The algebraic diagrammatic construction scheme for the polarization propagator for the calculation of excited states

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The algebraic diagrammatic construction (ADC) scheme for the polarization propagator provides a series of *ab initio* methods for the calculation of excited states based on perturbation theory. In recent years, the second-order ADC(2) scheme has attracted attention in the computational chemistry community because of its reliable accuracy and reasonable computational effort in the calculation of predominantly singly excited states. Owing to their size-consistency, ADC methods are suited for the investigation of large molecules. In addition, their Hermitian structure and the availability of the intermediate state representation (ISR) allow for straightforward computation of excited-state properties. Recently, an efficient implementation of ADC(3) has been reported, and its high accuracy for typical valence excited states of organic chromophores has been demonstrated. In this review, the origin of ADC-based excited-state methods in propagator theory is described, and an intuitive route for the derivation of algebraic expressions via the ISR is outlined and comparison to other excited-state methods is made. Existing computer codes and implemented ADC variants are reviewed, but most importantly the accuracy and limits of different ADC schemes are critically examined. © 2014 John Wiley & Sons, Ltd.

INTRODUCTION

The development of accurate, predictive, and, at the same time, computationally efficient theoretical approaches for the calculation of excited electronic states of medium-sized and large organic molecules is an active field of research in contemporary theoretical chemistry,[1–6] which addresses one of its greatest challenges: the study of photochemistry of large molecules with more than approximately 25 atoms of the second row of the periodic table.[7,8] Here, one faces a serious dilemma when different excited electronic states of a molecule are to be computed: any approximation made to the Hamiltonian introduces imbalances in their description, and, clearly, the more severe an approximation is, the less balanced is the description of different excited states.[2] Computations on large molecules, however, require severe approximations to be technically feasible at all. Hence, for the computation of excited states of large molecules in reasonable time, it is necessary to find a compromise between accuracy and feasibility, or in other words, a theoretical method, that is computationally efficient and at the same time accurate enough to deliver a conclusive solution to the investigated photochemical problem. For excited states of large molecules this is particularly difficult, because their excited states are usually close in energy but possess very different electronic structures (e.g., $\pi\pi^*$, $n\pi^*$, charge transfer, Rydberg, or doubly excited), requiring in general quite accurate calculations. A plethora of quantum chemical approaches exist already for the calculation of excited states (see for example Refs 1–8). However, their

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accuracy and hence their reliability and predictive power vanish quickly with increasing level of approximation. In most cases it is thus not possible to identify a single quantum chemical method to describe all excited states with similar high accuracy, and one is usually forced to focus only on those states relevant to the investigated problem.

In the late 1990s great enthusiasm existed about linear-response (LR) time-dependent density functional theory (TDDFT),[9–11] because accurate calculations of absorption spectra were reported at very low computational cost.[12] TDDFT using standard exchange-correlation functionals rapidly became the method of choice for the calculation of excited states of medium-sized and large molecules with up to 250 atoms of the second row of the periodic table, i.e., far more than 1000 basis functions.[13,14] However, due to the approximate nature of the xc-functionals and the nowadays well-known problems of LR TDDFT with charge-transfer excited states,[15,16] doubly excited states,[13] its accuracy is essentially unpredictable and reliable theoretical benchmarks are generally required.[2] Despite the large number of available xc-functionals and their different levels of sophistication, DFT-based methods are also generally not systematically improvable.

A valuable alternative is offered by efficient semiempirical methods, for example the intermediate neglect of differential overlap/screened approximation (INDO/S),[17,18] the orthogonalization method 2 (OM2)/MRCI,[19–21] or DFT/MRCI.[22,23] In particular, the last two approaches have shown great potential in the investigation of multi-reference problems,[24] but it is clear that also these require accurate benchmarks for an initial assessment of the accuracy, due to the underlying high levels of semiempirical approximations.

For large molecules, accurate benchmarks are nowadays mostly generated by wave function-based *ab initio* methods following the theoretical approaches of multi-configuration self-consistent field (MCSCF), configuration interaction (CI), coupled cluster (CC) or, as we will see below, most recently also the algebraic diagrammatic construction (ADC) approach.[25–27] These comprise well-known methods like complete-active space self-consistent field (CASSCF)[26,28] in combination with second-order perturbation theory (CASPT2),[29,30] the approximate coupled-cluster schemes of second and third order, CC2[31–36] and CC3,[37–39] respectively, or equation-of-motion (EOM)[40–45] and LR[46–48] CC methods, for instance. Most recently, also propagator-based approaches have gained more attention, the second-order polarization propagator approximation (SOPPA)[49–52] and the ADC scheme of the polarization propagator in second and third order of perturbation theory [ADC(2) and ADC(3)].[43–57]

The interest in the ADC scheme of the polarization propagator has been triggered by recent efficient implementations of the second-order scheme ADC(2)-s into widespread quantum chemical program packages such as Turbomole,[58] Q-Chem,[59,60] and Psi4.[61] It turned out to be a slightly more efficient alternative to CC2 exhibiting a similar accuracy for singly excited states with a mean error (±standard deviation) of 0.22 ± 0.38 eV.[35,62] In addition, its Hermitian structure offers advantages in the computation of excited-state properties, such as nuclear gradients or dipole moments[35,63] and the inclusion of environmental effects via polarizable continuum models,[64] for example. Furthermore, it has recently been demonstrated that the ADC formalism is also applicable in the computation of molecular response properties such as polarizabilities[65] and indirect nuclear spin–spin coupling constants.[66] Despite the increasing interest in the application of ADC-based methods, its theoretical foundations, the basic concepts, as well as their accuracies and application ranges are known to an expert group of quantum chemists only. Hence, it is our intention here to introduce ADC schemes for the polarization propagator to a broad computational community, for whom it may provide a useful method for the calculation of excited electronic states and the comprehensive investigation of photochemical problems.

