase approximation (RPA) which has a relative error of about 50% (corresponding to 400 a.u.). They still overestimate the static polarizability significantly by more than 30% (about 250 a.u.). The use of coupled-cluster amplitudes within these methods lowers the value of the polarizability in all cases, but the magnitude of the effect varies strongly for the different variants. While SOPPA(CCSD) yields better results than Geertsen’s coupled-cluster polarization propagator approximation (CCSDPPA) variant,²⁰ this also holds true for the ADC(2) variant with CCD, but not for the one with CCSD amplitudes. In the latter case, the polarizability is underestimated by more than 40% or 350 a.u. With CCD amplitudes, the underestimation is less than 25% (200 a.u.). A further improvement can be observed for the variants in which the amplitudes are only substituted in the modified transition moments **F**. While for the F/CCSD-ADC(2) the error is still –30% (about 240 a.u.), the best result of all compared methods could be obtained with F/CCD-ADC(2), where the underestimation of 6% (50 a.u.) is even smaller than for SOPPA(CCSD) with 8% (65 a.u.). It can already be seen in this system that the amplitudes in the **F** vectors play a larger role than the ones in the secular matrix, since the change in going from standard ADC(2) to F/CCD-ADC(2) is already almost 300 a.u., and when the amplitudes

TABLE I. Static dipole polarizability (in a.u.) of Li^- calculated with different methods.

Method	α
RPA ^a	1198.39
SOPPA ^a	1061.70
CCSDPPA ^a	620.80
SOPPA(CCSD) ^a	732.60
ADC(2)	1039.17
CCD-ADC(2)	601.66
F/CCD-ADC(2)	747.59
CCSD-ADC(2)	448.38
F/CCSD-ADC(2)	558.30
FCI ^a	797.77

^aTaken from Ref. 20.

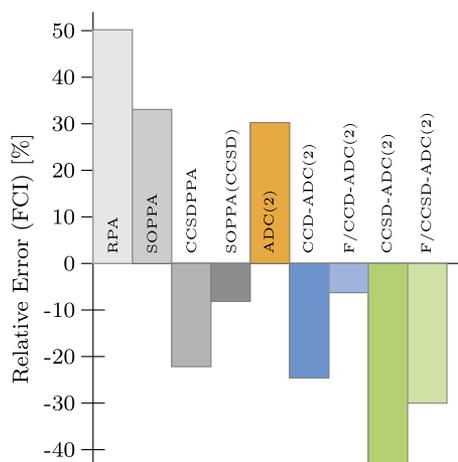


FIG. 1. The relative error of the static dipole polarizability α for Li^- of results presented in Table I with respect to FCI.

are additionally substituted in the secular matrix in CCD-ADC(2), the polarizability decreases by another 145 a.u. For CCSD amplitudes, this trend is even more pronounced: the difference between ADC(2) and F/CCSD-ADC(2) amounts to 480 a.u., and between F/CCSD-ADC(2) and “full” CCSD-ADC(2) only 110 a.u.

However, the results obtained with the different methods do not appear to be very systematic, and especially, the best result obtained with the F/CCD-ADC(2) variant seems rather fortuitous. Since the lithium anion is a system with a diffuse charge cloud that is easily polarizable, it is understandable that the computed polarizability is very sensitive to small changes in the parameters. This makes it, however, questionable whether the Li^- ion is really an ideal test case and whether the observed improvements were obtained for the right reasons and not fortuitously. Furthermore, Li^- is isoelectronic to the beryllium atom which, in turn, is known to be a strongly correlated system, and therefore, perturbation theories at low order and even single-reference coupled-cluster approaches may not be appropriate such that in this case a real multireference treatment would be needed.

In order to further investigate the CC-ADC methods and deduce some general trends when using different t -amplitudes within ADC, additional calculations on more standard chemical systems have been carried out and analyzed as shall be discussed in the following.

2. Neon and hydrogen fluoride

We turn our attention to two more small systems, namely, neon and hydrogen fluoride. The static dipole polarizabilities of Ne and HF have been calculated with various ADC methods, and the results are compared to FCI. The basis sets used here are only of double-zeta quality, but since the reference FCI values were calculated in the same one-particle basis, the deviations from FCI stem solely from the approximations in the respective ADC method. Table II shows the static dipole polarizability of the Ne atom calculated with the d-aug-cc-pVDZ basis set,^{40,41} and the relative error is depicted

TABLE II. Static dipole polarizability (in a.u.) of Ne (d-aug-cc-pVDZ basis set) and HF (aug-cc-pVDZ basis set) obtained with different variants of the ADC scheme compared to FCI.

