Coupled-cluster Green's function: Analysis of properties originating in the exponential parametrization of the ground-state wave function

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In this paper we derive basic properties of the Green's-function matrix elements stemming from the exponential coupled-cluster (CC) parametrization of the ground-state wave function. We demonstrate that all intermediates used to express the retarded (or, equivalently, ionized) part of the Green's function in the ω representation can be expressed only through connected diagrams. Similar properties are also shared by the first-order ω derivative of the retarded part of the CC Green's function. Moreover, the first-order ω derivative of the CC Green's function can be evaluated analytically. This result can be generalized to any order of ω derivatives. Through the Dyson equation, derivatives of the corresponding CC self-energy operator can be evaluated analytically. In analogy to the CC Green's function, the corresponding CC self-energy operator can be represented by connected terms. Our analysis can easily be generalized to the advanced part of the CC Green's function.

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I. INTRODUCTION

Coupled-cluster (CC) methods [1–7] have evolved into a method of choice in studies of various aspects of chemical problems, including ground-state potential-energy surfaces [8], excited states [7], molecular properties [9], and multireference and strongly correlated systems [10–13]. Significant progress has also been achieved in the development of reduced-scaling CC methods employing the local character of ground-state correlation effects [14–17]. The key factor that contributes to the success of the CC formulations is its efficiency in capturing various types of correlation effects that enable the development of hierarchical classes of CC approximations. This has been illustrated in numerous studies with ground-state CC formulations, multireference CC methods, linear-response CC formalisms, and excited-state equation-of-motion CC formalisms (EOMCC; see Ref. [7]).

More recently, CC formalisms began to permeate various embedding methods (fragment molecular-orbital approach [18,19], effective fragment potential method [20], coupled-cluster/molecular-mechanics (CC/MM) methods [21,22], polarizable embedding formulations [23], wave-function-theory-in-density-functional-theory (WFT-in-DFT) [24,25]), offering a detailed description of correlation effects in studies of chemical transformations in solutions, reactions in active centers of proteins, and localized electronic states in solids, to mention only a few applications. Important progress in the development of reliable embedding schemes is associated with the utilization of the Green's-function formalism [26–57]. Recently, considerable interest has been attracted by the possibility of utilizing highly correlated methodologies to describe local Green's function or corresponding self-energies in dynamical mean-field theories [58–64]. Several highly correlated methods have been employed to account for many-body correlation effects in self-energy calculations for impurity regions [57,63]. This effort also includes CC Green's-function formulation utilizing the sum-over-state approach [65]. In our earlier works [66,67], which follow the formalism introduced by Nooijen and Snijders [68–70] (see also Ref. [71]), we demonstrated that the CC Green's function with singles and doubles (GFCCSD) can be evaluated analytically. This algorithm makes the GFCCSD approach applicable to any energy regime and is extendable to the whole complex plane. We have also explored the possibility of reducing the computational effort associated with the need to solve N_s (N_s stands for the number of spin orbitals) linear equations for ionization-potential EOMCC (IP-EOMCC) [72] type operators $X_p(\omega)$ and N_s linear equations for electron-affinity EOMCC (EA-EOMCC) [73] type operators $Y_q(\omega)$. The resulting block approximation (B-GFCCSD), which requires $X_p(\omega)$ and $Y_q(\omega)$ operators be calculated for only active spin orbitals, was shown to significantly reduce numerical overhead of the full GFCCSD approach while preserving its pole structure.

In this paper we would like to further extend the analysis of the CC Green's function. We will entirely focus on the IP or retarded part of the CC Green's function (the present analysis can easily be extended to the EA or advanced part of CC Green's function) and prove several properties stemming from the exponential parametrization of the ground-state wave functions. These properties include (1) the connected character of the CC Green's-function matrix elements originating from the connected form of the equations for intermediates $X_p(\omega)$ and $Y_q(\omega)$, (2) the connected character of the first-order ω derivative of the CC Green's-function matrix originating from exponential parametrization of the $(1 + \Lambda)$ deexcitation operator, and (3) the connected character of higher-order ω derivatives of the CC Green's-function matrix. By employing Dyson equations we will also show that the above properties can be extended to the corresponding self-energy operator. We will also discuss the possibility of exponential parametrization of the retarded GFCC.

II. COUPLED-CLUSTER GREEN'S-FUNCTION APPROACH

In this section, we will give the basic tenets of the CC Green's-function formalism introduced by Nooijen and Snijders [68–70]. The CC Green's-function formalism hinges

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upon the CC bivariational formalism [74–76] utilizing different parametrizations of the bra ($\langle\Psi_0^{(N)}|$) and ket ($|\Psi_0^{(N)}\rangle$) ground-state wave functions of a N-electron system,

$$\left\langle\Psi_0^{(N)}\right| = \langle\Phi|(1+\Lambda)e^{-T}, \tag{1}$$

$$\left|\Psi_0^{(N)}\right\rangle = e^{T}|\Phi\rangle. \tag{2}$$

In the exact formulation, the T and Λ operators are represented as sums of their many-body components (T_n and Λ_n)

$$T = \sum_{n=1}^{N} T_n, \tag{3}$$

$$\Lambda = \sum_{n=1}^{N} \Lambda_n, \tag{4}$$

where again N stands for the total number of correlated electrons in the system of interest. The T_n and Λ_n operators can be given by the following expressions:

$$T_n = \frac{1}{(n!)^2} \sum_{\substack{i_1,\ldots,i_n;\\ a_1,\ldots,a_n}} t_{a_1\cdots a_n}^{i_1\cdots i_n} a_{a_1}^{\dagger}\cdots a_{a_n}^{\dagger} a_{i_n}\cdots a_{i_1}, \tag{5}$$

$$\Lambda_n = \frac{1}{(n!)^2} \sum_{\substack{i_1,\ldots,i_n;\\ a_1,\ldots,a_n}} \lambda_{i_1\cdots i_n}^{a_1\cdots a_n} a_{i_1}^{\dagger}\cdots a_{i_n}^{\dagger} a_{a_n}\cdots a_{a_1}, \tag{6}$$

where $t_{a_1\cdots a_n}^{i_1\cdots i_n}$ and $\lambda_{i_1\cdots i_n}^{a_1\cdots a_n}$ are antisymmetric amplitudes determining T and Λ operators. The indices $i,j,k,\ldots$ $(i_1,i_2,\ldots)$ and $a,b,c,\ldots$ $(a_1,a_2,\ldots)$ correspond to occupied and unoccupied spin orbitals in the reference function $|\Phi\rangle$, respectively. The a_p ($a_p^{\dagger}$) operator is the annihilation (creation) operator for the electron in the pth state. The cluster operator T, CC energy $E_0^{(N)}$, and deexcitation operator Λ are determined from the standard CC equations that are solved in the following order:

$$Qe^{-T}He^{T}|\Phi\rangle = 0, \tag{7}$$

$$E_0^{(N)} = \langle\Phi|e^{-T}He^{T}|\Phi\rangle, \tag{8}$$

$$\langle\Phi|(1+\Lambda)e^{-T}He^{T}Q = E_0^{(N)}\langle\Phi|(1+\Lambda)Q, \tag{9}$$

