Coupled Cluster Green’s function formulations based on the effective Hamiltonians

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We demonstrate that the effective Hamiltonians obtained with the downfolding procedure based on double unitary coupled cluster (DUCC) ansatz can be used in the context of Green’s function coupled cluster (GFCC) formalism to calculate spectral functions of molecular systems. This combined approach (DUCC-GFCC) provides a significant reduction of numerical effort and good agreement with the corresponding all-orbital GFCC methods in energy windows that are consistent with the choice of active space. These features are demonstrated on the example of two benchmark systems: H2O and N2, where DUCC-GFCC calculations were performed for active spaces of various sizes.

I. INTRODUCTION

Although the Green’s function formalism has been introduced as a tool to analyze properties of molecular systems more than five decades ago,[1–18] it remains an active area of development. Recently, a considerable effort has been expended to provide accurate representations of the Green’s function or self-energies for many-electron systems in situations where a detailed characterization of correlation effects in molecular systems is necessary to achieve the required level of accuracy. [19–23] This includes a significant progress achieved in the developments of (1) various diagrammatic techniques and linked cluster theorems for perturbative expansions,[24, 25] (2) stochastic approaches to evaluate the self energies,[26] (3) cumulant representation,[27, 28] and (4) explicitly correlated formulations[26, 29] to calculate self-energies or Green’s functions of molecular systems. Another important impulse to developed high-accuracy representation of Green’s function/self-energy is associated with the development of more accurate embedding techniques related to dynamical mean-field theories (DMFT) [21, 30] and self-energy embedding theory (SEET),[31, 32] where the utilization of high-accuracy self-energies has been recently tested in studies of molecular systems. The accurate Green’s function algorithms have been developed for conventional computer architectures and more recently for quantum computing.[33, 34]

A very promising way of introducing correlation effects to Green’s function theory stems from the utilization of accurate coupled cluster (CC) expansions for the ground-state wave function.[35–43] The coupled cluster Green’s function formulation originally introduced by Nooijen and Snijders in a series of papers published in the early nineties [44–46] (see also Ref. [47]) has been recently re-adopted by several groups in studies of atomic/molecular,[48–53] and condensed phase and periodic systems,[19, 54] where the efficiency of models built upon inclusion hierarchy of collective many-body effect has been examined.

Recent progress in CC theory led to the emergence of techniques for downfolding or dimensionality reduction of the electronic Hamiltonians. These techniques draw heavily on the utilization of a tailored double unitary coupled cluster (DUCC) expansion to integrate out high-energy wave-function components from low-energy ones in the effective (or downfolded) Hamiltonians. In this paper, we examine a variant of the GFCC formulations that utilize this class of effective Hamiltonians. In particular, our focus is on the active-space GFCC formulations that utilize standard GFCC models that build upon single, double (GFCCSD)[44–46, 49] and single, double, and internal triple excitations (the so-called GFCC-i(2,3) approximation of Ref. [55]). Using water molecule and N2 systems as benchmarks, we demonstrate the efficiency of using downfolded Hamiltonians in recovering all features of spectral functions obtained in full GFCCSD and GFCC-i(2,3) calculations in energy windows that correspond to the active space used.

II. THEORY

The main idea behind the DUCC-GFCC formalism is to use DUCC downfolded/effective Hamiltonians in the GFCC calculations limited to the active space employed in the DUCC ansatz. Below, we describe the DUCC formalism, GFCC methodology, and combined DUCC-GFCC framework.