In the following section, the origin of ADC in Green's function theory is briefly outlined, motivating its otherwise unusual name. Subsequently, a more intuitive derivation of the ADC equations and a conceptual access to excited-state properties is provided, when the concept of the intermediate state representation (ISR) is explained. To make a connection to more familiar excited-state methods, the structure of the ADC matrices at several approximation levels is first discussed, and then the general properties of CI, CC, and ADC methods are compared. Most importantly, the computational accuracy of ADC methods is discussed, and the limitations of their applicability are pointed out. Finally, existing ADC implementations are reviewed.

THE ORIGIN OF THE METHOD IN PROPAGATOR THEORY

The ADC scheme of the polarization propagator for electronically excited states originates from

many-body Green's function theory.[53] Green's functions are a useful mathematical technique to solve inhomogeneous differential equations.[67] Although in many-body systems, like the electronic Hamiltonian of molecules, a unique Green's function cannot be defined, it is still possible to identify building blocks, which are usually called propagators, which yield solutions to certain classes of problems.[68,69] The one-electron propagator, for instance, measures the probability of the electron to travel within a certain time t from one place to another, while the two-electron propagator does the same for two correlated electrons. Hence it is clear that knowledge of the exact one-electron and two-electron propagators allows to calculate exact expectation values of one and two-particle operators.[70] In addition, the electron propagator provides access to ionization potentials and electron affinities, typical one-electron properties.[71–73]

The polarization propagator describes the time evolution of the polarization of a many-electron system, which from a more abstract perspective corresponds to time-dependent fluctuations of the ground-state electron density or wavefunction of the otherwise unperturbed system.[68] To be more explicit, the polarization propagator acts on the time-dependent ground-state wavefunction and propagates time-dependent density fluctuations of the many-body system. Their mathematical description in the eigenstate basis of the corresponding electronic Hamiltonian requires the wavefunctions of the excited electronic states. Thus, the polarization propagator implicitly contains information about the electronic excited states of the many-electron system, i.e., the corresponding molecule. This is readily apparent in the well-known spectral representation of the polarization propagator which, if expressed as a matrix function, is given by[68]:

$$\Pi_{pq,rs}(\omega) = \sum_{n \neq 0} \frac{\left\langle \psi_0 | c_q^\dagger c_p | \psi_n \right\rangle \left\langle \psi_n | c_r^\dagger c_s | \psi_0 \right\rangle}{\omega + E_0^N - E_n^N}$$
$$+ \sum_{n \neq 0} \frac{\left\langle \psi_0 | c_r^\dagger c_s | \psi_n \right\rangle \left\langle \psi_n | c_q^\dagger c_p | \psi_0 \right\rangle}{-\omega + E_0^N - E_n^N} \quad (1)$$

where ψ_0 is the electronic many-body ground state of the molecule with energy E_0^N. The creation and annihilation operators $c_q^\dagger$ and c_p, respectively, create or annihilate an electron in the corresponding one-electron state, which are typically associated with canonical Hartree-Fock orbitals. The sum is carried out over *all* electronically excited states ψ_n with total energy E_n^N. This so-called Lehmann

representation of the polarization propagator contains information on the excitation spectrum, as it possesses poles at the vertical excitation energies $\omega_n = E_n^N - E_0^N$, while the residues are the transition probabilities of the corresponding excitation. Both sums on the right-hand side of Eq. (1) contain identical information, hence it is sufficient to consider only one of them. Since in Eq. (1), the polarization propagator is expressed in the eigenstates of the molecular system, i.e., the ones that diagonalize the molecular Hamiltonian, it is usually called 'diagonal' representation of the polarization propagator and compactly written as

$$\Pi(\omega) = \mathbf{x}^\dagger (\omega - \mathbf{\Omega})^{-1} \mathbf{x} \quad (2)$$

where $\mathbf{\Omega}$ is the diagonal matrix of vertical excitation energies ω_n and $\mathbf{x}$ is the matrix of transition amplitudes, or also called 'spectroscopic' amplitudes. For the derivation of ADC approximation schemes,[53] Eq. (2) is to be formulated in a 'non-diagonal' representation according to

$$\Pi(\omega) = \mathbf{f}^\dagger (\omega - \mathbf{M})^{-1} \mathbf{f}, \quad (3)$$

which fits to the representation of the polarization propagator in terms of Feynman-Goldstone diagrammatic perturbation series. The existence of such a representation needs to be postulated here. $\mathbf{M}$ is a 'non-diagonal' matrix representation of an 'effective' Hamiltonian and $\mathbf{f}$ is the matrix of the 'effective' transition moments.[53] At this point in the original derivation, diagrammatic perturbation theory comes into play, and the 'effective' Hamiltonian and transition amplitudes are expanded independently with respect to their perturbation-theoretical order in the fluctuation potential,[53] which is the correlation energy according to the typical Møller-Plesset partitioning of the Hamiltonian

$$\mathbf{M} = \mathbf{M}^{(0)} + \mathbf{M}^{(1)} + \mathbf{M}^{(2)} + \dots$$
$$\mathbf{f} = \mathbf{f}^{(0)} + \mathbf{f}^{(1)} + \mathbf{f}^{(2)} + \dots \quad (4)$$

