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Closed-form intermediate representations of many-body propagators and resolvent matrices

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A new type of "intermediate" state, $|\tilde{\Psi}_J\rangle$, is introduced in the representation of many-body propagators and related resolvent matrix elements. A simple algebraic procedure is presented for constructing the unitary transformation matrix $\underline{Q}$ that relates the intermediate states and the exact energy eigenstates, $|\Psi_n\rangle$, of the interacting system. Here the starting point is the matrix $\underline{X}$ of generalized spectroscopic amplitudes $\langle\Psi_n|\hat{C}_J|\Psi_0^N\rangle$, where $\hat{C}_J$ denotes a physical excitation operator and $|\Psi_0^N\rangle$ is the N-electron ground state. A block QR decomposition [G. H. Golub and C. F. von Loan, *Matrix Computations* (Johns Hopkins University, Baltimore, 1989)] of $\underline{X}$ according to the equation $\underline{X}=\underline{Q}\,\underline{F}$ allows one to determine explicit expressions for the subblocks of $\underline{Q}$ and the intermediate propagator representations constituted by a nondiagonal effective interaction matrix $\underline{C}$ and an effective spectroscopic matrix $\underline{f}$. These effective quantities $\underline{f}$ and $\underline{C}$ are formulated entirely in terms of ground-state density-matrix elements and related energy expectation values. The relevance of the intermediate representations as a means for deriving computational schemes is based on the regularity and compactness of the perturbation expansions for the effective matrices $\underline{f}$ and $\underline{C}$. These basic properties also establish that the intermediate representations are closed-form versions of the algebraic-diagrammatic construction approximation schemes derived previously as a reformulation of the original diagrammatic propagator perturbation series. The intermediate representations represent a link between algebraic and diagrammatic approaches in the field of propagator methods and are expected to be useful also in the development of nonperturbative approximations.

I. INTRODUCTION

In the language of Green's-function and propagator methods[1] the many-electron problem of atoms and molecules is formulated in terms of ground-state expectation values of Heisenberg operator products which after Fourier transformation take essentially the form of many-body resolvent matrix elements. The propagators allow for a direct access to the basic excitation processes in the considered system, such as single electron removal or attachment by the one-particle Green's function $\underline{G}(\omega)$; electronic excitation by the polarization propagator $\underline{\Pi}(\omega)$; double ionization or attachment by the two-particle (hole) propagator $\underline{P}(\omega)$. Another advantage, being particularly important in applications to larger system, is the emergence of "size-consistent" approximation schemes, leading to results that scale correctly with the number of particles in the system.

The usefulness of the propagator approach depends, of course, crucially on the quality of the available approximation schemes. Diverse computational schemes have been developed and used in the field of applications to atoms and molecules, and the reader is referred to recent review articles[2-6] and textbooks[7,8] as an introduction. One may distinguish essentially between an algebraic approach for deriving approximation schemes and methods based on diagrammatic perturbation theory. In the former family of methods, a widely adopted procedure is to rewrite the propagator as a superoperator resolvent and to apply inner projection techniques for its evaluation.[9,10] Approximations result by truncating the operator spaces employed in the inner projection of the operator inverse and by the choice of a reference state replacing the exact ground state. Fully equivalent approximation schemes have been obtained in the context of the equation-of-motion (EOM) method.[11,12] The diagrammatic approach, on the other hand, is based on the perturbation series for the considered propagator, which—as is well known—can be formulated in terms of Feynman diagrams. In general, useful approximation schemes cannot be obtained by a finite summation of these series, but one must resort to summations through infinite order of certain classes of diagrams. The prototype of such an infinite partial summation is the random-phase approximation (RPA) for the polarization propagator.[13] However, the RPA summation is complete only through first order,[11] which is completely unsatisfactory for the treatment of finite electronic systems.

Within the framework of the diagrammatic approach, practical higher-order approximation schemes have been obtained by a method referred to as algebraic diagrammatic construction (ADC).[14-16] The ADC method reformulates the diagrammatic perturbation series according to a simple algebraic form which may be viewed as a nondiagonal representation of the considered propagator. The ADC form introduces a constant Hermitian secular matrix (effective interaction matrix) $\underline{C}$ and a matrix of effective spectroscopic amplitudes $\underline{f}$. Approximations for these quantities can be successively determined by comparing the perturbation expansion of the ADC form with the original diagrammatic series through finite order. Hereby one arrives quite naturally at systematic approximation schemes [ADC(n)] representing infinite summations complete through order n for the propagator perturbation expansion. Diagonalization of the effective interaction matrix then leads to the spectral representation in which the physical information of the propagator becomes explicit: excitation (ionization) energies are obtained directly as the eigenvalues; the associated spectroscopic (spectral intensity) amplitudes result from a linear combination of eigenvector components and effective amplitudes. The ADC approximations combine two distinct numerical elements, namely the diagonalization of a (Hermitian) secular matrix and finite perturbation expansions of its matrix elements. An essential feature of the perturbation expansions is the absence of so-called dangerous denominators (which makes these expansions practical). The merit of the ADC secular problem is the compactness of the explicit configuration spaces required for a consistent nth-order treatment.

While the explicit ADC reformulation of propagator perturbation expansions through low orders of perturbation theory has lead to practical approximation schemes, questions of more theoretical interest, e.g., those concerning the feasibility and uniqueness of this construction in higher order, remained unanswered. Of particular interest is the question of whether one can find direct closed-form expressions for the ADC transformation and the corresponding effective quantities. This would make it possible to replace the cumbersome indirect procedure of deriving higher-order schemes by a more practical direct approach. Attempts to solve this problem were presented recently by Tarantelli and Cederbaum.[17] Motivated by the obvious correspondence of quasidegenerate perturbation theory (QDPT) and the ADC in the (exactly solvable) case of noninteracting particles, these authors applied essentially block-diagonalization procedures to suitable chosen blocks in the configuration-interaction (CI) representation of a propagator secular matrix. In this way, explicit nonperturbative algebraic expressions could be derived for the effective quantities introduced on the level of the third-order [ADC(3)] scheme. An extension beyond that level was envisaged by adopting their general noninteracting particle scheme also in the case of interacting particles. However, no proof has been given so far that this approach leads to the basic properties of the ADC representations. Another algebraical approach recently proposed by Mukherjee and Kutzelnigg[18] seems to be relevant in the present context. These authors consider the resolvent of an effective Liouvillean superoperator and introduce a special ("consistent") operator manifold in the representation of this resolvent. According to Mukherjee and Kutzelnigg, their perturbative procedure for the construction of the considered propagator reproduces the ADC schemes. An explicit proof of this assertion is still not available, which makes it difficult to compare their formalism with the approach discussed below.

In this article a surprisingly simple algebraic solution will be presented for the problem of determining a direct nonperturbative access to the ADC representation of propagators and related quantities. The starting point is the matrix $\underline{X}$ of generalized exact transition matrix elements (spectroscopic amplitudes) for suitably chosen excitation operators. A unitary matrix $\underline{Q}$ can then be constructed essentially by applying a block Gram-Schmidt orthogonalization (or block QR decomposition) procedure to $\underline{X}$, where the underlying block structure of $\underline{X}$ is defined by the affiliation of the matrix elements with distinct classes of physical excitations. The unitary matrix $\underline{Q}$ transforms the exact excited energy eigenstates $|\Psi_n\rangle$ to "intermediate" states $|\tilde{\Psi}_J\rangle$ generating a corresponding intermediate representation for the considered propagator which, as will be shown here, possesses the basic ADC properties. The block QR decomposition (BQRD) is quite practical and allows one to determine successively simple algebraic expressions for the blocks of $\underline{Q}$ and also for the blocks of the effective matrices $\underline{f}$ and $\underline{C}$. The intermediate representations thereby obtained represent a link between the algebraic and diagrammatic approaches, and may prove to be useful as a starting point for new approximation schemes of both a perturbative and a nonperturbative kind.

An outline of this paper is as follows. Section II reviews the diagrammatical derivation of the ADC for the illustrative example of the one-particle Green's function. In Sec. III the block QR decomposition and the resulting intermediate representation is introduced and discussed. The generality of the BQRD representations is outlined in Sec. IV. Here the treatment of the polarization propagator and the two-particle propagator is briefly addressed. Some conclusions are given in Sec. V. Two appendices A and B are used to collect, respectively, the explicit ADC(2) equations for $\underline{G}(\omega)$ and the results for the blocks of the BQRD-matrices $\underline{Q}$, $\underline{f}$, and $\underline{C}$ that are required for a consistent fourth-order treatment of $\underline{G}(\omega)$, $\underline{\Pi}(\omega)$, and $\underline{P}(\omega)$.

II. ALGEBRAIC DIAGRAMMATIC CONSTRUCTION (ADC) FOR THE ONE-PARTICLE GREEN'S FUNCTION

The ADC reformulation of propagator perturbation expansions has been described previously for the polarization propagator,[14] the self-energy part of the one-particle Green's function,[15] and the pp propagator.[16] A brief review of the ADC approach will be given here, for which the ADC treatment of the one-particle Green's function $\underline{G}(\omega)$ may serve as a particular pedogogical example.