A. DUCC formalism

In Ref. [56], we introduced the unitary extension of the sub-system embedding sub-algebra CC approach (SE-CC) [57] which utilizes the double unitary CC expansion

\[ |\Psi\rangle = e^{\sigma_{\text{ex}}^\text{ext}} e^{\sigma_{\text{int}}} |\Phi\rangle. \]  

(1)

The character of the expansion (1) is similar to the expansion discussed in the single-reference formulation of the active-space coupled cluster formalism,[58, 59] (see Refs. [60, 61]) which also utilizes the decomposition of...
the cluster operator into internal and external parts. Additionally, using the Campell-Baker-Hausdorff formula, expansion (1) can be viewed as yet another unitary CC ansatz with a specific form of unitary cluster amplitudes (see Eq. (47) in Ref. [56])

In analogy to Ref. [56], $\sigma_{int}$ and $\sigma_{ext}$ are the anti-Hermitian operators ($\sigma_{int}^{\dagger} = -\sigma_{int}$ and $\sigma_{ext}^{\dagger} = -\sigma_{ext}$) defined by excitations/de-excitations within and outside of active space, respectively. To be more precise, the amplitudes defining the $\sigma_{ext}$ operator must carry at least one inactive spin-orbital index. Using Ansatz 1 in Schrödinger’s equation, one obtains equations for cluster amplitudes and the corresponding energy, i.e.,

$$Q e^{-\sigma_{ext}} e^{-\sigma_{int}} H e^{\sigma_{ext}} e^{\sigma_{int}} |\Phi\rangle = 0,$$

$$\langle \sigma_{int} | e^{-\sigma_{ext}} e^{-\sigma_{int}} H e^{\sigma_{ext}} e^{\sigma_{int}} |\Phi\rangle = E.$$  

where $Q$ is a projection operator on the space spanned by determinants that are orthogonal to the reference function $|\Phi\rangle$. In these and subsequent equations, we consider the case of the exact limit ($\sigma_{int}$ and $\sigma_{ext}$ include all possible excitations). In Ref. [56], we showed that when $\sigma_{int}$ contains all possible excitations/de-excitations within the active space, the energy of the system Eq. (3) can be obtained by diagonalizing the DUCC effective Hamiltonian

$$\overline{H}_{ext}^{\text{eff(DUCC)}} e^{\sigma_{int}} |\Phi\rangle = E e^{\sigma_{int}} |\Phi\rangle,$$

where

$$\overline{H}_{ext}^{\text{eff(DUCC)}} = (P + Q_{int}) \overline{H}_{ext}^{\text{DUCC}} (P + Q_{int})$$

and

$$\overline{H}_{ext}^{\text{DUCC}} = e^{-\sigma_{ext}} He^{\sigma_{ext}}.$$  

In the above eigenvalue problem, the $e^{\sigma_{int}} |\Phi\rangle$ expansion defines the corresponding eigenvector and $P$ and $Q_{int}$ are projection operators onto the reference function $|\Phi\rangle$ and excited determinants in the active space that orthogonal to $|\Phi\rangle$, respectively.

To prove this property, it is sufficient to introduce the resolution of identity $e^{\sigma_{int}} e^{-\sigma_{int}}$ to the left of the $\overline{H}_{ext}^{\text{DUCC}}$ operator in

$$(P + Q_{int}) \overline{H}_{ext}^{\text{DUCC}} e^{\sigma_{int}} |\Phi\rangle = E(P + Q_{int}) e^{\sigma_{int}} |\Phi\rangle,$$

where we employed the fact that

$$(P + Q_{int}) e^{\sigma_{int}} |\Phi\rangle = e^{\sigma_{int}} |\Phi\rangle,$$

and to notice that $e^{\sigma_{int}} \overline{H}_{ext}^{\text{DUCC}} e^{\sigma_{int}} = e^{-\sigma_{int}} e^{-\sigma_{ext}} H e^{\sigma_{ext}} e^{\sigma_{int}}$. Next, using matrix representation of the $\sigma_{int}$ operator in the CAS space, denoted as $\sigma_{int}$, this equation can be re-written as

$$[e^{\sigma_{int}}]|y\rangle = 0,$$  

where the first component of the $|y\rangle$ vector is equivalent to $\langle \sigma_{int} | e^{-\sigma_{ext}} H e^{\sigma_{ext}} e^{\sigma_{int}} |\Phi\rangle = E$ while the remaining components correspond to projections of $e^{-\sigma_{int}} e^{-\sigma_{ext}} H e^{\sigma_{ext}} e^{\sigma_{int}} |\Phi\rangle$ onto excited configurations belonging to $Q_{int}$. The $[e^{\sigma_{int}}]$ matrix is also non-singular, which is a consequence of the formula

$$\det(e^{\sigma_{int}}) = e^{\text{Tr}(\sigma_{int})} = 1$$

and the anti-Hermitian character of the $\sigma_{int}$ matrix, i.e., $\text{Tr}(\sigma_{int}) = 0$ (where real character of $\sigma_{int}$ cluster amplitudes is assumed). Given the non-singular character of the $[e^{\sigma_{int}}]$ matrix (see also Ref. [56]), this proves the equivalence of these two representations.