A perturbation-theoretical order analysis of the expansion of $\Pi(\omega)$ yields explicit algebraic expressions for the matrix elements $(\mathbf{M})_{\mu\nu}^{(n)}$ and $\mathbf{f}_\mu^{(n)}$, where the indices μ and ν refer to certain excitation classes, i.e., singly, doubly, etc. excited. The order of an ADC approximation scheme, ADC(n), accounts for all terms and blocks required for a perturbation theoretically consistent description of $\Pi(\omega)$ through order n. The ADC schemes can thus be seen as a specific reformulation of the diagrammatic perturbation series of the polarization propagator. Having now explicit algebraic expressions for the matrix M available, and

knowing that the polarization propagator has poles at the excitation energies, the latter can be obtained simply by diagonalization of the matrix $\mathbf{M}$ at a desired order of perturbation theory. Hence, the solution of the Hermitian eigenvalue problem

$$\mathbf{MY} = \mathbf{Y}\Omega; \quad \mathbf{Y}^\dagger \mathbf{Y} = 1 \qquad (5)$$

yields vertical excitation energies ω_n and eigenvectors $\mathbf{y}$, which give access to spectroscopic amplitudes $\mathbf{x}$ via

$$\mathbf{x} = \mathbf{y}^\dagger \mathbf{f} \ . \qquad (6)$$

Summarizing the line of thought of this derivation briefly, the polarization propagator of a molecular system carries information about the exact excited states. The ADC scheme allows for a perturbation-theoretical consistent reformulation of approximations for the polarization propagator, which then in turn contain only approximate information on the excited states. Diagrammatic analysis of the perturbation-theoretical series yields explicit algebraic expressions, and hence, a mathematical framework to compute excitation spectra. Naturally, the higher the order of perturbation theory, the more accurate the results for the excitation energies and transition amplitudes can be expected to be.

The derivation outlined above also points toward the origin of the name of the methodology: ADC scheme, since diagrammatic perturbation theory is employed to construct consistent levels of approximations to propagators. Of course, the polarization propagator is only one possible propagator. ADC can be applied to, and it has already been used for other propagators as well. For example, the electron propagator yields algebraic expressions for the calculation of electron affinities,[74] while the hole propagator delivers ionization potentials[75] and the two hole propagator gives direct access to double ionization potentials,[76] and so forth. All these schemes are usually referred to as ADC, thus requiring to name the underlying propagator. In the following, however, we will concentrate on ADC for the polarization propagator only, i.e., on the calculation of excited electronic states.

THE INTERMEDIATE STATE REPRESENTATION

Today, an alternative route of the derivation of the algebraic ADC expressions exists via the so-called ISR.[55,63,77,78] This route does not require knowledge about propagators and is thus more easily comprehensible for students and computational scientists with a more standard quantum chemical training.

In the previous derivation, the excited-state basis $\{\tilde{\psi}_J\}$, in which the ADC equations are defined was not known, and apparently, this is not necessary to obtain excitation energies and spectroscopic amplitudes. However, without knowledge of these basis functions, the wavefunctions of the excited states are not accessible, as it is otherwise not possible to construct them from the ADC eigenvectors $\mathbf{y}$ according to

$$\psi_n = \sum_J y_{nJ} \tilde{\psi}_J \ . \qquad (7)$$

The explicit form of the basis functions, the so-called intermediate states (IS) $\{\tilde{\psi}_J\}$, was later derived.[55,77] Starting from the correlated ground-state wavefunction ψ_0, a correlated excited-state basis $\{\psi_J^0\}$, can in general be generated by acting on it with excitation operators $\{\hat{C}_J\} \equiv \{\hat{c}_a^\dagger \hat{c}_k, \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_k \hat{c}_l, ...\}$ representing physical single, double, etc … excitations

$$\psi_J^0 = \hat{C}_J \psi_0. \qquad (8)$$

These correlated excited states $\{\psi_J^0\}$ are generally not orthogonal, but can be successively orthogonalized via Gram-Schmidt (GS) orthogonalization yielding directly the orthogonal intermediated state basis $\{\tilde{\psi}_J\}$. The concept of the ISR is very general, and obviously, the previously defined 'effective' quantities $\mathbf{M}$ and $\mathbf{f}$ can now be expressed directly exploiting the IS basis as follows:

$$(\mathbf{M})_{IJ} = \left\langle \tilde{\psi}_I | \hat{H} - E_0^N | \tilde{\psi}_J \right\rangle , \qquad (9)$$

$$(\mathbf{f})_{J,pq} = \left\langle \tilde{\psi}_J | \hat{c}_p^\dagger \hat{c}_q | \psi_0 \right\rangle , \qquad (10)$$

with Eqs (9) and (10) being the ISRs of the shifted Hamiltonian and the effective transition amplitudes, respectively. The latter can be contracted with the dipole operator to obtain transition dipole moments. Choosing now the nth order Møller-Plesset ground state as starting point for the derivation of the IS basis, one arrives at the nth order ADC(n) scheme for excitation energies. For example, starting with the MP2 ground-state wavefunction and the MP2 ground-state energy, ADC(2) is obtained. Hence, one can state that ADC(2) can be seen as 'MP2 for excited states'. It is important to note that the ADC(n) methods converge to full-CI with increasing order.

As is immediately obvious, the ISR concept offers new possibilities,[63,78] not available in previous propagator approaches and the previous derivation of ADC. In particular, the ISR opens an avenue for convenient and efficient calculation of excited state and transition properties, since every operator $\hat{O}$ can be represented in the IS, in analogy to Eqs (9) and (10)

$$(\mathbf{O})_{IJ} = \left\langle \tilde{\psi}_I | \hat{O} | \tilde{\psi}_J \right\rangle, \tag{11}$$

and the corresponding expectation value is simply obtained by contraction with the corresponding ADC eigenvalues

$$\langle O \rangle_{nm} = \mathbf{y}_n^\dagger \mathbf{O} \mathbf{y}_m \ . \tag{12}$$

When, for example, $\hat{O}$ is chosen to be the dipole operator in Eq. (11), the static dipole moments of the excited states ($n = m$) and the transition dipole moments between excited states ($n \neq m$) are obtained via Eq. (12).[78] Most importantly, though, the excited state many-body wavefunctions can now be explicitly constructed according to Eq. (7). This allows for the calculation of one-electron densities, transition densities, difference densities, or detachment/attachment density plots, which greatly facilitate the interpretation of the electronic structure of excited states.[79,80]