A. Spectral representation

For an N-electron system with a nondegenerate ground state $|\Psi_0^N\rangle$ the matrix elements of the one-particle Green's function $\underline{G}(\omega)$ are defined in energy representation according to[1]

$$\underline{G}_{pq}(\omega)=\langle \Psi_0^N|c_q^\dagger(\omega-E_0^N+\hat{H}-i\eta)^{-1}c_p|\Psi_0^N\rangle + \langle \Psi_0^N|c_p(\omega+E_0^N-\hat{H}+i\eta)^{-1}c_q^\dagger|\Psi_0^N\rangle \ . \tag{1}$$

Here $c_p^\dagger$ (c_p) are the creation (annihilation) operators of second quantization associated with a basis of single-particle states $|\varphi_p\rangle$ usually chosen as the ground-state Hartree-Fock (HF) orbitals; $\hat{H}$ is the Hamiltonian of the system, E_0^N denotes the ground-state energy, and η is a positive infinitesimal required for the convergence of the Fourier transform between time and energy representation. According to Eq. (1), $\underline{G}(\omega)$ consists of two parts,

$$\underline{G}(\omega)=\underline{G}^{-}(\omega)+\underline{G}^{+}(\omega)\ , \tag{2}$$

containing physical information on the $(N-1)$-particle and $(N+1)$-particle systems, respectively. The physical content of $\underline{G}(\omega)$ becomes explicit in the well-known spectral representation[1] obtained by inserting complete sets of $(N\pm1)$-particle states $|\Psi_n^{N\pm1}\rangle$ on the right-hand side of Eq. (1). For $\underline{G}^{-}(\omega)$ the result is

$$G^{-}_{pq}(\omega)=\sum_{n\in\{N-1\}}\frac{x_p^{(n)}x_q^{(n)*}}{\omega-e_n-i\eta}\ . \tag{3a}$$

Here the (negative) pole positions

$$-e_n=E_n^{N-1}-E_0^N \tag{3b}$$

correspond to the ionization energies of the system, while the residue amplitudes

$$x_p^{(n)}=\langle\Psi_n^{N-1}|c_p|\Psi_0^N\rangle \tag{3c}$$

referred to as spectroscopic amplitudes are related to spectral intensities. Similar expressions apply to the case of the $(N+1)$-particle part $\underline{G}^{+}(\omega)$.

B. ADC approximation

The ADC(3) and ADC(4) approximations derived previously[15] for the one-particle Green's function combined the ADC approach for the self-energy part $\underline{\Sigma}(\omega)$ and the Dyson equation relating $\underline{G}(\omega)$ and $\underline{\Sigma}(\omega)$:

$$\underline{G}(\omega)=\underline{G}^{0}(\omega)+\underline{G}^{0}(\omega)\underline{\Sigma}(\omega)\underline{G}(\omega)\ . \tag{4}$$

Here $\underline{G}^{0}(\omega)$ is the free one-particle Green's function defined with respect to noninteracting HF particles. In the following we apply the ADC reformulation directly to the part $\underline{G}^{-}(\omega)$ or $\underline{G}^{+}(\omega)$. Though this is certainly less useful for deriving higher-order approximations, it is the better suited for the purpose of demonstration. The treatment of $\underline{G}^{-}(\omega)$ and $\underline{G}^{+}(\omega)$ is completely analogous, and we may confine our discussion to the former part.

The spectral representation (3) of $\underline{G}^{-}(\omega)$ can be cast in a more compact matrix notation:

$$\underline{G}^{-}(\omega)=\underline{x}^{\dagger}(\omega\underline{1}-\underline{\Omega})^{-1}\underline{x}\ , \tag{5a}$$

where $\underline{\Omega}$ denotes the diagonal matrix of the (negative) ionization energies

$$\Omega_{nn}=e_n\ , \tag{5b}$$

and $\underline{x}$ is the matrix of spectral amplitudes

$$x_{n,r}=x_r^{(n)}=\langle\Psi_n^{N-1}|c_r|\Psi_0^N\rangle\ . \tag{5c}$$

The infinitesimal η is no longer essential and has been dropped. The one-particle states r in Eq. (5c) may be distinguished according to their HF occupation numbers $n_r=1$ (hole states) and $\bar{n}_r=1-n_r=1$ (particle states), respectively. Correspondingly, the matrix $\underline{x}$ is composed of two parts:

$$x=(\underline{x}(h),\underline{x}(p))\ , \tag{6}$$

where the hole (or physical) part (h) and the particle (or unphysical) part (p) comprise the columns of $\underline{x}$ with $n_r=1$ and 0, respectively. This organization of $\underline{x}$ is depicted in Fig. 1.

The ADC formulation replaces the special (diagonal) form (5) of the spectral representation by the more general nondiagonal ADC form

$$\underline{G}^{-}(\omega)=\underline{f}^{\dagger}(\omega\underline{1}-\underline{K}-\underline{C})^{-1}\underline{f}\ . \tag{7}$$

Here $\underline{C}$ is a Hermitian matrix referred to as "effective" interaction matrix, and $\underline{K}$ is the diagonal matrix of zeroth-order ionization energies specified further below. The configuration space of the matrices $\underline{K}$ and $\underline{C}$ is the space of all $(N-1)$-particle configurations $|\phi_J^{N-1}\rangle$ further subdivided into one-hole $(1h)$ excitations, two-hole–one-particle $(2h$-$1p)$ excitations, and so forth, with respect to the N-electron HF ground state. The matrix $\underline{f}$ in Eq. (7) is referred to as the matrix of "effective" spectroscopic amplitudes $f_{J,r}$. Its first index J labels the

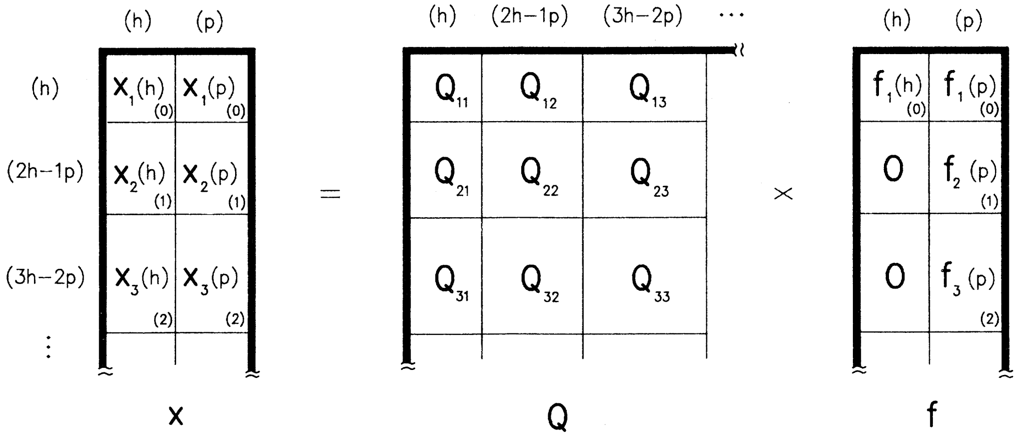

FIG. 1. Schematic representation of the ADC equation (24a) relating the exact and effective spectroscopic matrix $\underline{x}$ and $\underline{f}$ by the unitary transformation $\underline{Q}$. The order relations of the subblocks in $\underline{x}$ and $\underline{f}$ are indicated by the numbers in brackets.

$(N-1)$-particle configurations, while the second index r refers to one-particle states. As for $\underline{x}$, we may divide $\underline{f}$ into a physical (hole) part $\underline{f}(h)$ and an unphysical (particle) part $\underline{f}(p)$:

$$\underline{f}=(\underline{f}(h),\underline{f}(p)) \ . \tag{8}$$

The matrix inversion in Eq. (7) is equivalent to the Hermitian eigenvalue problem

$$(\underline{K}+\underline{C})\underline{Y}=\underline{Y}\underline{\Omega} \ , \quad \underline{Y}^{\dagger}\underline{Y}=1 \ . \tag{9}$$

Here $\underline{Y}$ denotes the eigenvector matrix and $\underline{\Omega}$ is the diagonal matrix of eigenvalues Ω_{mm}. The matrix $\underline{x}$ of the spectroscopic amplitudes is obtained from $\underline{f}$ and $\underline{Y}$ by the operation

$$\underline{x}=\underline{Y}^{\dagger}\underline{f} \ . \tag{10}$$

Obviously, the eigenvector matrix $\underline{Y}$ may be viewed as a unitary transformation relating the explicit diagonal and the ADC representation.

How can the effective quantities $\underline{f}$ and $\underline{C}$ be determined? For this task we consider their perturbation expansions

$$\underline{f}=\underline{f}^{(0)}+\underline{f}^{(1)}+\underline{f}^{(2)}+\cdots \ , \tag{11a}$$

$$\underline{C}=\underline{C}^{(1)}+\underline{C}^{(2)}+\underline{C}^{(3)}+\cdots \tag{11b}$$

based on the usual (Møller-Plesset) decomposition

$$\hat{H}=\hat{H}_0+\hat{H}_I \tag{12}$$

of the Hamiltonian $\hat{H}$ into an unperturbed (HF) part $\hat{H}_0$ and an interaction part $\hat{H}_I$. The expansion of $\underline{C}$ begins in first order, since all zeroth-order terms are comprised in the diagonal matrix $\underline{K}$ with the elements

$$\begin{aligned} &K_{l,l}=\epsilon_l \ , \quad n_l=1 \\ &K_{jkl,jkl}=-\epsilon_j+\epsilon_k+\epsilon_l \ , \quad \bar{n}_j n_k n_l=1 \ , \end{aligned} \tag{13}$$

and so forth. Expanding the matrix $(\omega\underline{1}-\underline{K}-\underline{C})^{-1}$ of the ADC form (7) in powers of $(\omega\underline{1}-\underline{K})^{-1}\underline{C}$ and inserting the perturbation expansions (11) for $\underline{f}$ and $\underline{C}$, yields the following perturbation expansion of the ADC form for $\underline{G}^{-}(\omega)$:

$$\underline{G}^{-}(\omega)=\underline{f}^{(0)^{\dagger}}(\omega\underline{1}-\underline{K})^{-1}\underline{f}^{(0)}+\underline{f}^{(0)^{\dagger}}(\omega\underline{1}-\underline{K})^{-1}\underline{C}^{(1)}(\omega\underline{1}-\underline{K})^{-1}\underline{f}^{(0)}+\underline{f}^{(1)^{\dagger}}(\omega\underline{1}-\underline{K})^{-1}\underline{f}^{(0)}+\underline{f}^{(0)^{\dagger}}(\omega\underline{1}-\underline{K})^{-1}\underline{f}^{(1)}+\cdots \ . \tag{14}$$

By comparing this expansion with the original diagrammatic perturbation series for $\underline{G}^{-}(\omega)$ through a finite, say, nth-order one may successively determine the terms in the perturbaton expansions of $\underline{f}$ and $\underline{C}$. Inserting these finite expansions $\underline{f}(n)$ and $\underline{C}(n)$ obtained through order n in the general ADC equations [(7), (9), and (10)] one obtains systematic approximations for $\underline{G}^{-}(\omega)$ referred to as ADC(n) schemes. According to their construction, the ADC(n) schemes sum up the perturbation expansion for $\underline{G}^{-}(\omega)$ completely through nth order and represent infinite though only partial summations of higher-order terms.