Method	Ne α	HF		
		α_{xx}	α_{zz}	$\bar{\alpha}$
ADC(2)	2.83	4.55	6.71	5.27
CCD-ADC(2)	2.78	4.43	6.47	5.11
F/CCD-ADC(2)	2.78	4.43	6.48	5.11
CCSD-ADC(2)	2.83	4.53	6.58	5.21
F/CCSD-ADC(2)	2.83	4.53	6.59	5.22
ADC(3/2)	2.70	4.29	6.32	4.97
F/CCD-ADC(3/2)	2.65	4.19	6.12	4.84
F/CCSD-ADC(3/2)	2.70	4.28	6.21	4.93
FCI ^a	2.67	4.29	6.21	4.93

^aTaken from Refs. 11 and 39.

in Fig. 2. The deviation of the standard ADC(2) result from FCI of 6% (0.16 a.u.) is improved by 0.05 a.u. when using CCD amplitudes such that the deviation is only 4% or 0.11 a.u. When CCSD doubles amplitudes are employed, the polarizability increases again to the same value as standard ADC(2) and hence no improvement is observed. We can see, however, that the results for both CCD-ADC(2) and F/CCD-ADC(2) as well as for CCSD-ADC(2) and F/CCSD-ADC(2) are the same, underlining the greater importance of the amplitudes in the modified transition moments F compared to the ones in the secular matrix M for the calculation of the polarizability. The same trend as for ADC(2) is observed for the third-order variants, where standard ADC(3/2) slightly overestimates the static polarizability by 1.0% compared to FCI. The use of CCD amplitudes within the second-order modified transition moments F lowers the obtained value and improves it slightly with a relative error of -0.7% , whereas with F/CCSD-ADC(3/2), the same value as for standard ADC(3/2) is obtained.

The dipole polarizability of hydrogen fluoride was calculated with the aug-cc-pVDZ basis set,⁴² and the results can also be found in Table II and Fig. 2. Again, the results for the CC-ADC and F/CC-ADC variants are almost identical. Focusing first on the isotropic polarizability of HF $\bar{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$, with $\alpha_{xx} = \alpha_{yy}$ for symmetry reasons, standard ADC(2) overestimates its value by 6.9% or 0.34 a.u. As before, the use of CC amplitudes in ADC lowers the static polarizability and thus improves its value compared to standard ADC. CCD amplitudes again yield a better result in ADC(2) than CCSD ones, with the error of the former being only 3.7% (0.18 a.u.) compared to about 5.8% (0.28 a.u.) of the latter. So again, when CCSD amplitudes are employed, the polarizability is raised compared to CCD ones, making the result more similar to standard ADC(2). A similar trend is observed for the ADC(3/2) method. Here, however, F/CCD-ADC(3/2) underestimates the polarizability by 1.9% or 0.09 a.u. due to the already very good result of standard ADC(3/2), having an error of only 0.8% or 0.04 a.u. The F/CCSD-ADC(3/2) method again raises the value of the polarizability to some extent compared to F/CCD-ADC(3/2) and is in this case in almost perfect agreement (relative error $<0.1\%$) with the FCI result of 4.93 a.u. for the isotropic polarizability.

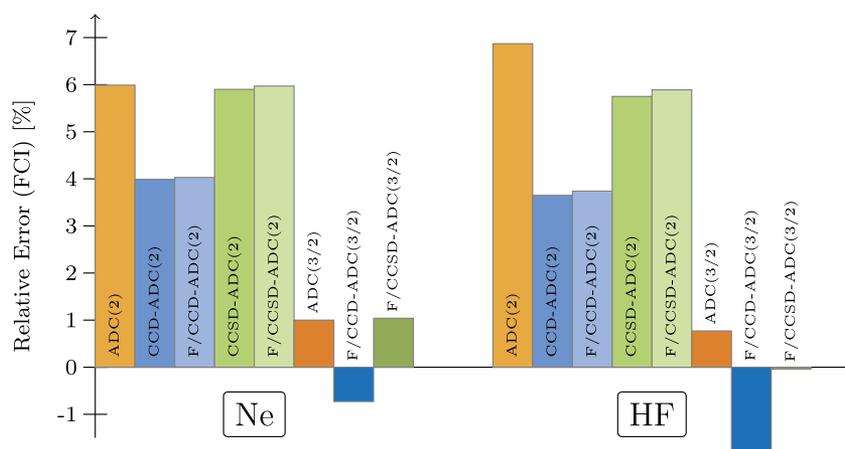


FIG. 2. Relative error of the isotropic polarizability $\tilde{\alpha}$ for Ne and HF of results presented in Table II with respect to FCI.