Beyond the calculation of excited-state properties, the ISR also provides a rigorous mean to derive open-shell ADC schemes.[81–83] This has not been possible previously via the original algebraic diagrammatic pathway, because the required open-shell polarization propagator is not known. Via the ISR, on the contrary, the derivation of unrestricted algebraic diagrammatic construction (UADC) schemes is intriguingly simple using Eq. (8). In the unrestricted case, the reference ground state corresponds to an unrestricted MP ground state, and the excitation operators have to refer to spin orbitals rather than spatial orbitals as in the restricted case. As a consequence, the excitation operators acquire an additional spin index $\left\{ \hat{C}_J \right\} \equiv \left\{ \hat{c}_{a\sigma}^\dagger \hat{c}_{k\sigma}, \hat{c}_{a\sigma}^\dagger \hat{c}_{k\sigma} \hat{c}_{b\tau}^\dagger \hat{c}_{l\tau}, ... \right\}$ and one has to take care that subsequent annihilation and creation operators act on same-spin orbitals being both either α or β orbitals. Following the same derivation steps as outlined above yields unrestricted ADC equations. Along the same line of thought spin-flip ADC equations can in principle be derived. In that case, the triplet MP ground state serves as starting point, in which the two unpaired electrons are said to possess α spin. To generate now the singlet IS basis from the triplet ground state via the ISR formalism, the excitation operators of Eq. (8) must be ensured to flip the spin of one of the excited electrons from α to β.

THE STRUCTURE OF THE ADC MATRIX

For the derivation of the explicit expressions of the matrix elements of the ADC matrix, the formalism of second quantization is usually exploited and strings of creation and annihilation operators need to be evaluated to construct the IS basis and to represent the shifted Hamiltonian in them.[53,77] Explicit expressions of the matrix elements $(\mathbf{M})_{\mu\nu}^{(n)}$ are given elsewhere[53,56] and shall not be discussed in detail here. Instead, a more general discussion of the structure of the ADC matric at different levels of perturbation theory appears to be more useful.

As can be seen in Figure 1, the matrices of the ADC(2)-s, ADC(2)-x, and ADC(3) schemes have the same size, i.e., the dimension of a CI singles plus doubles matrix. In other words, they comprise singly excited Φ_i^a, so-called particle-hole (p-h) states, and doubly excited Φ_{ij}^{ab}, so-called two particle-two hole (2p-2h) intermediate states. The ADC schemes differ, however, in the order of perturbation theory to which the matrix elements of each individual block are expanded. In the strict ADC(2)-s scheme, which is rigorously derived when starting from the MP2 ground state, the (p-h) block is expanded to second order of perturbation theory, the (p-h, 2p-2h) coupling block to first order and the (2p-2h) block to zeroth order. As a consequence, the (2p-2h) block is diagonal containing only the orbital energy differences on the diagonal (Figure 1).

The extended ADC(2)-x scheme is an *ad hoc* extension of the ADC(2)-s scheme without rigorous theoretical justification.[54] In ADC(2)-x, the matrix elements of the (2p-2h) block are now expanded up to first order of perturbation theory, while all other matrix elements of the ADC(2)-s scheme remain unchanged (Figure 1). As a consequence, the (2p-2h) block is no longer diagonal and the computational effort for the diagonalization of the ADC(2)-x matrix increases from $O(N^5)$ for ADC(2)-s to $O(N^6)$. However, the inclusion of the coupling between the doubly excited states improves their theoretical description, that is, a substantial lowering of their excitation energies is observed. As we will see below, this *ad hoc* extension leads to an overall unbalanced description of the excitation spectrum and a consistent underestimation of excitation energies.

Originally, the third-order ADC(3) scheme has been derived using the diagrammatic path,[56,57] of course algebraic expression can also be obtained via the ISR pathway, when the MP3 ground state is used as starting point for the construction of the IS basis. In ADC(3), the matrix elements of all blocks are

FIGURE 1 | Structures of the ADC matrix in the strict and extended second-order schemes ADC(2)-s and ADC(2)-x, as well as the third-order scheme ADC(3). The matrices of these schemes have the dimension of a CISD matrix, as they stay within the singles and doubles manifolds. For the individual blocks the level of perturbation theory is given (white: zeroth order; yellow: first order; orange: second order; red: third order).
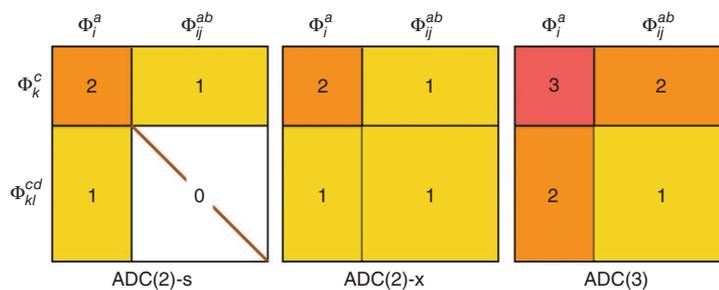
expanded consistently to one order of perturbation theory higher than in ADC(2)-s. Singly excited states are thus treated in third order of perturbation theory, while doubly excited states are computed to first order. Their coupling is treated consistently up to second order (Figure 1). However, the dimension of the ADC(3) matrix remains in the singles and doubles excitation manifolds. The computational effort of ADC(3) scales in analogy to ADC(2)-x like $O(N^6)$, though exhibiting a slightly bigger prefactor. In general, every calculation at ADC(2)-x level can also be done at ADC(3) level. In contrast to ADC(2)-x, ADC(3) offers a balanced description of the valence excitation spectrum and, as will be demonstrated below, with a much higher accuracy.