For $n=2$ this program can readily be performed.[19] There is a single second-order Feynman diagram giving rise to $\frac{1}{2}(4!)=12$ time-ordered diagrams contributing to $\underline{G}^{-}(\omega)$ which can readily be evaluated and compared with the formal expansion [Eq. (14)] of the ADC representation. The resulting explicit ADC(2) expressions for $\underline{f}$ and $\underline{C}$ are given in Appendix A. The case $n=3$ is somewhat more involved, as here already 60 time-ordered diagrams emerge for each of the three third-order Feynman diagrams. A report on the third-order ADC scheme for $\underline{G}^{\pm}(\omega)$ will be given elsewhere.

C. Basic properties of the ADC scheme

The ADC approximations combine perturbation theory and secular matrix diagonalization. The particular usefulness of these schemes relies on two basic properties referred to as the compactness of the ADC(n) configuration spaces and the regularity of the perturbation expansions for the effective quantities $\underline{f}$ and $\underline{C}$. Let us consider these properties in some detail. Compactness means that the explicit configuration space required in the nth-order ADC treatment [for $\underline{G}^{-}(\omega)$] is restricted according to the following rule: for $n=2\nu$ and $n=2\nu+1$, $\nu=0,1,2,\ldots$, the ADC configuration space comprises the $\nu+1$ lowest classes of excitations $1h, 2h\text{-}1p, \ldots, (\nu+1)h\text{-}\nu p$. This means that in each even order the next higher class of $(N-1)$-particle excitations comes explicitly into play, beginning with the $1h$ excitations for $n=0$ and 1. For comparison, the consistent nth-order treatment of $(N-1)$-particle states within the conventional wave-function approach would require configuration-interaction (CI) expansions up to the class of $(2\nu+1)h\text{-}(2\nu)p$ excitations for $n=2\nu, 2\nu+1$ $(2\nu<N)$. We see that the ADC configuration space is smaller than that of a comparable CI expansion and grows only half as fast. The finite perturbation expansions $\underline{f}(n)$ and $\underline{C}(n)$ account both for higher excitation classes not explicitly considered and for ground-state correlation.

The compactness of the ADC configuration spaces is a consequence of a remarkable order relation for the exact spectroscopic amplitudes stating that for a state $|\Psi_{(\mu)}^{N-1}\rangle$ deriving from an unperturbed $(\mu+1)h\text{-}\mu p$ excitation $|\phi_{(\mu)}^{N-1}\rangle$, the spectroscopic amplitude $x_{(\mu)r}$ is of the order μ:

$$x_{(\mu)r}=\langle \Psi_{(\mu)}^{N-1}|c_r|\Psi_0^N\rangle \simeq O(\mu) \ . \tag{15}$$

A proof of this assertion, supposing a two-particle interaction in $\hat{H}$ and a nondegenerate ground state, has been given in Ref. 15. The essential step here is to recast the perturbation expansion for (15) into a sum of matrix elements

$$A(\mu,l)=\langle \phi_{(\mu)}^{N-1}|[[\cdots[c_r,\hat{H}]\cdots],\hat{H}]|\phi_0^N\rangle \tag{16}$$

involving repeated commutators and HF states $|\phi_0^N\rangle$ and $|\phi_{(\mu)}^{N-1}\rangle$; here l denotes the number of commutators. For a two-particle Hamiltonian $\hat{H}$ the action of an l-times repeated commutator on $|\phi_0^N\rangle$ results at most in a $(l+1)h$-lp excitation, which means that $A(\mu,l)$ vanishes for $l<\mu$; a nonvanishing contribution $A(\mu,l)$ can arise for the first time in μth order. This result can readily be extended to other spectroscopic amplitudes, e.g., those of the polarization and *pp* propagator (see Secs. IV A and IV B), and to other Hamiltonians, e.g., those including three- and more-body interactions. A particularly simple result is obtained for a pure one-particle operator (see Sec. IV C).

The order relation (15) for the spectroscopic amplitudes $x_{(\mu)r}$ of a $(\mu+1)h$-μp excitation means for the perturbation expansion of $\underline{G}^-(\omega)$ that this class of states [represented by terms with denominators $(\omega-K_{(\mu)})^{-1}$] appears for the first time in the order $n=2\mu$. This property is preserved in the ADC reformulation of the perturbation expansion; here the relation (15) is transferred to the corresponding effective spectroscopic amplitudes, that is,

$$f_{J,r}\sim O(\mu) \tag{17}$$

for a $(\mu+1)h$-μp configuration J.

The other basic property of the ADC concerns the behavior of perturbation expansions for the effective quantities $\underline{f}$ and $\underline{C}$. As is well known, direct Rayleigh-Schrödinger (RS) perturbation expansions for the $(N-1)$-particle states and energies are in general not useful, since they introduce terms with "dangerous denominators," that is, contributions of the form $V_{ab}(\epsilon_a-\epsilon_b)^{-1}$, where $V_{ab}\neq 0$, and the energy difference $|\epsilon_a-\epsilon_b|$ can become small or even vanish. For example, the mixing of $1h$ excitations (r) and $2h$-$1p$ excitations (jkl) introduces contributions

$$V_{rjkl}(\epsilon_r-\epsilon_j-\epsilon_k-\epsilon_l)^{-1}n_r\bar{n}_j n_k n_l \tag{18}$$

that are of this kind; here V_{rjkl} is the usual notation for Coulomb integrals. The mixing of $1h$ and $3h$-$2p$ excitations, on the other hand, does not lead to dangerous denominators, since the coupling matrix elements vanish unless the respective energies differ by a double excitation energy. An example for a well-behaved perturbation series is the RS expansion for the N-particle ground state $|\Psi_0^N\rangle$ (of a closed-shell system), since here the absolute values of the denominators are bounded from below by the energy gap Δ between the occupied and unoccupied (HF) orbitals. The diagrammatic perturbation expansion for $\underline{G}^-(\omega)$ is free of dangerous denominators, as can be seen by inspecting the rules for drawing and evaluating the diagrams.[20] This property is maintained in the ADC reformulation, leading to well-behaved expansions for the matrix elements of $\underline{f}$ and $\underline{C}$. Like in the RS expansion for the N-particle ground state, the absolute values of the denominators are not smaller than the ground-state HF energy gap Δ.

D. Intermediate ADC states and comparison with other representations

The spectral representation (5) was obtained by inserting the complete set of exact $(N-1)$-particle states on the right-hand side of Eq. (1). Similarly, the ADC form of Eq. (7) can be viewed as the result of instead inserting a complete set of "intermediate" states $|\tilde{\Psi}_J^{N-1}\rangle$. Then, the effective interaction $\underline{C}$ may be expressed as the representation of $E_0^N-\hat{H}$ in the intermediate basis,

$$(K+C)_{J,J'}=\langle\tilde{\Psi}_J^{N-1}|E_0^N-\hat{H}|\tilde{\Psi}_{J'}^{N-1}\rangle\ , \tag{19a}$$

and the effective spectroscopic amplitudes read

$$f_{J,r}=\langle\tilde{\Psi}_J^{N-1}|c_r|\Psi_0^N\rangle\ . \tag{19b}$$

The two sets of exact and intermediate states are connected by a unitary transformation

$$|\Psi_m^{N-1}\rangle=\sum_J Q_{mJ}|\tilde{\Psi}_J^{N-1}\rangle\ , \tag{20}$$

where $\underline{Q}=(Q_{mJ})$ is readily identified as the Hermitian conjugate $\underline{Y}^\dagger$ of the ADC eigenvector matrix introduced in Eq. (9). Obviously, the unitary transformation $\underline{Q}$ completely determines the ADC representation of $\underline{G}^-(\omega)$.

How can $\underline{Q}$ and thus the intermediate states be chosen so that the basic ADC properties are obtained? Before we turn to this question in Sec. III, let us contrast the ADC with two opposing choices for $\underline{Q}$ not fulfilling the ADC requirements. The spectral representation (5) itself may be viewed as a special, namely, diagonal "ADC" form ($\underline{Q}=\underline{1}$). This leads to the usual RS perturbation expansions for the exact energies $\Omega_{mm}=E_0^N-E_m^{N-1}$ and spectroscopic amplitudes $x_{mr}=\langle\tilde{\Psi}_m^{N-1}|c_r|\Psi_0^N\rangle$. As discussed above, these expansions introduce dangerous denominators and, thus, do not represent a practical means of calculation. An opposite choice is the CI representation

$$\underline{G}^-(\omega)=\underline{y}^\dagger(\omega\underline{1}+\underline{H}-E_0^N\underline{1})^{-1}\underline{y}\ , \tag{21a}$$

$$H_{J,J'}=\langle\phi_J^{N-1}|\hat{H}|\phi_{J'}^{N-1}\rangle\ , \tag{21b}$$

$$y_{J,r}=\langle\phi_J^{N-1}|c_r|\Psi_0^N\rangle\ , \tag{21c}$$

obtained by inserting [on the left-hand side of Eq. (1)] the complete set of unperturbed (HF) configurations $|\phi_J^{N-1}\rangle$, $J\in\{1h,2h\text{-}1p,\ldots\}$. This corresponds to putting $\underline{Q}=\underline{S}^\dagger$, where $\underline{S}$ is the eigenvector matrix of the CI problem

$$\underline{H}\,\underline{S}=\underline{S}(E_0^N\underline{1}-\underline{\Omega})\ . \tag{22}$$

Here the "effective" quantities $\underline{H}-E_0^N\underline{1}$ and $\underline{y}$ require RS expansions only for E_0^N and $|\Psi_0^N\rangle$ which, of course, are well behaved. However, the CI representation does not fulfill the compactness property of the ADC, since its explicit configuration space grows twice as fast with increasing order n. The CI and spectral representation represent two extremes, namely maximal (full) diagonalization and maximal perturbation theory (no diagonalization), respectively. The ADC representation, on the other hand, mediates between these opposing cases and might be characterized as introducing as much perturbation theory as possible and as much diagonalization as necessary.