### B. GFCC methodology

Our GFCC implementations follow the basic tenets of the original GFCC formalism introduced by Nooijen et al. [44–46] and its features discussed in Refs. [48, 49, 55, 62–65]. Using CC bi-variational approach, the corresponding frequency-dependent Green’s function for an $N$-particle system can be expressed as

$$G_{pq}(\omega) = \langle \sigma_{int} | (1 + \Lambda)e^{-T} a^\dagger_q (\omega + (H - E_o) - i\eta)^{-1} a_p e^{-T}|\Phi\rangle + \langle \sigma_{int} | (1 + \Lambda)e^{-T} a_p (\omega - (H - E_o) + i\eta)^{-1} a^\dagger_q e^{-T}|\Phi\rangle,$$

where the $a_q$ ($a^\dagger_q$) operator is the annihilation (creation) operator for an electron in the $p$-th spin orbital. The $\omega$ parameter denotes the frequency, and the imaginary part $\eta$ is often called a broadening factor. The cluster operator $T$ and de-excitation operator $\Lambda$ define correlated ket ($|\Psi\rangle$) and bra ($\langle\Psi|$) ground-state wave functions for the $N$-electron system

$$|\Psi\rangle = e^T |\Phi\rangle,$$

$$\langle\Psi| = \langle\Phi|(1 + \Lambda)e^{-T}.$$

The ground-state energy $E_o$, and the amplitudes defining $T$ and $\Lambda$ operators are obtained from the following sequence of CC equations

$$Q e^{-T} H e^T |\Phi\rangle = 0,$$

$$\langle\Phi|e^{-T} H e^T |\Phi\rangle = E_o,$$

$$\langle\Phi|(1 + \Lambda)e^{-T} H e^T Q = E_o \langle\Phi|(1 + \Lambda)Q,$$

where the $T$ and $\Lambda$ operators are defined as

$$T = \sum_{n=1}^{N} \frac{1}{[n!]^2} \sum_{\begin{array}{c} \underbrace{i_{1}\ldots i_{n}}_{a_{1}\ldots a_{n}} ; \\
\end{array}} \phi_{a_{1}\ldots a_{n}} a_{i_{1}}^\dagger \ldots a_{i_{n}}^\dagger a_{i_{n}} \ldots a_{i_{1}}$$

$$\Lambda = \sum_{n=1}^{N} \frac{1}{[n!]^2} \sum_{\begin{array}{c} \underbrace{i_{1}\ldots i_{n}}_{a_{1}\ldots a_{n}} ; \\
\end{array}} \lambda_{a_{1}\ldots a_{n}} a_{i_{1}}^\dagger \ldots a_{i_{n}}^\dagger a_{i_{n}} \ldots a_{i_{1}}$$

with $\phi_{a_{1}\ldots a_{n}}$ and $\lambda_{a_{1}\ldots a_{n}}$ being the antisymmetric amplitudes, and the indices $i, j, k, \ldots (i_1,i_2,\ldots)$ and $a, b, c, \ldots (a_1,a_2,\ldots)$ corresponding to occupied and unoccupied
spin orbitals in the reference function \( |\Phi\rangle \), respectively. The projection operator \( Q \) is defined as,

\[
Q = \sum_{n=1}^{N} \frac{1}{\langle n \mid n \rangle^2} \sum_{a_1, \ldots, a_n} |\Phi_{a_1, \ldots, a_n}^{n} \rangle \langle \Phi_{a_1, \ldots, a_n}^{n}|,
\]

and represents the projection onto the subspace spanned by excited configurations \( |\Phi_{a_1, \ldots, a_n}^{n}\rangle \) defined as

\[
a_{a_1}^\dagger \cdots a_{a_n}^\dagger a_{a_n} \cdots a_{a_1}|\Phi\rangle.
\]