One possibility to further reduce the computational effort of ADC(2) calculations is to exploit the spin-opposite-scaling (SOS) approach, which has been established previously for MP2[84] and CIS(D)[85] and which has recently also been applied to ADC(2) and CC2.[86] Having understood the gist of the ISR derivation, it is clear that it can be followed also starting from the SOS-MP2 ground state. This yields a 'rigorous' ISR-SOS-ADC(2) scheme, which contains the SOS scaling factor only in the second-order expansion terms of the (p-h) block.[87] However, this derivation route does not provide any substantial improvement, neither in computational efficiency nor in accuracy. Hence, an additional approximation is made to the ADC matrix elements in that the same-spin components are also neglected in the (2p-2h) contributions. This makes the introduction of two further semiempirical parameters for the rescaling of the remaining opposite-spin components necessary (Figure 2). Along this line of thought, SOS-ADC(2)-s as well as SOS-ADC(2)-x have been developed, and the corresponding scaling factors have been fitted to an existing benchmark set. In particular, SOS-ADC(2)-x has been designed to reproduce the excitation energies of singly- and doubly excited states of linear polyenes as accurately as possible,[87] which is a notoriously difficult task for quantum chemical methods.

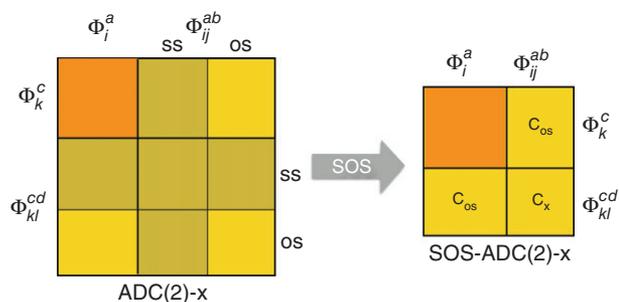If the interest lies only in a particular class of excited electronic states, it is generally possible to

FIGURE 2 | Effect of spin-opposite scaling (SOS) on the size and structure of the ADC(2)-x matrix. Neglect of the same-spin (ss) component and scaling of the opposite-spin (os) components leads to a reduction of the matrix dimension and the possibility to fit the semiempirical scaling factors (c_{os} and c_x) to known benchmark data. The color of the blocks represents the order of perturbation theory (yellow: first order; orange: second order). The shaded parts of the original ADC(2)-x matrix (left) are neglected in the SOS approximation.

reduce the complexity of the ADC matrix further. One example is the calculation of core-excited electronic states, i.e., such states in which an electron is promoted from a core orbital to a valence orbital. Such excited states are important for the computation of X-ray absorption spectra, for example. The calculation of core-excited states is generally difficult with standard implementations of excited-states methods, because their solution algorithms are typically designed to yield the energetically lowest excited states of the spectrum.[88] Hence for the calculation of the energetically high-lying core-excited states, which are located in the middle of the energy spectrum, the full ADC matrix would need to be diagonalized, which is computationally very inefficient and practically not feasible. A practical and very efficient work-around is offered by the core-valence separation (CVS) approximation, which exploits the fact that core and valence orbitals are energetically and spatially decoupled making the corresponding coupling elements in the ADC matrix vanishingly small.[89–91] Within the CVS approximation, these couplings are set to exactly zero, and as a consequence, the ADC matrix can be diagonalized in the space of core-valence excited states only (Figure 3). This leads to substantial
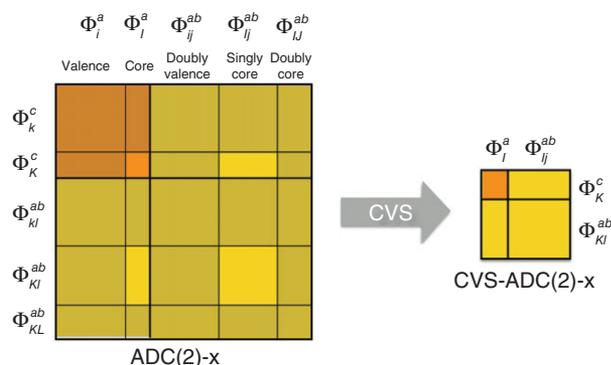
$$\Phi_i^a \quad \Phi_I^a \quad \Phi_{ij}^{ab} \quad \Phi_{Ij}^{ab} \quad \Phi_{IJ}^{ab}$$

Valence Core Doubly Singly Doubly
valence core core

Φ_k^c
Φ_K^c
Φ_{kl}^{ab}
Φ_{Kl}^{ab}
Φ_{KL}^{ab}

ADC(2)-x

CVS →

$\Phi_I^a \quad \Phi_{Ij}^{ab}$

Φ_K^c
Φ_{Kl}^{ab}

CVS-ADC(2)-x

FIGURE 3 | Effect of the core-valence-separation (CVS) approximation on structure and size of the ADC(2)-x matrix. The restriction of one of the indexes of the occupied orbitals to correspond to a core orbital results in a significant reduction of the matrix dimension. The color of the blocks represents the order of perturbation theory (yellow: first order; orange: second order) and the shaded parts of the original ADC(2)-x matrix (left) are set to zero in the CVS approximation.