III. A CLOSED-FORM ADC TRANSFORMATION

In the preceding section we have considered the unitary matrix $\underline{Q}$ with matrix elements

$$Q_{mJ}=\langle \Psi_m^{N-1}|\tilde{\Psi}_J^{N-1}\rangle \tag{23}$$

transforming the exact $(N-1)$-electron states into the intermediate states of the ADC representation. According to Eqs. (9) and (10), which read, if $\underline{Q}$ is replacing $\underline{Y}^{\dagger}$,

$$\underline{x}=\underline{Q}\,\underline{f}\ , \tag{24a}$$

$$\underline{K}+\underline{C}=\underline{Q}^{\dagger}\underline{\Omega}\,\underline{Q}\ . \tag{24b}$$

The transformation $\underline{Q}$ relates the ADC quantities $\underline{f}$ and $\underline{K}+\underline{C}$ the exact spectroscopic amplitudes $\underline{x}$ and ionization energies $\underline{\Omega}$, respectively, thereby defining the ADC representation of $\underline{G}^{-}(\omega)$. Our aim now is to determine a closed-form expression for $\underline{Q}$ (and thus for $\underline{f}$ and $\underline{K}+\underline{C}$). What we have to show is that the resulting ADC(n) schemes fulfill the two basic properties, that is, the proper order relations for the blocks of $\underline{f}$ guaranteeing the compactness of the configuration spaces and the absence of dangerous denominators in the perturbation expansions of $\underline{f}$ and $\underline{C}$.

A. The generalized resolvent matrix

Equation (24a) suggests to seek $\underline{Q}$ in the form of an appropriate decomposition of the matrix $\underline{x}$ of the exact spectroscopic amplitudes given in closed form by Eq. (5c). However, the inspection of the different sizes of the (rectangular) matrix $\underline{x}$ and the (quadratic) matrix $\underline{Q}$ makes clear that this procedure cannot succeed. One is thus lead to an obvious generalization of the original problem: instead of $\underline{x}$, we have to consider the (quadratic) matrix $\underline{X}$ of generalized spectroscopic amplitudes

$$X_{m,J}=\langle \Psi_m^{N-1}|\hat{C}_J|\Psi_0^N\rangle\ . \tag{25}$$

Here $\hat{C}_J$ is a short-hand notation for the operator products of the form

$$\{\hat{C}_J\}=\{c_k, c_j^{\dagger}c_kc_l, c_i^{\dagger}c_j^{\dagger}c_kc_lc_m,\ldots\} \tag{26}$$

corresponding to the physical $1h,2h\text{-}1p,3h\text{-}2p,\ldots$ excitations of $N-1$ electrons; the indices of the creation operators ($c_i^{\dagger}$) and annihilation operators (c_l) are restricted, respectively, to particle states ($\bar{n}_i=1$) and hole states ($n_l=1$). Similarly, we may introduce the matrix $\underline{F}$ of generalized effective spectroscopic amplitudes,

$$F_{J,J'}=\langle \tilde{\Psi}_J^{N-1}|\hat{C}_{J'}|\Psi_0^N\rangle\ . \tag{27}$$

Using these definitions we readily arrive at the following generalization of Eq. (24a):

$$\underline{X}=\underline{Q}\,\underline{F}\ , \tag{28}$$

which represents the basic equation for our further considerations. It should be noted that the matrices $\underline{X}$ and $\underline{F}$ may be viewed as arising in representations of a generalized resolvent matrix $\underline{\Gamma}^{-}(\omega)$, defined according to

$$\Gamma^{-}(\omega)_{JJ'}=\langle \Psi_0^N|\hat{C}_J^{\dagger}(\omega\underline{1}+\hat{H}-E_0^N\underline{1})^{-1}\hat{C}_{J'}|\Psi_0^N\rangle\ . \tag{29}$$

B. Block QR decomposition of $\underline{X}$

The matrix $\underline{X}$ has a block structure induced by the configuration spaces of $1h,2h\text{-}1p,3h\text{-}2p,\ldots$ excitations. For the second matrix index the assignment to blocks is obvious; the block assignment of the first matrix entry can be performed at least formally according to the perturbation theoretical genealogy of the exact states but is not relevant for the final result. By simply numbering the classes of configuration spaces $\nu=1,2,3,\ldots,N$ according to the number of holes [$\nu\equiv\nu h\text{-}(\nu-1)p$], the matrix $\underline{X}$ may be viewed as being composed of blocks $\underline{X}_{\nu\mu}$ (Fig. 2) arranged in their natural order (see Fig. 2). In a similar manner we may define blocks $\underline{F}_{\nu\mu}$ of $\underline{F}$ and $\underline{Q}_{\nu\mu}$ of $\underline{Q}$. For further reference we also introduce the notation $\underline{X}_1$, $\underline{X}_2$, $\underline{X}_3,\ldots$ (and $\underline{Q}_1$, $\underline{Q}_2$, $\underline{Q}_3,\ldots$) for the columns of $1h,2h\text{-}1p,3h\text{-}2p$ blocks, respectively. In Sec. II B we have discussed the order structure of the spectroscopic amplitudes $\underline{x}$. We have seen that the blocks of the first column $\underline{X}_1$ fulfill the order relations

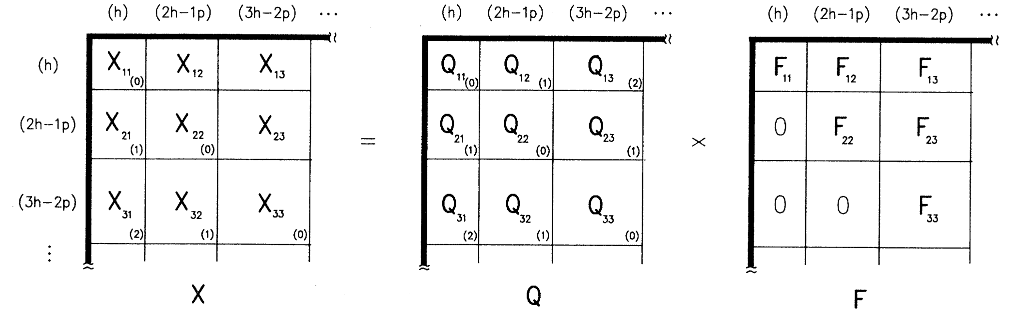

FIG. 2. Schematic representation of the block QR decomposition [Eq. (28)] transforming the generalized spectroscopic matrix $\underline{X}$ into the upper block-triangular matrix $\underline{F}$. The order relations of the subblocks $\underline{X}$ and $\underline{Q}$ are indicated by the numbers in brackets.

$$\underline{X}_{\nu 1} \simeq O(\nu-1)\ , \quad \nu=1,2,\ldots\ . \tag{30}$$

By an obvious extension of the previous proof[15] to the generalized amplitudes (25) we arrive at the following order relations for diagonal and subdiagonal blocks of $\underline{X}$:

$$\underline{X}_{\nu\mu} \simeq O(\nu-\mu)\ , \quad \nu=\mu,\mu+1,\ldots\ . \tag{31}$$

In Fig. 2 the order structure of the blocks of $\underline{X}$ is indicated by the numbers in brackets.

Now we may attempt to decompose the matrix $\underline{X}$ of the exact spectroscopic amplitudes in the form suggested by Eq. (28). How can this be achieved? The simple answer is by Gram-Schmidt orthogonalization[21] of the columns $\underline{X}_i$ of blocks combined with symmetric orthogonalization within each column $\underline{X}_i$. This leads to a QR decomposition[21] of the blocks of $\underline{X}$ resulting in the upper triangular block structure

$$\underline{F}_{ij}=\underline{0} \quad \text{for } i>j \tag{32}$$

for the matrix $\underline{F}$ as indicated in Fig. 2. We shall see that this procedure transfers the order relation of $\underline{X}$ to $\underline{Q}$ providing one thus with the desired compactness property of the ADC, and collects in $\underline{Q}$ all terms of $\underline{X}$ introducing dangerous denominators so that well-behaved perturbation expansions results for the matrix elements of $\underline{F}$.

The first step of the Gram-Schmidt orthogonalization procedure sets out from the equation

$$\underline{X}_1=\underline{Q}_1\underline{F}_{11} \tag{33}$$

for the first column $\underline{Q}_1$ of the blocks $\underline{Q}_{\nu 1}$ of $\underline{Q}$. Obviously the symmetric orthonormalization

$$\underline{X}_1=\underline{X}_1(\underline{X}_1^\dagger\underline{X}_1)^{-1/2}(\underline{X}_1^\dagger\underline{X}_1)^{1/2} \tag{34a}$$

for the columns of $\underline{X}_1$ leads to the desired result and one readily identifies $\underline{Q}_1$ and $\underline{F}_{11}$ as

$$\underline{Q}_1=\underline{X}_1(\underline{X}_1^\dagger\underline{X}_1)^{-1/2}\ , \tag{34b}$$

$$\underline{F}_{11}=(\underline{X}_1^\dagger\underline{X}_1)^{1/2}\ . \tag{34c}$$

Using Eq. (25) the matrix elements of $\underline{X}_1^\dagger\underline{X}_1$ may be further evaluated as follows:

$$\begin{aligned}(\underline{X}_1^\dagger\underline{X}_1)_{r,r'}&=\sum_m \langle \Psi_0^N|c_r^\dagger|\Psi_m^{N-1}\rangle\langle\Psi_m^{N-1}|c_{r'}|\Psi_0^N\rangle\\ &=\langle\Psi_0^N|c_r^\dagger c_{r'}|\Psi_0^N\rangle\ .\end{aligned} \tag{35}$$

Thus, we see that $\underline{X}_1^\dagger\underline{X}_1$ can be identified with the physical block $\underline{\rho}(h,h)$ of the one-particle density matrix:

$$\underline{X}_1^\dagger\underline{X}_1=\rho(h,h)\ , \tag{36a}$$

$$\rho(h,h)_{r,r'}=\langle\Psi_0^N|c_r^\dagger c_{r'}|\Psi_0^N\rangle\ , \quad n_r=n_{r'}=1\ . \tag{36b}$$