where Q is the projection operator onto the subspace spanned by Slater determinants generated by the T operator when acting on the reference function $|\Phi\rangle$, i.e.,

$$Q = \sum_{n=1}^{N} Q_n = \sum_{n=1}^{N} \frac{1}{(n!)^2} \sum_{\substack{i_1,\ldots,i_n;\\ a_1,\ldots,a_n}} \left|\Phi_{i_1\cdots i_n}^{a_1\cdots a_n}\right\rangle\left\langle\Phi_{i_1\cdots i_n}^{a_1\cdots a_n}\right|, \tag{10}$$

where the excited Slater determinant $|\Phi_{i_1\cdots i_n}^{a_1\cdots a_n}\rangle$ is defined as $a_{a_1}^{\dagger}\cdots a_{a_n}^{\dagger}a_{i_n}\cdots a_{i_1}|\Phi\rangle$. Algebraically, the system of equations defining cluster amplitudes $t_{a_1\cdots a_n}^{i_1\cdots i_n}$ can be represented as

$$\left\langle\Phi_{i_1\cdots i_n}^{a_1\cdots a_n}\right|\bar{H}_N|\Phi\rangle = 0\ \forall\, n\in\{1,\ldots,N\},$$
$$\forall\, i_1,\ldots,i_n,\forall\, a_1,\ldots,a_n. \tag{11}$$

The Λ operator has been extensively discussed in the literature [77]. In particular, the Λ operator is defined by linked diagrams (in the present context, linked diagrams refer to the open diagrams which do not contain a disconnected closed part). In the limit of the exact theory discussed in this paper, $\langle\Phi|(1+\Lambda)$ is equivalent to the exponential ansatz based on the deexcitation cluster operator S, i.e.,

$$\langle\Phi|(1+\Lambda) = \langle\Phi|e^{S}. \tag{12}$$

Since the equations for the S operator,

$$\langle\Phi|\bar{\bar{H}}Q = \langle\Phi|e^{S}\bar{H}e^{-S}Q = \langle\Phi|(e^{S}\bar{H})_C Q = 0, \tag{13}$$

obtained upon the substitution of expansion (12) into the left CC equations for the Λ operator, are explicitly connected, the deexcitation cluster operator S is also connected. In analogy to Eq. (11), the explicitly projected form of Eq. (13) takes the form

$$\left\langle\Phi|\bar{\bar{H}}\right|\Phi_{i_1\cdots i_n}^{a_1\cdots a_n}\right\rangle = 0\ \forall\, n\in\{1,\ldots,N\},$$
$$\forall\, i_1,\ldots,i_n,\forall\, a_1,\ldots,a_n. \tag{14}$$

The $\bar{H}$ and $\bar{\bar{H}}$ operators are the so-called similarity transformed Hamiltonians,

$$\bar{H} = e^{-T}He^{T}, \tag{15}$$

$$\bar{\bar{H}} = e^{S}e^{-T}He^{T}e^{-S} = e^{S}\bar{H}e^{-S}. \tag{16}$$

The above representation of the $1+\Lambda$ operator will greatly facilitate the discussion of diagrams contributing to the CC Green's-function matrix. Although the above exponential expansion bears a resemblance to the extended CC (ECC) formulations of Arponen [74], in the present context the equations for the cluster operator T are decoupled from the equations for the S operator.

By employing the CC bivariational approach, the corresponding Green's function can be expressed as

$$G_{pq}(\omega) = \langle\Phi|(1+\Lambda)e^{-T}a_q^{\dagger}[\omega+(H-E_0)-i\eta]^{-1}a_p e^{T}|\Phi\rangle + \langle\Phi|(1+\Lambda)e^{-T}a_p[\omega-(H-E_0)+i\eta]^{-1}a_q^{\dagger}e^{T}|\Phi\rangle.$$

Let's focus on $G_{pq}^{R}(\omega)$, the retarded part of $G_{pq}(\omega)$, which is defined as

$$G_{pq}^{R}(\omega) = \langle\Phi|(1+\Lambda)e^{-T}a_q^{\dagger}[\omega+(H-E_0)-i\eta]^{-1}a_p e^{T}|\Phi\rangle. \tag{17}$$

Introducing resolution of the identity $1 = e^{-T}e^{T}$ and the normal product form representation of $\bar{H}$, the Green's function can be rewritten as (for simplicity, in the following we will omit the complex factor $i\eta$)

$$G_{pq}^{R}(\omega) = \langle\Phi|(1+\Lambda)\bar{a}_q^{\dagger}(\omega+\bar{H}_N)^{-1}\bar{a}_p|\Phi\rangle, \tag{18}$$

where the similarity-transformed operators $\bar{a}_p$, $\bar{a}_p^{\dagger}$, and $\bar{H}_N$ are given by the equations

$$\bar{a}_p = e^{-T}a_p e^{T}, \tag{19}$$

$$\bar{a}_p^{\dagger} = e^{-T}a_p^{\dagger}e^{T}, \tag{20}$$

$$\bar{H}_N = e^{-T}He^{T} - E_0. \tag{21}$$

Using the Campbell-Baker-Hausdorff formula

$$e^{-B}Ae^{B} = A + [A,B] + \tfrac{1}{2}[[A,B],B] + \cdots, \tag{22}$$

one can derive explicit forms of the similarity-transformed creation and annihilation operators $\bar{a}_p$ an $\bar{a}_p^\dagger$ as

$$\bar{a}_p = a_p + [a_p, T], \tag{23}$$

$$\bar{a}_p^\dagger = a_p^\dagger + [a_p^\dagger, T]. \tag{24}$$

A connected nature of cluster amplitudes defining cluster operator T in conjunction with the connected character of the operator that is transformed [A operator in Eq. (22)] leads to the connected character of the nested commutator expansion. In particular, the expansion for $\bar{H}_N$ [Eq. (21)] contains only connected diagrams. It is also easy to verify that due to the pairwise character of the interelectron interactions it naturally terminates after terms containing fourth powers of cluster operator T. Analogously, similarity-transformed annihilation and creation operators ($\bar{a}_p$ and $\bar{a}_p^\dagger$) are also expressed in terms of connected expressions.

To evaluate the $G^R_{pq}(\omega)$ matrix elements in a numerically efficient way, a set of intermediate operators $X_p(\omega)$ defined in the Hilbert space of $N-1$ particles is defined as follows:

$$(\omega + \bar{H}_N)X_p(\omega)|\Phi\rangle = \bar{a}_p|\Phi\rangle, \tag{25}$$

where the second-quantized form of $X_p(\omega)$ is identical to the form of the IP-EOMCC excitation operator,

$$X_p(\omega) = \sum_i x^i(\omega)_p\, a_i + \sum_{i<j,a} x^{ij}_a(\omega)_p\, a_a^\dagger a_j a_i + \cdots. \tag{26}$$

This leads to the following compact expression for the retarded CC Green's-function matrix elements:

$$G^R_{pq}(\omega) = \langle\Phi|(1+\Lambda)\bar{a}_q^\dagger X_p(\omega)|\Phi\rangle. \tag{27}$$

Another interesting feature is that only connected diagrams are involved in the above representation, which will be shown in the next section.