TABLE 1 | Comparison of General Properties of Configuration Interaction (CI), Coupled Cluster (CC) and Algebraic Diagrammatic Construction (ADC) Methods

	CI(n)	CC(n)	ADC(n)
Size consistency	No	(Yes)	Yes
Hermiticity	Yes	No	Yes
Compactness	n	$m+1^1/m+2^2$	$m+1^{1,\,2}$
Ground state	CI(n)	CC(n)	MPn

[1] For even order $n = 2m$.
[2] For odd order $n = 2m + 1$.

reduction of the ADC matrix dimension and substantial computational savings without relevant loss of accuracy, and gives direct access to core-excited states. Recent work has shown that in particular the CVS-ADC(2)-x scheme in combination with the 6-311++G** basis set yields core-excitation spectra in excellent quantitative agreement with experimentally recorded ones of medium-sized and large molecules.[92]

COMPARISON WITH OTHER EXCITED-STATE APPROACHES

After the introduction of the basic concept and the mathematical structure of ADC, we are in the position to discuss basic general properties of ADC and to compare them with CI and coupled cluster (CC)-based methods. It is well known that correlated CI methods, except full CI of course, are not size-consistent.[27] As the ground-state correlation energy, also excitation energies, transition moments as well as excited-state properties are not size-consistent. On the other hand, as CI methods are Hermitian, the computation of excited-state properties and transition moments is straightforward.[27]

The CC-based excited-state methods comprise three related approaches referred to as coupled-cluster linear response (CCLR),[46–48] equation-of-motion coupled cluster (EOM–CC),[40–42] and symmetry-adapted cluster configuration interaction (SAC–CI),[93–95] which yield identical algebraic expressions for the excitation energies but differ in the calculation of properties.[96] All of them are non-Hermitian methods and thus lead to a twofold wavefunction representation of the excited states, corresponding to right and left eigenvectors of the non-Hermitian CC secular matrix. Hence, for a rigorous calculation of excited-state properties, both the right and left excited-state representations have to be computed.[97] In other words, the excited states need to be computed twice. However, the accuracy of the calculated properties is independent of the non-Hermiticity. Turning to size-consistency, excitation energies are size-consistent within all CC schemes; however, ground-state transition moments and excited-state properties are size-consistent only in the case of CCLR.[98–100]

In contrast to CC methods, the ADC(n) schemes are Hermitian and fully size-consistent with respect to excitation energies, transition moments and excited-state properties.[97,101] Hence, the computation of excited states and, in particular, of their properties is straightforward, since the ADC equations need to be solved only once. Another advantage of ADC over CI and CC is its compactness (Table 1). Compactness is in general defined as the explicit size of the configuration space that is needed for a consistent perturbation-theoretical description of the singly excited states to specific order n.[55,101] For CI methods, the required configuration space always corresponds to n, i.e., for treatment of singly excited states in nth order perturbation theory n-tuply excited configurations need to be taken into account. CC and ADC approaches are generally more compact. For an even order $n = 2m$, both require configuration spaces of $m + 1$ only, which means that for a treatment of the singly excited states in fourth-order perturbation theory 'only' triply excited configurations need to be considered. For an odd order $n = 2m + 1$, ADC requires again configuration spaces of $m + 1$, while CC methods have to go to $m + 2$. This is noticeable already in third-order methods. While EOM-CCSDT or CC(3) need to include triply excited (3p-3h) configurations, ADC(3) stays within the doubly excited-state manifold, i.e., the (2p-2h) space. ADC

TABLE 2 | Comparison of the Characteristics of ADC Schemes and CC Models

Method	Space	E_0	p-h	2p-2h	Properties	Scaling
CCS	p-h	1	1	–	0	n^4
ADC(1)	p-h	1	1	–	1	n^4
ADC(2)	2p-2h	2	2	0	2	n^5
CC2	2p-2h	2	2	0	1	n^5
ADC(2)-x	2p-2h	2	2	1	2	n^6
CCSD	2p-2h	3	2	1	2	n^6
ADC(3)	2p-2h	3	3	1	3	n^6
CC3	3p-3h	4	3	2	3	n^7

The configuration space, order of perturbation theory of the ground-state energy (E_0), the singly (p-h) and doubly (2p-2h) excited states as well as of response properties are given together with the scaling of the computational effort with the number of orbitals n.

schemes represent thus the most compact methods for excited states (see also Table 2).

In Table 2, a comparison of the general characteristics of CC and ADC schemes is made. It is readily apparent that CC and ADC methods have both advantages and disadvantages. The biggest advantage of CC methods is certainly the improved description of the ground state, which is for example consistent to fourth order of perturbation theory in CC3, while it is only third order in ADC(3).[97] Concomitantly, also the (2p-2h) configurations are better described. However, owing to the higher compactness of ADC compared to CC, the scaling of the computational effort with number of molecular orbitals is more favorable for ADC(3) than for CC3. Most remarkable, though, is the consistently high order of perturbation-theoretical treatment of the excited-state properties in the ADC schemes, which is always as high as the one of the (p-h) configurations.

Let us briefly inspect the relation of the second-order methods CIS(D), ADC(2)-s, and CC2 in a bit more detail, which are closely related both from a theoretical and computational point of view.[35] Mathematically, the ADC(2)-s matrix $\mathbf{M}^{\text{ADC}(2)}$ can be derived from the corresponding CC2 Jacobian $\mathbf{A}^{\text{CC2}}$, which is a non-symmetric matrix in a bi-orthogonal representation. Neglect of the t_1 amplitudes present in the CC2 Jacobian yields in a first step the $\text{CIS}(D_\infty)$ Jacobian $\mathbf{A}^{\text{CIS}(D_\infty)}$.[35] Eventually, the ADC(2)-s matrix is obtained by symmetrization

$$\mathbf{M}^{\text{ADC}(2)} = \frac{1}{2} \left[\mathbf{A}^{\text{CIS}(D_\infty)} + \mathbf{A}^{\text{CIS}(D_\infty)\dagger} \right]. \qquad (13)$$

A systematic $\text{CIS}(D_n)$ class of approximate second-order methods can be derived from $\text{CIS}(D_\infty)$ through inversion of the diagonal (2p-2h) block and binomial expansion up to order n.[102] Thereby the

doubles are eliminated from explicit consideration and the 'dressed' singles matrix needs to be solved in the space of single excitations only. However, apart from $\text{CIS}(D_0)$ a generalized, energy-dependent eigenvalue problem has to be solved iteratively. Not surprisingly, ADC(2)-s and $\text{CIS}(D_\infty)$ yield very similar excitation energies, while the results obtained with $\text{CIS}(D_0)$ and $\text{CIS}(D_1)$ deviate more strongly due to the additional approximations.[35,85] In general, CC2 yields slightly more accurate results for excitation energies with the smallest mean absolute errors.[35,62] The advantage of ADC(2)-s compared to CC2 that the excitation energies are obtained as eigenvalues of a Hermitian secular matrix results in a physically correct description of conical intersections between states of the same symmetry.