Having a look at the individual values of the polarizability tensor, all ADC(2) variants describe the components of the polarizability perpendicular to the molecular axis (that is, α_{xx} and α_{yy}) better than the component parallel to the axis, α_{zz} . The relative improvement when using CCD amplitudes, however, is larger for the parallel z component than for the perpendicular ones. A similar observation holds for the ADC(3/2) method. Here, however, the standard version is already in agreement with FCI for the diagonal x and y components of the polarizability, whereas the error of the z component amounts to 0.11 a.u. When using CCSD amplitudes in the F vectors, the perpendicular components remain virtually unchanged, whereas the parallel z component is lowered to be in perfect agreement with the FCI value as well.

B. Comparison with experiment

In the following, we will evaluate the accuracy of the CC-ADC methods for molecular systems of increasing size and with larger basis sets and compare the obtained results to the ones obtained in

experiments, often by means of the dipole oscillator strength distribution (DOSD).²⁴ Since no FCI results are available for these systems, the results of the third-order approximate coupled cluster (CC3) method⁴³ were taken as a theoretical reference when they were available. Additionally, the polarizability anisotropy defined as

$$\Delta\alpha = \sqrt{\frac{(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2}{2}} \quad (9)$$

is compared. Previous studies have shown that ADC(2) yields, in general, rather large discrepancies in the anisotropies due to a poor reproduction of longitudinal polarizability components.^{11,12}

1. Water and carbon monoxide

Let us start with the investigation of the water molecule, using the rather large d-aug-cc-pVTZ basis set⁴¹ in order to allow for a proper comparison of theory and experiment.¹¹ The results obtained for H₂O are shown in Table III, and the relative error with respect to

TABLE III. Static dipole polarizability (in a.u.) of H₂O and CO calculated with different ADC variants (d-aug-cc-pVTZ basis set) compared to CC3 and experiment.

Method	H ₂ O					CO			
	α_{xx}	α_{yy}	α_{zz}	$\tilde{\alpha}$	$\Delta\alpha$	α_{xx}	α_{zz}	$\tilde{\alpha}$	$\Delta\alpha$
ADC(2)	9.79	10.41	10.17	10.13	0.54	11.88	17.32	13.70	5.43
CCD-ADC(2)	9.48	9.97	9.83	9.76	0.44	11.45	16.92	13.27	5.47
F/CCD-ADC(2)	9.48	9.97	9.85	9.77	0.45	11.47	17.07	13.34	5.61
CCSD-ADC(2)	9.81	10.11	10.05	9.99	0.28	11.51	17.14	13.38	5.63
F/CCSD-ADC(2)	9.81	10.12	10.06	10.00	0.28	11.55	17.27	13.46	5.72
ADC(3/2)	9.30	10.09	9.71	9.70	0.69	12.07	16.35	13.50	4.29
F/CCD-ADC(3/2)	9.03	9.70	9.43	9.39	0.58	11.68	16.28	13.21	4.59
F/CCSD-ADC(3/2)	9.33	9.82	9.63	9.59	0.43	11.78	16.45	13.33	4.67
CC3 ^a	9.38	9.96	9.61	9.65	0.51	11.95	15.57	13.16	3.62
Experiment ^a				9.83	0.67			13.08	3.59

^aTaken from Refs. 11 and 44–48.

CC3 is depicted in Fig. 3. Compared to CC3, the standard ADC(2) variant overestimates the polarizability by almost 5%. This can be significantly improved to almost 1% by using CCD amplitudes, independent of whether they are used everywhere or only in the F vectors. When using CCSD amplitudes, the results are with a relative error of about 3.5% worse, but still better than for the standard ADC(2) variant. ADC(3/2), however, yields a result very similar to CC3, having a relative error of only 0.5%. The trend of using CCD or CCSD amplitudes within ADC(3/2) is the same as for the pure second-order method. Here, however, this means a deterioration in the case of CCD amplitudes, since the polarizability is underestimated by about 2.7%. F/CCSD-ADC(3/2) has roughly the same relative error compared to CC3 as the standard variant, just with the opposite sign.

