Sub-system quantum dynamics using coupled cluster downfolding techniques

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(Dated: March 24, 2020)

In this paper, we discuss extending the sub-system embedding sub-algebra coupled cluster (SES-CC) formalism and the double unitary coupled cluster (DUCC) ansatz to the time domain. As we demonstrated in earlier studies, it is possible, using these formalisms, to calculate the energy of the entire system as an eigenvalue of downfolded/effective Hamiltonian in the active space, that is identifiable with the sub-system of the composite system. In these studies, we demonstrated that downfolded Hamiltonians integrate out Fermionic degrees of freedom that do not correspond to the physics encapsulated by the active space. We extend these results to the time-dependent Schrödinger equation, showing that a similar construct is possible to partition a system into a sub-system that varies slowly in time and a remaining subsystem that corresponds to fast oscillations. This time dependent formalism allows coupled cluster quantum dynamics to be extended to larger systems and for the formulation of novel quantum algorithms based on the quantum Lanczos approach, which have recently been considered in the literature.

INTRODUCTION

The coupled cluster (CC) theory [1–7] has evolved into one of the most accurate many-body formulations to describe correlated behavior of chemical [7] and nuclear systems.[8] Over the last few decades, applications of the CC formalism in quantum chemistry have grown enormously, embracing molecular structure optimization, the description of chemical reactivity, simulations of spectroscopic properties, and computational models of strongly correlated systems. A great deal of effort has been exerted towards developing hierarchical families of approximations which provide an increasing level of accuracy by including high-rank collective phenomena in cluster operator(s).[7] Significant advances in describing properties, quasi-degenerate and excited electronic states were possible thanks to extensions of CC formalism to linear-response theory,[9, 10] equation-of-motion CC formulations, [11–14] and multi-reference CC methods.[15–31] Significant progress has also been achieved in developing reduced scaling CC methods, mainly in applications to ground- and excited-state problems.[32–34] The existence of hierarchical structures of approximations that allow one to reach the exact, full configuration interaction (FCI), limit for a given basis set is an appealing feature of the CC formalism that drives the development of most formulations.

Parallel to these advances, one could also witness significant progress in developing explicitly time-dependent CC (TD-CC) formulations of the time-dependent Schrödinger equation (TDSH)

\[
i\hbar \frac{\partial}{\partial t} |\Psi(t)\rangle = H |\Psi(t)\rangle ,
\]

where

\[
|\Psi(t)\rangle = e^{T(t)}|\Phi\rangle
\]

represents the time-dependent wave function with the time-dependent cluster operator \(T(t)\). This CC formulation has been explored in CC linear response theory [9, 10] for molecular systems, X-ray spectroscopy and Green’s function theory,[35] nuclear physics,[36–38] condensed matter physics,[39] and quantum dynamics of molecular systems in external fields.[40–44] These studies have also initiated an intensive effort towards understanding many-aspects of the TD-CC formalism including addressing fundamental problems such as the form of the action functional, form of the time-dependent molecular basis, various-rank approximations of the cluster operator, and numerical stability of time integration algorithms. One of the milestone achievements in developing time-dependent CC formalism was Arponen’s action functional for the bi-variational coupled cluster formalism. [39] In the last decade, this formalism was further extended by Kvaal [41] by introducing the orbital adaptive time-dependent coupled cluster formalism and ensuing approximations. These developments made the TD-CC formalism a complementary approach to well established wave-function-based time-dependent multi-configurational approaches, [45–53] configuration interaction formulations, [54–58], and density matrix renormalization group (DMRG) method. [59–62]

The sub-system embedding sub-algebra CC (SES-CC) formalism [63] and its unitary variant based on the double unitary coupled cluster (DUCC) ansatz [64] enabled new features of CC equations that are strictly related to the active space concept to be identified. The critical observation is related to the fact that energies of CC methods (such as CCSD,[5] CCSDTQ,[65, 66] etc.) can be obtained, in contrast to the standard CC energy expression, by diagonalizing reduced-dimensionality effective (or downfolded) Hamiltonians in the corresponding active space. Both SES-CC and DUCC methods provide rigorous expressions defining these Hamiltonians. Additionally, downfolded Hamiltonians integrate out external Fermionic degrees of freedom (specifically,
all cluster amplitudes that correspond to excitations outside of the active space). Besides these fundamental properties, the SES-CC formalism naturally introduces the concept of seniority numbers discussed recently in the context of configuration interaction methods [67] and CC formulations.[68–70] The so-called SES-CC flow equations [63] and Ducc formalisms were used to define approximations to calculate ground- and excited-states energies as well as spectral functions in a recent Green’s function Ducc extension.[71] The Ducc Hamiltonians have also been intensively tested on the subject of quantum computing simulations with reduced-dimensionality Hamiltonians.[64, 72] The SES-CC methods complement/extend the active space coupled cluster methods and SES-CC see Refs.[63, 64]).

In this manuscript, we present the time evolution of the system using SES-CC and Ducc wave function representations. As in previous studies, where SES-CC/Ducc methods decoupled Fermionic degrees of freedom corresponding to various energy or localization regimes, we discuss formulations, using SES-CC and Ducc approaches, which decouple slow- and fast-varying components of the wave function. Additionally, the Ducc formalism provides a rigorous many-body characterization of the time-dependent action functional to describe the dynamics of the entire system in time modes captured by the corresponding active space. This approach and corresponding approximations can not only reduce the cost of TD-CC simulations for larger molecular applications but can also be employed in the imaginary time evolution, which has recently been intensively studied in the context of quantum computing.[77] The flexibility associated with the choice of the active space can also be advantageous for the generalization of time-dependent SES-CC/Ducc formulations (TD-SES-CC and TD-ucc, respectively) beyond slow-varying components of the wave functions. In analogy to TDCC formulations discussed in Refs.[38, 40], we also analyze the properties of TD-SES-CC and TD-ucc methods based on fixed (time-independent) orthogonal spin orbitals.