The (1,1) block of $\underline{F}$ can be written as

$$\underline{F}_{11}=\rho(h,h)^{1/2}\ , \tag{37}$$

which makes explicit that the perturbation expansions for the elements of $\underline{F}_{11}$ behave like the ground-state RS series. The equation

$$\underline{X}_2=\underline{Q}_1\underline{F}_{12}+\underline{Q}_2\underline{F}_{22} \tag{38}$$

of the second step allows us to determine directly the block

$$\begin{aligned}\underline{F}_{12}&=\underline{Q}_1^\dagger\underline{X}_2\\ &=(\underline{X}_1^\dagger\underline{X}_1)^{-1/2}\underline{X}_1^\dagger\underline{X}_2\\ &=\rho(h,h)^{-1/2}\rho(h,2h\text{-}1p)\ ,\end{aligned} \tag{39a}$$

where $\rho(h,2h\text{-}1p)$ denotes a density-matrix block with the elements

$$\begin{aligned}&\rho(h,2h\text{-}1p)_{r,jkl}=\langle\Psi_0^N|c_r^\dagger c_j^\dagger c_k c_l|\Psi_0^N\rangle\ ,\\ &n_r=\bar{n}_j n_k n_l=1\ .\end{aligned} \tag{39b}$$

The quantities $\underline{Q}_2$ and $\underline{F}_{22}$ are obtained by symmetric orthonormalization of the matrix

$$\underline{\tilde{X}}_2=\underline{X}_2-\underline{Q}_1\underline{F}_{12}\ , \tag{40a}$$

leading to

$$\underline{Q}_2=\underline{\tilde{X}}_2(\underline{\tilde{X}}_2^\dagger\underline{\tilde{X}}_2)^{-1/2}\ , \tag{40b}$$

$$\underline{F}_{22}=(\underline{\tilde{X}}_2^\dagger\underline{\tilde{X}}_2)^{1/2}\ . \tag{40c}$$

The quantity $\underline{\tilde{X}}_2^\dagger\underline{\tilde{X}}_2$ may be further evaluated, yielding

$$\underline{\tilde{X}}_2^\dagger\underline{\tilde{X}}_2=\underline{X}_2^\dagger\underline{X}_2-\underline{F}_{12}^\dagger\underline{F}_{12}\ , \tag{41a}$$

which in turn can be expressed in terms of density matrices according to

$$\begin{aligned}\underline{\tilde{X}}_2^\dagger\underline{\tilde{X}}_2=&\ \rho(2h\text{-}1p,2h\text{-}1p)\\ &-\rho(2h\text{-}1p,h)\rho(h,h)^{-1}\rho(h,2h\text{-}1p)\ .\end{aligned} \tag{41b}$$

Here $\rho(2h\text{-}1p,2h\text{-}1p)$ is the density matrix of the physical $2h$-$1p$ operators [defined analogously to (36b)] and

$$\rho(2h\text{-}1p,h)=\rho(h,2h\text{-}1p)^\dagger\ . \tag{41c}$$

Again it is clear that the matrix elements of $\underline{F}_{22}$ are subject to well-behaved perturbation expansions.

Let us now consider the general, say, nth step leading to the equation

$$\underline{X}_n=\sum_{i=1}^{n-1}\underline{Q}_i\underline{F}_{in}+\underline{Q}_n\underline{F}_{nn}\ , \tag{42}$$

where $\underline{Q}_i$, $i=1,\ldots,n-1$ have already been determined. The blocks $\underline{F}_{in}$, $i=1,\ldots,n-1$ of $\underline{F}$ are given by

$$\underline{F}_{in}=\underline{Q}_i^\dagger\underline{X}_n\ , \quad i=1,2,\ldots,n-1\ , \tag{43}$$

and as before $\underline{Q}_n$ and $\underline{F}_{nn}$ result from the symmetric orthonormalization of

$$\underline{\tilde{X}}_n=\underline{X}_n-\sum_{i=1}^{n-1}\underline{Q}_i^\dagger\underline{F}_{in}\ , \tag{44a}$$

that is,

$$\underline{Q}_n=\underline{\tilde{X}}_n(\underline{\tilde{X}}_n^\dagger\underline{\tilde{X}}_n)^{-1/2}\ , \tag{44b}$$

$$\underline{F}_{nn}=(\underline{\tilde{X}}_n^\dagger\underline{\tilde{X}}_n)^{1/2}\ . \tag{44c}$$

The product $\underline{\tilde{X}}_n^\dagger\underline{\tilde{X}}_n$ may be written more explicitly as

$$\underline{\tilde{X}}_n^\dagger \underline{\tilde{X}}_n = \underline{X}_n^\dagger \underline{X}_n - \sum_{i=1}^{n-1} \underline{F}_{in}^\dagger \underline{F}_{in} \; . \tag{45}$$

Proceeding in this way until $n=N$ is reached, one can successively determine explicit expressions for the columns $\underline{Q}_i$ and the (upper) blocks of $\underline{F}$. The blocks (i,j) of $\underline{K}+\underline{C}$ can readily be evaluated using Eq. (24b) once $\underline{Q}_i$ and $\underline{Q}_j$ have been determined (see Sec. III D). In Appendix B the resulting expressions for $i,j \leq 3$ are collected.

C. Proof of the ADC properties

We have seen that the blocks $\underline{F}_{11}$, $\underline{F}_{12}$, and $\underline{F}_{22}$ of $\underline{F}$ could be expressed entirely in terms N-electron ground-state density matrices. One can easily convince oneself that this assertion holds for all (nonvanishing) blocks of $\underline{F}$. The proof is as follows: Let us assume that the assertion is true for the blocks $\underline{F}_{i(n-1)}$, $i \leq n-1$, generated in the Gram-Schmidt steps 1 through $n-1$. The ensuing step n introduces the blocks $\underline{F}_{in}$, $i=1,\ldots,n-1$ according to Eq. (43) and the block $\underline{F}_{nn}$ according to Eqs. (44a) and (44c). For the first new block $\underline{F}_{1n}$ we may write explicitly

$$\begin{aligned}\underline{F}_{1n} &= \underline{Q}_1^\dagger \underline{X}_n \\ &= (\underline{X}_1^\dagger \underline{X}_1)^{-1/2} \underline{X}_1^\dagger \underline{X}_n \\ &= \rho(h,h)^{-1/2} \rho(h, nh\text{-}(n-1)p) \; ,\end{aligned} \tag{46}$$

which proves our assertion for $\underline{F}_{1n}$ and for the product $\underline{Q}_1^\dagger \underline{X}_n$. For any of the other blocks $\underline{F}_{ln}$ with $l<n$ we find using Eqs. (43), (44a) and (44b)

$$\begin{aligned}\underline{F}_{ln} &= \underline{Q}_l^\dagger \underline{X}_n \\ &= (\underline{\tilde{X}}_l^\dagger \underline{\tilde{X}}_l)^{-1/2} \underline{\tilde{X}}_l^\dagger \underline{X}_n \\ &= \underline{F}_{ll}^{-1} \left[\underline{X}_l^\dagger \underline{X}_n - \sum_{j=1}^{l-1} \underline{F}_{jl}^\dagger \underline{F}_{jn} \right] \; .\end{aligned} \tag{47}$$

The product $\underline{X}_l^\dagger \underline{X}_n$ on the right-hand side of Eq. (47) is given by the density matrix of the physical lh-$(l-1)p$ and nh-$n-1)p$ excitations

$$\underline{X}_l^\dagger \underline{X}_n = \rho(lh\text{-}(l-1)p, nh\text{-}(n-1)p) \; , \tag{48}$$

and we may conclude (by induction) that all blocks $\underline{F}_{ln}$, $l=1,\ldots,n-1$ have the desired property. Using this result for the remaining diagonal block $\underline{F}_{nn}$ [Eqs. (44c) and (45)] and noting that

$$\underline{X}_n^\dagger \underline{X}_n = \rho(nh\text{-}(n-1)p, nh\text{-}(n-1)p) \tag{49}$$

completes the proof. The property that the (nonvanishing) blocks of $\underline{F}$ can be written in terms of ground-state density matrices means in particular that the perturbation expansions for the matrix elements of $\underline{F}$ are free of dangerous denominators. In a similar way, this property may also be shown for the effective interaction $\underline{K}+\underline{C}=\underline{Q}^\dagger \underline{\Omega}\, \underline{Q}$.

The other basic property is the order structure of the unitary transformation matrix $\underline{Q}$. One can easily convince oneself that the construction of block columns $\underline{Q}_n$ according to Eqs. (43) and (44),

$$\underline{Q}_n = \left[\underline{X}_n - \sum_{i=1}^{n-1} \underline{Q}_i \underline{F}_{in} \right] (\underline{F}_{nn})^{-1} \; ,$$

transfers the order structure of the diagonal and subdiagonal blocks $\underline{X}_{\nu n}$, $\nu \geq n$, of $\underline{X}$ to the corresponding blocks of $\underline{Q}$, that is,

$$\underline{Q}_{\nu n} \simeq \underline{X}_{\nu n} \simeq O(\nu - n) \; , \quad \text{for } \nu = n, n+1, \ldots \; . \tag{50}$$

The unitary of $\underline{Q}$ then requires the symmetrical order structure

$$\underline{Q}_{\nu\mu} \sim O(|\nu-\mu|) \; , \quad \nu,\mu = 1,\ldots,N \tag{51}$$

for the blocks of $\underline{Q}$ (see Fig. 2). In the following section we shall see that the order structure (51) of $\underline{Q}$ gives rise to the compactness property of the ADC.