Using the resolution of identity \( \mathbb{1} = e^{-T} e^{T} \), the algebraic expression for matrix elements of the Green’s function can be re-written as

\[
G_{pq}(\omega) = \langle \Phi | (1 + \Lambda)\bar{a}_q^\dagger (\omega + \Pi_N - i\eta)^{-1} \bar{a}_p | \Phi \rangle + \langle \Phi | (1 + \Lambda)\bar{a}_p^\dagger (\omega - \Pi_N + i\eta)^{-1} \bar{a}_q | \Phi \rangle,
\]

where the similarity transformed operator \( \Pi_N \) (in normal product form representation), \( \bar{a}_p \) and \( \bar{a}_q \) are defined as

\[
\Pi_N = e^{-T} H e^{T} - E_0,
\]

\[
\bar{a}_p = e^{-T} a_p e^{T},
\]

\[
\bar{a}_q = e^{-T} a_q^\dagger e^{T}.
\]

Note that by using Campbell-Baker-Hausdorff formula

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

one can derive the explicit forms of Eqs. (22) and (23) where

\[
\bar{\pi}_p = a_p + [a_p, T]
\]

\[
\bar{a}_q = a_q^\dagger + [a_q^\dagger, T].
\]

Now we define frequency dependent ionization-potential equation-of-motion CC (IP-EOMCC) type operators \( X_p(\omega) \) and frequency dependent electron-affinity EOMCC (EA-EOMCC) type operators \( Y_q(\omega) \)

\[
X_p(\omega) = \sum_{i} x^i(p, \omega) a_i + \sum_{i<j,a} x^{ij}_a(p, \omega) a_{a}^\dagger a_{a}^\dagger a_i a_i + \ldots
\]

\[
Y_q(\omega) = \sum_{i} y_a(q, \omega) a_a^\dagger + \sum_{i,a<b} y^{i}_{a}(q, \omega) a_{a}^\dagger a_{a}^\dagger a_i a_i + \ldots
\]

defined as

\[
(\omega + \Pi_N - i\eta)X_p(\omega)|\Phi\rangle = \bar{\pi}_p |\Phi\rangle,
\]

\[
(\omega - \Pi_N + i\eta)Y_q(\omega)|\Phi\rangle = \bar{a}_q^\dagger |\Phi\rangle.
\]

Note that the amplitudes \( x^i(p, \omega), x^{ij}_a(p, \omega), \ldots \), and \( y_a(q, \omega), y^{i}_{a}(q, \omega), \ldots \) are defined on the entire complex plane, and are functions of a spin-orbital index and frequency. Consequently, we can express Eq. (20) in a compact form

\[
G_{pq}(\omega) = \langle \Phi | (1 + \Lambda)\bar{a}_q^\dagger X_p(\omega) | \Phi \rangle + \langle \Phi | (1 + \Lambda)\bar{\pi}_p^\dagger Y_q(\omega) | \Phi \rangle.
\]

C. GFCC methodology utilizing DUCC effective Hamiltonians

For simplicity, let designate the second quantized representation of the \( H_{\text{ext}}^{\text{Ducc}}(\text{DUCC}) \) operator by \( \Gamma \). We will also consider the case when the set of active orbitals consists of all occupied orbitals and a small subset of active virtual orbitals (containing \( n_{\text{act}}^{v} \) active virtual orbitals), where, in general, \( n_{\text{act}}^{v} \ll n_{\text{v}} \), where \( n_{\text{v}} \) designates the total number of virtual orbitals.

