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

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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 retarded (or equivalently, ionized) part of the Green's function in the ω-representation can be expressed through connected diagrams only. Similar properties are also shared by the first order ω-derivative of the retarded part of the CC Green's function. Moreover, 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 analogyto the CC Green's function, the corresponding CC self-energy operator can be represented by connected terms. Our analysis can be easily generalized to the advanced part of the CC Green's function.

I. INTRODUCTION

Coupled cluster methods[1–7] has 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] multi-reference and strongly correlated systems.[10–13] Significant progress has also been achieved in the development of reduced scaling CC methods employing 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 enables a development of hierarchical classes of CC approximations. This has been illustrated on numerous studies with ground-state CC formulations, multi-reference 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 orbitals approach,[18, 19] effective fragment potential method,[20] CC/MM methods,[21, 22] polarizable embedding formulations,[23] 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 few applications. An important progress in the development of reliable embedding schemes is associated with the utilization of the Green's function formalism.[26–57] Recently, a considerate 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 (DMFT).[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 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 GFCCSD approach applicable to any energy regime and is extendable to the whole complex plane. We have also explored possibility of reducing computational effort associated with the need of solving N_s (N_s stands for the number of spinorbitals) 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 calculated for active spinborbitals only, 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:

- connected character of the CC Green's function matrix elements originating from the connected form of the equations for intermediates $X_p(\omega)$ and $Y_q(\omega)$,
- connected character of the first order ω-derivative of CC Green's function matrix originating from exponential parametrization of the $(1 + \Lambda)$ de-excitation operator,
- connected character of higher-order ω-derivatives of CC Green's function matrix.

By employing Dyson equations we will also show that the above properties can be extended to the corresponding

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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 *et al.*[68–70]. The CC Green's function formalism hinges upon the CC bi-variational 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,

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

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

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

$$T_n = \frac{1}{(n!)^2} \sum_{\substack{i_1,\ldots,i_n;\\ a_1,\ldots,a_n}} t^{i_1\ldots i_n}_{a_1\ldots a_n} a^\dagger_{a_1}\ldots a^\dagger_{a_n} a_{i_n}\ldots a_{i_1} \tag{5}$$

$$\Lambda_n = \frac{1}{(n!)^2} \sum_{\substack{i_1,\ldots,i_n;\\ a_1,\ldots,a_n}} \lambda^{a_1\ldots a_n}_{i_1\ldots i_n} a^\dagger_{i_1}\ldots a^\dagger_{i_n} a_{a_n}\ldots a_{a_1} \ , \tag{6}$$

where $t^{i_1\ldots i_n}_{a_1\ldots a_n}$ and $\lambda^{a_1\ldots a_n}_{i_1\ldots i_n}$ 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 spinorbitals in the reference function $|\Phi\rangle$ respectively. The a_p ($a_p^\dagger$) operator is the annihilation (creation) operator for electron in the p-th 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.,

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

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

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

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 disconnected closed part). In the limit of the exact theory discussed in this paper, the $\langle\Phi|(1+\Lambda)$ is equivalent to the exponential ansatz based on the de-excitation 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 Λ operator, are explicitly connected, the de-excitation cluster operator S is also connected. In analogy to Eq.(11), the explicitly projected form of Eq.(13) takes the form:

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

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 bear the resemblance to the extended CC (ECC) formulations by Arponen,[74] in the present context the equations for the cluster operator T are decoupled from the equations for the S operator.

By employing CC bi-variational approach, the corresponding Green's function can be expressed as

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

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

$$G^R_{pq}(\omega) = \langle\Phi|(1+\Lambda)e^{-T}a_q^\dagger(\omega+(H-E_0)-i\eta)^{-1}a_pe^T|\Phi\rangle \tag{17}$$

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

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

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

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

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

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

Using Campbell-Baker-Hausdorff formula

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

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 connected character of the operator that is transformed (A operator in Eq.(22)) leads to the connected character of nested commutator expansion. In particular, expansion for $\bar{H}_N$ (Eq.(21)) contains connected diagrams only (it is also easy to verify that due to the pairwise character of the inter-electron 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 on 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 second-quantized form of the $X_p(\omega)$ is identical with the form of IP-EOMCC excitation operator