The single reference CC (SR-CC) ansatz is predicated on the assumption that there exists a single Slater determinant \( |\Phi \rangle \) that provides a reasonable approximation of the correlated electronic ground-state \( |\Psi \rangle \) to justify its exponential CC parametrization

\[
|\Psi \rangle = e^T |\Phi \rangle ,
\]

where \( T \) is the so-called cluster operator, which in general can be expressed in terms of its many-body components \( T_k \)

\[
T = \sum_{k=1}^{m} T_k .
\]

In the exact wave function limit, the excitation level \( m \) is equal to the number of correlated electrons \( (N) \) while in the approximate formulations \( m \ll N \). Several standard approximations fall into this category, i.e., CCSDT \((m = 2),[5]\) CCSDT \((m = 3),[78–80]\), CCSDTQ \((m = 4),[65, 66]\) etc. Using the language of second quantization, the \( T_k \) components can be expressed as

\[
T_k = \frac{1}{(k!)^2} \sum_{i_1, \ldots, i_k} t^{i_2 \cdots i_k}_{a_{i_1} \cdots a_k} E^{a_1 \cdots a_k}_{i_1 \cdots i_k} ,
\]

where indices \( i_1, i_2, \ldots, (a_1, a_2 \ldots, ) \) refer to occupied (unoccupied) spin orbitals in the reference function \( |\Phi \rangle \). The excitation operators \( E^{a_1 \cdots a_k}_{i_1 \cdots i_k} \) are defined through strings of standard creation \( \langle a_p \) and annihilation \( \langle a_p \) operators

\[
E^{a_1 \cdots a_k}_{i_1 \cdots i_k} = a^\dagger_{a_1} \cdots a^\dagger_{a_k} a_{i_k} \cdots a_{i_1} ,
\]

where creation and annihilation operators satisfy the following anti-commutation rules

\[
[a_p, a_q]_+ = [a^\dagger_p, a^\dagger_q]_+ = 0 ,
\]

\[
[a_p, a^\dagger_q]_+ = \delta_{pq} .
\]

After substituting Ansatz (3) into the Schrödinger equation one gets the energy-dependent form of the CC equations:

\[
(P + Q)He^T |\Phi \rangle = E(P + Q)e^T |\Phi \rangle ,
\]

where \( P \) and \( Q \) are projection operators onto the reference function \( \langle \Phi \| \langle \Phi \) and onto excited configurations (with respect to \( |\Phi \rangle \)) generated by the \( T \) operator when acting onto the reference function,

\[
Q = \sum_{k=1}^{m} \sum_{i_1 < i_2 < \ldots < i_k; a_1 < a_2 \ldots < a_k} |\Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} \rangle \langle \Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} | ,
\]

where

\[
|\Phi^{a_1 \cdots a_k}_{i_1 \cdots i_k} \rangle = E^{a_1 \cdots a_k}_{i_1 \cdots i_k} |\Phi \rangle .
\]
Diagrammatic analysis [81] leads to an equivalent \((at \ the \ solution)\), energy-independent form of the CC equations for cluster operators

\[
Q e^{-T} H e^T \Phi = Q(H e^T)_C \Phi = 0 ,
\]  
and energy expression

\[
E = \langle \Phi | e^{-T} H e^T | \Phi \rangle ,
\]
where \(C\) designates a connected form of a given operator expression. In the forthcoming discussion, we refer to \(e^{-T} H e^T\) as a similarity transformed Hamiltonian \(\tilde{H}\).

The SES-CC formalism hinges upon the notion of excitation sub-algebra of algebra \(g^{(N)}\) generated by \(E_{\alpha i}^{\dagger} = a^\dagger \alpha_{i} a_{\alpha i}\) operators (for a more detailed discussion of many-body Lie algebras the reader is referred to Refs.[82–84]). The SES-CC formalism utilizes an important class of sub-algebras of \(g^{(N)}\), which contain all possible excitations \(E_{\alpha i_1, \ldots , \alpha i_m}\) that excite electrons from a subset of active occupied orbitals (denoted as \(R\) to a subset of active virtual orbitals (denoted as \(S\)). These sub-algebras will be designated as \(g^{(N)}(R, S)\). In the following discussion, we will use \(R\) and \(S\) notation for subsets of occupied and virtual active orbitals \(\{R_{i}, i = 1, \ldots , x\}\) and \(\{S_{i}, i = 1, \ldots , y\}\) respectively (sometimes it is convenient to use alternative notation \(g^{(N)}(x_{R}, y_{S})\) where numbers of active orbitals in \(R\) and \(S\) orbital sets, \(x\) and \(y\), respectively, are explicitly called out). As discussed in Ref.[63] configurations generated by elements of \(g^{(N)}(x_{R}, y_{S})\) along with the reference function span the complete active space (CAS) referenced to as the CAS\((R, S)\).

Each sub-algebra \(\mathfrak{h} = g^{(N)}(x_{R}, y_{S})\) induces partitioning of the cluster operator into internal \((T_{\text{int}}(\mathfrak{h})\ or \ T_{\text{int}}\ for \ short)\) part belonging to \(\mathfrak{h}\) and external \((T_{\text{ext}}(\mathfrak{h})\ or \ T_{\text{ext}}\ for \ short)\) part not belonging to \(\mathfrak{h}\), i.e.,

\[
T = T_{\text{int}}(\mathfrak{h}) + T_{\text{ext}}(\mathfrak{h}) .
\]

In Ref.[63] it was shown that if two criteria are met:

1. the \(|\Psi(\mathfrak{h})\rangle = e^{T_{\text{int}}(\mathfrak{h})} |\Phi\rangle\) is characterized by the same symmetry properties as \(|\Psi\rangle\) and \(|\Phi\rangle\) vectors (for example, spin and spatial symmetries),

2. the \(e^{T_{\text{ext}}(\mathfrak{h})}|\Phi\rangle\) ansatz generates FCI expansion for the sub-system defined by the CAS corresponding to the \(\mathfrak{h}\) sub-algebra,

then \(\mathfrak{h}\) is called a sub-system embedding sub-algebra (SES) for cluster operator \(T\). For any SES \(\mathfrak{h}\) we proved the equivalence of representations of the CC equations at the solution, standard

\[
\langle \Phi | \tilde{H} | \Phi \rangle = E ,
\]
\[
Q_{\text{int}} \tilde{H} | \Phi \rangle = 0 ,
\]
\[
Q_{\text{ext}} \tilde{H} | \Phi \rangle = 0 ,
\]
and hybrid

\[
(P + Q_{\text{int}}) \tilde{H}_{\text{ext}} e^{T_{\text{int}}}|\Phi\rangle = E(P + Q_{\text{int}}) e^{T_{\text{int}}}|\Phi\rangle ,
\]
\[
Q_{\text{ext}} \tilde{H} | \Phi \rangle = 0 ,
\]
where

\[
\tilde{H}_{\text{ext}} = e^{-T_{\text{ext}}H} e^{T_{\text{ext}}}
\]

and the two projection operators \(Q_{\text{int}}(h)\) and \(Q_{\text{ext}}(h)\) \((Q_{\text{int}}\ and \ Q_{\text{ext}}\ for \ short)\) are spanned by all excited configurations generated by acting with \(T_{\text{int}}(\mathfrak{h})\) and \(T_{\text{ext}}(\mathfrak{h})\) onto reference function \(|\Phi\rangle\), respectively. The \(Q_{\text{int}}\) and \(Q_{\text{ext}}\) projections operators satisfy the condition

\[
Q = Q_{\text{int}} + Q_{\text{ext}} .
\]