The main idea behind the combined GFCC and DUCC formalism (DUCC-GFCC) is to replace \( T, \Lambda \), and \( H \) operators in Eq. (11) by cluster, de-excitation and \( \Gamma \) operators acting in the active space only. To avoid possible conflict with the notation convention used in Ref. [7] to define the \( \sigma_{\text{int}} \) operator, we will denote the active-space counterparts of the \( T \) and \( \Lambda \) operators by \( T_{\text{int}} \) and \( \Lambda_{\text{int}} \), respectively. The equations (14)-(16) are replaced by their "active" counterparts

\[
Q_{\text{int}} e^{-T_{\text{int}}^{\dagger}} \Gamma e^{T_{\text{int}}} |\Phi\rangle = 0,
\]

\[
\langle \Phi | e^{-T_{\text{int}}^{\dagger}} \Gamma e^{T_{\text{int}}} | \Phi \rangle = E_{0}^{\text{int}},
\]

\[
\langle \Phi | (1 + \Lambda_{\text{int}}) e^{-T_{\text{int}}^{\dagger}} \Gamma e^{T_{\text{int}}} Q_{\text{int}} |\Phi\rangle = E_{0}^{\text{int}} \langle \Phi | (1 + \Lambda_{\text{int}}) Q_{\text{int}} |\Phi\rangle.
\]

Now, the coupled cluster Green’s function employing the DUCC Hamiltonian \( \Gamma \) can be expressed as for active orbitals as follows

\[
G_{PQ}^{\text{DUCC}}(\omega) = \langle \Phi | (1 + \Lambda_{\text{int}}) e^{-T_{\text{int}}^{\dagger}} a_{Q}^{\dagger} (\omega + (\Gamma - E_{0}^{\text{int}}) - i\eta)^{-1} a_{P} e^{T_{\text{int}}} |\Phi\rangle + \langle \Phi | (1 + \Lambda_{\text{int}}) e^{-T_{\text{int}}^{\dagger}} a_{P} (\omega - (\Gamma - E_{0}^{\text{int}}) + i\eta)^{-1} a_{Q}^{\dagger} e^{T_{\text{int}}} |\Phi\rangle
\]

where indices \( P, Q, \ldots \) designate active spin orbitals. Again, applying the resolution of identity \( e^{-T_{\text{int}}^{\dagger}} e^{T_{\text{int}}} \) in the above equation, one gets the following expressions for DUCC Green’s function matrix elements

\[
G_{PQ}^{\text{DUCC}}(\omega) = \langle \Phi | (1 + \Lambda_{\text{int}}) \bar{a}_{Q}^{\dagger} \bar{T}_{\text{int}} \bar{T}_{\text{int}}^{\dagger} \bar{T}_{\text{int}} \bar{T}_{\text{int}}^{\dagger} |\Phi\rangle + \langle \Phi | (1 + \Lambda_{\text{int}}) \bar{a}_{P} \bar{T}_{\text{int}} \bar{T}_{\text{int}}^{\dagger} |\Phi\rangle
\]

where we used the following definitions

\[
\bar{T}_{\text{int}} = e^{-T_{\text{int}}^{\dagger}} \Gamma e^{T_{\text{int}}},
\]

\[
\bar{\Gamma}_{\text{int}} = \bar{T}_{\text{int}}^{\dagger} \Gamma \bar{T}_{\text{int}}^{\dagger},
\]

\[
\bar{a}_{P}^{\dagger} = e^{-T_{\text{int}}^{\dagger}} a_{P} e^{T_{\text{int}}},
\]

\[
\bar{a}_{Q}^{\dagger} = e^{-T_{\text{int}}^{\dagger}} a_{Q} e^{T_{\text{int}}}.
\]