D. Application to the one-particle Green's function

Now we may return to the case of the one-particle Green's function $\underline{G}^-(\omega)$. Equation (24a) establishes the relation between the exact and effective spectroscopic amplitudes $\underline{x}$ and $\underline{f}$, respectively. Using the notation introduced by Eqs. (6) and (8) we obtain the following relation for the hole parts of $\underline{x}$ and $\underline{f}$:

$$\underline{f}(h) = \underline{Q}^\dagger \underline{x}(h) = \underline{Q}^\dagger \underline{X}_1 = \underline{F}_{11} \; . \tag{52}$$

This means that all blocks of $\underline{f}(h)$ vanish except for the first (1-hole) block $\underline{f}_1(h)$:

$$\underline{f}_1(h) = \underline{F}_{11} = \rho(h,h)^{1/2} \; , \tag{53a}$$

$$\underline{f}_l(h) = \underline{0} \quad \text{for } l > 1 \; . \tag{53b}$$

For the unphysical particle part we have

$$\underline{f}(p) = \underline{Q}^\dagger \underline{x}(p) \; , \tag{54}$$

and the first block here simply reads

$$\underline{f}_1(p) = \rho(h,h)^{-1/2} \rho(h,p) \; , \tag{55}$$

$\rho(h,p)$ being the (h,p) block of the one-particle density matrix. Explicit expressions for the blocks $\underline{f}_2$ and $\underline{f}_3$ are given in Appendix B. By contrast to $\underline{f}(h)$, the blocks of $\underline{f}(p)$ do not vanish. Let us consider a specific block $\underline{f}_\nu(p)$ of νh-$(\nu-1)p$ excitations

$$\underline{f}_\nu(p) = \underline{Q}_\nu^\dagger \underline{x}(p) = \sum_j \underline{Q}_{j\nu}^\dagger \underline{x}_j(p) \; . \tag{55$'$}$$

The order relations (51) of the blocks $\underline{Q}_{j\nu}^\dagger$ and those of $\underline{x}_j(p)$ [Eq. (15)] are seen to combine to the relation

$$\underline{f}_\nu(p) \simeq O(\nu) \tag{56}$$

for $\underline{f}_\nu(p)$. This means that $\underline{f}$ has the same order structure as $\underline{x}$, which guarantees the compactness property of the ADC(n) configuration spaces.

The matrix $\underline{K}+\underline{C}$ of the effective interaction can be obtained from the relation (24b). For a particular block $(\underline{K}+\underline{C})_{nm}$ this relation becomes

$$(\underline{K}+\underline{C})_{nm} = \underline{Q}_n^\dagger \underline{\Omega}\, \underline{Q}_m \; , \tag{57}$$

which allows for a straightforward evaluation once the columns $\underline{Q}_n$ and $\underline{Q}_m$ of $\underline{Q}$ have been constructed. For example, the result for the first diagonal block reads

$$(\underline{K}+\underline{C})_{11}=\rho(h,h)^{-1/2}\chi(h,h)\rho(h,h)^{-1/2}\ , \tag{58a}$$

where $\chi(h,h)$ denotes a matrix of energy expectation values

$$\begin{aligned}\chi(h,h)_{r,s}&=\langle\Psi_0^N|c_r^\dagger(E_0^N-\hat{H})c_s|\Psi_0^N\rangle\\&=\langle\Psi_0^N|c_r^\dagger[c_s,\hat{H}]|\Psi_0^N\rangle\end{aligned} \tag{58b}$$

for the physical one-hole states ($n_r=n_s=1$). Explicit expressions for the further blocks of $\underline{f}$ and $\underline{K}+\underline{C}$ are given in Appendix B.

It is interesting to compare the expressions for $\underline{f}$ and $\underline{C}$ determined diagrammatically [see Eqs. (A1) and (A2) in Appendix A] with the closed-form results obtained by the block QR decomposition. Through second order, both sets of results are identical, which is consistent with the observation that the diagrammatical construction of $\underline{f}$ and $\underline{C}$ is unique through second order.[14,16] In third (and higher) order the diagrammatic construction may lead to expressions for $\underline{f}$ and $\underline{C}$ that differ from those of the closed-form representation. This shows that the ADC procedure is not uniquely determined by the two basic conditions of compact and regular perturbation expansions. Obviously, the closed-form ADC representations obtained using the BQRD is a distinguished, highly symmetrical form. The order-by-order procedure of the diagrammatic construction, on the other hand, may result in less symmetrical though possibly simpler perturbation theoretical expressions. Of course, the symmetrical form can always be enforced in the course of the diagrammatic construction by suitable algebraic manipulations.

IV. GENERALIZATIONS

The closed-form ADC representation for the one-particle Green's-function parts $\underline{G}^{\pm}(\omega)$ presented in the preceding Section can readily be generalized to the treatment of other propagators, and we will briefly discuss the polarization propagator $\Pi(\omega)$ and the two-particle (hole)-propagator $\underline{P}(\omega)$. In both cases explicit second-order ADC equations are available;[14,16] third-order [ADC(3)] equations for $\underline{P}(\omega)$ were derived recently by Tarantelli and Cederbaum.[22]

A. Polarization propagator

The spectral representation for the polarization propagator $\underline{\Pi}(\omega)$ can be written in the form given by Eqs. (2), (3), and (5):

$$\underline{\Pi}(\omega)=\underline{\Pi}^{+}(\omega)+\underline{\Pi}^{-}(\omega)\ , \tag{59}$$

$$\underline{\Pi}^{+}(\omega)=\underline{x}^{\dagger}(\omega\underline{1}-\underline{\Omega})^{-1}\underline{x}\ . \tag{60a}$$

Here, $\underline{\Omega}$ is the diagonal matrix of the exact (N-electron) excitation energies

$$\Omega_{mm}=E_m^N-E_0^N\ ,\quad m\neq 0\ , \tag{60b}$$

and $\underline{x}$ is the matrix of spectroscopic amplitudes

$$x_{m,rs}=\langle\Psi_m^N|c_r^\dagger c_s|\Psi_0^N\rangle\ ,\quad m\neq 0\ . \tag{60c}$$

The part $\underline{\Pi}^{-}(\omega)$ is related to $\underline{\Pi}^{+}(\omega)$ according to the relation

$$\Pi^{-}_{rs,r's'}(\omega)=\Pi^{+}_{s'r',sr}(-\omega)\ . \tag{61}$$

The ADC form for $\underline{\Pi}^{+}(\omega)$ is obtained by the unitary transformation

$$\underline{X}=\underline{Q}\,\underline{f}\ , \tag{62a}$$

$$\underline{K}+\underline{C}=\underline{Q}^{\dagger}\underline{\Omega}\,\underline{Q}\ , \tag{62b}$$

where $\underline{Q}$ relates the exact excited N-electron states $|\Psi_m^N\rangle$, $m\neq 0$, and the ADC intermediate states $|\tilde{\Psi}_m^N\rangle$, leading to the ADC form

$$\underline{\Pi}^{+}(\omega)=\underline{f}^{\dagger}(\omega\underline{1}-\underline{\Omega})^{-1}\underline{f}\ . \tag{63}$$

As in Eqs. (6) and (8), we distinguish a physical (p-h) part and an unphysical (up) part of $\underline{x}$ (and $\underline{f}$) according to the values $\bar{n}_r n_s=1$ and $\bar{n}_r n_s=0$, respectively, of the single particle indices r,s in Eq. (60c):

$$\underline{x}=(x(p\text{-}h),\underline{x}(up))\ , \tag{64a}$$

$$\underline{f}=(f(p\text{-}h),\underline{f}(up))\ . \tag{64b}$$

The unphysical part may be decomposed further in h-p, h-h, and p-p parts, respectively. In analogy to Eq. (25), we now consider the matrix $\underline{X}$ of generalized spectroscopic amplitudes

$$X_{m,J}=\langle\Psi_m^N|\hat{C}_J|\Psi_0^N\rangle\ ,\quad m\neq 0 \tag{65}$$

where C_J denotes excitation operators of the set

$$\{\hat{C}_J\}=\{c_j^\dagger c_l,c_i^\dagger c_j^\dagger c_l c_k,\ldots\} \tag{66}$$

comprising all physical p-h, $2p$-$2h$, $3p$-$3h$, . . . excitations. The same generalization leads to the matrix $\underline{F}$ of effective spectroscopic amplitudes

$$F_{J,J'}=\langle\tilde{\Psi}_J^N|\hat{C}_{J'}|\Psi_0^N\rangle\ . \tag{67}$$

Again, the basic equation for determining $\underline{Q}$ is

$$\underline{X}=\underline{Q}\,\underline{F}\ . \tag{68}$$

Labeling the classes of np-nh states by $\nu=1,2,3\ldots$ the block structure of these matrices is identical with that of $\underline{G}^{-}(\omega)$, and the BQRD as described in the preceding section can just be transferred to the present case. In particular, the order relations

$$\underline{X}_{\nu\mu}\simeq O(\nu-\mu)\ ,\quad \nu=\mu,\mu+1,\mu+2,\ldots \tag{69}$$

for the lower triangular blocks of $\underline{X}$ are the same as those for $\underline{G}^{-}(\omega)$ stated in Eq. (31). Explicit expressions for the columns $\underline{Q}_i$ and the blocks $\underline{f}_i$ and $(\underline{K}+\underline{C})_{ij}$, $i,j\leq 3$ are collected in Appendix B.

B. Two-particle (hole) propagator

In a completely analogous way we can treat the case of the pp propagator[16]

$$\underline{P}(\omega)=\underline{P}^{+}(\omega)-\underline{P}^{-}(\omega)\,, \tag{70}$$

where the two parts $\underline{P}^{\pm}(\omega)$ contain information on the removal or attachment of two electrons, respectively. We may confine ourselves here to the $(N-2)$-particle part $\underline{P}^{-}(\omega)$. Its spectral representation takes the familiar matrix form

$$\underline{P}^{-}(\omega)=\underline{x}^{\dagger}(\omega\underline{1}-\underline{\Omega})^{-1}\underline{x}\,, \tag{71a}$$

where

$$-\Omega_{mm}=E_{m}^{N-2}-E_{0}^{N} \tag{71b}$$

are double-ionization energies and

$$x_{m,rs}=\langle\Psi_{m}^{N-2}|c_{r}c_{s}|\Psi_{0}^{N}\rangle \tag{71c}$$

are corresponding spectroscopic amplitudes, which, according to $n_r n_s=1$ or 0, belong to the physical part $\underline{x}(2h)$ or unphysical part $\underline{x}(up)$ of $\underline{x}$, respectively. The set of physical excitation operators

$$\{\hat{C}_{J}\}=\{c_{l}c_{k},c_{j}^{\dagger}c_{l}c_{h}c_{k},\ldots\} \tag{71d}$$

here comprises the classes of $2h, 3h\text{-}1p, 4h\text{-}2p, \ldots$ excitations of $N-2$ particles. The corresponding generalized spectroscopic amplitudes read

$$X_{m,J}=\langle\Psi_{m}^{N-2}|\hat{C}_{J}|\Psi_{0}^{N}\rangle\,. \tag{72}$$

All equations given above for the BQRD of $\underline{G}^{-}(\omega)$ [and $\underline{\Pi}^{+}(\omega)$] can be formally transferred to the present case if the $(\nu+1)h\text{-}(\nu-1)p$ states are labeled by $\nu=1,2,3,\ldots$. For explicit expressions of $\underline{Q}$, $\underline{f}$, and $\underline{K}+\underline{C}$ the reader is referred to Appendix B.