The above equivalence shows that the CC energy can be calculated by diagonalizing effective Hamiltonian \(H^{\text{eff}}\) defined as

\[
H^{\text{eff}} = (P + Q_{\text{int}}) \tilde{H}_{\text{ext}}(P + Q_{\text{int}})
\]
in the complete active space corresponding to any SES of CC formulation defined by cluster operator \(T\). One should also notice that: (1) the non-CAS related CC wave function components (referred here as external degrees of freedom) are integrated out and encapsulated in the form of \(H^{\text{eff}}\) and (2) the internal part of the wave function, \(e^{T_{\text{int}}}|\Phi\rangle\) is fully determined by diagonalization of \(H^{\text{eff}}\) in the CAS. Separation of external degrees of freedom in the effective Hamiltonians is a desired feature especially from the point of building reduced-dimensionality Hamiltonian for quantum computing (QC). However, a factor that impedes the use in QC of the \(H^{\text{eff}}\) is its non-Hermitian character.

In order to assure the Hermitian character of the CC effective Hamiltonian that also provides a separation of Fermionic degrees of freedom, in Ref.[64] we have introduced double unitary coupled cluster ansatz

\[
|\Psi\rangle = e^{\sigma_{\text{ext}}(\mathfrak{h})} e^{\sigma_{\text{int}}(\mathfrak{h})} |\Phi\rangle ,
\]
where

\[
\sigma_{\text{int}} = T_{\text{int}} - T_{\text{int}}^{\dagger} ,
\]
\[
\sigma_{\text{ext}} = T_{\text{ext}} - T_{\text{ext}}^{\dagger} ,
\]
and \(T_{\text{int}}\) and \(T_{\text{ext}}\) have the same structure as in the single-reference SEC-CC case discussed earlier. By their construction, both \(\sigma_{\text{int}}\) and \(\sigma_{\text{ext}}\) operators are anti-Hermitian, i.e.,

\[
\sigma_{\text{int}}^{\dagger} = -\sigma_{\text{int}} ,
\]
\[
\sigma_{\text{ext}}^{\dagger} = -\sigma_{\text{ext}} .
\]

Assuming that \(\mathfrak{h}\) is a SES for the \(T\) operator, we showed in Ref.[64] that the DUCC expansion allows effective Hamiltonians to be constructed in a similar way as in
single reference SES-CC. It can be proven that both the energy and the $e^{\sigma_{\text{int}}}|\Phi\rangle$ FCI CAS state can be obtained by diagonalizing DUCC effective Hamiltonian in the complete active space

$$H_{\text{eff}} e^{\sigma_{\text{int}}}|\Phi\rangle = E e^{\sigma_{\text{int}}}|\Phi\rangle,$$

(28)

where

$$H_{\text{eff}} = (P + Q_{\text{int}})\tilde{H}_{\text{ext}} (P + Q_{\text{int}})$$

(29)

and

$$\tilde{H}_{\text{ext}} = e^{-\sigma_{\text{ext}}} H e^{\sigma_{\text{ext}}}.$$

(30)

In analogy to the SES-CC formalism, the energy and the CAS wave functions are obtained by diagonalizing DUCC effective Hamiltonian in the complete active space. Also, in the construction of the DUCC effective Hamiltonian only the external cluster operator ($\sigma_{\text{ext}}$) is used. In further analysis, for both SES-CC and DUCC formalisms we will be using the same notation for the $H_{\text{ext}}$ and $H_{\text{eff}}$ operators, and their form will follow from the context of the discussed equations.

**TIME-DEPENDENT FORMULATIONS EMPLOYING DOWNFOLDED HAMILTONIANS**

To derive properties of the time-dependent Schrödinger equations utilizing SES-CC and DUCC representations of the time-dependent wave functions, we will (in analogy to Refs.[35, 38, 40] focus on the simplest case where orbitals and the reference function $|\Phi\rangle$ are time-independent, which can be expressed as

$$\frac{\partial}{\partial t} a_p = \frac{\partial}{\partial a_q} a_q = 0, \quad \frac{\partial}{\partial t} |\Phi\rangle = 0.$$

(31)

The above assumptions indicate that the CAS and corresponding SES $H$ do not change in time.

**Time-dependent Schrödinger equation in the SES-CC representation**

In this subsection, we derive the time-dependent extension of the SES-CC and DUCC wave function representations. First, we start from the time-dependent CC parametrization of the wave function:

$$|\Psi_{\text{CC}}(t)\rangle = e^{T(t)}|\Phi\rangle,$$

(32)

where

$$T(t) = \sum_{k=0}^{m} T_k(t).$$

(33)

As in the stationary SES-CC formulation, we will assume the decomposition of the time-dependent cluster operator $T(t)$ into internal ($T_{\text{int}}(t)$) and external ($T_{\text{ext}}(t)$) parts, i.e.,

$$|\Psi_{\text{CC}}(t)\rangle = e^{T_{\text{ext}}(t)+T_{\text{int}}(t)}|\Phi\rangle$$

(34)

and

$$= e^{T_{\text{ext}}(t)} e^{T_{\text{int}}(t)}|\Phi\rangle,$$

(35)

For the sake of generality, we also include a time-dependent scalar phase factor ($T_0(t)$) in the definition of $T_{\text{int}}(t)$ operator. As pointed out by Hoodbhoy and Negele in Refs.[36, 37] this phase factor is not needed when calculating physical observables.