When taking the experimental value as reference, which was obtained using refractive index data,^{45,47} similar trends are observed. ADC(2) overestimates the polarizability by 3% or 0.3 a.u., and the use of CC amplitudes again lowers the obtained values, thus generally improving the results. As for Ne and HF, CCD amplitudes yield better results than CCSD ones and the difference between the CC- and F/CC-ADC variants is negligible. CCSD-ADC(2), however, still overestimates the static polarizability by about 1.6% (0.16 a.u.), whereas the variants with CCD amplitudes now *underestimate* its value by 0.06 a.u. Overall, (F)/CCD-ADC(2) yields the best results of all compared methods with a relative error of only about -0.65%. In fact, the result with CCD-ADC(2) agrees even better with experiment than the CC3 one, which for the previously studied systems yielded results almost identical to FCI, but here underestimates the polarizability by 1.8% (0.18 a.u.) compared to experiment.^{11,39} A significant difference to previous results is observed for the third-order ADC scheme. The effect of the CC amplitudes of lowering the values is still the same, but since standard ADC(3/2) already underestimates the polarizability compared to experiment by 1.3% (0.13 a.u., thus being still more accurate than CC3); in this case, the results deviate stronger when using CCD or CCSD amplitudes within the second-order F vectors. Deviations from experiment of -0.44 and -0.24 a.u. corresponding to relative errors of -4.5% and

-2.4% were obtained for F/CCD-ADC(3/2) and F/CCSD-ADC(3/2), respectively.

Having a look at the polarizability anisotropy $\Delta\alpha$, standard ADC(2) yields the best result of 0.54 a.u. with respect to CC3 or experiment compared to all other second-order methods. CCD amplitudes lower this value only by 0.1 a.u., but with CCSD amplitudes, the result is with 0.28 a.u. the worst of all. Standard ADC(3/2) yields the best result of all with respect to experiment, even better than CC3. Taking CC3 as a reference, on the other hand, the ADC(3/2) value can be slightly improved by using CC amplitudes.

Another molecular system under investigation here is carbon monoxide, which was also calculated using the d-aug-cc-pVTZ basis set. As can be seen from the results for the isotropic polarizability shown in Table III and the relative error with respect to CC3 depicted in Fig. 3, standard ADC(2) overestimates its value significantly by 4.1% or 0.34 a.u. The use of CCD amplitudes in both the F vectors and the secular matrix \mathbf{M} of ADC(2) lowers this error significantly to 0.11 a.u., yielding again the best result of all ADC(2) variants compared to CC3 with a relative error of only about 0.9%. With CCSD amplitudes, the deviation is 1.7% (0.22 a.u.), which is still less than half as large as for standard ADC(2). The difference between the CC-ADC(2) and F/CC-ADC(2) variants is for CO larger than for Ne or HF, but the trend is the same as for Li^- : employing CC amplitudes only in the modified transition moments has the largest influence and lowers the value of the dipole polarizability significantly, with F/CCD-ADC(2) and F/CCSD-ADC(2) resulting in a relative error of about 1.3% and 2.3%, respectively, while the additional substitution in the secular matrix \mathbf{M} has the same effect, but to a smaller extent. Going to the third-order description in the secular matrix only yields a small improvement compared to pure second-order; the error of standard ADC(3/2) still amounts to 2.6% or 0.34 a.u. Replacing the MP amplitudes in the second-order transition moment vectors by CC ones gives an improvement for both CCD and CCSD doubles amplitudes. In this case, however, the variant with CCD amplitudes yields better result than that with CCSD ones. While F/CCSD-ADC(3/2) still deviates from experiment by 1.3%

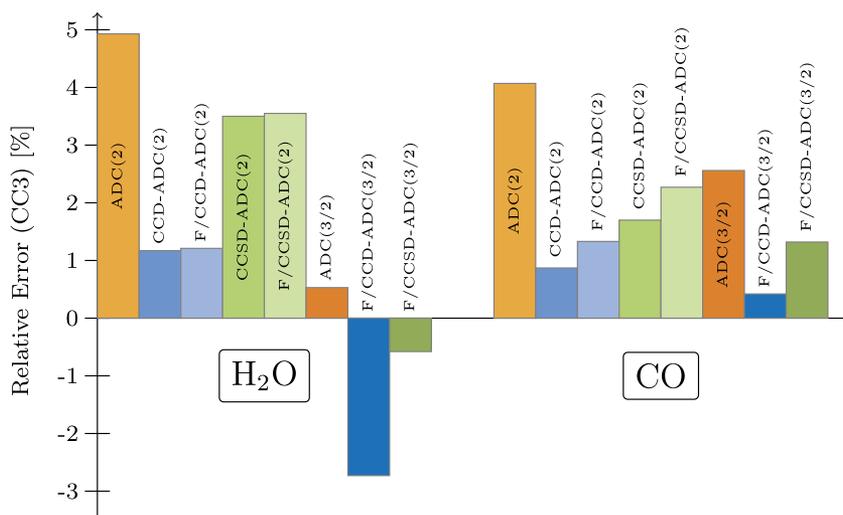


FIG. 3. Relative error of the isotropic polarizability $\bar{\alpha}$ of H_2O and CO of results presented in Table III with respect to CC3.