III. CONNECTED DIAGRAM EXPANSION FOR THE RETARDED PART OF THE COUPLED-CLUSTER GREEN's FUNCTION

The connectedness of the CC Green's-function matrix elements can be proven in two steps, in which we utilize features of the similarity-transformed Hamiltonian $\bar{H}_N$ stemming from the form of CC equations (7) for cluster operator T. First, let us decompose the $\bar{H}_N X_p(\omega)|\Phi\rangle$ term of Eq. (25) into the form

$$\bar{H}_N X_p(\omega)|\Phi\rangle = [\bar{H}_N X_p(\omega)]_C|\Phi\rangle + [\bar{H}_N X_p(\omega)]_{DC}|\Phi\rangle, \tag{28}$$

where subscripts C and DC denote connected and disconnected parts of a given operator expression, respectively. Typical diagrams contributing to the connected and disconnected parts are shown in Fig. 1. It can be observed that the only disconnected terms stem from diagrams that contain vertices corresponding to $\langle\Phi^{a_1\cdots a_n}_{i_1\cdots i_n}|\bar{H}_N|\Phi\rangle$ matrix elements of $\bar{H}_N$, which are equal to zero as they represent the equations for

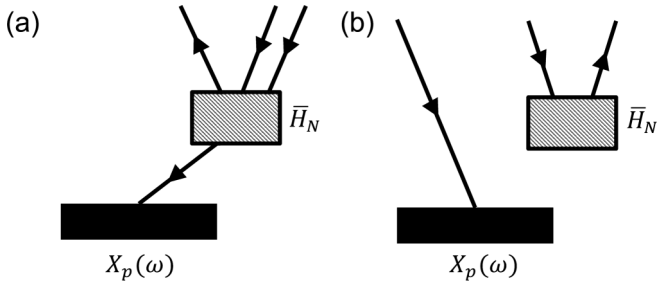

FIG. 1. Typical examples of (a) connected and (b) disconnected diagrams contributing to $(\omega + \bar{H}_N)X_p(\omega)|\Phi\rangle = \bar{a}_p|\Phi\rangle$.

cluster amplitudes defining cluster operator T. Thus, the left-hand side of Eq. (25) is defined by only connected diagrams. As discussed in the previous section, the similarity-transformed annihilation operator $\bar{a}_p$ is expressed in terms of connected expressions. Therefore, Eq. (25) is represented by only the connected diagrams,

$$\{(\omega + \bar{H}_N)X_p(\omega)\}_C|\Phi = \bar{a}_p|\Phi\rangle, \tag{29}$$

and consequently, the $X_p(\omega)$ operator is determined by only connected contributions. Second, we will show that the $\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger$ term [or the $\langle\Phi|e^S\bar{a}_q^\dagger$ term when using the exponential parametrization given by Eq. (12)] in the expression for the retarded part of the Green's function (27) is represented by linked diagrams. This is a consequence of the fact that in contrast to the Λ and S operators, the $\bar{a}_q^\dagger$ operator is a particle-number-nonconserving operator. For this reason (and the fact that $\bar{a}_q^\dagger$ has to be fully contracted with the S operators; otherwise, it would lead to a zero contribution) it cannot be fully contracted with the S operator or its products to produce the disconnected closed part of the diagram. If we additionally recall that the $\bar{a}_q^\dagger$ operator is expressed in terms of

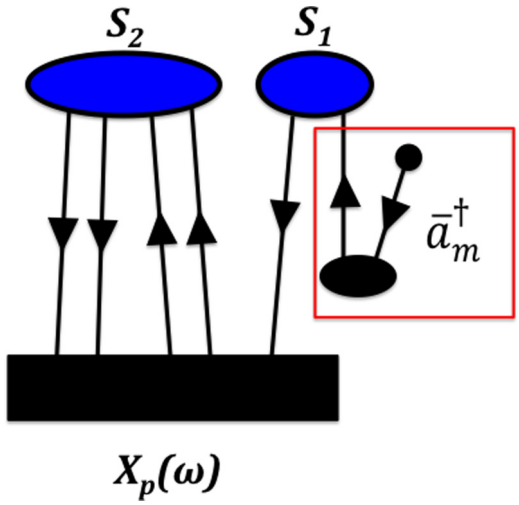

FIG. 2. An example of a connected diagram contributing to the $G_{pm}(\omega)$ matrix element of the CC Green's function (p represents the general spin-orbital index, while index m corresponds to the occupied spin-orbital index). The red box represents a typical particle-nonconserving diagram contributing to $\bar{a}_m^\dagger$.

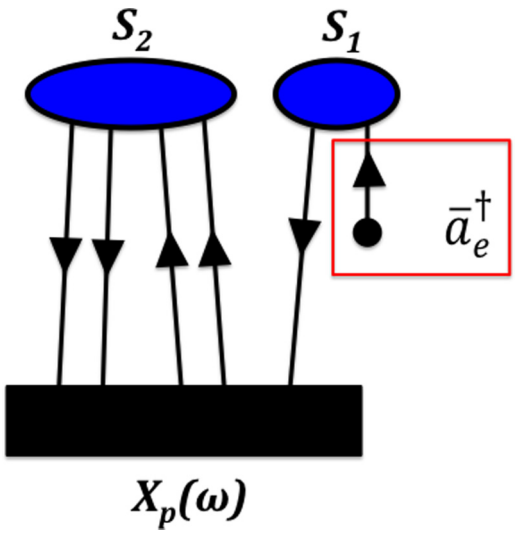

FIG. 3. An example of a connected diagram contributing to the $G_{pe}(\omega)$ matrix element of the CC Green's function (p represents the general spin-orbital index, while index e corresponds to the unoccupied spin-orbital index). The red box contains particle-nonconserving operator $\bar{a}_e^\dagger$.

connected diagrams, we can write that

$$\langle\Phi|S\cdots S\bar{a}_q^\dagger = \langle\Phi|[S\cdots S\bar{a}_q^\dagger]_L \tag{30}$$

(where L designates the linked part of a given operator expression), and consequently,

$$\langle\Phi|e^S\bar{a}_q^\dagger = \langle\Phi|[e^S\bar{a}_q^\dagger]_L\ . \tag{31}$$

Combining the above observations and the fact that the full contractions between linked and connected operators lead to connected diagrams (see Figs. 2 and 3), one can readily notice that the matrix element $G^R_{pq}(\omega)$ is determined by only connected diagrams, which can be symbolically expressed as

$$\begin{aligned} G^R_{pq}(\omega) &= \langle\Phi|[(1+\Lambda)\bar{a}_q^\dagger X_p(\omega)]_C|\Phi\rangle \\ &= \langle\Phi|[e^S\bar{a}_q^\dagger X_p(\omega)]_C|\Phi\rangle. \end{aligned} \tag{32}$$

This provides an alternative proof of the linked-diagram theorem for the one-body Green's function.