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

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

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

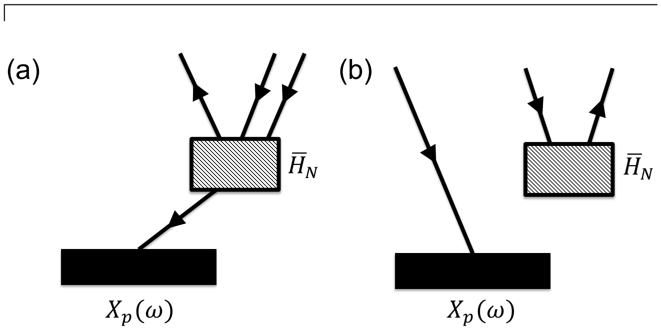

FIG. 1. Typical examples of connected (inset (a)) and disconnected (inset (b)) diagrams contributing to the $(\omega + \bar{H}_N)X_p(\omega)|\Phi\rangle = \bar{a}_p|\Phi\rangle$.

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 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 similarity transformed Hamiltonian $\bar{H}$ 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) in 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 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 $\langle\Phi^{a_1\ldots a_n}_{i_1\ldots i_n}|\bar{H}_N|\Phi\rangle$ matrix elements of $\bar{H}_N$, which are equal to zero as they represent the equations for cluster amplitudes defining cluster operator T. Thus the left hand side of Eq.(25) is defined by connected diagrams only. As discussed in the previous section, the similarity transformed annihilation operator $\bar{a}_p$ is expressed in terms of connected expressions. Therefore, the equation (25) is represented by the connected diagrams only,

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

and consequently $X_p(\omega)$ operator is determined by connected contributions only. Second, we will show that the $\langle\Phi|(1+\Lambda)\bar{a}_q^\dagger$ term (or $\langle\Phi|e^S\bar{a}_q^\dagger$ one when using 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

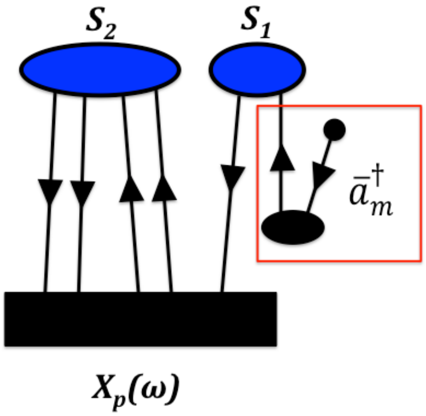

FIG. 2. An example of a connected diagram contributing to the $G_{pm}(\omega)$ matrix element of CC Green's function (p represents general spinorbital index while index m corresponds to the occupied spinorbital index). The red box represents a typical particle non-conserving diagram contributing to $\bar{a}_m^\dagger$.

fact that in contrast to Λ and S operators, the $\bar{a}_q^\dagger$ operator is particles number non-conserving 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 S operator or its products to produce disconnected closed part of the diagram. If we additionally recall that the $\bar{a}_q^\dagger$ operator is expressed in terms of connected diagrams we can write that

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

(where "L" designates 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, one can readily notice that the matrix element $G_{pq}^R(\omega)$ is determined by connected diagrams only, which can be symbolically expressed as

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

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 $G_{pq}^R(\omega)$ matrix element with respect to ω

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

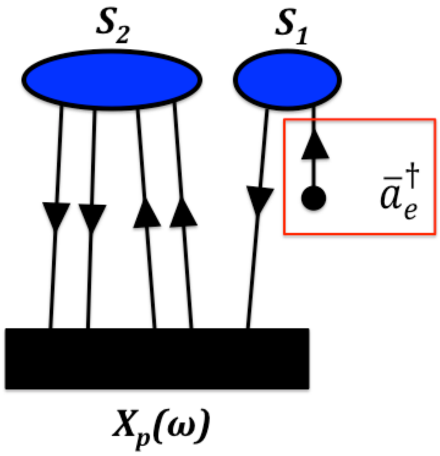

FIG. 3. An example of a connected diagram contributing to the $G_{pe}(\omega)$ matrix element of CC Green's function (p represents general spinorbital index while index e corresponds to the unoccupied spinorbital index). The red box contains particle non-conserving operator $\bar{a}_e^\dagger$.

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

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

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)

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

By invoking similar arguments as those we used in proving 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,
2. left hand side contains linked terms only.