(0.17 a.u.), F/CCD-ADC(3/2) yields the best result of all presented ADC variants with a deviation of only 0.05 a.u., corresponding to a relative error of about 0.4%. It is also remarkable at this point that all “hybrid” CC-ADC variants, even the pure second-order ones, yield better results than the (third-order) standard ADC(3/2) method. For example, the relative error of F/CCD-ADC(3/2) is only one third of the standard ADC(3/2) one, and the relative error of CCD-ADC(2) is about half as large as the one of standard ADC(3/2) and only one third of the standard ADC(2) one. All observed trends and results hold as well when taking experiment^{11,46} as a reference for the isotropic polarizability, just that the absolute deviation is 0.08 a.u. larger for all ADC variants.

A different picture is observed for the individual components of the polarizability tensor. For the two components perpendicular to the molecular axis, α_{xx} and α_{yy} , the standard ADC approaches with MP amplitudes have a smaller deviation from the CC3 results than the ones with CC amplitudes, the order of magnitude of the deviation for the former being about 0.1 a.u., whereas for the latter, it is up to 0.5 a.u. However, for the component along the molecular axis, α_{zz} , the largest difference can be observed between the pure second-order ADC variants and the ADC(3/2) ones. The third-order description of the secular matrix \mathbf{M} significantly improves the description of α_{zz} by about 1.0 a.u. for the standard ADC approaches. The influence of the chosen amplitudes in the \mathbf{F} vectors on the ADC(3/2) results is rather negligible. At the ADC(2) level, this influence is somewhat larger, and the largest improvement is again obtained with CCD amplitudes replacing the MP ones everywhere, with the error of CCD-ADC(2) being 0.4 a.u. smaller than the one of the standard ADC(2) variant. These differences, of course, explain the changes in the polarizability anisotropy. While all ADC variants overestimate its value compared to experiment^{11,48} or also CC3,⁴⁴ the use of CC amplitudes within ADC generally raises $\Delta\alpha$, thus worsening the results. For CCSD amplitudes, the effect is more pronounced than for CCD ones.

2. Aromatic systems

Finally, we turn our attention now to some larger chemical systems: aromatic and heteroaromatic compounds. Due to the lack of

CC3 or similar values in the literature for these systems, they are compared to experimental values only. The prototype of aromatic systems is, of course, the benzene molecule, which is considered as a first example using the Sadlej-pVTZ basis set.⁵² Experimental values in the literature were obtained by applying ultraviolet Stark spectroscopy⁴⁹ or through a series of experimental and theoretical data using the DOSD technique.⁵⁰ For standard ADC methods, the benzene molecule has proven to be a difficult case,¹² which can be seen in the results shown in Table IV and Fig. 4 (left). Compared to the DOSD value, standard ADC(2) overestimates the static polarizability significantly by 5.14 a.u., corresponding to a relative error of 7.6%. Expanding the secular matrix \mathbf{M} to third order in standard ADC(3/2) improves the result only slightly and still overestimates $\bar{\alpha}$ notably by 6.1% or absolutely by 4.13 a.u. Using CC amplitudes within ADC again improves the values for the polarizability significantly by lowering the computed values. Here, the difference between CCD and CCSD amplitudes is replacing the MP ones either only in the \mathbf{F} vectors or both in \mathbf{F} and the secular matrix \mathbf{M} is rather negligible, with the difference between the two corresponding CC-ADC(2) and F/CC-ADC(2) variants being $\leq 0.1\%$. Using CC amplitudes within ADC(2) in the modified transition moment vectors only yields a deviation from experiment of about 3.2% (2.2 a.u.), whereas the error is about 2.9% (less than 2.0 a.u.) when the amplitudes are replaced everywhere in CC-ADC(2). A significant improvement is also observed when using CC amplitudes in the \mathbf{F} vectors of the ADC(3/2) variant, with the deviation from experiment being merely about 2.2% (1.5 a.u.), thus yielding the best results for all compared ADC variants. Hence, the improvement obtained when using CC amplitudes within ADC for the calculation of the static polarizability lies in the order of 63%, which is the most significant one of all systems compared so far. Again, all CC-ADC variants show a substantial improvement over the standard ones with the relative error of CC-ADC(2) methods being only about half as large as the one for standard ADC(3/2). A possible explanation for the better performance of the CC-ADC variants compared to the standard ADC ones is the better description of excitation energies, especially for the lowest ones, as shown in Paper I.¹⁷ Yet, the transition moments seem to be a more important factor. They are, however, hard to compare with the literature or especially experiment.