C. A special case

We finally consider the special case where the interaction part $\hat{H}_I$ of the Hamiltonian $\hat{H}$ is a nondiagonal one-particle operator

$$\hat{H}_{I}=\sum_{i,j}W_{ij}c_{i}^{\dagger}c_{j}\,. \tag{73}$$

In this case the matrices $\underline{X}$ for any of the propagators considered here have already the upper triangular block form:

$$\underline{X}_{\nu\mu}=\underline{0}\quad\text{for } \nu>\mu\,. \tag{74}$$

The BQRD procedure here leads to a block-diagonal matrix $\underline{Q}$, that is, $\underline{Q}_{\nu\mu}=\underline{0}$ for $\nu\neq\mu$, and the diagonal blocks are given by

$$\underline{Q}_{nn}=\underline{X}_{nn}(\underline{X}_{nn}^{\dagger}\underline{X}_{nn})^{-1/2}\,. \tag{75}$$

Of special interest is the case of the one-particle propagator $\underline{G}^{-}(\omega)$ [or $\underline{G}^{+}(\omega)$] where one can readily establish a direct relation to the problem of quasidegenerate perturbation theory (QDPT) or block diagonalization. A more detailed discussion of this connection is planned to be given elsewhere.[23]

V. CONCLUSIONS

A new type of intermediate many-electron state $|\tilde{\Psi}_J\rangle$ has been introduced in the representation of propagators and related quantities, augmenting the familiar spectral and CI representations associated with the exact states $|\Psi_n\rangle$ (eigenstates of the full Hamiltonian) and the HF states $|\phi_J\rangle$ (eigenstates of the HF Hamiltonian), respectively. Here the unitary matrix $\underline{Q}$ relating the exact and intermediate states is constructed by a simple algebraic procedure consisting in a block QR decomposition (BQRD) of the generalized spectroscopic matrix $\underline{X}$. The BQRD procedure generates successively the blocks of the effective spectroscopic and interaction matrices $\underline{f}$ and $\underline{C}$, respectively, which constitute the intermediate propagator representations. As a result, explicit closed-form expressions have been derived for these quantities formulated entirely in terms of ground-state density matrices and related energy expectation values.

The relevance of the intermediate representations as a means for deriving approximation schemes arises from two basic properties, namely the regularity and the compactness of the perturbation expansions for the effective matrix elements. Regularity means the absence of terms with dangerous denominators which would disqualify these perturbation expansions as a computational method. The BQRD procedure provides a mechanism to automatically separate dangerous and well-behaved contributions both contained in the original spectroscopic matrix $\underline{X}$. All terms with dangerous denominators are collected in the unitary matrix $\underline{Q}$ leaving the upper triangle matrix $\underline{F}$ and the effective matrices $\underline{f}$ and $\underline{C}$ well behaved. The compactness property, on the other hand, restricts the size of the explicit intermediate configuration space required for a consistent nth-order treatment of the considered propagator. Indeed, one may say that the nth-order intermediate configuration space is the minimal space compatible with the regularity requirement for the respective perturbation expansions of the effective matrix elements. Clearly, the compactness property does not apply to the CI representation. We recall that in the usual case of a two-particle interaction the CI space for a consistent nth-order treatment grows in each even order by two next higher classes of configurations, whereas only one higher class is required in the explicit intermediate configuration space. The compactness requirement discards also other apparent possibilities to define an "intermediate" representation, such as the simple choice $\underline{X}(\underline{X}^{\dagger}\underline{X})^{-1/2}$ for the unitary transformation $\underline{Q}$.

The regularity and compactness properties prove the intermediate representations to be closed forms of the algebraic diagrammatic construction (ADC) introduced previously[14–16] as a reformulation of the diagrammatic propagator perturbation series. The closed-form ADC representations provide us with a direct access to determine the effective spectroscopic and interaction matrices $\underline{f}$ and $\underline{C}$, and may be used instead of the original indirect procedure, which consisted in comparing the diagrammatic series and the perturbation expansion of the ADC representation. This will be very useful for deriving higher-order approximation schemes. A particularly important aspect here is that it is no longer necessary to resort to the lengthy and numerically impractical perturbation theoretical expressions for the matrix elements of $\underline{f}$ and $\underline{C}$. Instead one may code only the building blocks, that is, the perturbation expansions for the density matrix ρ and the matrix χ of the related energy expectation values and then assemble numerically—according to the formulas in Appendix B—the required effective quantities.

Besides the more practical consequences, there are theoretical aspects concerning the existence, uniqueness, and convergence of the ADC approach. The first point is manifestly demonstrated by the closed form presented here. Uniqueness, on the other hand, does not follow as the consequence of the defining regularity and compactness conditions, as the example of different third-order schemes has shown. It is clear, however, that the BQRD procedure leads to a distinguished highly symmetrical form, which is reflected by the Hermiticity of the diagonal blocks $\underline{F}_{\nu\nu}$ in the generalized effective spectroscopic matrix $\underline{F}$. QR decompositions with less symmetrical forms of $\underline{F}$ may be obtained by modifying the symmetric orthonormalization used here within a column of blocks of $\underline{Q}$. With respect to the convergence properties of the ADC schemes, the explicit expressions of the intermediate representation show that the effective matrix element expansions behave essentially like the Rayleigh-Schrödinger perturbation series for the N-electron ground state. It should be recalled here that the perturbation expansions of a finite-order ADC representation account both for ground- and final-state correlation.

In several respects, the intermediate representations go beyond the original concept of the ADC reformulation of propagator perturbation series. For instance, the BQRD procedure can be applied in cases where a (diagrammatic) perturbation expansion is not readily available. More importantly, this approach may be useful even in cases where the ground-state pertubation series and hence the effective matrix element expansions do not converge. The closed-form representation allows one to evaluate the effective quantities without resorting to perturbation theory, e.g., by introducing a suitable multiconfiguration representation of the N-electron ground state. Future work must show whether the intermediate representations introduced here will serve as a useful starting point for developing such nonperturbative approximations.

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APPENDIX A: ADC(2) EQUATIONS FOR THE ONE-PARTICLE GREEN'S FUNCTION

The $(N-1)$-particle part $\underline{G}^{-}(\omega)$ will be considered here. The ADC(2) configuration space comprises the $1h$ and $2h$-$1p$ configurations specified by the sets of one-particle quantum numbers

$$(k)\ ,\quad \text{where } n_k=1\ ;$$

$$(j,k,l)\ ,\quad \text{where } \bar{n}_j n_k n_l=1 \text{ and } k<l\ .$$

Here $n_k=1-\bar{n}_k$ are ground-state HF occupation numbers. In the following equations, $V_{ij[kl]}=V_{ijkl}-V_{ijlk}$ denotes the antisymmetrized Coulomb integral, ϵ_i are HF energies, and

$$\gamma_{ijkl}=\frac{V_{ij[kl]}}{\epsilon_i+\epsilon_j-\epsilon_k-\epsilon_l}$$

serves for a short notation.

(i) Effective spectroscopic amplitudes

$1h$ block:

$$\begin{aligned} f_{k,q}=\delta_{kq}&-\tfrac{1}{4}\sum_{v,r,s}\gamma^*_{kv[rs]}\gamma_{qv[rs]}n_v\bar{n}_r\bar{n}_s n_q \\ &+\tfrac{1}{2}\sum_{u,v,s}\gamma_{gs[uv]}\frac{V^*_{ks[uv]}}{\epsilon_k-\epsilon_q}\bar{n}_s n_u n_v \bar{n}_q \\ &+\tfrac{1}{2}\sum_{u,s,t}\gamma^*_{ku[st]}\frac{V_{qu[st]}}{\epsilon_k-\epsilon_q}n_u\bar{n}_s\bar{n}_t\bar{n}_q\ . \end{aligned}\tag{A1a}$$

$2h$-$1p$ block:

$$f_{jkl,q}=-\gamma_{qjkl}\bar{n}_q\ .\tag{A1b}$$

(ii) Effective interaction

$1h$ block:

$$(K+C)_{kk'}=\epsilon_k\delta_{kk'}-\tfrac{1}{2}\sum_{v,r,s}\gamma^*_{kv[rs]}\gamma_{k'v[rs]}(\epsilon_v-\epsilon_r-\epsilon_s+\tfrac{1}{2}\epsilon_k+\tfrac{1}{2}\epsilon_{k'})n_v\bar{n}_r\bar{n}_s\ .\tag{A2a}$$

$1h/2h$-$1p$ block:

$$(K+C)_{k,j'k'l'}=V^*_{kj'[k'l']}\ .\tag{A2b}$$

$2h$-$1p$ block:

$$(K+C)_{jkl,j'k'l'}=(-\epsilon_j+\epsilon_k+\epsilon_l)\delta_{jj'}\delta_{kk'}\delta_{ll'}-\delta_{jj'}V_{kl[k'l']}+(\delta_{kk'}V_{j'l[jl']}+\delta_{ll'}V_{j'k[jk']})-(k\leftrightarrow l)\ .\tag{A2c}$$

Here $(k\leftrightarrow l)$ means repeating the preceding term, but with k and l interchanged. It should be noted that the Coulomb terms in Eq. (A2c) are anticipated from the third-order scheme.