Consequently, $Z_q(\omega)$ operators are also determined by linked terms only. 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 $Z_q(\omega)$,

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

Eq. (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,

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

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

$$Z_{q,3}(\omega) = W_{q,3}(\omega) + \Lambda_1 W_{q,2}(\omega) + \Lambda_2 W_{1,q}(\omega) \; , \tag{41}$$

$$\ldots$$

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 general spinorbital index q belonging both to occupied ($q \in O$) and unoccupied/virtual ($q \in V$) spinorbitals. 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 spinorbitals.

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

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

$$W_i(\omega) = \sum_j m_{ji}^R(\omega)\bar{a}_j^\dagger + \gamma_i^R(\omega) \; , \tag{43}$$

which leads to a natural decomposition of $W_i(\omega)$ into lowest-order contributions and higher-terms included in the $\gamma_i^R(\omega)$ term. There are several ways of defining this decomposition, here we will follow the easiest one stemming from the decomposition of $W_{i,1}(\omega)$ (see Eq. (34)) where the $a_j^\dagger$ operators can be expressed in terms of $\bar{a}_j^\dagger$ operators (see Eq. (24)) according to the formula

$$a_j^\dagger = \bar{a_j}^\dagger - [a_j^\dagger, T] \; . \tag{44}$$

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

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

which upon substituting into the $W_i(\omega)$ operator leads to the following definition of $m_{ji}^R(\omega)$ and $\gamma_i^R(\omega)$ quantities

$$m_{ji}^R(\omega) = w_j(\omega)_i \; , \tag{46}$$

$$\gamma_i^R(\omega) = -\sum_j w_j(\omega)_i[a_j^\dagger, T] + \sum_{n=2}^N W_{i,n}(\omega) \; . \tag{47}$$

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

$$\begin{aligned} \langle\Phi|Z_i(\omega) &= \langle\Phi|(1+\Lambda)W_i(\omega) \\ &= \langle\Phi|(1+\Lambda)\left(\sum_j m_{ji}^R(\omega)\bar{a}_j^\dagger + \gamma_i^R(\omega)\right) . \end{aligned} \tag{48}$$

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

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

$$W_a(\omega) = \sum_{n=1} W_{a,n}(\omega) = \gamma_a^R(\omega) \; , \tag{49}$$

where

$$\gamma_a^R(\omega) = \sum_{n=1} W_{a,n}(\omega) \; . \tag{50}$$

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

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

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 electronic Hamiltonian can be expressed as the sum of one-particle part and two-particle part, $H_N = F_N + V_N$ with $F_N = \sum_r \epsilon_r N[a_r^\dagger a_r]$, $V_N = \frac{1}{4}\sum_{p,q,r,s} v_{pq}^{rs} N[a_u^\dagger a_v^\dagger a_s a_r]$ with v_{pq}^{rs} are antisymmetrized 2-electron integrals, and $N[\ldots]$ designating normal ordered form of a given second-quantized expression. Its similarity-transformed counterpart can then be partitioned into two groups of diagrams

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

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

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

where

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

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

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

$$\cdots$$

For canonical orbitals, the $\bar{H}_N^{(1)}$ is represented only by the $V_{N,d}$ term. In the following, we will put our emphasize on analytical expressions for the 0-th and 1st orders contributions to $X_p(\omega)$ and $W_p(\omega)$ operators.

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

To calculate $X_p^{(0)}(\omega)$ and $X_p^{(1)}(\omega)$ we will refer to 0-th and 1st orders of Eq. (25). We will consider two distinct cases: (1) p belongs to occupied spinorbitals and (2) p is virtual spinorbital index.

1. $X_p^{(0)}(\omega)$ *and* $X_p^{(1)}(\omega)$ *operators for p corresponding to occupied spinrobital*

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 0-th order equation, which becomes

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

The only non-vanishing 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 corresponding amplitudes defined as

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

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

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

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 virtual spinrobital*

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 previous subsection, we have $X_p^{(0)}(\omega) = 0$.

The first order term satisfying the equation

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

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 similar procedure, the perturbative expansions for the $W_q^{(\omega)}$ operators can be extracted from the equation

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

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

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

In analogy to the $X_p(\omega)$ analysis, the 0-th order contribution $W_q^{(0)}(\omega)$ is determined by one-body contributions only, *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 is identical with the 0-th order estimate of the $X_p(\omega)$ operator (see Eq. (58)).