Upon introducing expansion (35) into time-dependent Schrödinger equation (TDSE) one obtains

$$i\hbar \frac{\partial}{\partial t} e^{T_{\text{ext}}(t)+T_{\text{int}}(t)}|\Phi\rangle = H e^{T_{\text{ext}}(t)+T_{\text{int}}(t)}|\Phi\rangle,$$

(36)

which can be further transformed (after differentiating its left hand side over $t$)

$$i\hbar \left(\frac{\partial T_{\text{int}}(t)}{\partial t} + \frac{\partial T_{\text{ext}}(t)}{\partial t}\right) e^{T_{\text{ext}}(t)+T_{\text{int}}(t)}|\Phi\rangle = H e^{T_{\text{ext}}(t)+T_{\text{int}}(t)}|\Phi\rangle,$$

(37)

After premultiplying both sides by $e^{-T_{\text{ext}}(t)}$, we obtains a convenient form of TDSE

$$i\hbar \left(\frac{\partial T_{\text{int}}(t)}{\partial t} + \frac{\partial T_{\text{ext}}(t)}{\partial t}\right) e^{T_{\text{int}}(t)}|\Phi\rangle = \tilde{H}_{\text{ext}} e^{T_{\text{int}}(t)}|\Phi\rangle,$$

(38)

where

$$\tilde{H}_{\text{ext}}(t) = e^{-T_{\text{ext}}(t)} H e^{-T_{\text{ext}}(t)}.$$

(39)

Now, we focus our attention on the projection of Eq.(38) onto time-independent subspace $(P + Q_{\text{int}})$, which leads to the equations:

$$i\hbar (P + Q_{\text{int}}) \left(\frac{\partial T_{\text{int}}(t)}{\partial t} + \frac{\partial T_{\text{ext}}(t)}{\partial t}\right) e^{T_{\text{int}}(t)}|\Phi\rangle$$

$$= (P + Q_{\text{int}}) \tilde{H}_{\text{ext}} e^{T_{\text{int}}(t)}|\Phi\rangle.$$

(40)

Taking into account the fact that $T_{\text{ext}}(t)$ and $\frac{\partial}{\partial t} T_{\text{ext}}(t)$ produce "external" excitations (defined by strings of creation-annihilation operators containing at least one inactive spin-orbital index) we have

$$(P + Q_{\text{int}}) \frac{\partial T_{\text{ext}}(t)}{\partial t} e^{T_{\text{int}}(t)}|\Phi\rangle = 0$$

(41)

and therefore the time-evolution of $e^{T_{\text{int}}(t)}|\Phi\rangle$ corresponds to the non-unitary evolution in time-independent ($P + Q_{\text{int}}$) space

$$i\hbar (P + Q_{\text{int}}) \frac{\partial T_{\text{int}}(t)}{\partial t} e^{T_{\text{int}}(t)}|\Phi\rangle = (P + Q_{\text{int}}) \tilde{H}_{\text{ext}} e^{T_{\text{int}}(t)}|\Phi\rangle$$

(42)

or

$$i\hbar \frac{\partial}{\partial t} e^{T_{\text{int}}(t)}|\Phi\rangle = H_{\text{eff}}(t) e^{T_{\text{int}}(t)}|\Phi\rangle,$$

(43)
where we used the fact that
\[
(P + Q_{\text{int}})e^{T_{\text{int}}(t)}|\Phi\rangle = e^{T_{\text{int}}(t)}|\Phi\rangle
\] (44)
and
\[
H^{\text{eff}}(t) = (P + Q_{\text{int}})\tilde{H}_{\text{ext}}(t)(P + Q_{\text{int}}).
\] (45)
We will refer to equation (43) as embedded sub-system time evolution (ESTV).

**Time-dependent Schrödinger equation in the DUCC representation**

The non-Hermitian character of $\tilde{H}_{\text{ext}}(t)$ may limit the application areas of ESTV. In analogy to the DUCC formalism studied in Refs.\[64, 71, 72\] let us represent normalized time-dependent wave function $|\Psi_{\text{DUCC}}(t)\rangle$ in the following form
\[
|\Psi_{\text{DUCC}}(t)\rangle = e^{\sigma_{\text{int}}(t)}e^{\sigma_{\text{int}}(t)}|\Phi\rangle,
\] (46)
where $\sigma_{\text{int}}(t)$ and $\sigma_{\text{ext}}(t)$ are time-dependent anti-Hermitian cluster operators, i.e.,
\[
\sigma_{\text{int}}(t)\dagger = -\sigma_{\text{int}}(t),
\] (47)
\[
\sigma_{\text{ext}}(t)\dagger = -\sigma_{\text{ext}}(t).
\] (48)
Introducing (46) into the TDSE leads to the equation
\[
i\hbar\left(\frac{\partial e^{\sigma_{\text{int}}(t)}}{\partial t}e^{\sigma_{\text{int}}(t)} + e^{\sigma_{\text{int}}(t)}\frac{\partial e^{\sigma_{\text{int}}(t)}}{\partial t}\right)|\Phi\rangle = H e^{\sigma_{\text{int}}(t)}e^{\sigma_{\text{int}}(t)}|\Phi\rangle,
\] (49)
In contrast to the standard single reference formalism, where all $T$ operators are represented by commuting components and calculations of time derivatives of exponential operators are pretty straightforward, the unitary case, where components of $\sigma_{\text{ext}}(t)$ and $\sigma_{\text{int}}(t)$ are non-commuting operators, poses a significant challenge. In our analysis, we will use the following identity for calculating derivatives of exponential operators (see Refs.\[85, 86\] for more details)
\[
\frac{\partial}{\partial t} e^{X(t)} = e^{X(t)} \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+1)!} (ad_X)^k \frac{\partial X(t)}{\partial t}
\] (50)
\[
= e^{X(t)} \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+1)!} I_k(X(t), \frac{\partial X(t)}{\partial t})
\] (51)
where the adjoint action $ad_X$ is defined as
\[
ad_A(B) = [A, B]
\] (52)
and $k$-commutator term $I_k(X(t), \frac{\partial X(t)}{\partial t})$ is given by the formula
\[
I_k(X(t), \frac{\partial X(t)}{\partial t}) = [X(t), [X(t), \ldots [X(t), \frac{\partial X(t)}{\partial t}]\ldots]]_{k \text{ times}}.
\] (53)
It is easy to notice that the first terms in the expansion (51) are given by the expressions
\[
I_0(X(t), \frac{\partial X(t)}{\partial t}) = \frac{\partial X(t)}{\partial t},
\] (54)
\[
I_1(X(t), \frac{\partial X(t)}{\partial t}) = [X(t), \frac{\partial X(t)}{\partial t}],
\] (55)
and for $k \geq 1$ recursive formula is satisfied
\[
I_k = [X(t), I_{k-1}(t)].
\] (56)
Henceforth, for the simplicity of notation, we will use $I_k$ and $I_k(X(t), \frac{\partial X(t)}{\partial t})$ interchangeably.