APPENDIX B: EXPLICIT INTERMEDIATE REPRESENTATION RESULTS OBTAINED BY THREE BQRD STEPS

In the following we collect the explicit results obtained by the first three steps of the block QR decomposition for the intermediate representation of single-particle Green's-function $\underline{G}(\omega)$ (Sec. III), the polarization propagator $\underline{\Pi}(\omega)$ (Sec. IV A) and the two-particle (hole)-propagator $\underline{P}(\omega)$ (Sec. IV B). A common notation may be used for all three cases. As in Secs. III and IV, $\nu=1,2,3,\ldots$ refers to the successive classes of excitations, that is,

$$\nu\equiv\begin{cases} \nu h\text{-}(\nu-1)p & \text{for } \underline{G}^{-}(\omega) \\ \nu p\text{-}\nu h & \text{for} \underline{\Pi}^{+}(\omega) \\ (\nu+1)h\text{-}(\nu-1)p & \text{for } \underline{P}^{-}(\omega) \; . \end{cases} \tag{B1}$$

The short-hand notation $\rho(\nu,\mu)$ is used for the matrix of ground-state density matrix elements

$$\begin{aligned}\rho(\nu,\mu)_{I,J}=&\langle \Psi_0^N|\hat{C}_I^{\dagger}\hat{C}_J|\Psi_0^N\rangle \\ &-\langle \Psi_0^N|\hat{C}_I^{\dagger}|\Psi_0^N\rangle\langle \Psi_0^N|\hat{C}_J|\Psi_0^N\rangle \; ,\end{aligned} \tag{B2}$$

where $\hat{C}_I$ and $\hat{C}_J$ are physical excitation operators from the classes ν and μ, respectively; the second term on the right-hand side of (B2) applies only to the case of the polarization propagator. Similarly, $\chi(\nu,\mu)$ denotes the matrix of the corresponding energy expectation values

$$\chi(\mu,\nu)_{I,J}=\pm\langle \Psi_0^N|\hat{C}_I^{\dagger}(\hat{H}-E_0^N)\hat{C}_J|\Psi_0^N\rangle \; . \tag{B3}$$

Here a positive sign on the right-hand side applies to $\underline{\Pi}^{+}(\omega)$ and a negative to $\underline{G}^{-}(\omega)$ and $\underline{P}^{-}(\omega)$. Finally, density matrix blocks $\rho(\nu,\bar{1})$ have to be introduced where the second entry corresponds to an unphysical excitation operator, more specifically:

$$\bar{1}\equiv\begin{cases} p & \text{for } \underline{G}^{-}(\omega) \\ h\text{-}p,h\text{-}h,p\text{-}p & \text{for } \underline{\Pi}^{+}(\omega) \\ h\text{-}p,p\text{-}h,p\text{-}p & \text{for } \underline{P}^{-}(\omega) \; . \end{cases} \tag{B4}$$

The modifications of the notations (B1) and (B4) for the case of $\underline{G}^{+}$ and $\underline{P}^{+}$ are obvious.

(i) Generalized effective spectroscopic amplitudes $\underline{F}_{\nu\mu}$

$$\underline{F}_{11}=\rho(1,1)^{1/2} \; , \tag{B5a}$$

$$\underline{F}_{12}=\rho(1,1)^{-1/2}\rho(1,2) \; , \tag{B5b}$$

$$\underline{F}_{22}=[\rho(2,2)-\rho(2,1)\rho(1,1)^{-1}\rho(1,2)]^{1/2} \; , \tag{B5c}$$

$$\underline{F}_{13}=\rho(1,1)^{-1/2}\rho(1,3) \; , \tag{B5d}$$

$$\underline{F}_{23}=\tilde{\rho}(2,2)^{-1/2}\tilde{\rho}(2,3) \; , \tag{B5e}$$

$$\underline{F}_{33}=[\rho(3,3)-\rho(3,1)\rho(1,1)^{-1}\rho(1,3)-\tilde{\rho}(3,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)]^{1/2} \; . \tag{B5f}$$

Here and in the following quantities

$$\tilde{\rho}(2,2)=\rho(2,2)-\rho(2,1)\rho(1,1)^{-1}\rho(1,2) \; , \tag{B6a}$$

$$\tilde{\rho}(2,3)=\tilde{\rho}(3,2)^{\dagger}=\rho(2,3)-\rho(2,1)\rho(1,1)^{-1}\rho(1,3) \; , \tag{B6b}$$

$$\tilde{\rho}(3,3)=\rho(3,3)-\tilde{\rho}(3,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)-\rho(3,1)\rho(1,1)^{-1}\rho(1,3) \tag{B6c}$$

are used.

(ii) Unitary transformation matrix $\underline{Q}$

$$\underline{Q}_{1}=\underline{X}_{1}\rho(1,1)^{-1/2} \; , \tag{B7a}$$

$$\underline{Q}_{2}=[\underline{X}_{2}-\underline{Q}_{1}\rho(1,1)^{-1/2}\rho(1,2)]\tilde{\rho}(2,2)^{-1/2} \; , \tag{B7b}$$

$$\underline{Q}_{3}=[\underline{X}_{3}-\underline{Q}_{1}\rho(1,1)^{-1/2}\rho(1,3)-\underline{Q}_{2}\tilde{\rho}(2,2)^{-1/2}\tilde{\rho}(2,3)]\tilde{\rho}(3,3)^{-1/2} \; . \tag{B7c}$$

According to Sec. III B, $\underline{X}_i$ are columns of blocks $\underline{X}_{\mu i}$ of the generalized spectroscopic matrix $\underline{X}$ [Eqs. (25), (65), and (72)].

(iii) Effective spectroscopic amplitudes $\underline{f}$

Physical part:

$$\underline{f}_{1}(1)=\rho(1,1)^{1/2} \; , \tag{B8a}$$

$$\underline{f}_{\nu}(1)=\underline{0} \quad \text{for } \nu>1 \; . \tag{B8b}$$

Unphysical part:

$$\underline{f}_{1}(\bar{1})=\rho(1,1)^{-1/2}\rho(1,\bar{1}) \; , \tag{B8c}$$

$$\underline{f}_{2}(\bar{1})=\tilde{\rho}(2,2)^{-1/2}[\rho(2,\bar{1})-\rho(2,1)\rho(1,1)^{-1/2}\underline{f}_{1}(\bar{1})] \; , \tag{B8d}$$

$$\underline{f}_{3}(\bar{1})=\tilde{\rho}(3,3)^{-1/2}[\rho(3,\bar{1})-\rho(3,1)\rho(1,1)^{-1/2}\underline{f}_{1}(\bar{1})-\tilde{\rho}(3,2)\tilde{\rho}(2,2)^{-1/2}\underline{f}_{2}(\bar{1})] \; . \tag{B8e}$$

(iv) Effective interaction matrix $\underline{K}+\underline{C}$

$$(\underline{K}+\underline{C})_{11}=\rho(1,1)^{-1/2}\chi(1,1)\rho(1,1)^{-1/2}\ , \tag{B9a}$$

$$(\underline{K}+\underline{C})_{12}=\rho(1,1)^{-1/2}[\chi(1,2)-\chi(1,1)\rho(1,1)^{-1}\rho(1,2)]\tilde{\rho}(2,2)^{-1/2}\ , \tag{B9b}$$

$$\begin{aligned}(\underline{K}+\underline{C})_{22}=\tilde{\rho}(2,2)^{-1/2}[&\chi(2,2)-\chi(2,1)\rho(1,1)^{-1}\rho(1,2)\\&-\rho(2,1)\rho(1,1)^{-1}\chi(1,2)+\rho(2,1)\rho(1,1)^{-1}\chi(1,1)\rho(1,1)^{-1}\rho(1,2)]\tilde{\rho}(2,2)^{-1/2}\ ,\end{aligned} \tag{B9c}$$

$$(\underline{K}+\underline{C})_{13}=\rho(1,1)^{-1/2}[\chi(1,3)-\chi(1,1)\rho(1,1)^{-1}\rho(1,3)-\tilde{\chi}(1,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)]\tilde{\rho}(3,3)^{-1/2}\ , \tag{B9d}$$

$$\begin{aligned}(\underline{K}+\underline{C})_{23}=\tilde{\rho}(2,2)^{-1/2}[&\chi(2,3)-\rho(2,1)\rho(1,1)^{-1}\chi(1,3)\\&-\tilde{\chi}(2,1)\rho(1,1)^{-1}\rho(1,3)-\tilde{\chi}(2,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)]\tilde{\rho}(3,3)^{-1/2}\ ,\end{aligned} \tag{B9e}$$

$$\begin{aligned}(\underline{K}+\underline{C})_{33}=\tilde{\rho}(3,3)^{-1/2}\{&\chi(3,3)+\rho(3,1)\rho(1,1)^{-1}\chi(1,1)\rho(1,1)^{-1}\rho(1,3)+\tilde{\rho}(3,2)\tilde{\rho}(2,2)^{-1}\tilde{\chi}(2,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)\\&-[\chi(3,1)\rho(1,1)^{-1}\rho(1,3)+\tilde{\chi}(3,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)\\&\quad-\rho(3,1)\rho(1,1)^{-1}\tilde{\chi}(1,2)\tilde{\rho}(2,2)^{-1}\tilde{\rho}(2,3)]-(\text{h.c.})\}\tilde{\rho}(3,3)^{-1/2}\ .\end{aligned} \tag{B9f}$$

For notational brevity the quantities

$$\tilde{\chi}(1,2)=\tilde{\chi}(2,1)^{\dagger}=\rho(1,1)^{1/2}(\underline{K}+\underline{C})_{12}\tilde{\rho}(2,2)^{1/2}\ , \tag{B9g}$$

$$\tilde{\chi}(2,2)=\tilde{\rho}(2,2)^{1/2}(\underline{K}+\underline{C})_{22}\tilde{\rho}(2,2)^{1/2}\ , \tag{B9h}$$

$$\tilde{\chi}(2,3)=\tilde{\chi}(3,2)^{\dagger}=\tilde{\rho}(2,2)^{1/2}(\underline{K}+\underline{C})_{23}\tilde{\rho}(3,3)^{1/2} \tag{B9i}$$

are introduced in Eqs. (B9d)–(B9f).

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