A. Algebraic diagrammatic construction

Originally, the so-called direct ADC procedure was developed within the Green's function (GF) formalism [1, 2]. It provides a framework to develop a hierarchy ADC(n) of approximations for the one-electron propagator, which are complete through the order n of the perturbation theory (PT) but include infinite partial summations needed to recover the correct simple poles analytical structure of the propagator, which is lost in the traditional diagrammatic approach. The method can be readily applied to construct multi-electron GF [3, 4] or the polarization propagator [5, 6]. A detailed and pedagogical account on ADC and related many-body methods is available in the excellent recent book by J. Schirmer [7]. In the present work, we employ the alternative ISR-ADC formulation [8, 9], which we describe for the specific case of single ionization.

The approach can be conveniently explained in comparison with the configuration interaction (CI) expansion [10], which represents the most straightforward approach to describe electronic correlation in quantum chemistry. Consider the Hartree-Fock (HF) ground state $|\Phi_0\rangle$ of the N-electron system. Using the so-called physical excitation operators,

$$\left\{\hat{C}_J\right\} = \left\{c_k; c_a^\dagger c_k c_l, k < l; c_a^\dagger c_b^\dagger c_j c_k c_l, j < k < l; \dots\right\}, \tag{1}$$

a complete orthonormal set of $(N-1)$-electron basis functions (also called HF configurations) can be derived as

$$|\Phi_J\rangle = \hat{C}_J|\Phi_0\rangle. \tag{2}$$

The indices j, k, l, ... and a, b, ... correspond to the occupied and virtual HF orbitals, respectively. It follows that the basis functions are naturally classified as *one-hole* ($1h$), *two-hole-one-particle* ($2h1p$) and so on according to the degree of excitation. The common notation is that J denotes individual configuration while $[J] = \mu$ stands for the whole $\mu h - (\mu - 1)p$ excitation class.

The basis set (2) is used in the CI method for expansion of the correlated $(N-1)$-electron wave functions $|\Psi_q^{(N-1)}\rangle$ (q denoting the complete set of quantum numbers specifying the ionized state). The principal drawback of such a direct approach is slow convergence and, once truncated after some specific excitation class $[J]$, lack of size consistency. The slow convergence is rooted in the fact that the HF configurations are uncorrelated and, therefore, every ionized state is constructed "from scratch". To improve, ISR-ADC employs a basis

set of the so-called correlated excited states (CESs),

$$|\Psi_J^0\rangle = \hat{C}_J|\Psi_0\rangle, \tag{3}$$

where $|\Psi_0\rangle$ is the exact N-electron ground state. The intuitive idea underlying the use of CESs is that the removal of an electron affects the correlation with respect to the initial N-electron ground state but not totally alter it. Therefore, the information on the correlation in the N-electron system conveyed by the CESs should result in faster convergence of the expansion of the $(N-1)$-electron wave functions [7].

In contrast to the HF configurations (2), the CESs (3) are not orthonormal. It is the specific *excitation class orthogonalization* (ECO) procedure that leads to an orthonormal basis of intermediate states (ISs) $|\tilde{\Psi}_J\rangle$, providing the sought-after size-consistent and fast-convergent expansion of $|\Psi_q^{(N-1)}\rangle$. ECO is an iterative process consisting of Gram-Schmidt orthogonalization between different excitation classes and symmetric orthogonalization of the resulting *precursor states* within each excitation class. For more details, see Refs. [7, 11].

Using the complete manifold of excitation operators (1), the basis of ISs provides an exact representation of the secular matrix (shifted Hamiltonian with E_0 being the exact neutral ground state energy),

$$M_{IJ} = \langle\tilde{\Psi}_I|\hat{H} - E_0|\tilde{\Psi}_J\rangle \tag{4}$$

as well as of the $(N-1)$-electron wave functions,

$$|\Psi_q^{(N-1)}\rangle = \sum_J Y_{q,J}|\tilde{\Psi}_J\rangle. \tag{5}$$

A practical computation scheme is obtained by replacing the exact neutral ground state $|\Psi_0\rangle$ by its PT expansion for the neutral ground state through the order n,

$$|\Psi_0\rangle = |\Phi_0\rangle + |\Psi_0^{(1)}\rangle + \cdots + |\Psi_0^{(n)}\rangle + O(n+1), \tag{6}$$

which in turn leads naturally to PT expansions of the ISs, the ground state energy E_0, and the matrix elements M_{JI} of Eq. (4). Similarly, the wave function expansion (5) has to be truncated after some specific excitation class, restricting the active configuration space. Ionization energies and the corresponding $(N-1)$-electron eigenstates are then obtained by diagonalising the resulting finite matrix $\boldsymbol{M}$.