The $W_q^{(1)}(\omega)$ depends on (**a**) the 1st 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 (**b**) the 1st 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, the $W_q^{(1)}(\omega)$ can be determined from the 1st order representation of Eq. (63)

$$\langle\Phi|\Lambda_2^{(1)}a_q^\dagger=\langle\Phi|\left(\Lambda_2^{(1)}W_q^{(0)}(\omega)(\omega+F_{N,\mathrm{d}})+W_q^{(1)}(\omega)(\omega+F_{N,\mathrm{d}})+W_q^{(0)}(\omega)V_{N,\mathrm{d}}\right). \tag{65}$$

It is interesting to observe that all non-zero 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 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 non-zero 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 virtual spinorbital

In analogy to $X_q(\omega)$ operators, the 0-th 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 doubles 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 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 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-ODER ω-DERIVATIVES OF CC GREEN'S FUNCTION

In order to prove 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 remaining part of our discussion)

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

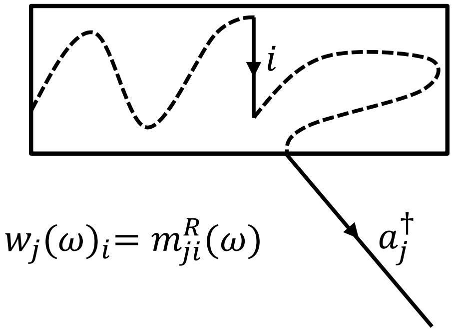

FIG. 4. An example of connected diagram contributing to the $w_j(\omega)_i = m^R_{ij}(\omega)$ amplitude. Indices i and j correspond to occupied spinorbitals.

and the fact that 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

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

where the free term on the left hand side $\langle\Phi|e^S\bar{a}_q^\dagger e^{-S}$ and the $e^S\bar{H}_N e^{-S}$ operator contain connected terms only. 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 (**a**) matrix elements of $e^S\bar{H}_N e^{-S}$ that correspond to Eq. (13) and therefore numerically disappear, and (**b**) fully contracted $\left(e^S\bar{H}_N\right)_C$ 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 in terms of connected diagrams only and consequently all $W_q(\omega)$ amplitudes (including $m^R_{ji}(\omega)$ ones) contain connected terms only. To reflect this fact symbolically, Eq. (71) can be written as

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

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 de-excitation associated with the $a_j^\dagger$ 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 NON-HOMOGENEOUS 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 re-express Eq. (36) in the general form as

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

which in matrix form representation can be cast in the form of non-homogeneous of 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 CC Green's function matrix and $\mathbf{M}^R(\omega)$ and $\mathbf{\Gamma}^R(\omega)$

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

and

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

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

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

As we discussed earlier, the first term on the right hand side of equation (74) contains lowest-order contributions while the second expression introduces higher-order coupling terms between O-O, O-V,V-O,V-V block of the 1st 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.

The equation (74) represents non-homogeneous linear system of ordinary differential equations (ODEs), which is solved in two steps:

- First, we solve the homogeneous system of ODEs

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

  with the solution which can be written as

  $$\mathbf{G}_h^R(\omega) = \mathbf{G}_{\text{init}}^R e^{-\int_0^\omega \mathbf{M}^R(\bar{\omega})d\bar{\omega}} , \quad (81)$$

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

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

$$\mathbf{G}^R(\omega) = \{1 - \int_0^\omega \mathbf{\Gamma}^R(\bar{\omega})\mathbf{G}_h^R(\bar{\omega})^{-1}d\bar{\omega}\}\mathbf{G}_h^R(\omega) \quad (82)$$

$$= \{1 + \mathbf{A}^R(\omega)\}\mathbf{G}_{\text{init}}^R e^{\mathbf{C}^R(\omega)} , \quad (83)$$

  where

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

  and

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

Using perturbative analysis in previous sections we demonstrated that $m_{ji}^R(\omega)$ elements are dominated by 0-th order contributions. In specific situations these matrix elements can be evaluated in a different way. Assuming that in the Hilbert space of $N-1$ particles the $\bar{H}_N$ operator can be represented in the form of the following spectral resolution

$$\bar{H}_N = \sum_p |R_p^{(N-1)}\rangle\omega_p\langle L_p^{(N-1)}| , \quad (86)$$

where $|R_p^{(N-1)}\rangle$ and $\langle L_p^{(N-1)}|$ are right and left eigenvectors of $\bar{H}_N$ and ω_p represents corresponding ionization potential. If K-th state of $N-1$ electron system is dominated by single k-th single de-excitation (i.e., a_k operator acting onto the reference determinant $|\Phi\rangle$) then projecting Eq. (42) from the right onto $|R_K^{(N-1)}\rangle$ leads to a rough estimate for the corresponding $m_{ki}^R(\omega)$ matrix element

$$m_{ki}^R(\omega) \simeq \frac{\langle\Phi|e^S\bar{a}_i^+|R_K^{(N-1)}\rangle}{(\omega+\omega_K)\langle\Phi|e^S\bar{a}_k^+|R_K^{(N-1)}\rangle} . \quad (87)$$