Finally let us briefly comment on the relation between ADC(2)-s and SOPPA, which are both second-order polarization propagator approaches based on Møller-Plesset perturbation theory. The most striking difference between these schemes lies in the dimension of the corresponding matrix representations. While ADC(2)-s spans the space of p-h and 2p-2h configurations, in other words, the matrix has the same dimension as the CISD matrix, in SOPPA also h-p and 2h-2p configurations are included.[49,50] As a consequence, the matrix dimension is twice as large as the one of ADC(2)-s, however, both exhibit very similar accuracy.[51] The relation between the ADC(2)-s and SOPPA matrices is similar to the one between the ADC(1) or CIS and the random phase approximation (RPA) or time-dependet Hartree-Fock (TDHF), in which the neglect of the h-p configurations in the latter approaches yields the working equations of ADC(1) or CIS.[13]

ACCURACY AND LIMITATIONS OF ADC SCHEMES

The excited-state methods ADC(2)-s, ADC(2)-x, and ADC(3), as well as the spin-opposite-scaled variants SOS-ADC(2)-s and SOS-ADC(2)-x, which have been introduced above, offer elegant Hermitian computation schemes for excitation energies and properties of medium-sized and large molecules. However, as any other excited-state method, also these schemes possess a clear range of accuracy and applicability, which shall be briefly discussed in the following section.

Before going to the individual ADC schemes in detail, it should be pointed out that one limitation is set by the ground-state treatment. Since all ADC schemes are built upon perturbation theory according to the Møller-Plesset scheme, it is clear that ADC(n) methods can only be expected to

yield reasonable results for molecules whose electronic ground state is reasonably well described by the corresponding MP*n* method. This excludes molecules with pronounced ground-state multi-reference character, i.e., small HOMO-LUMO gaps. However, this limitation may be overcome in the near future by using spin-flip approaches as outlined above. Nevertheless, the conventional ADC methods are applicable to most organic and inorganic molecules with energetically well separated closed- or open-shell electronic ground states covering a huge range of photochemistry.

The accuracy of the ADC schemes has recently been thoroughly evaluated by comparison to Thiel's benchmark set[103,104] of medium-sized molecules.[62] This augments previous evaluations, which were mainly done with respect to full CI data of atoms and diatomic molecules.[54,57] In general, however, similar accuracies have been found. Going through the different ADC variants, the second-order approach ADC(2)-s is applicable to fairly large molecules owing to its comparably low computational effort. ADC(2)-s turns out to be a robust and reliable method exhibiting typical mean errors (±standard deviation) of 0.22 ± 0.38 and 0.12 ± 0.16 eV for the singlet and triplet states, respectively, of the representative 28 organic molecules of Thiel's benchmark set (Table 3).[103,104] Application of the SOS approximation yields the SOS-ADC(2)-s scheme, which extends the accessible range of molecular sizes substantially and allows for fitting of the scaling parameters to the benchmark data (see above). This leads to a substantial reduction of the errors, 0.00 ± 0.15 and 0.06 ± 0.10 eV for the singlet and triplet states, respectively.[87] However, one should keep in mind that the scaling factors have been fitted for this benchmark set, so that, generally, similar accuracy cannot be taken for granted for other classes of molecules. SOS methods are semiempirical methods and require thorough benchmarking for each new application.

The extended second-order ADC(2)-x scheme turned out to exhibit a rather large mean error for the benchmark data with -0.70 ± 0.37 eV for its singlet states and -0.55 ± 0.20 eV for its triplet states.[62] This large, though consistent, underestimation of excitation energies originates from the previously described *ad hoc* extension of the (2p-2 h)-block of the ADC(2)-s matrix to first-order perturbation theory. However, ADC(2)-x is still useful in identifying doubly excited states, since their excitation energies are significantly lowered. Therefore, ADC(2)-x is recommended to be exploited as diagnostic tool for the presence of doubly excited states in the low energy region of the excitation spectrum.[105] When no states with pronounced double excitation character

TABLE 3 | Comparison of the Mean Errors and Their Standard Deviation of Singlet and Triplet Excitation Energies Computed with Different ADC Schemes

	Singlets	Triplets
ADC(2)-s	0.22 ± 0.38[1]	0.12 ± 0.16[1]
SOS-ADC(2)-s	0.00 ± 0.15[2]	0.06 ± 0.10[2]
UADC(2)-s	0.25 ± 0.20[3,4]	
ADC(2)-x	-0.70 ± 0.37[1]	-0.55 ± 0.20[1]
SOS-ADC(2)-x	-0.11 ± 0.18[2]	-0.04 ± 0.12[2]
UADC(2)-x	0.32 ± 0.20[3,4]	
ADC(3)	0.12 ± 0.28[1]	-0.18 ± 0.16[1]

The excitation energies are given in eV.
[1] Reprinted with permission from Ref 62.
[2] Reprinted with permission from Ref 87.
[3] These errors refer to doublet states.
[4] Reprinted with permission from Refs 81 and 83.

are present, ADC(2)-s or CC2 should be used for the calculation of the complete spectrum. Again, the SOS approximation can be used turning ADC(2)-x into a semiempirical method. Fitting the parameters in the same way as for SOS-ADC(2)-s before yields a substantial improvement of the accuracy for the benchmark set of -0.11 ± 0.18 and -0.04 ± 0.12 eV for triplet states, respectively.[87] Special attention in the fitting of the SOS scaling parameters has however been paid to doubly excited state of linear polyenes. Of course, the same statement as above also holds for SOS-ADC(2)-x, and care must be taken when it is applied to molecules outside the benchmark set by careful testing of the accuracy.