One of the defining properties of the ADC method are the *canonical order relations* (COR), according to which the PT expansion of the off-diagonal ($[I] \neq [J]$) matrix elements

(SI) | $1h$ | $2h1p$ | **(DI)** | $2h$ | $3h1p$ | **(TI)** | $3h$ | $4h1p$

	$1h$	$2h1p$		$2h$	$3h1p$		$3h$	$4h1p$
$1h$	$M_{11}^{(0,2)}$	$M_{12}^{(1)}$	$2h$	$M_{11}^{(0,1,2)}$	$M_{12}^{(1)}$	$3h$	$M_{11}^{(0,1,2)}$	$M_{12}^{(1)}$
$2h1p$	$M_{21}^{(1)}$	$M_{22}^{(0,1)}$	$3h1p$	$M_{21}^{(1)}$	$M_{22}^{(0,1)}$	$4h1p$	$M_{21}^{(1)}$	$M_{22}^{(0,1)}$

TABLE I. Block structures of the ADC(2)x secular matrices $\mathbf{M}$ for single (SI, [2]), double (DI, [3]), and triple (TI, [4]) ionization. The upper indices give the PT orders included, i.e., $M_{11}^{(0,2)} = M_{11}^{(0)} + M_{11}^{(2)}$, with the zeroth order being given by the HF orbital energies.

of the secular matrix follow the general rule

$$M_{IJ} \sim O(|[I] - [J]|). \tag{7}$$

COR dictates at which order and excitation class the expansions (6) and (5) have to be truncated, respectively, to obtain ionization energies consistent through the required PT order. If $|\Psi_q^{(N-1)}\rangle$ is an eigenstate belonging to the excitation class $[I]$ (i.e., its expansion is dominated by class $[I]$ ISs), truncation of the configuration space after the excitation class $[J] > [I]$ introduces an error of order $2(J + 1 - I)$. Specifically for main $1h$ states ($I = 1$) this means an error of order $2J$, which can be compared to an error of the order $(J + 1)$ for the slower converging CI expansion.

The most widely used ISR-ADC scheme is the extended second-order scheme [ADC(2)x, ADC(2)-E]. The configuration space is spanned by the $1h$ and $2h1p$ ISs, and the $1h/1h$ block of the secular matrix contains corrections up to the second-order of PT while the $1h/2h1p$ and $2h1p/2h1p$ blocks only up to the first order. At this level, the energies of the $1h$-like states are determined through the second-order while those of the $2h1p$-like states through the first order of PT only. To remedy this shortcoming, we have recently introduced the ADC(2,2) approximation [11] which, through the inclusion of the $3h2p$ excitation class and appropriate order structure of the resulting secular matrix $\boldsymbol{M}$ (see Tab. I in Ref. [11]), allows for a balanced description of both $1h$ and $2h1p$-like states through second order of PT.

ISR-ADC schemes for multi-electron Green's functions are derived fully analogously using an appropriate manifold of excitation operators in place of Eq (1). Specifically, for double ionization, the ADC(2)x schemes comprise $2h$ and $3h1p$ classes of ISs, derived from the

manifold

$$\left\{\hat{C}_J\right\} = \left\{c_k c_l, k < l; c_a^\dagger c_k c_l c_m, k < l < m\right\}, \tag{8}$$

and similarly for triple ionization. The block structures of the three ADC(2)x schemes are summarized in Tab. I. For each charge state, the working equations for the secular matrix elements are derived and implemented independently. Using the same level of the ADC scheme ensures consistency of the calculated ionization potentials, which is essential for the correct determination of the energy windows and would be difficult to achieve using any other methodology.

In the present work, the ionization potentials were obtained by block-Lanczos diagonalization [12] of the secular matrices. The procedure is initialized with a block of starting vectors covering the whole main subspace, e.g., all $1h$ ISs for single ionization. Iterative multiplication of the starting block by the Hamiltonian matrix generates the so-called Krylov space. Corresponding smaller, band-diagonal representation of the Hamiltonian is then easily diagonalized to obtain approximate eigenvalues of the original matrix. In the present work, convergence in the spectral regions of interest was typically reached after 100-150 iterations for the inner-valence and core regions, less than 50 iterations are usually sufficient to accurately determine the lowest triple ionization potential.

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