In the active-space driven DUCC-GFCC approach, the \( X_p(\omega) \) and \( Y_q(\omega) \) operators are replaced by \( X^{\text{Ducc}}(\omega) \) and \( Y^{\text{Ducc}}(\omega) \), respectively, which are given by the following expressions:
\[ X_P^{\text{int}}(\omega) = \sum_I x_I^P(P,\omega)^{\text{int}} a_I + \sum_{I,J,A} x_{IJ}^A(P,\omega)^{\text{int}} a_I^\dagger a_J a_I + \ldots , \]  

\[ Y_Q^{\text{int}}(\omega) = \sum_A y_A(Q,\omega)^{\text{int}} a_A^\dagger + \sum_{I,A,B} y_{AB}^I(Q,\omega)^{\text{int}} a_A^\dagger a_B a_I + \ldots , \]  

where indices \( I, J, \ldots \) and \( A, B, \ldots \) refer to active occupied and unoccupied spin orbitals indices, respectively (again, in the present discussion we assume that all occupied spin orbitals are treated as active). These operators satisfy

\[ (\omega + \Gamma_N - i\eta)X_P^{\text{int}}(\omega)\Phi = \overline{\overline{X}_P^{\text{int}}} \Phi , \]

\[ (\omega - \Gamma_N + i\eta)Y_Q^{\text{int}}(\omega)\Phi = a_Q^{\dagger} \Phi , \]

and the \( G_{PQ}^{\text{DUCC}}(\omega) \) is given by the expression

\[ G_{PQ}^{\text{DUCC}}(\omega) = \langle \Phi | (1 + \Lambda_{\text{int}}) a_Q^{\dagger} X_P^{\text{int}}(\omega) | \Phi \rangle + \langle \Phi | (1 + \Lambda_{\text{int}}) \overline{\overline{X}_P^{\text{int}}} Y_Q^{\text{int}}(\omega) | \Phi \rangle . \]

### III. APPROXIMATIONS AND IMPLEMENTATION DETAILS

In the present study, we will consider the following approximations for the form of the \( \Gamma \) operator and from of the \( \overline{T}_{\text{int}}, \overline{\Lambda}_{\text{int}}, X_P^{\text{int}}(\omega) \) and \( Y_Q^{\text{int}}(\omega) \) operators:

- The \( \Gamma \) operator only considers to by one- and two-body terms defined in Eq. (65) of Ref. [56]. The \( \Gamma \) operator is limited to the downfolding of inactive virtual orbitals.
- \( \overline{T}_{\text{int}} \) and \( \overline{\Lambda}_{\text{int}} \) operators are represented by single and double excitations within the active space (the

\[ A(\omega) = -\frac{1}{\pi} \text{Tr}_{\text{act}} \left[ \Im \left( G^{\text{DUCC (IP)}}(\omega) \right) \right] \approx -\frac{1}{\pi} \sum_{I} \Im \left( G_{II}^{\text{DUCC (IP)}}(\omega) \right) , \]

where summation under trace (\( \text{Tr}_{\text{act}} \)) includes summation over active spin orbitals only.

Recently, we have introduced new class of GFCC approximations where locations of poles are improved by extending the excitation level of inner auxiliary operators \( (X_P(\omega), Y_Q(\omega)) \). [55] These approximations can be generally categorized as GFCC-i(n, m) method, where the excitation level of the inner auxiliary operators (m) used to describe the ionization potentials and electron affinities effects in the \( N-1 \) and \( N+1 \) particle Hilbert spaces is higher than the excitation level (n) used to represent the ground-state coupled cluster wave function for the \( N \)-electron system. We also derived the so-called "n+1" rule (or the GFCC-i(n,n+1) class of methods), which states that in order to maintain size-extensivity of the Green's function matrix elements, the excitation level of inner auxiliary operators \( X_p(\omega) \) and \( Y_q(\omega) \) cannot be larger than \( n+1 \). We demonstrated that the GFCC-i(2,3) approximation can significantly improve the location of satellite peaks compared to the GFCCSD formalism. [55] For this reason we decided to combine the GFCC-i(2,3) approach with the DUC effective Hamiltonians (DUC-GFCC-i(2,3) approach).