For the diagonal $m_{kk}^R(\omega)$ element, the above form is analogous to the 0-th order estimate given by Eq.(64) with ω_K ionization potential being replaced by the inverse of corresponding orbital energy $-\epsilon_k$.

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

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

$$\frac{d^{(n)}G_{pq}^R(\omega)}{d\omega^{(n)}} = (-1)^n\langle\Phi|e^S\bar{a}_q^\dagger(\omega+\bar{H}_N)^{-(n+1)}\bar{a}_p|\Phi\rangle \quad (88)$$

$$= (-1)^n\langle\Phi|e^S\bar{a}_q^\dagger(\omega+\bar{H}_N)^{-n}X_p(\omega)|\Phi\rangle \quad (89)$$

Introducing set of recursive intermediates $\{W_q^{[i]}(\omega)\}_{i=1}^n$ satisfying

$$\langle\Phi|e^S W_q^{[i-1]}(\omega) = \langle\Phi|e^S W_q^{[i]}(\omega)(\omega+\bar{H}_N) \quad (90)$$

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

$$\frac{d^nG_{pq}^R(\omega)}{d\omega^n} = (-1)^n\langle\Phi|e^S W_q^{[n]}(\omega)X_p(\omega)|\Phi\rangle \quad (91)$$

contains connected terms only.

IX. CONNECTED CHARACTER OF THE CC SELF-ENERGY OPERATOR

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

$$\mathbf{G}(\omega) = \mathbf{G}_0(\omega) + \mathbf{G}_0(\omega)\mathbf{\Sigma}(\omega)\mathbf{G}(\omega) \ , \tag{92}$$

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 Dyson equation with respect to ω

$$\frac{d\mathbf{G}(\omega)}{d\omega} = \frac{d\mathbf{G}_0(\omega)}{d\omega} + \frac{d\mathbf{G}_0(\omega)}{d\omega}\mathbf{\Sigma}(\omega)\mathbf{G}(\omega) + \mathbf{G}_0(\omega)\frac{d\mathbf{\Sigma}(\omega)}{d\omega}\mathbf{G}(\omega) + \mathbf{G}_0(\omega)\mathbf{\Sigma}(\omega)\frac{d\mathbf{G}(\omega)}{d\omega} \ , \tag{93}$$

and taking into account connected character of the CC Green's function and its first derivative with respect to ω we obtain connected form of the equation for the $\frac{d\mathbf{\Sigma}(\omega)}{d\omega}$, which can be evaluated analytically by solving Eq. (93) for matrix elements of $\frac{d\mathbf{\Sigma}(\omega)}{d\omega}$. 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 arbitrary order of ω-derivative (see Fig.5).

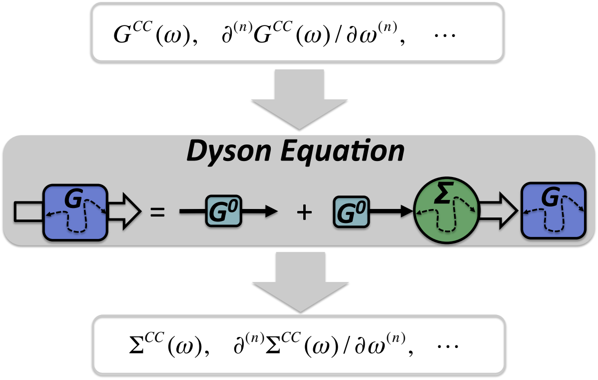

FIG. 5. Schematic representation of the Dyson equation for calculating CC self-energies and their derivatives.

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 connected diagrams only. This is a consequence of connected nature of cluster operator, 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 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 de-excitation (S) operators. 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 CC Green's function satisfies non-homogeneous system of linear ordinary differential equations where all coefficients are determined by connected expressions, which may suggest possibility of exponential parametrization of the coupled cluster Green's function. Through Dyson equation, ω-derivatives of CC self-energies can be determined analytically as functions of ω-derivatives of 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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