Formula (51) will be used to evaluate the
\[
\frac{\partial e^{\sigma_{\text{int}}(t)}}{\partial t} e^{\sigma_{\text{int}}(t)}
\] (57)
term in Eq.(49), which using formula (51) can be rewritten in the form:
\[
e^{\sigma_{\text{int}}(t)} A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) e^{\sigma_{\text{int}}(t)}
\] (58)
where
\[
A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) = \sum_{k=0}^{\infty} \frac{(-1)^k}{(k+1)!} I_k(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}).
\] (59)
Given the fact that both $\sigma_{\text{ext}}(t)$ and $\frac{\partial \sigma_{\text{ext}}(t)}{\partial t}$ operators are anti-Hermitian, it is easy to show the same is true for $I_k(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})$ and $A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})$ operators, i.e.,
\[
I_k(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})\dagger = -I_k(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}),
\] (60)
\[
A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})\dagger = -A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}).
\] (61)
By introducing Eq.(58) into Eq.(49), multiplying both sides by $e^{-\sigma_{\text{int}}(t)}$, and projecting resulting equations onto $(P + Q_{\text{int}})$, one gets the equation for time evolution of the sub-system $e^{\sigma_{\text{int}}(t)}|\Phi\rangle$
\[
i\hbar\frac{\partial}{\partial t} e^{\sigma_{\text{int}}(t)}|\Phi\rangle = H^{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) e^{\sigma_{\text{int}}(t)}|\Phi\rangle,
\] (62)
where the Hermitian effective (or downfolded) operator $H^{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})$ is given by the expression
and
\[
H^\text{eff}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) = (P + Q_{\text{int}})\{\bar{H}_{\text{ext}}(t) - i\hbar A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})\}(P + Q_{\text{int}}) \tag{63}
\]

In deriving the above equations we employed the fact that
\[
e^{\sigma_{\text{int}}(t)}|\Phi\rangle = (P + Q_{\text{int}})e^{\sigma_{\text{int}}(t)}|\Phi\rangle. \tag{64}
\]

One should also notice that \(H^\text{eff}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})\) is an Hermitian operator.

Common features of TD-SES-CC and TD-DUCC formulations

In previous subsections, we showed that when the orbital basis is time-independent then for both TD-SES-CC and TD-DUCC cases the dynamics of the sub-system (defined by appropriately chosen SES \(\mathfrak{h}\) or equivalently active space) can be described by the effective/downfolded Hamiltonians acting in the active space. While in the TD-SES-CC case the dynamic is generated by a non-Hermitian Hamiltonian, for the TD-DUCC formalism, the downfolded Hamiltonian is Hermitian and contains "external-velocity" dependent term (i.e., \(\frac{\partial \sigma_{\text{ext}}(t)}{\partial t}\) dependent term - \(A\) operator in Eq.\(63\)). In both cases one can observe a rigorous decomposition of external Fermionic degrees of freedom (\(T_{\text{ext}}(t)\) and \(\sigma_{\text{ext}}(t)\) operators) from those defining sub-system time-dependent wave function (\(T_{\text{int}}(t)\) and \(\sigma_{\text{int}}(t)\)) in the time-dependent downfolded Hamiltonian. By the appropriate choice of the active space, these approaches can be used to separate the description of the sub-system that slowly evolves in time (representing low-energy modes) from the components of the entire system that correspond to fast-varying components (representing high-energy modes) of the entire system. As suggested by earlier analysis (see Ref.\[64\]) parameters corresponding to fast-varying parts can be effectively described by perturbation techniques. Simulations of these sub-systems can be performed employing explicit time-propagation techniques described in Refs.\[35–37, 40\].

ARPONEN'S ACTION FUNCTIONAL FOR TD-SES-CC AND TD-DUCC FORMULATIONS

The form of optimal time evolution (or optimal equations of motion) for approximate theories describing time-dependent wavefunction \(|\Psi\rangle\) can be determined by using the Dirac-Frenkel time-dependent variational principle (TDVP),\[87, 88\] (for a detailed discussion see also Refs.\[45, 88–93\]) where one varies the action integrals
\[
S[\Psi(t)] = \int_{t_1}^{t_2} \langle \Psi(t)|i\hbar \frac{\partial}{\partial t} - H|\Psi(t)\rangle dt. \tag{66}
\]
to obtain the equations of motion for parameters describing time-dependent wave function. This functional has paved the way for time-dependent formulations including various variants of time-dependent multi-configurational methods.\[45, 48–51, 55, 94\] In the above formulation the normalization of the time-dependent wave function,
\[
\langle \Psi(t)|\Psi(t)\rangle = 1, \tag{67}
\]
is assumed, which significantly simplifies the utilization of TDVP since for this type of domain the \(i\hbar \frac{\partial}{\partial t}\) operator is the Hermitian operator and \(S[\Psi(t)]\) functional assumes real values. The functional Dirac-Frenkel functional has been extended to bi-variational formulations by Arponen et al.\[39\]
\[
S[\Psi(t), \Psi'(t)] = \int_{t_1}^{t_2} \langle \Psi'(t)|i\hbar \frac{\partial}{\partial t} - H|\Psi(t)\rangle dt. \tag{68}
\]
where the trial wave functions \(\langle \Psi(t)|\) and \(|\Psi(t)\rangle\) satisfy the normalization condition
\[
\langle \Psi'(t)|\Psi(t)\rangle = 1. \tag{69}
\]
The Arponen’s functional provides a theoretical foundation especially for time-dependent formulations of the coupled cluster theory. Recently, Kvaal and Pedersen used this functional to develop orbital adaptive time-dependent coupled cluster approximations \[41\] and symplectic integrators for TDCC equations.\[42\] The real-action functional introduced by Sato et al. in studies of TDCC theory also invokes the bi-orthogonal form of the Arponen’s functional.\[44\] Both functionals \((66)\) and \((68)\) are very useful in situations where one also considers time evolution of reference function and molecular basis.