TABLE IV. Static dipole polarizability (in a.u.) of benzene, pyridine, and naphthalene calculated with different ADC variants (Sadlej-pVTZ basis set) compared to DOSD values.

Method	Benzene				Pyridine					Naphthalene				
	α_{xx}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$
ADC(2)	86.32	46.14	72.93	40.18	82.64	42.21	78.49	67.78	38.53	182.3	134.4	69.2	128.6	98.3
CCD-ADC(2)	81.68	45.99	69.78	35.69	78.41	42.09	74.67	65.05	34.60	172.8	128.5	69.4	123.6	89.8
F/CCD-ADC(2)	81.90	46.08	69.96	35.82	78.51	42.14	74.88	65.18	34.69	171.0	128.7	69.6	123.1	88.2
CCSD-ADC(2)	81.79	45.57	69.72	36.22	78.70	41.83	75.20	65.24	35.26	172.9	129.0	68.9	123.6	90.4
F/CCSD-ADC(2)	82.14	45.75	70.01	36.39	78.96	41.97	75.54	65.49	35.41	171.6	129.5	69.3	123.4	89.1
ADC(3/2)	84.89	45.97	71.92	38.92	80.91	41.95	76.59	66.48	36.99	178.1	130.7	68.6	125.8	95.2
F/CCD-ADC(3/2)	80.91	46.08	69.30	34.82	77.27	42.07	73.46	64.27	33.46	168.3	126.0	69.3	121.2	86.1
F/CCSD-ADC(3/2)	81.12	45.75	69.33	35.37	77.67	41.87	74.05	64.53	34.13	168.8	126.6	68.9	121.4	86.8
Experiment ^a			67.79	31.5				62.88					117.4	86.8

^aTaken from Refs. 24 and 49–51.

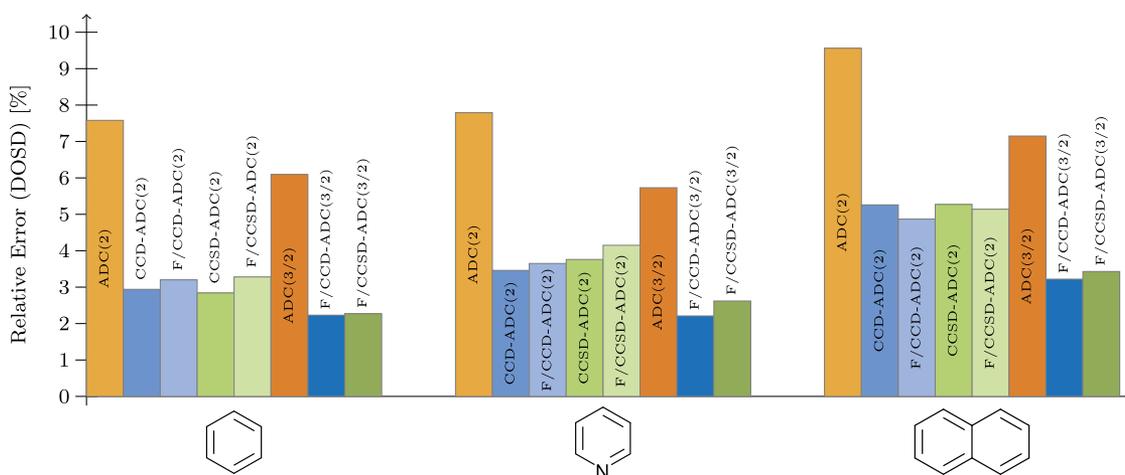


FIG. 4. Relative error of the isotropic polarizability $\bar{\alpha}$ for benzene, pyridine, and naphthalene of results presented in Table IV with respect to DOSD values.

In Ref. 9, only oscillator strengths were compared, but those also depend linearly on the excitation energy.

Not only the isotropic polarizability but also its anisotropy is improved significantly compared to the experimental value⁴⁹ when using CC amplitudes in ADC. While it does not seem to play a significant role whether they are employed both in the secular matrix and the modified transition moments, CCD amplitudes again yield slightly better results than the corresponding versions with CCSD amplitudes. Other experimental results give the polarizability anisotropy of benzene as 35.02 a.u.,^{51,53} which is in almost perfect agreement with CCD-ADC(2) or F/CCSD-ADC(3/2) results, for instance.