IV. FIRST-ORDER ω DERIVATIVE OF THE RETARDED CC GREEN'S FUNCTION

In the next step, we will focus on the first derivative of the $G^R_{pq}(\omega)$ matrix element with respect to ω,

$$\begin{aligned} \frac{dG^R_{pq}(\omega)}{d\omega} &= -\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger(\omega+\bar{H}_N)^{-2}\bar{a}_p|\Phi\rangle \\ &= -\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger(\omega+\bar{H}_N)^{-1}X_p(\omega)|\Phi\rangle. \end{aligned} \tag{33}$$

In analogy to the $X_p(\omega)$ operator, let us introduce operator $Z_q(\omega)$,

$$\begin{aligned} Z_q(\omega) &= Z_{q,1}(\omega) + Z_{q,2}(\omega) + \cdots \\ &= \sum_i z_i(\omega)_q\ a_i^\dagger + \sum_{i<j,a} z^a_{ij}(\omega)_p\ a_i^\dagger a_j^\dagger a_a + \cdots, \end{aligned} \tag{34}$$

which is defined as a solution of the linear equation

$$\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger = \langle\Phi|Z_q(\omega)(\omega+\bar{H}_N) \tag{35}$$

and which leads to a very simple form of the derivative (33),

$$\frac{dG^R_{pq}(\omega)}{d\omega} = -\langle\Phi|Z_q(\omega)X_p(\omega)|\Phi\rangle. \tag{36}$$

By invoking arguments similar to those we used to prove the connectedness of X_p operators, we can easily show that (1) the right-hand side of Eq. (35) is expressed in terms of linked diagrams and (2) the left-hand side contains only linked terms. Consequently, $Z_q(\omega)$ operators are also determined by only linked terms. This can be easily proven using the induction with respect to the iteration number in the case Eq. (35) is solved iteratively. A direct consequence of the linked character of the $Z_q(\omega)$ is that the first derivatives of the CC Green's function matrix elements contain connected diagrams only.

Our next step will involve decomposition of $Z_q(\omega)$ operators into the following form:

$$\langle\Phi|Z_q(\omega) = \langle\Phi|(1+\Lambda)W_q(\omega), \tag{37}$$

where $W_q(\omega)$ operators are represented in the same way as $Z_q(\omega)$,

$$\begin{aligned} W_q(\omega) &= W_{q,1}(\omega) + W_{q,2}(\omega) + \cdots \\ &= \sum_i w_i(\omega)_q\ a_i^\dagger + \sum_{i<j,a} w^a_{ij}(\omega)_q\ a_i^\dagger a_j^\dagger a_a + \cdots. \end{aligned} \tag{38}$$

Equation (37) can be used to establish a one-to-one correspondence between many-body components $Z_{q,i}(\omega)$ and $W_{q,i}(\omega)$ of $Z_q(\omega)$ and $W_q(\omega)$ operators, respectively,

$$Z_{q,1}(\omega) = W_{q,1}(\omega), \tag{39}$$

$$Z_{q,2}(\omega) = W_{q,2}(\omega) + \Lambda_1 W_{q,1}(\omega), \tag{40}$$

$$\begin{aligned} Z_{q,3}(\omega) &= W_{q,3}(\omega) + \Lambda_1 W_{q,2}(\omega) + \Lambda_2 W_{1,q}(\omega), \\ &\cdots. \end{aligned} \tag{41}$$

In the next section we will prove that $W_q(\omega)$ operators are connected quantities.

In analogy to Eq. (25), poles of $W_q(\omega)$ operators obtained from the equation

$$\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger = \langle\Phi|(1+\Lambda)W_q(\omega)(\omega+\bar{H}_N) \tag{42}$$

correspond to the EOMCC ionization potentials. For these ω values, amplitudes defining $W_q(\omega)$ operators ($\eta = 0$) assume singular values.

All results discussed so far are valid for the general spin-orbital index q belonging to both occupied ($q \in O$) and virtual ($q \in V$) spin orbitals. In the next step, we will focus on the explicit algebraic form of the $Z_q(\omega)$ or $W_q(\omega)$ operators for q indices belonging to occupied and unoccupied spin orbitals.

A. $Z_q(\omega)$ and $W_q(\omega)$ operators for q corresponding to the occupied spin orbital ($q = i$)

In this case the $W_i(\omega)$ operator can be formally decomposed as

$$W_i(\omega) = \sum_j m^R_{ji}(\omega)\bar{a}^\dagger_j + \gamma^R_i(\omega), \tag{43}$$

which leads to a natural decomposition of $W_i(\omega)$ into lowest-order contributions and higher-order terms included in the $\gamma^R_i(\omega)$ term. There are several ways to define this decomposition; here we will follow the easiest one stemming from the decomposition of $W_{i,1}(\omega)$ [see Eq. (38)] where the $a^\dagger_j$ operators can be expressed in terms of $\bar{a}^\dagger_j$ operators [see Eq. (24)] according to the formula

$$a^\dagger_j = \bar{a}_j{}^\dagger - [a^\dagger_j, T]. \tag{44}$$

Using the above formula, the $W_{i,1}(\omega)$ operator can be expressed as

$$W_{i,1}(\omega) = \sum_j w_j(\omega)_i(\bar{a}^\dagger_j - [a^\dagger_j, T]), \tag{45}$$

which upon substitution into the $W_i(\omega)$ operator leads to the following definition of the $m^R_{ji}(\omega)$ and $\gamma^R_i(\omega)$ quantities:

$$m^R_{ji}(\omega) = w_j(\omega)_i, \tag{46}$$

$$\gamma^R_i(\omega) = -\sum_j w_j(\omega)_i[a^\dagger_j, T] + \sum_{n=2}^{N} W_{i,n}(\omega). \tag{47}$$

It can easily be shown that the lowest-order contributions to $W_i(\omega)$ are captured by $m^R_{ji}(\omega)$ (see Secs. V and VII). The final forms of the $Z_i(\omega)$ and $W_i(\omega)$ operators can be represented as

$$\begin{aligned}\langle\Phi|Z_i(\omega) &= \langle\Phi|(1+\Lambda)W_i(\omega) \\ &= \langle\Phi|(1+\Lambda)\left[\sum_j m^R_{ji}(\omega)\bar{a}^\dagger_j + \gamma^R_i(\omega)\right].\end{aligned} \tag{48}$$

B. $Z_q(\omega)$ and $W_q(\omega)$ operators for q corresponding to the virtual spin orbital ($q = a$)

For $q \in V$ we will also represent $Z_a(\omega)$ and $W_a(\omega)$ operators in forms given by Eqs. (34) and (38). However, in contrast to the $q \in O$ case, the $\bar{a}^\dagger_a$ operator cannot be naturally extracted from the expansion for $W_a(\omega)$. Therefore, $W_a(\omega)$ is represented only by the γ^R_a term, which in analogy to the previous case ($q \in O$) includes higher-order contributions,

$$W_a(\omega) = \sum_{n=1} W_{a,n}(\omega) = \gamma^R_a(\omega), \tag{49}$$

where

$$\gamma^R_a(\omega) = \sum_{n=1} W_{a,n}(\omega). \tag{50}$$

Finally, $Z_a(\omega)$ and $W_a(\omega)$ operators take the form

$$\langle\Phi|Z_a(\omega) = \langle\Phi|(1+\Lambda)W_a(\omega) = \langle\Phi|(1+\Lambda)\gamma^R_a(\omega). \tag{51}$$