In this section, we will employ functionals \((66)\) and \((68)\) to study stationary conditions for TD-SES-CC and TD-DUCC formulations, respectively, and to describe time evolution of sub-system described by the internal type excitations. The Frenkel-Dirac functional for normalized DUCC wave function takes the following form
\[
S[\sigma_{\text{int}}(t), \sigma_{\text{ext}}(t)] = \langle \Phi|e^{-\sigma_{\text{int}}(t)}e^{-\sigma_{\text{ext}}(t)(i\hbar \frac{\partial}{\partial t}\bar{H})}e^{\sigma_{\text{ext}}(t)}e^{\sigma_{\text{int}}(t)}|\Phi\rangle \tag{70}
\]
where, as stated earlier, we assume that one-particle orbital basis is time-independent. Since the DUCC wave function is normalized, the \(S[\sigma_{\text{int}}(t), \sigma_{\text{ext}}(t)]\) assumes real
values. In the next step, we will re-write functional (70) using results of the previous section (see Eqs. (51), (57), (58), (59))

\[ i\hbar e^{-\sigma_{\text{ext}}(t)} \frac{\partial}{\partial t} e^{\sigma_{\text{int}}(t)} = i\hbar \frac{\partial}{\partial t} + i\hbar A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) , \]  

which after substituting to Eq.(70) leads to the expression

\[ S[\sigma_{\text{int}}(t), \sigma_{\text{ext}}(t)] = \langle \Phi | e^{-\sigma_{\text{int}}(t)} \{ i\hbar \frac{\partial}{\partial t} - [\hat{H}_{\text{ext}}(t) - i\hbar A(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})] \} e^{\sigma_{\text{int}}(t)} | \Phi \rangle . \]  

The above expression can be represented in an equivalent form using (63) and (65)

\[ S[\sigma_{\text{int}}(t), \sigma_{\text{ext}}(t)] = \langle \Phi | e^{-\sigma_{\text{int}}(t)} \{ i\hbar \frac{\partial}{\partial t} - \hat{H}^{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}, t) \} e^{\sigma_{\text{int}}(t)} | \Phi \rangle , \]  

which can be interpreted in terms of slow and fast varying parts of the wave function represented in terms of \( \sigma_{\text{int}}(t) \) and \( \sigma_{\text{ext}}(t) \) operators if "energetic" definition of the active space (or SES) is utilized. Namely, if the fast-varying in time part of the wave function (or \( \sigma_{\text{ext}}(t) \)-dependent part of the wave function) is known or can be efficiently approximated then the slow-varying dynamic (captured by the proper choice of the active space and \( \sigma_{\text{int}}(t) \) operator) of the entire system can be described as a sub-system dynamics generated by the Hermitian \( \hat{H}^{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t}) \) operator. This decoupling of various time regimes (slow vs. fast varying components) is analogous to the de-coupling of high- and low-energy Fermionic degrees of freedom in stationary formulations of the SES-CC and DUCC formalisms (see Refs.[64, 72]). This result indicates that there exist universal mechanisms in coupled cluster theory that naturally lead to the decoupling of various temporal, energy, and spatial scales as shown in present analysis and in Refs.[63, 64].

Properties of the Arponen’s functional draw heavily on the representations of the bra and ket states. Here we will analyze the standard approach analyzed in references [38, 39, 41, 42, 44] where ket state is represented by standard CC expansion (3) while the bra is represented using a standard de-excitation \( \Lambda(t) \) operator [39]

\[ \langle \Psi'(t) | = \langle \Phi |(1 + \Lambda(t))e^{-T_{\text{int}}(t)} \] 

\[ = \langle \Phi |(1 + \Lambda_{\text{int}}(t) + \Lambda_{\text{ext}}(t))e^{-T_{\text{int}}(t)}e^{-T_{\text{ext}}(t)} , \]  

which leads to the following form of the Arponen’s functional

\[ S[\Lambda_{\text{int}}(t), \Lambda_{\text{ext}}(t), T_{\text{int}}(t), T_{\text{ext}}(t)] = \langle \Phi |(1 + \Lambda_{\text{int}}(t) + \Lambda_{\text{ext}}(t))e^{-T_{\text{int}}(t)}e^{-T_{\text{ext}}(t)}(i\hbar \frac{\partial}{\partial t} - \hat{H})e^{T_{\text{int}}(t)}e^{T_{\text{ext}}(t)} | \Phi \rangle . \]  

Comparing the above expression for the current functional with the DUCC one (73) leads to the observation that the DUCC functional can be expressed directly in terms of a sub-system perspective, where the dynamics for the sub-system is generated by \( \hat{H}_{\text{ext}} - i\hbar A \) whereas for the TD-SES-CC case only the first term in Eq.(77) can be interpreted in a similar way. The remaining term in the Eq.(77) introduces explicit coupling between \( \Lambda_{\text{ext}}(t) \) and \( T_{\text{int}}(t) \) operators and cannot be considered in terms of sub-system dynamics as in the case of DUCC functional. As mentioned earlier the algebraic form and properties of Arponen’s functional depends on the parametrization used for the bra state \( \langle \Psi'(t) | \).
APPROXIMATIONS AND IMAGINARY TIME EVOLUTION GENERATED BY DOWNFOLDLED HAMILTONIANS

Before discussing main approximations of TD-SES-CC and TD-DUCC approaches, let us focus on the stationary conditions for the $\sigma_{\text{int}}(t)$ operator stemming from functional (72). Since the definition of $e^{\sigma_{\text{int}}(t)}$ is an exact wave function in the complete active space, it can be equivalently represented by the active-space FCI expansion

$$|\Psi_{\text{int}}(t)\rangle = e^{\sigma_{\text{int}}(t)}|\Phi\rangle = C_{\text{int}}(t)|\Phi\rangle,$$

where $C_{\text{int}}(t)$ is the configuration interaction type operator that produces all possible excitations/configurations within CAS and which satisfies the normalization condition

$$\langle \Psi_{\text{int}}(t)|\Psi_{\text{int}}(t)\rangle = \langle \Phi|C_{\text{int}}(t)\rangle C_{\text{int}}|\Phi\rangle = 1.$$

In the $(C_{\text{int}}(t), \sigma_{\text{ext}}(t))$ parametrization, the functional (72) takes the form

$$\sigma_{\text{ext}}(t)$$

and describe evolution, of $C_{\text{int}}(t)|\Phi\rangle$ or $e^{\sigma_{\text{int}}(t)}|\Phi\rangle$ (Eq.(81) or Eq.(62)) using modified TD-MCSCF or TD-CASSCF implementations. In these simulations, the time-dependent $H_{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}}{\partial t})$ operator is used to generate the sub-system dynamics, which can be employed for example in studies of decoherence effects in open-systems. This can be achieved by analyzing density matrix corresponding to $C_{\text{int}}|\Phi\rangle$ wave function.