Another system closely related to benzene is the six-membered heteroaromatic compound pyridine, the geometry of which has been optimized using the Gaussian 09 program package⁵⁴ at the MP2/cc-pVTZ level of theory. For the calculation of the static polarizability again the Sadlej-pVTZ basis set was used, the results are shown next to the ones for benzene in Table IV and the relative errors are depicted in Fig. 4. The experimental value of its isotropic polarizability was obtained using the DOSD method.²⁴ However, no value for the individual components or its anisotropy could be found in the literature. The deviation of the standard ADC(2) method from the DOSD value is with 7.8% or 4.9 a.u., very similar to the one for the benzene molecule, while the deviation of the standard ADC(3/2) variant is with 5.7% (3.6 a.u.) slightly smaller (0.5 a.u. in absolute numbers) for pyridine than for benzene. However, a clear improvement is observed again for all ADC variants when using CC instead of MP amplitudes. The difference between the individual variants is slightly larger in this case than for benzene, though all variants are still very similar. The best result for the pure second-order ADC method is again obtained when CCD amplitudes are used throughout, i.e., CCD-ADC(2). Here, the error amounts to 3.46% (2.17 a.u.), as compared to 3.76% (2.36 a.u.) when CCSD amplitudes are used, or 3.65% and 4.15% corresponding to 2.30 and 2.61 a.u. when CCD or CCSD amplitudes are used in the F vectors only, respectively. This corresponds to an improvement of up to 55% compared to

the relative error of the standard ADC(2) method. Another significant improvement is observed when F/CCD-ADC(3/2) is employed. With a deviation from experiment of 2.21% (1.39 a.u.), the F/CCD-ADC(3/2) variant again yields the best result, which corresponds to an improvement of 61% as compared to the standard ADC(3/2) variant. The F/CCSD-ADC(3/2) variant yields a comparable result with a relative error of 2.62%. Again, the results obtained with all hybrid CC-ADC variants show a significant improvement over the standard ones, even CC-ADC(2) over standard ADC(3/2), at a lower overall computational cost.

The results for the last and largest system discussed here, the naphthalene molecule, are summarized in Table IV and Fig. 4, as well calculated with the Sadlej-pVTZ basis set. As noted by Millefiori and Alparone,⁵¹ experimental results of the polarizability and its anisotropy were obtained from the Cotton-Mouton effect,⁵⁵ molar Kerr constants, and refractions,^{56,57} as well as from laser Stark spectroscopy.^{58,59} Concerning the isotropic polarizability, the standard ADC(2) variant has an even larger deviation from experiment than for benzene and pyridine, the relative overestimation amounting to 9.6%, its absolute error being 11.22 a.u. As previously, significant improvement is obtained when CC amplitudes are used. For CCD-ADC(2), CCSD-ADC(2), and F/CCSD-ADC(2), the relative error lies between 5.1% and 5.3%, with the absolute error between 6.0 and 6.2 a.u. In this case, the F/CCD-ADC(2) variant again stands somewhat out, having the smallest error of all compared methods with 4.9% or 5.72 a.u. Thus, the improvement obtained when using CC amplitudes is up to almost 50% compared to the standard ADC(2) variant. The standard third-order ADC(3/2) method again shows no significant improvement compared to standard ADC(2) and has an error of 7.2% corresponding to 8.4 a.u. The use of CC amplitudes within the second-order F vectors improves notably upon this value, yielding the best result of all compared methods with 3.2% corresponding to 3.8 a.u. As for the aromatic systems studied before, all CC-ADC variants yield better results compared to experiment than the standard ones, especially CC-ADC(2) yields better results than standard ADC(3/2) while the computational cost remains

significantly lower. On the other hand, an improvement in the relative error of more than 50% is obtained when going from standard ADC(3/2) to F/CCD-ADC(3/2) at a computational cost increase that only amounts to about 1% in this case. Again, a possible explanation for the improved description of the polarizability is the improvement in excitation energies.¹⁷ Even more pronounced than for benzene, significantly improved results for the polarizability anisotropy $\Delta\alpha$ compared to experiment are obtained when using CC amplitudes within ADC, especially in the ADC(3/2) scheme where the F/CCSD-ADC(3/2) variant is in perfect agreement with the experimental value.

Two more related aromatic systems, quinoline and isoquinoline, have been calculated as well (see the [supplementary material](#) for the results), and the results show the same trends and improvements for the CC-ADC methods, underlining the consistency of the improvement for this class of molecules.