V. PERTURBATIVE ANALYSIS OF $X_p(\omega)$ AND $W_q(\omega)$ INTERMEDIATES

In the following analysis we will assume that canonical Hartree-Fock (HF) orbitals are employed, which significantly simplifies the analysis of low-order contributions to $X_p(\omega)$ and $W_q(\omega)$ operators. In the HF molecular basis the normal-ordered form of the electronic Hamiltonian can be expressed as the sum of the one-particle and two-particle parts, $H_N = F_N + V_N$, with $F_N = \sum_r \epsilon_r N[a^\dagger_r a_r]$ and $V_N = \frac{1}{4}\sum_{p,q,r,s} v^{rs}_{pq} N[a^\dagger_p a^\dagger_q a_s a_r]$, where v^{rs}_{pq} are antisymmetrized two-electron integrals and $N[\cdots]$ designating normal ordered form of a given second-quantized expression. Its similarity-transformed counterpart can then be partitioned into two groups of diagrams,

$$\begin{aligned}\bar{H}_N &= e^{-T}H_N e^T = e^{-T}(F_N + V_N)e^T \\ &= F_N + [F_N,T] + [[F_N,T],T] + V_N + [V_N,T] \\ &\quad + \tfrac{1}{2}[[V_N,T],T] + \tfrac{1}{6}[[[V_N,T],T],T] \\ &\quad + \tfrac{1}{24}[[[[V_N,T],T],T],T] \\ &= (F_{N,CC} + V_{N,CC} + [F_N,T]_{CC} + [[F_N,T],T]_{CC} \\ &\quad + [V_N,T]_{CC} + \tfrac{1}{2}[[V_N,T],T]_{CC} + \cdots)_{\mathrm{I}} \\ &\quad + (F_{N,\mathrm{d}} + [F_N,T]_{\mathrm{d}} + V_{N,\mathrm{d}} + [V_N,T]_{\mathrm{d}} \\ &\quad + \tfrac{1}{2}[[V_N,T],T]_{\mathrm{d}} + \cdots)_{\mathrm{II}}.\end{aligned} \tag{52}$$

where all terms in part I contribute to the CC equations and show no deexcitation lines, while in part II we collect all terms containing at least one deexcitation line (these terms will be denoted by a subscript d). Note that only part II will survive if CC equations are satisfied. Then we can expand $\bar{H}_N$ in perturbative series,

$$\bar{H}_N = \bar{H}^{(0)}_N + \bar{H}^{(1)}_N + \bar{H}^{(2)}_N + \cdots, \tag{53}$$

where

$$\bar{H}^{(0)}_N = F_{N,\mathrm{d}}, \tag{54}$$

$$\bar{H}^{(1)}_N = [F_N, T^{(1)}]_{\mathrm{d}} + V_{N,\mathrm{d}}, \tag{55}$$

$$\bar{H}^{(2)}_N = [V_N, T^{(1)}]_{\mathrm{d}}, \quad \cdots \tag{56}$$

where $T^{(i)}$ represents the ith-order contribution to the T operator. For canonical orbitals, $\bar{H}^{(1)}_N$ is represented only by the $V_{N,d}$ term. In the following, we will put our emphasis on analytical expressions for the zeroth- and first-order contributions to $X_p(\omega)$ and $W_p(\omega)$ operators.

A. Algebraic expressions for $X^{(0)}_p(\omega)$ and $X^{(1)}_p(\omega)$ operators

To calculate $X^{(0)}_p(\omega)$ and $X^{(1)}_p(\omega)$ we will refer to the zeroth and first orders of Eq. (25). We will consider two distinct cases: (1) p belongs to occupied spin orbitals, and (2) p is a virtual spin-orbital index.

1. $X_p^{(0)}(\omega)$ and $X_p^{(1)}(\omega)$ operators for p corresponding to the occupied spin orbital

In this case, a_p and T operators commute ($[a_p,T]=0$), and $\bar{a}_p|\Phi\rangle$ becomes $a_p|\Phi\rangle$. This term contributes to the zeroth-order equation, which becomes

$$(\omega + F_{N,\mathrm{d}})X_p^{(0)}(\omega)|\Phi\rangle = a_p|\Phi\rangle. \tag{57}$$

The only nonvanishing contribution to $X_p^{(0)}(\omega)$ ($p \in O$) corresponds to the single excitations $[X_p^{(0)}(\omega) = \sum_m x^{m,(0)}(\omega)_p a_m|\Phi\rangle]$, with the corresponding amplitudes defined as

$$x^{m,(0)}(\omega)_p = \frac{\delta_{pm}}{\omega - \epsilon_m}. \tag{58}$$

The $X_p^{(1)}(\omega)$ operator can be obtained by collecting first-order contributions in Eq. (25),

$$V_{N,\mathrm{d}}X_p^{(0)}(\omega)|\Phi\rangle = -(\omega + F_{N,\mathrm{d}})X_p^{(1)}(\omega)|\Phi\rangle, \tag{59}$$

which leads to the $X_p^{(1)}(\omega)$ operator containing only two-body terms $[X_p^{(1)}(\omega) = \sum_{i<j,a} x_a^{ij,(1)}(\omega)_p a_a^\dagger a_j a_i|\Phi\rangle]$, where two-body amplitudes are given by the formula

$$x_a^{ij,(1)}(\omega)_p = \frac{v_{pa}^{ij}}{(\omega - \epsilon_p)(\omega + \epsilon_a - \epsilon_j - \epsilon_i)}. \tag{60}$$

2. $X_p^{(0)}(\omega)$ and $X_p^{(1)}(\omega)$ operators for p corresponding to the virtual spin orbital

In this case, the free term on the right-hand side of Eq. (25) is given by the expression $\bar{a}_p|\Phi\rangle = [a_p,T]_C|\Phi\rangle = (a_pT)_C|\Phi\rangle$, where the lowest- (first-) order contribution stems from the term $a_pT^{(1)}|\Phi\rangle = (a_pT_2^{(1)})_C|\Phi\rangle$, with $T_2^{(1)} = \sum_{i<j,a<b} t_{ab}^{ij(1)} a_a^\dagger a_b^\dagger a_j a_i$ and $t_{ab}^{ij(1)} = \frac{v_{ab}^{ij}}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$. Therefore, in contrast to the previous section, we have $X_p^{(0)}(\omega) = 0$.

The first-order term satisfying the equation

$$(\omega + F_{N,\mathrm{d}})X_p^{(1)}(\omega)|\Phi\rangle = \left(a_pT_2^{(1)}\right)_C|\Phi\rangle \tag{61}$$

is given by the formula

$$x_a^{ij,(1)}(\omega)_p = \frac{v_{pa}^{ij}}{(\omega + \epsilon_a - \epsilon_i - \epsilon_j)(\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_p)} \tag{62}$$

for $i < j$ and $p \in V$.