The working equations for the DUC-GFCC-i(2,3) method represent a simple modification of the GFCC-i(2,3) approach. For example, for the ionized part of the Q_int operator of Eqs. (32) and (34) is replaced by the projection operator onto singly and doubly excited configurations belonging to the active space \( Q_{(1)\text{int}} \) and \( Q_{(2)\text{int}} \), respectively. Moreover, we also assumed that \( \Lambda_{\text{int}} = \overline{T}_{\text{int}}^\dagger \) (the efficiency of this approximation was discussed in Refs. [55]).
Green’s functions considered here

\[
Q^{(N-1)}_{(1)^{\text{int}}} (\omega + \Gamma_N - i\eta)(X^{\text{int}}_{P,1}(\omega) + X^{\text{int}}_{P,2}(\omega) + X^{\text{int}}_{P,3}(\omega))|\Phi\rangle = Q^{(N-1)}_{(1)^{\text{int}}} \tilde{\Gamma}^{\text{int}}|\Phi\rangle, \tag{48}
\]

\[
Q^{(N-1)}_{(2)^{\text{int}}} (\omega + \Gamma_N - i\eta)(X^{\text{int}}_{P,1}(\omega) + X^{\text{int}}_{P,2}(\omega) + X^{\text{int}}_{P,3}(\omega))|\Phi\rangle = Q^{(N-1)}_{(2)^{\text{int}}} \tilde{\Gamma}^{\text{int}}|\Phi\rangle, \tag{49}
\]

\[
Q^{(N-1)}_{(3)^{\text{int}}} \{(\omega + F_N(\Gamma)_D - i\eta)X^{\text{int}}_{P,3}(\omega) + (\Gamma_{N,2}X^{\text{int}}_{P,2}(\omega)) + (\Gamma_{N,2}\tilde{\Gamma}^{\text{int}} X^{\text{int}}_{P,1}(\omega))\}|\Phi\rangle = Q^{(N-1)}_{(3)^{\text{int}}} \tilde{\Gamma}^{\text{int}}|\Phi\rangle,
\]

where the \( F_N(\Gamma)_D \) is diagonal part of the one-particle \( \Gamma \)-operator-dependent Fock operator in a normal product form, \( \Gamma_{N,2} \) is two-particle part of \( \Gamma_N \), and subscript "C" designates connected part of a given operator expression. The \( X^{\text{int}}_{P,3}(\omega) \) and \( Y^{\text{int}}_{Q}(\omega) \) are internal triply excited components of the \( X^{\text{int}}_{P}(\omega) \) and \( Y^{\text{int}}_{Q}(\omega) \) operators. One should mention that in analogy to the GFCC-i\((2,3)\) case, the DUCC-GFCC-i\((2,3)\) expression is given by DUCC-GFCCSD expression (Eq. (46)), the only difference is in the fact that now the \( X_{P,1}(\omega) \) and \( X_{P,2}(\omega) \) are iterated in the presence of the \( X_{P,3}(\omega) \) operator.

IV. RESULTS AND DISCUSSION

To illustrate the performance of the DUCC-GFCCSD formalism we performed calculations for two benchmark systems: \( H_2O \) and \( N_2 \) molecules in cc-pVDZ basis sets.\cite{68} In both cases, we calculated spectral functions for DUCC Hamiltonians defined by active spaces of various sizes. For the water molecule, we tested two active spaces including 7 and 9 active orbitals (spanned by 5 occupied and 2 virtual orbitals and 5 occupied and 4 virtual orbitals, respectively). For \( N_2 \) molecules we used three active spaces composed of 10, 11, and 17 orbitals. For \( N_2 \) we have also performed GFCCSD calculations employing bare Hamiltonians in the same active spaces. The conventional GFCCSD results employing all orbitals are shown in Figs. 1 and 2 in black lines.

It is intriguing to see that for both systems, DUCC-GFCCSD spectral functions (see Figs. 1 and 2) approach monotonically conventional GFCCSD spectral functions as the size of active space is increased. Additionally, all features of the conventional GFCCSD formulation correlating all orbitals are reproduced by DUCC-GFCCSD approaches. This concerns not only the main peaks in the energy range [-20,-10] eV but also all three satellite peaks located below -30 eV.