Since recently, also an efficient computer program of ADC(3) is available and its accuracy for excitation energies and oscillator strengths has been tested using again Thiel's benchmark set.[62] Previous tests with a pilot implementation for atomic and diatomic molecules found the deviations from full CI data to be consistently below 0.2 eV.[57] This accuracy is largely corroborated for the much bigger benchmark set of typical organic molecules, as well. ADC(3) exhibits a quite impressive low mean error of only 0.12 ± 0.28 eV for singlet and -0.18 ± 0.16 eV for triplet states. This deviation from the theoretical best estimates falls in the range of the expected error of the benchmark data itself, which are mostly CC3 and CASPT2 numbers. For example, when CC3 is reevaluated against the theoretical best estimates, which are not CC3 numbers, its deviation amounts to 0.23 ± 0.21 eV for the singlet states and 0.12 ± 0.10 eV for triplet states, which is similar to the one of ADC(3). Hence it is clear that ADC(3) is a highly accurate method with a computational effort of $O(N^6)$ which is only slightly higher than ADC(2)-x owing to a slightly

larger prefactor. ADC(3) is a big step forward in the available methods for excited-state calculations, as it is accurate and reliable, and in addition a black-box method, which does not require selection of molecular orbitals or configuration spaces. We are convinced that ADC(3) will soon become the benchmark method of choice for medium-sized closed-shell molecules.

Let us finally have a look at the accuracy of the unrestricted second-order ADC schemes, UADC(2)-s and UADC(2)-x (Table 3). The accuracy of both schemes has not been evaluated against a large benchmark set as the restricted ADC variants previously, but only against a limited set of existing experimental gas-phase absorption spectra of 11 medium-sized radicals[81] and gas-phase photo-electron spectra of small closed-shell molecules.[83] However, for these investigated cases, both schemes provide a similar accuracy with a mean error of about 0.3 ± 0.2 eV. As is typical for unrestricted single-reference excited-state methods, the UADC(2) schemes are sensitive to spin contamination, and the $\langle \hat{S}^2 \rangle$ of the unrestricted Hartree-Fock reference should not deviate too much from its expected value. It has been observed that values of below 1.25 for doublet radicals are still fine.[81]

IMPLEMENTED ADC METHODS AND EXISTING PROGRAMS

Today, efficient implementations of ADC(2)-s, ADC(2)-x, and ADC(3) are available in different quantum chemistry program packages. ADC(2)-s has been implemented in Turbomole,[58] Q-Chem,[59,60] and Psi4.[61] The most efficient implementation is currently the one in Turbomole based on the existing CC2 code exploiting the resolution-of-the-identity approximation.[33–35] The most complete ADC implementation offering most features is the one in Q-Chem using a general tensor contraction engine,[106] as ADC(2)-x and ADC(3) are only available in Q-Chem at the moment.

Turbomole and Q-Chem offer a similar set of excited-state properties at the ADC(2)-s level of theory, for example, excited-state gradients,[35] state-to-state transition and static excited-state dipole moments,[63] spin-orbit coupling elements,[107] and two-photon-absorption cross sections.[63] Since recently, ADC calculations can also be performed in combination with continuum solvation models.[64] In a development version of Q-Chem all these properties are also implemented at the ADC(2)-x and ADC(3) level of theory, which after thorough testing will be

soon included in the next official Q-Chem release. The spin-opposite-scaled variant SOS-ADC(2)-s is also available in Turbomole and Q-Chem, while SOS-ADC(2)-x is currently only present in the recent version of Q-Chem. Core-valence-separated (CVS) ADC(2)-s and ADC(2)-x especially well suited for the calculation of core-excitation spectra are currently being tested in a development version of Q-Chem,[92] and will also be made available soon.

CONCLUSION

The *ab initio* ADC schemes for the polarization propagator represent a new family of methods for the calculation of excited electronic states of molecular systems. They combine, in some sense, CI concepts with many-body perturbation theory. They offer the advantage to be fully size-consistent, Hermitian, and systematically improvable. However, also ADC has clear limitations owing to the single-reference character of the underlying Møller-Plesset electronic ground state. Hence, for a successful ADC calculation a reasonable description of the ground state by MP theory is a necessary prerequisite. For molecules with significant multi-reference character, standard ADC schemes are not the methods of choice, and one should instead resort to approaches such as CASSCF and MRCI. Still, ADC is applicable to organic and inorganic closed-shell molecules covering a broad range of photochemistry.

The ISR formulation of ADC paves the road to the efficient calculation of excited-state properties like state-to-state transition dipole moments, two-photon absorption cross sections, spin-orbit coupling elements to name a few. Also gradients can be computed, which allow for efficient optimization of excited-state equilibrium geometries and excited-state reaction pathways. While the second-order ADC(2)-s scheme represents a robust and reliable excited-state method, ADC(2)-x serves as a diagnostic for the presence of states with pronounced double excitation character in the low energy region of the excitation spectrum. The recently implemented ADC(3) scheme is a big step forward in theoretical photochemistry owing to its high accuracy at moderate computational cost of $O(N^6)$ for a third-order method. It can be expected that ADC(3) will soon be the benchmark method of choice to evaluate the accuracy of computationally more efficient approaches such as TDDFT and semiempirical methods such as OM2/MRCI, DFT/MRCI, and SOS-ADC schemes.

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