B. Algebraic expressions for $W_q^{(0)}(\omega)$ and $W_q^{(1)}(\omega)$ operators

Following a similar procedure, the perturbative expansions for the $W_q(\omega)$ operators can be extracted from the equation

$$\begin{aligned}\langle\Phi|(1+\Lambda^{(1)}+\Lambda^{(2)}+\cdots)(a_q^\dagger + [a_q^\dagger,T]_C) \\ = \langle\Phi|(1+\Lambda^{(1)}+\Lambda^{(2)}+\cdots)\big[W_q^{(0)}(\omega)+W_q^{(1)}(\omega)+W_q^{(2)}(\omega) \\ + \cdots\big](\omega + F_{N,\mathrm{d}} + V_{N,\mathrm{d}} + [V_N,T]_\mathrm{d} + \cdots),\end{aligned} \tag{63}$$

where $\Lambda^{(i)}$ represents the ith-order contribution to the Λ operator.

1. $W_q^{(0)}(\omega)$ and $W_q^{(1)}(\omega)$ operators for q corresponding to the occupied spin orbital

In analogy to the $X_p(\omega)$ analysis, the zeroth-order contribution $W_q^{(0)}(\omega)$ is determined by only one-body contributions, i.e., $W_q^{(0)}(\omega) = \sum_{a,i<j} w_m^{(0)}(\omega)_q a_m^\dagger$, where amplitudes $w_m^{(0)}(\omega)_q$ are expressed as

$$w_m^{(0)}(\omega)_q = \frac{\delta_{qm}}{\omega - \epsilon_m} \tag{64}$$

and are identical to the zeroth-order estimate of the $X_p(\omega)$ operator [see Eq. (58)].

$W_q^{(1)}(\omega)$ depends on (1) the first-order of the free term $\langle\Phi[a_q^\dagger,T]$, which is $\langle\Phi|[a_q^\dagger,T^{(1)}]_C = \langle\Phi|[a_q^\dagger,T_2^{(1)}]_C = 0$, and (2) the first-order term in the Λ operator, which can be expressed as $\Lambda^{(1)} = \Lambda_2^{(1)} = \sum_{i<j,a<b} \lambda_{ij}^{ab(1)} a_i^\dagger a_j^\dagger a_b a_a$, with $\lambda_{ij}^{ab(1)} = \frac{v_{ij}^{ab}}{\epsilon_i+\epsilon_j-\epsilon_a-\epsilon_b}$. Then, $W_q^{(1)}(\omega)$ can be determined from the first-order representation of Eq. (63),

$$\begin{aligned}\langle\Phi|\Lambda_2^{(1)}a_q^\dagger = \langle\Phi|\big[\Lambda_2^{(1)}W_q^{(0)}(\omega)(\omega + F_{N,\mathrm{d}}) \\ + W_q^{(1)}(\omega)(\omega + F_{N,\mathrm{d}}) + W_q^{(0)}(\omega)V_{N,\mathrm{d}}\big].\end{aligned} \tag{65}$$

It is interesting to observe that all nonzero three-body contributions stemming from the linked but disconnected $\langle\Phi|\Lambda_2^{(1)}a_q^\dagger$, $\langle\Phi|[\Lambda_2^{(1)}W_q^{(0)}(\omega)(\omega + F_{N,\mathrm{d}})]$, and $\langle\Phi|W_q^{(0)}(\omega)V_{N,\mathrm{d}}$ cancel each other. The cancellation of linked terms bears a resemblance to the order-by-order cancellation of disconnected diagrams in the perturbative expansion of the correlation energy that eventually leads to the linked cluster theorem [78,79].

The only nonzero contribution to $W_q^{(1)}(\omega)$ corresponds to double excitations $W_q^{(1)}(\omega) = \sum_{i<j,a} w_{ij}^{a,(1)}(\omega)_q a_i^\dagger a_j^\dagger a_a$, where

$$w_{ij}^{a,(1)}(\omega)_q = \frac{v_{ij}^{qa}}{(\omega - \epsilon_q)(\omega + \epsilon_a - \epsilon_i - \epsilon_j)} \tag{66}$$

for $i < j$ and $q \in O$.

2. $W_q^{(0)}(\omega)$ and $W_q^{(1)}(\omega)$ operators for q corresponding to the virtual spin orbital

In analogy to the $X_q(\omega)$ operators, the zeroth-order contribution vanishes. The first-order terms originate from the equation

$$\langle\Phi|\Lambda_2^{(1)}a_q^\dagger = \langle\Phi|W_q^{(1)}(\omega)(\omega + F_{N,\mathrm{d}}), \tag{67}$$

which results in double excitations $W_q^{(1)}(\omega) = \sum_{i<j,a} w_{ij}^{a,(1)}(\omega)_q a_i^\dagger a_j^\dagger a_a$, where

$$w_{ij}^{a,(1)}(\omega)_q = \frac{v_{ij}^{qa}}{(\epsilon_i + \epsilon_j - \epsilon_q - \epsilon_a)(\omega + \epsilon_a - \epsilon_i - \epsilon_j)} \tag{68}$$

for $i < j$ and $q \in V$.

Summarizing, we observed that in the lowest orders of the perturbation theory all $W_q^{(i)}(\omega)$ ($i = 0,1$) contributions are determined by connected diagrams. Moreover, for $W_q^{(1)}(\omega)$ we observed an interesting cancellation of disconnected (yet linked) terms appearing in the triply excited part of first-order equations. This may suggest that all $W_q(\omega)$ operators can

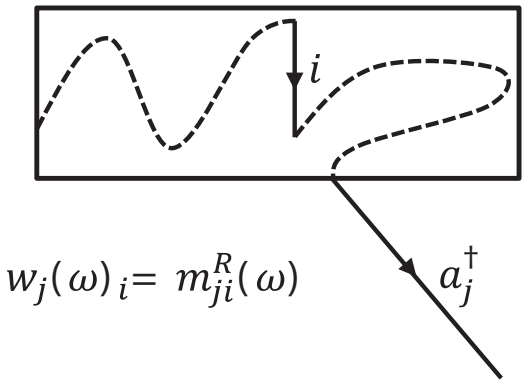

FIG. 4. An example of a connected diagram contributing to the $w_j(\omega)_i = m^R_{ij}(\omega)$ amplitude. Indices i and j correspond to occupied spin orbitals.

be expressed in terms of connected diagrams. We prove this conjecture in the next section.

VI. CONNECTED FORM OF THE $W_q(\omega)$ OPERATORS AND CONNECTED CHARACTER OF THE FIRST-ORDER ω DERIVATIVES OF THE CC GREEN's FUNCTION