It is interesting to notice that the monotonic behavior of the DUCC-GFCCSD spectral functions is a consequence of the "correlated" character of the DUCC Hamiltonians, which also capture the dynamical correlation effects outside of active space. To illustrate this fact for the \( N_2 \) molecule we performed GFCCSD in the same active spaces using bare Hamiltonians, where the corresponding spectral functions are shown in Fig. 2 by dotted lines. In contrast to the DUCC-GFCCSD formalism, the spectral functions for GFCC approaches utilizing bare Hamiltonian in active spaces are no longer monotonically approaching full GFCCSD results. In some cases the position of peaks disclose an irregular behavior. For example, the first main peak of \( N_2 \) obtained with 11 active orbitals (see Fig. 2 blue line) overestimates the ionization energy obtained with the full GFCCSD approach whereas for 17 active orbitals case (see Fig. 2 red line) this quantity is underestimated. Similar behavior can be observed for the satellite peak of \( N_2 \) located between -30 and -35 eV.

To assess to what extent DUCC-GFCC-i\((2,3)\) formalism can reproduce the effects due to the higher-order excitations (for example, triple excitation) in the calculated spectral functions, we performed the DUCC-GFCC-i\((2,3)\) calculations for the \( N_2 \) system which was used in the original GFCC-i\((2,3)\) studies. To make a comparison with the previous DUCC-GFCC calculations we used the same active spaces employed in the DUCC-GFCCSD case. Our results are shown in Fig. 3, where the exact GFCC-i\((2,3)\) spectral function is marked in gray. As one can see, all active spaces can reproduce all the basic features of the full GFCC-i\((2,3)\) approach. It regards not only the main peaks but also all satellite peaks (below -25 eV), of which two were not detected by the GFCCSD method. The results obtained with the 17 orbitals active space are in a good agreement with the full GFCC-i\((2,3)\) results. One should emphasize that this agreement was possible to obtain with a very simple form of the effective Hamiltonians used in the simulations (see Eq. (65) of Ref. [55]).

V. CONCLUSIONS

We demonstrated that the utilization of the effective Hamiltonian stemming from the DUCC downfolding procedure can be used to reproduce the main features of the standard GFCCSD spectral function. In a series of test calculations, we demonstrated that increasing active space size leads to monotonic improvements in the location of peaks obtained with the DUCC-GFCCSD approach with respect to the full GFCCSD results. We contribute this behavior to the presence of dynamical (out-of-active-space) correlation effects encapsulated in each of DUCC effective Hamiltonians. In contrast to the DUCC-GFCCSD formalism, the utilization of active space bare Hamiltonians results in a less regular behavior of calculated peaks. The utilization of the DUCC effec-
FIG. 1. Spectral functions of the water molecule in the valence energy regimes directly computed by the close-shell GFCCSD and DUCC-GFCCSD methods with cc-pVDZ basis set. The conventional GFCCSD results with 24 total number of molecular orbitals are shown as a black line at the bottom. The DUCC-GFCCSD results with 7 and 9 internal molecular orbitals (including all the five occupied molecular orbitals) are shown in green and blue lines, respectively.

FIG. 2. Spectral functions of the nitrogen molecule in the valence energy regimes directly computed by the closed-shell GFCCSD and DUCC-GFCCSD methods with cc-pVDZ basis set. The conventional GFCCSD results with 28 total number of molecular orbitals are shown as a black line at the bottom. The DUCC-GFCCSD results with 10, 11, and 17 internal molecular orbitals (including all the seven occupied molecular orbitals) are shown in green, blue, and red lines, respectively, with their bare Hamiltonian counter parts being shown in the dashed line with same colors.

FIG. 3. Spectral functions of the nitrogen molecule in the valence energy regimes directly computed by the closed-shell GFCC-i(2,3) and DUCC-GFCC-i(2,3) methods with cc-pVDZ basis set. The conventional GFCC-i(2,3) results with 28 total number of molecular orbitals are shown as a black line at the bottom. The DUCC-GFCC-i(2,3) results with 10, 11, and 17 internal molecular orbitals (including all the seven occupied molecular orbitals) are shown in green, blue, and red lines, respectively.

development of quantum computing algorithms for correlated Green’s function [33, 34] makes reduced-dimension DUCC-GFCC formulations a possible target for early quantum computing applications.

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