IV. SUMMARY

In this work, the existing implementation of the algebraic-diagrammatic construction scheme for the polarization propagator with coupled-cluster amplitudes¹⁷ has been extended to molecular properties and in this special case tested for dipole polarizabilities recently implemented for standard ADC using the damped response formalism.¹² Furthermore, in addition to CCD, CCSD amplitudes can be used as well, also in the second-order transition moments of the ADC(3/2) method. This new approach is inspired by similar works done on the SOPPA method by Geertsen, Oddershede, and Sauer.^{19,20} In the new CC-ADC(2) variants, the Møller–Plesset correlation coefficients that occur in ADC are replaced by either CCD or CCSD amplitudes; in the F/CC-ADC(2) and F/CC-ADC(3/2) variants, they are replaced only in the second-order modified transition moments \mathbf{F} , but not in the secular matrix \mathbf{M} . In order to test the performance of the new CC-ADC variants, the static dipole polarizabilities of several small- to medium-sized chemical systems have been calculated and compared to FCI, CC3, DOSD, or experimental reference values. As a first test case, the Li^- ion was chosen since it served previously as a reference.²⁰ In our opinion, however, this is not a good test case since the results are very sensitive with respect to the amplitudes employed in the calculation, and hence, the values vary very strongly and unsystematically. Although the result obtained with the F/CCD-ADC(2) variant is very close to FCI, this seems to be rather fortuitous than systematic and hence does not allow for many general conclusions regarding the use of CC amplitudes within ADC, except that the polarizability becomes smaller when using CC amplitudes. For the ten-electron systems neon and hydrogen fluoride, the standard ADC methods show a relatively large deviation from FCI that could be improved when employing CCD amplitudes. Since, however, the third-order ADC(3/2) scheme already provided very good results with relative errors $\leq 1\%$, no significant improvement was obtained with CC amplitudes in the \mathbf{F} vectors. A slightly different picture is obtained when experimental values are used as reference. While for the water molecule notable improvements, especially with CCD amplitudes, could be observed for the second-order ADC method, an increased deviation is observed for ADC(3/2) because the standard variant already underestimates the static polarizability by about 1%, and the use of CC amplitudes in the \mathbf{F} vectors generally lowers

its absolute value even more. For carbon monoxide and, in particular, the aromatic systems benzene, pyridine, and naphthalene, which have proven to be very problematic cases for standard ADC,¹² very consistent improvements for all CC-ADC variants compared to the standard schemes are obtained. The CCD-ADC(2) results, for instance, even exhibit a notably smaller relative error than the considerably more expensive ADC(3/2) method. For benzene, the relative errors of both the CC-ADC(2) and F/CC-ADC(3/2) variants amounted only to about 35%–50% compared to the one of standard ADC(3/2).

Due to the less favorable scaling of CCD/CCSD compared to MP2, the CC-ADC(2) variants are, of course, computationally somewhat more demanding than standard ADC(2), but still significantly cheaper than the standard third-order ADC(3/2) or equation-of-motion (EOM)-CC methods. At this point, it seems appropriate to consider some computational efficiency aspects of the different standard ADC, CC-ADC, and standard (EOM)-CC approaches in terms of their formal scaling with system size a bit more in detail. Both MP2 and ADC(2) scale as $\mathcal{O}(N^5)$ (the latter in an iterative manner, however), whereas ADC(3) and both (EOM)-CCSD and CCD scale as $\mathcal{O}(N^6)$, where N is the number of basis functions. The price that has thus to be paid for the improvement of the results for the static polarizability with CC-ADC(2) is the $\mathcal{O}(N^6)$ iterative ground-state calculation with CCD or CCSD instead of just the single $\mathcal{O}(N^5)$ MP2 one. The successive excited-state calculation, however, scales more favorably for ADC(2) than for ADC(3) or CCSD. Thus, while the ground-state calculation has become one order of magnitude more expensive compared to MP2, the excited-state calculation still scales as $\mathcal{O}(N^5)$ and the results obtained with the CC-ADC(2) variants are notably better than the ones for standard ADC(3/2). In this way, one obtains very good results at an overall lower cost than standard third-order ADC or CCSD methods which are sometimes even comparable to the very accurate iterative CC3 method that, however, scales very unfavorably as $\mathcal{O}(N^7)$. As an example, in the ADC(2) and CC-ADC(2) computations of the aromatic systems, the central processing unit (CPU) time needed for the ADC (and CC) calculations amounts to only about 1% compared to ADC(3/2). On the other hand, the additional time needed for the CC calculation in F/CC-ADC(3/2) also amounts to only about 1% of the total time, and the improvement in the results is remarkable.

We thus believe that especially the CC-ADC(2) variants will become useful and versatile alternatives to standard ADC in the calculation of molecular properties such as polarizabilities since it combines a reliable iterated CC ground state and retains the advantageous features of ADC with its Hermitian eigenvalue problem and low computational cost.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for geometries of all considered molecules as well as additional results for the static polarizabilities of the quinoline and isoquinoline molecules.

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