In order to prove the connected character of $W_q(\omega)$ operators, one should invoke Eq. (42), where $\langle\Phi|(1+\Lambda)$ is replaced by its exponential form $\langle\Phi|e^S$ (this convention will be employed in the remainder of our discussion),

$$\langle\Phi|e^S\bar{a}^\dagger_q = \langle\Phi|e^S W_q(\omega)(\omega + \bar{H}_N), \tag{69}$$

and the fact that the S and $W_q(\omega)$ operators commute,

$$[S, W_q(\omega)] = 0. \tag{70}$$

Multiplying both sides of Eq. (69) by e^{-S}, one can rewrite

$$\langle\Phi|e^S\bar{a}^\dagger_q e^{-S} = \langle\Phi|W_q(\omega)(\omega + e^S\bar{H}_N e^{-S}), \tag{71}$$

where the free term on the left-hand side $\langle\Phi|e^S\bar{a}^\dagger_q e^{-S}$ and the $e^S\bar{H}_N e^{-S}$ operator contain only connected terms. Moreover, the only disconnected contributions to Eq. (71) [in the $\langle\Phi|W_q(\omega)(\omega + e^S\bar{H}_N e^{-S})$ term] stem from (1) matrix elements of $e^S\bar{H}_N e^{-S}$ that correspond to Eq. (13) and therefore numerically disappear and (2) the fully contracted $(e^S\bar{H}_N)_C$ term, which, again, is numerically equal to zero on the basis of Eq. (7). In effect, the equations for $W_q(\omega)$ operators are expressed only in terms of connected diagrams, and consequently, all $W_q(\omega)$ amplitudes [including the $m^R_{ji}(\omega)$ ones] contain only connected terms. To reflect this fact symbolically, Eq. (71) can be written as

$$\langle\Phi|(e^S\bar{a}^\dagger_q)_C = \langle\Phi|[W_q(\omega)(\omega + e^S\bar{H}_N e^{-S})]_C. \tag{72}$$

A straightforward order-by-order perturbative analysis shows also that each diagram contributing to any $W_q(\omega)$ amplitude must contain index q.

A particular case of connected $W_q(\omega)$ amplitudes refers to $w_j(\omega)_i$ amplitudes [or $m^R_{ji}(\omega)$ matrix elements, given by Eq. (46)], where $q = i$. One should realize that while in connected diagrams defining $w_j(\omega)_i$ amplitudes the j index corresponds to the external index producing deexcitation associated with the $a^\dagger_j$ operator, the i index is associate with the internal structure of a connected diagram as shown in Fig. 4. Similar results hold for $q \in V$.

VII. RETARDED CC GREEN's FUNCTION AS A SOLUTION OF THE NONHOMOGENEOUS SYSTEM OF LINEAR ORDINARY DIFFERENTIAL EQUATIONS

By combining Eqs. (48) and (51) with the expression for the CC Green's-function derivatives (36) with respect to ω one can reexpress Eq. (36) in the general form as

$$\begin{aligned}\frac{dG^R_{pq}(\omega)}{d\omega} &= -\sum_r m^R_{qr}(\omega)\langle\Phi|e^S\bar{a}^\dagger_r X_p(\omega)|\Phi\rangle \\ &\quad - \langle\Phi|e^S\gamma^R_q(\omega)X_p(\omega)|\Phi\rangle \\ &= -\sum_r m^R_{rq}(\omega)G^R_{pr}(\omega) - \langle\Phi|e^S\gamma^R_q(\omega)X_p(\omega)|\Phi\rangle,\end{aligned} \tag{73}$$

which in the matrix-form representation can be cast in the form of nonhomogeneous linear ordinary differential equations,

$$\frac{d\mathbf{G}^R(\omega)}{d\omega} = -\mathbf{G}^R(\omega)\mathbf{M}^R(\omega) - \mathbf{\Gamma}^R(\omega), \tag{74}$$

where the $\mathbf{G}^R(\omega)$ matrix represents the CC Green's-function matrix and $\mathbf{M}^R(\omega)$ and $\mathbf{\Gamma}^R(\omega)$ are

$$m^R_{rq}(\omega) = \begin{cases} w_r(\omega)_q & \text{for } r,q \in O, \quad (75)\\ 0 & \text{for other cases,} \quad (76)\end{cases}$$

and

$$\Gamma^R_{pq}(\omega) = \langle\Phi|e^S\gamma^R_q(\omega)X_p(\omega)|\Phi\rangle, \tag{77}$$

where $\gamma^R_q(\omega)$ is defined as

$$\gamma_q(\omega) = \begin{cases} -\sum_i w_i(\omega)_q[a^\dagger_i, T] + \sum_{n=2} W_{q,n}(\omega) & \text{for } q \in O, \quad (78)\\ \sum_{n=1} W_{q,n}(\omega) & \text{for } q \in V. \quad (79)\end{cases}$$

As we discussed earlier, the first term on the right-hand side of Eq. (74) contains the lowest-order contributions, while the second expression introduces higher-order coupling terms between O-O, O-V, V-O, and V-V blocks of the first-order derivative of $\mathbf{G}^R(\omega)$ with respect to ω. Moreover, all elements of the $\mathbf{M}^R(\omega)$ and $\mathbf{\Gamma}^R(\omega)$ matrices are represented by connected quantities.

Equation (74) represents the nonhomogeneous linear system of ordinary differential equations (ODEs), which is solved in two steps:

(1) First, we solve the homogeneous system of ODEs

$$\frac{d\mathbf{G}^R(\omega)}{d\omega} = -\mathbf{G}^R(\omega)\mathbf{M}^R(\omega), \tag{80}$$

with a solution which can be written as

$$\mathbf{G}^R_h(\omega) = \mathbf{G}^R_{\rm init} e^{-\int_0^\omega \mathbf{M}^R(\bar\omega)d\bar\omega}, \tag{81}$$

where $\mathbf{G}^R_{\rm init} = \mathbf{G}^R(\omega = 0)$.

(2) In the second step, the solution to Eq. (74) can be represented as

$$\mathbf{G}^R(\omega) = \left\{1 - \int_0^\omega \mathbf{\Gamma}^R(\bar\omega)\mathbf{G}^R_h(\bar\omega)^{-1}d\bar\omega\right\}\mathbf{G}^R_h(\omega) \tag{82}$$

$$= \{1 + \mathbf{A}^R(\omega)\}\mathbf{G}^R_{\rm init} e^{\mathbf{C}^R(\omega)}, \tag{83}$$

where

$$\mathbf{C}^R(\omega) = -\int_0^\omega \mathbf{M}^R(\bar\omega)d\bar\omega \tag{84}$$

and

$$\mathbf{A}^R(\omega) = -\int_0^\omega \mathbf{\Gamma}^R(\bar\omega)\mathbf{G}^R_h(\bar\omega)^{-1}d\bar\omega. \tag{85}$$

Using perturbative analysis in the previous sections, we demonstrated that $m^R_{ji}(\omega)$ elements are dominated by zeroth-order contributions. In specific situations these matrix elements can be evaluated in a different way. In the Hilbert space of $N-1$ particles the $\bar H_N$ operator can be represented in the form of the spectral resolution

$$\bar H_N = \sum_P \left|R^{(N-1)}_P\right\rangle \omega_P \left\langle L^{(N-1)}_P\right|, \tag{86}$$

where $|R^{(N-1)}_P\rangle$ and $\langle L^{(N-1)}_P|$ are right and left eigenvectors of $\bar H_N$ and ω_P represents the corresponding ionization potential. If the Kth state of the $N-1$ electron system is dominated by the kth single deexcitation (i.e., the a_k operator acting onto the reference determinant $|\Phi\rangle$), then projecting Eq. (42) from the right onto $|R^{(N-1)}_K\rangle$ leads to a rough estimate of the corresponding $m^R_{ki}(\omega)$ matrix element,

$$m^R_{ki}(\omega) \simeq \frac{\langle\Phi|e^S\bar a_i^+\left|R^{(N-1)}_K\right\rangle}{(\omega+\omega_K)\langle\Phi|e^S\bar a_k^+\left|R^{(N-1)}_K\right\rangle}. \tag{87}$$

For the diagonal $m^R_{kk}(\omega)$ element, the above form is analogous to the zeroth-order estimate given by Eq. (64), with the ω_K ionization potential being replaced by the inverse of the corresponding orbital energy $-\epsilon_k$.