Important features of the TD-DUCC formalism are associated with the behavior of the above formalism during imaginary time evolutions of equations (81) for $C_{\text{int}}(t)$ amplitudes. In analogy to the discussion by Pigg et al. [38] we use the imaginary Wick rotation $t \rightarrow -i\hbar \tau$ and re-write (81) in the form

$$i\hbar \frac{\partial C_{\text{int}}(t)}{\partial t} |\Phi\rangle = H_{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})C_{\text{int}}(t)|\Phi\rangle,$$

where $H_{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})$ operator is given by Eq.(63). The above equations corresponds to the equations (see Eq.(62)) defining dynamics of the $\sigma_{\text{int}}(t)$ operator when returning to the $(\sigma_{\text{int}}(t), \sigma_{\text{ext}}(t))$ parametrization. In view of decoupling internal and external wave function parameters in the $H_{\text{eff}}(\sigma_{\text{ext}}(t), \frac{\partial \sigma_{\text{ext}}(t)}{\partial t})$ operator a natural approximation is to use perturbative estimates of

$$\frac{\partial C_{\text{int}}(\tau)}{\partial \tau} |\Phi\rangle = -H_{\text{eff}}(\sigma_{\text{ext}}(\tau), \frac{\partial \sigma_{\text{ext}}(\tau)}{\partial \tau})C_{\text{int}}(\tau)|\Phi\rangle,$$

As soon as this approximation reaches the stationary limit (SL) for $\tau \rightarrow \infty$ (i.e. $\frac{\partial C_{\text{int}}(\tau)}{\partial \tau} = 0$ and $\frac{\partial \sigma_{\text{ext}}(\tau)}{\partial \tau} = 0$) and

$$\sigma_{\text{ext}}(\tau) \stackrel{\text{SL}}{\longrightarrow} \sigma_{\text{ext}},$$

then the the form of Eq.(82) for large values of $\tau$ is given by a simpler form

$$\frac{\partial C_{\text{int}}(\tau)}{\partial \tau} |\Phi\rangle = -(P+Q_{\text{int}})H_{\text{ext}}(\sigma_{\text{ext}}(\tau))(P+Q_{\text{int}})C_{\text{int}}(\tau)|\Phi\rangle,$$

which is a consequence of the fact that the "external-velocity" dependent term (i.e. $\frac{\partial \sigma_{\text{ext}}(\tau)}{\partial \tau}$-dependent term - the $A$ operator in Eq.(59)) disappears in the SL limit, i.e.,

$$A(\sigma_{\text{ext}}(\tau), \frac{\partial \sigma_{\text{ext}}(\tau)}{\partial \tau}) \stackrel{\text{SL}}{\longrightarrow} 0.$$
ditionally, since in the SL $\tilde{H}_{\text{ext}}(\sigma_{\text{ext}}(\tau))$ approaches $\tilde{H}_{\text{ext}}$, to get the ground state energy one can alternatively perform imaginary evolutions with the fixed-in-time Hamiltonian $\tilde{H}_{\text{ext}}$ in the active-space.

CONCLUSIONS

In this paper, we analyzed the extension of time-independent SES-CC and DUCC formalisms to the time domain. For a fixed-in-time orbital basis, we were able to prove that it is possible to describe the dynamics of the entire system in terms of sub-system dynamics generated by a downfolded Hamiltonian. If the active space separates slow modes from the fast ones, perturbative techniques can be used to define downfolded Hamiltonians. Although these results are valid for both TD-SES-CC and TD-DUCC methods, we put special emphasis on the TD-DUCC formalism where the operators defining the sub-system dynamics are Hermitian. Recognizing that if the $\sigma_{\text{ext}}(t)$ operator reaches the stationary limit, then the time-dependent Hamiltonian converges to the time-independent downfolded Hamiltonian, demonstrating the feasibility of imaginary time evolution. In the stationary limit, the $A$ operator, which depends linearly on the $\sigma_{\text{ext}}(t)$-velocity term, disappears, enabling the utilization of the time-dependent CASSCF codes to describe system dynamics in the time domain captured by the specific choice of the active space. Additionally, these results allow quantum Lanczos algorithms to be employed to identify the ground-state energy values.[77]

It is also interesting to look at the sub-system dynamics from the point of view of description decoherence effects, where the sub-system of interest is in contact with the surrounding environment described by the $\tilde{H}_{\text{eff}}(t)$ operator.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ACKNOWLEDGEMENT

This work was supported by the "Embedding Quantum Computing into Many-body Frameworks for Strongly Correlated Molecular and Materials Systems" project, which is funded by the U.S. Department of Energy (DOE), Office of Science, Office of Basic Energy Sciences, the Division of Chemical Sciences, Geosciences, and Biosciences. All calculations have been performed using computational resources at the Pacific Northwest National Laboratory (PNNL). PNNL is operated for the U.S. Department of Energy by the Battelle Memorial Institute under Contract DE-AC06-76RLO-1830.

Appendices

SUB-SYSTEM DYNAMICS WITH EXTENDED COUPLED CLUSTER FORMALISM

As a specific example of the SES-CC Arponen’s functional, we will focus on the bi-orthogonal formulation of TDVP given by the extended coupled cluster formalism where bra and ket states $|\Psi'(t)\rangle$ and $|\Psi(t)\rangle$ are parametrized as

$$\langle \Psi'(t)| \Psi(t) \rangle = \langle \Phi | e^{X(t)} e^{-T(t)} | \Phi \rangle ,$$

$$|\Psi'(t)| = e^{T(t)} |\Phi\rangle ,$$

where $T(t)$ and $X(t)$ are standard excitation and de-excitation operators. Expressions (86) and (87) for trial wave function automatically satisfies normalization condition (69) and the functional (68) can be viewed as a function of cluster amplitudes defining $T(t)$ and $X(t)$ cluster operators

$$S[T(t), X(t)] = \int_{t_1}^{t_2} \langle \Phi | e^{X(t)} e^{-T(t)} (i\hbar \frac{\partial}{\partial t} - H) e^{T(t)} |\Phi\rangle dt .$$

The stationary conditions provide equations of motion for the cluster amplitudes $T(t)$ and $X(t)$. Moreover, partial integration of (88) is required to obtain equations of motion for the $X(t)$ operator.

In analogy to standard excitation operator $T$, we will partition the de-excitation operator into its internal and external components (now the notion of sub-system embedding excitations should be replaced by the sub-system embedding de-excitations)

$$X(t) = X_{\text{int}}(t) + X_{\text{ext}}(t)$$

where all strings of de-excitation operators defining $X_{\text{int}}(t)$ contain active spin-orbital indices only. The Arponen’s functional for the ECC formalism takes the form

$$S[T_{\text{int}}(t), T_{\text{ext}}(t), X_{\text{int}}(t), X_{\text{ext}}(t)] =$$

$$\int_{t_1}^{t_2} \langle \Phi | e^{X_{\text{int}}(t)} e^{X_{\text{ext}}(t)} e^{-T_{\text{int}}(t)} e^{-T_{\text{ext}}(t)} (i\hbar \frac{\partial}{\partial t} - H) e^{T_{\text{ext}}(t)} e^{T_{\text{int}}(t)} |\Phi\rangle dt .$$
which is composed of time derivative $S_{\text{Dt}}[T_{\text{int}}(t), T_{\text{ext}}(t), X_{\text{int}}(t), X_{\text{ext}}(t)]$ part and energy term $S_{\text{H}}[T_{\text{int}}(t), T_{\text{ext}}(t), X_{\text{int}}(t), X_{\text{ext}}(t)]$ ($S = S_{\text{Dt}} + S_{\text{H}}$). In contrast to the real-valued DUCF functional, the expression above poses a significantly bigger challenge in extracting sub-system dynamics as shown in Eq.(73). There are two main reasons for that: (1) there are groups of non-commuting exponential operators, and (2) in the general case, functional (90) can assume complex values. While the latter problem has been recently explored by introducing real-action functional [44] (see also Ref.[42]), in order to define sub-system dynamic we will focus entirely on the first issue. For this purpose, let us rewrite $S_{\text{Dt}}$ and $S_{\text{H}}$ energy functional terms of (90) with the modified integration kernels ($I_{\text{Dt}}$ and $I_{\text{H}}$), $S = \int_{t_1}^{t_2} (I_{\text{Dt}}(t) + I_{\text{H}}(t)) dt$. For $I_{\text{Dt}} (t)$ we have

\[
I_{\text{Dt}}(t) = \langle \Phi | e^{X_{\text{int}}(t)} e^{X_{\text{ext}}(t)} e^{-T_{\text{int}}(t)} e^{-T_{\text{ext}}(t)} (-i\hbar \frac{\partial}{\partial t}) e^{T_{\text{ext}}(t)} e^{T_{\text{int}}(t)} | \Phi \rangle 
\]

\[
= i\hbar \langle \Phi | e^{X_{\text{int}}(t)} e^{X_{\text{ext}}(t)} \frac{\partial T_{\text{ext}}(t)}{\partial t} | \Phi \rangle + \langle \Phi | e^{X_{\text{int}}(t)} e^{-T_{\text{int}}(t)} (i\hbar \frac{\partial}{\partial t}) e^{T_{\text{int}}(t)} | \Phi \rangle 
\]

\[
= i\hbar \langle \Phi | e^{X_{\text{int}}(t)} e^{-T_{\text{int}}(t)} e^{T_{\text{ext}}(t)} e^{X_{\text{ext}}(t)} \frac{\partial T_{\text{ext}}(t)}{\partial t} | \Phi \rangle + \langle \Phi | e^{X_{\text{int}}(t)} e^{-T_{\text{int}}(t)} (i\hbar \frac{\partial}{\partial t}) e^{T_{\text{int}}(t)} | \Phi \rangle
\]

where $B(T_{\text{int}}(t), \frac{\partial T_{\text{ext}}(t)}{\partial t}, X_{\text{ext}}(t))$ (or $B$ term for short) is given by the formula

\[
B = e^{T_{\text{int}}(t)} (e^{X_{\text{ext}}(t)} \frac{\partial T_{\text{ext}}(t)}{\partial t}) e^{-T_{\text{int}}(t)}.
\]

Notice that only the active-space part of $B$ operator produces a non-zero contribution to Eq.(94), and therefore only the connected part of $e^{X_{\text{ext}}(t)} \frac{\partial T_{\text{ext}}(t)}{\partial t}$ produces non-zero contributions to the first term on the right hand side of Eq.(93) (disconnected components contain uncontracted external spin-orbital label which gives zero contribution when acting on either the active-space vector $\langle \Phi | e^{X_{\text{int}}(t)}$ or reference function $| \Phi \rangle$).

Using similar manipulations, the $I_{\text{H}} (t)$ term can be re-written as

\[
I_{\text{H}}(t) = \langle \Phi | e^{X_{\text{int}}(t)} e^{X_{\text{ext}}(t)} e^{-T_{\text{int}}(t)} e^{-T_{\text{ext}}(t)} H e^{T_{\text{ext}}(t)} e^{T_{\text{int}}(t)} | \Phi \rangle 
\]

\[
= \langle \Phi | e^{X_{\text{int}}(t)} e^{-T_{\text{int}}(t)} \tilde{H}_{\text{ECC}} e^{T_{\text{int}}(t)} | \Phi \rangle
\]

where

\[
\tilde{H}_{\text{ECC}} = e^{X_{\text{int}}(t)} e^{-T_{\text{int}}(t)} H e^{T_{\text{ext}}(t)} e^{-X_{\text{ext}}(t)}
\]

Although the above formula bears a resemblance to functional (72), by their definitions $\tilde{H}_{\text{ECC}}(t)$ and $B(t)$ mix internal and external Fermionic degrees of freedom, in contrast to the DUCF functional (72). Another important feature of the ECC formalism is the fact that $\tilde{H}_{\text{ECC}}(t)$, as given by Eq.(98), is defined by rather complicated algebraic many-body structure defined by two similarity transformations one involving singly-transformed auxil-
inary operator $X^{\text{int}}(t)$. Efficient coding of these expressions may require sophisticated symbolic algebra tools.
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