VIII. HIGHER-ORDER ω DERIVATIVES OF THE CC GREEN'S FUNCTION

The analysis in the previous sections can easily be generalized to any order derivative of the CC Green's function with respect to ω,

$$\frac{d^{(n)}G^R_{pq}(\omega)}{d\omega^{(n)}} = (-1)^n\langle\Phi|e^S\bar a_q^\dagger(\omega+\bar H_N)^{-(n+1)}\bar a_p|\Phi\rangle \tag{88}$$

$$= (-1)^n\langle\Phi|e^S\bar a_q^\dagger(\omega+\bar H_N)^{-n}X_p(\omega)|\Phi\rangle. \tag{89}$$

Introducing the set of recursive intermediates $\{W^{[i]}_q(\omega)\}^n_{i=1}$ satisfying

$$\langle\Phi|e^S W^{[i-1]}_q(\omega) = \langle\Phi|e^S W^{[i]}_q(\omega)(\omega+\bar H_N), \tag{90}$$

one can prove by induction that all $\{W^{[i]}_q(\omega)\}^n_{i=1}$ operators are represented by connected diagrams. We have proven this property in the previous sections for the $W^{[1]}_q(\omega)$ operator $[W^{[1]}_q(\omega) = W_q(\omega)]$; now let's assume that the $W^{[i-1]}_q(\omega)$ operator is given in terms of connected diagrams. From Eq. (90), employing the arguments in Sec. V, it is easy to show that the $W^{[i]}_q(\omega)$ operator is defined by connected terms. This leads to the conclusion that the nth-order derivative

$$\frac{d^nG^R_{pq}(\omega)}{d\omega^n} = (-1)^n\langle\Phi|e^S W^{[n]}_q(\omega)X_p(\omega)|\Phi\rangle \tag{91}$$

contains only connected terms.

An equivalent approach to calculate derivatives of GFCC (in the exact theory limit) is to focus on ket-intermediates. For example, if in the last term of Eq. (33) we introduce ket-type intermediate $\Omega_p(\omega)$ (of the same IP-type as $X_p(\omega)$ operators) defined as

$$(\omega+\bar H_N)\Omega_p(\omega)|\Phi\rangle = X_p(\omega)|\Phi\rangle, \tag{92}$$

then the first order derivative of CC Green's function is given by the expression:

$$\frac{dG^R_{pq}(\omega)}{d\omega} = -\langle\Phi|(1+\Lambda)\bar a_q^\dagger\Omega_p(\omega)|\Phi\rangle. \tag{93}$$

The connected form of this representation (stemming from the connected nature of $\Omega_p(\omega)$ operator) can be proven along the same line as the connected character of the CC Green's function discussed in Sec. III.

IX. CONNECTED CHARACTER OF THE CC SELF-ENERGY OPERATOR

In the previous sections we showed that both the CC Green's-function operator and its ω derivatives can be expressed in terms of connected diagrams. Using analogous techniques, one can prove that similar results also hold for the advanced part of the CC Green's function. From the Dyson equation

$$\mathbf{G}(\omega) = \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\Sigma(\omega)\mathbf{G}(\omega), \tag{94}$$

it immediately follows that the matrix elements of the CC self-energy operator satisfy connected equations. This is a consequence of the connected character of the CC Green's-function matrix elements. Differentiating both sides of the Dyson equation with respect to ω,

$$\frac{d\mathbf{G}(\omega)}{d\omega} = \frac{d\mathbf{G}_0(\omega)}{d\omega} + \frac{d\mathbf{G}_0(\omega)}{d\omega}\Sigma(\omega)\mathbf{G}(\omega) + \mathbf{G}_0(\omega)\frac{d\Sigma(\omega)}{d\omega}\mathbf{G}(\omega) + \mathbf{G}_0(\omega)\Sigma(\omega)\frac{d\mathbf{G}(\omega)}{d\omega}, \tag{95}$$

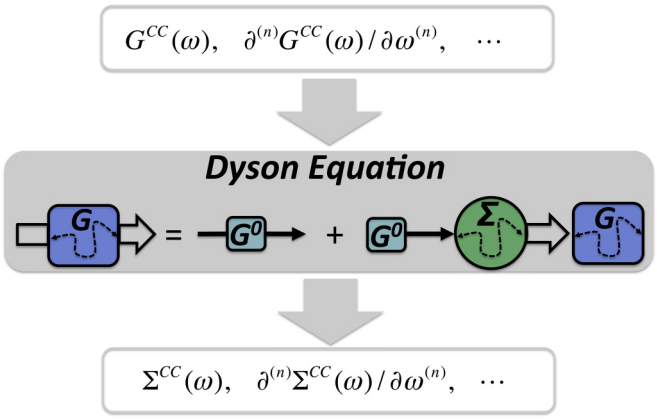

FIG. 5. Schematic representation of the Dyson equation for calculating CC self-energies and their derivatives.

and taking into account the connected character of the CC Green's function and its first derivative with respect to ω, we obtain the connected form of the equation for $\frac{d\Sigma(\omega)}{d\omega}$, which can be evaluated analytically by solving Eq. (95) for matrix elements of $\frac{d\Sigma(\omega)}{d\omega}$. This property of the CC self-energy is especially important in calculating, for example, pole strengths. By using chain rules and Eq. (91), we can generalize the above expression to an arbitrary order of ω derivative (see Fig. 5).

X. CONCLUSIONS

In this paper, we demonstrated that the exponential parametrization of the ground-state wave function results in several important properties of the corresponding Green's function. We have shown that the matrix elements of retarded CC Green's function are described in terms of only connected diagrams. This is a consequence of the connected nature of the cluster operator, the form of the CC equations, and connected equations for the $X_p(\omega)$. We derived this feature of the Green's function without invoking perturbative analysis. In a similar manner we showed that the first-order ω derivative of the CC Green's-function matrix can be calculated analytically, and using similar algebraic arguments, we demonstrated it is determined by connected expressions. The latter property is a direct consequence of the connected character of $W_q(\omega)$ operators, which have been introduced to deal with the second inverse of the $(\omega + \bar{H}_N)$ operator [see Eqs. (35) and (37)]. In analogy to the $X_p(\omega)$ operators, the connected nature of the $W_q(\omega)$ operators is a natural consequence of the equations that are satisfied by cluster (T) and cluster deexcitation (S) operators. A similar result can be generalized to any order of ω derivative of the CC Green's function. The same conclusions are also valid for block GFCC approximations. It is worth stressing that the CC Green's function satisfies the nonhomogeneous system of linear ordinary differential equations in which all coefficients are determined by connected expressions, which may suggest the possibility of exponential parametrization of the coupled-cluster Green's function. Through the Dyson equation, ω derivatives of CC self-energies can be determined analytically as functions of ω derivatives of the CC Green's function. This feature enables accurate calculation of CC Green's-function pole strengths without invoking sum-over-state techniques.

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